OCCASION

This publication has been made available to the public on the occasion of the 50th anniversary of the United Nations Industrial Development Organisation.

DISCLAIMER

This document has been produced without formal United Nations editing. The designations employed and the presentation of the material in this document do not imply the expression of any opinion whatsoever on the part of the Secretariat of the United Nations Industrial Development Organization (UNIDO) concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries, or its economic system or degree of development. Designations such as "developed", "industrialized" and "developing" are intended for statistical convenience and do not necessarily express a judgment about the stage reached by a particular country or area in the development process. Mention of firm names or commercial products does not constitute an endorsement by UNIDO.

FAIR USE POLICY

Any part of this publication may be quoted and referenced for educational and research purposes without additional permission from UNIDO. However, those who make use of quoting and referencing this publication are requested to follow the Fair Use Policy of giving due credit to UNIDO.

CONTACT

Please contact publications@unido.org for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org

16725

RESTRICTED

August 15, 1987

English

PYROLYSIS SYSTEM FOR POLYMETHYLMETACRYLATE

SI/CPR/86/028/11-51/32.1.H
PEOPLE'S REPUBLIC OF CHINA

Final report:

Prepared for the Government of the
People's Republic of China
By the United Nations Industrial Development Organization,
acting as an executing agency for the United Nations
Development Programme

Based on the work of Alfons G. Buekens,
expert in waste recycling

United Nations Industrial Development Organization
Vienna

691

This report has not been cleared with the United Nations Industrial Development Organization which does not, therefore, necessarily share the views presented.

ABSTRACT

In this final report a survey is given of the various phases of the development of a UNIDO/VUB-process for the pyrolysis of PMMA, conducted in close collaboration with SRRUC.

After a literature and patent survey, experimental testing and a preliminary design were conducted in parallel. On the basis of material and energy balances several alternative designs, involving directly and indirectly heated fluidized bed reactors were compared.

Although it has been shown that the new process features a superior yield and monomer quality some factors remain open for further optimization. Moreover, once that the pyrolysis plant has started up succesfully the constructive comments from the UNIDO-expert can be used for improving the environmental, safety and product quality aspects of the other divisions of the plant.

EXPLANATORY NOTES

The following abbreviations have been used consistently throughout the text.

Abbreviation	Entity or Material
MMA	methylmethacrylate monomer
PMMA	polymethylmethacrylate
PE	polyethylene
PS	polystyrene
PVC	polyvinylchloride
SRRUC	Shanghai Resource Recovery and Utilization Company
PRC	the People's Republic of China
VUB	Free University of Brussels

TABLE OF CONTENTS

INTRODUCTION

This project is a direct consequence of a former UNIDO-assignment, directed bij Prof. G. Patfoort, and devoted to the recycling of mixed plastics. During this mission in Shanghai (from August 23 to August 28, 1985) a need was identified to increase the yield and the purity of MMA monomer, obtained by the pyrolysis of cast PMMA. Also, the environmental and safety standards of the plant had to be improved.

A literature and patent study was conducted and after calculating some materials and energy balances experimental testing using a fluidized bed reactor was initiated.

During a first visit (from 18-28 July 1986) to SRRUC (Shanghai), dedicated to the PMMA problem, the plant was submitted to a complete operating, environmental and safety audit. It was concluded that numerous features of plant design and operation were to be improved, in conjuction with increasing product yield and purity. The latter would be obtained by converting to a more modern, continuous technology, developed with the aid from UNIDO/VUB. The design requirements, desired by SRRUC, were established (Mission Report of August 1, 1986 in Annexe A).

Advantages and disadvantages of various process concepts were evaluated and compared. A fluidized bed system using steam as a fluidizing agent was ultimately selected (Mission Report of November 15, 1986 in Annexe B)

In the meantime, SRRUC technical staff had experimented with an own, tin-bath technology. During a second visit of the UNIDO-Expert (23 December 1986 - 3 January 1987), these tests were continued and critically evaluated. Moreover, thanks to the diligence of SRRUC-staff a short full-scale experiment using the ancient cauldron technology was conducted, all tests being evaluated gas chromatographically (Mission Report of January 5, 1987 in Annexe C).

During a final mission (from 14 to 28 July 1987) all aspects of the new UNIDO/VUB technology, as adopted and co-developed by SRRUC, were discussed. Full agreement was reached in the design and testing of the individual parts of the plant, which has a more favourable situation from an environmental viewpoint. (Mission Report of July 31, 1987 in Annexe D).

Finally, the experimental results obtained at the VUB are briefly discussed in Annexe E, whereas the results obtained during the second mission in Shanghai are treated in Annexe C.

RECOMMENDATIONS

1. It is desirable that the collaboration between SRRUC and UNIDO would be continued. The direction and management as well as the technical staff of SRRUC have proved to be industrious, competent, realistic, flexible and keen to improve the local standards of technology. The best way for achieving the latter purpose is by promoting joint, UNIDO-sponsored, projects, based on local needs and ideas, and technical help and advice provided by UNIDO.

2. After the successful conclusion of the PMMA-pyrolysis project, it seems worthwhile to tackle another problem, which is similar in nature, but involves a more complex technology.

   The problem can be defined as "Improving the SRRUC-technology for the steam hydrolysis of nylon-6". The process has been developed by SRRUC, with the aid of East China University. Patents have been applied for the process.

   As a course for further UNIDO action it is suggested to:

   - contact compaines involved in caprolactam production and purification (I)
   - optimize the reaction conditions on a basis of fundamental study (II)
   - conduct experimental test work (III)
   - improve the auxiliary operations (IV).

   The latin figures between brackets refer to the successive stages of the project. The first and second stage (I) may be conducted within a limited budget and time, to be started as soon as possible.

1. SCOPE OF THE WORK

This work originated from the desire, expressed by the management of SRRUC, to dispose of a modern method of PMMA-pyrolysis, resulting in higher product yield and purity and in lower environmental damage.

Since such a method was not commercially available, it was proposed to develop a new fluidized bed technology, along methods developed previously at the Free University of Brussels (VUB). The latter has been succesfully derived and the resulting process has been termed UNIDO/VUB fluidized bed PMMA pyrolysis process.

As a second point, attention was paid to the various operations upstream and downstream of the pyrolysis unit proper, i.e.

- PMMA sorting, storage and feeding
- storage, distillation, rectification and salting out of crude MMA
- prepolymerization
- degassing and blending of MMA
- polymerization.

In the first mission report advice was given on all the other operations. Still, it should be recognized that the newly developed technology, assorted with some simple and straightforward advice, would do much to improve these operations.

Finally, at the conclusion of the study, a new topic was identified which could be tackled along the same lines as the present work.

2. EXPERIMENTAL RESULTS

2.1. Results of experiments on micro-scale

Several experimental methods have been proposed to study the pyrolysis of polymers. Experimental results on the pyrolysis of PMMA on a micro-scale (the amount PMMA used is never more than some milligrams) can be found in literature. The following techniques were used:

- pyrolysis gas chromatography (PyGC)
- thermal volatilization analysis (TVA)
- thermogravimetric analysis.

The main purpose of these experiments is to investigate the reaction mechanism. The various basic processes are listed below.

(I) chain-end initiation: $P \rightarrow R^\circ + X^\circ$

R° is the chain radical which will depropagate, X° is a small radical which distills out of the system;

(II) random scission initiation: $P \rightarrow 2R^\circ$

(III) depropagation: $R^\circ \rightarrow R^\circ + M$

M is a monomer molecule which distills out of the system;

(IV) termination by bimolecular interaction:

$R^\circ + R^\circ \rightarrow P$

(V) 'termination' by depropagation to the end of the polymer molecule, leaving a small radical which distills out of the system.

The reaction mechanism probably changes with temperature. At low temperatures (<400°C), the depropagation reaction is principally initiated at the ends of the molecules, and termination occurs by bimolecular interaction. At intermediate temperatures, chain scission becomes sufficiently important to account for most of the initiation steps, though bimolecular interaction is still the important termination mechanism. At high temperatures (>450°C), initiation by scission is the dominant initiation process, but the majority of the chains are effectively terminated by the diffusion out of the system of the ultimate radical remaining when a chain has completely depropagated.

Several PyGC experiments were also carried out at the VUB. The main practical conclusion from these experiments and the results in literature is that a high yield of monomer is possible. From the PyGC experiments one would infer that a high operating temperature is desirable. The later work at bench-scale, however, leads to the opposite conclusion.

Also some patents about possible industrial set-ups can be found (Annexe A and C). The used equipment is:

- cauldron with a lead-batch
- extruder.

2.2. Experiments on lab, bench and full scale

2.2.1. Experiment with cauldron technology

A full scale experiment (amount of PMMA charged: 30 kg) was carried out (Annexe C). In this experiment the yield was 88 %, the purity was not determined but can not be expected to be more then 90 %.

2.2.2. Experiments with tin batch technology

To evaluate the feasibility of the tin bath technology several experiments on a lab scale cauldron (volume: 3.5 dm^3) were carried out by SRRUC during the second mission of the UNIDO-expert (Annexe C). The most important results are given in the following table (the differences are due to the different kinds of PMMA used):

experiment	yield (%)	purity (%)	total MMA production (%)
A	99	95.9	94.9
B	93	91.6	85.2
C	90	89.2	80.3

It is also observed that the best product is generated during steady-state production, both initial and final product showing a lower grade. The amount of light products generated rises from the start until the end of the experiment. The heavy products show a different behaviour.

These observations were also made during the large scale experiment with the cauldron technology. The total MMA production of the large scale experiment is lower than in the lab scale experiments. This effect may be due to the lower surface to volume ratio of the large cauldron.

2.2.3. Experiments with fluid bed technology

Because a batch system gives much idle time (heating, charging and cooling of the reactor) a continuous operation is to be preferred. This can be obtained with:

- continuous tin bath
- fluidized bed.

The latter has superior characteristics with respect to heat transfer, residence time, the removal of fillers. Hence, experiments on this promising technique were carried out using the fluidized bed plant of the VUB. As a fluidizing agent steam was used. The results of the experiments with a PMMA flowrate of 990 g/h are given in following figures (more details are given in Annexe E).

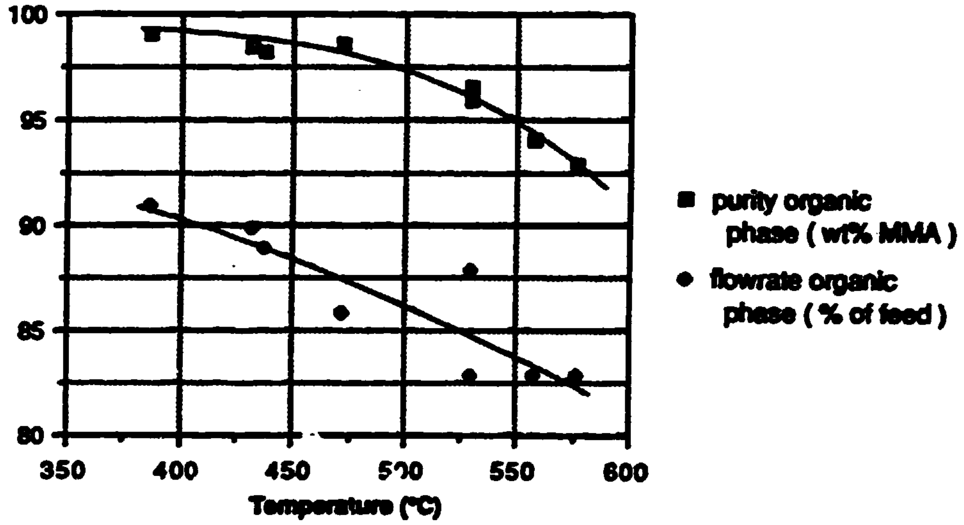


Figure 1 : yield and purity of the organic phase

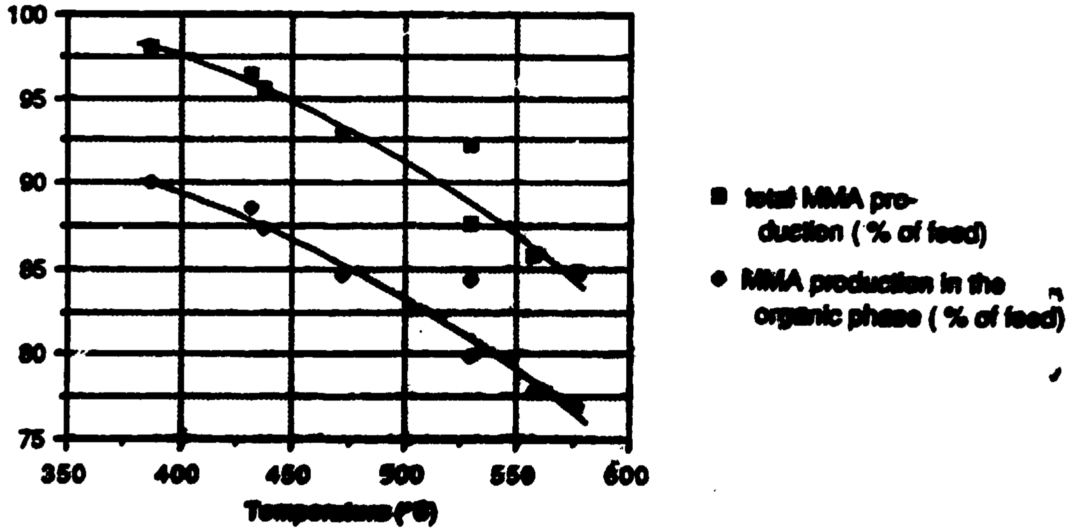


Figure 2 : amount of MMA produced

The yields obtained are much higher than those with the tin bath technology. Only experiment A of the tin bath experiments can compete with the fluidized bed experiments. Also with respect to yield a fluidized bed plant does not suffer from scale-up factors, as is the case with the tin bath technology. However, it must also be mentioned that the fluidized bed experiments were performed on PMMA free from pigments and fillers.

During the experiments the heat of reaccion was measured for the following reaction:

$$\text{PMMA } (293 \text{ K}) \rightarrow \text{MMA } (\text{T K})$$

It is given by:

$$\Delta H_r = 660 + 0{,}336\ T + 1.8\ 10^{-3}\ T^2 - 0.46\ 10^{-6}\ T^3 \quad \text{J/g}$$

This was a major unknown factor until now.

In annexe E some useful information about the distillation of water-MMA mixtures is given.

2.3. Conclusions

Since the fluid bed technology gives the highest yield and has many other advantages this type of process was selected by SRRUC/UNIDO. The fluid bed must be operated at low temperatures (about 400°C) and be filled with fine sand, in order to minimize the steam requirements necessary to fluidize the bed.

3. PROCESS DEVELOPMENT AND DESIGN

After selection of a fluidized bed as the most suitable solution for the problem posed, a preliminary design and general instruction were prepared at V.U.B. The collaboration of Mr. SAMYN is gratefully acknowledged. These data can be found in Annexe C. The final drawing of the fluidized bed unit is found on the following page, detailed drawings in Annexe F.

Because a coal fire was to be used for heating much attention was paid to the form of the distributor. It was designed in such way that the reactor bottom would be cooled by numerous steam jets directed downwards. Without this special distributor the bottom of the reactor would be destroyed rapidly. It could also be protected by an external fire-proof liner but in this case the surface for heat transfer would be reduced by about 10 % and radiant heat transfer would largely be lost. An ordinary distributor could be used if the reactor were heated electrically. In this case the steam should be produced externally.

The yields obtained are, much higher than those with the tin bath technology. Only experiment A of the tin bath experiments can compete with the fluidized bed experiments. Also with respect to yield a fluidized bed plant does not suffer from scale-up factors, as is the case with the tin bath technology. However, it must also be mentioned that the fluidized bed experiments were performed on PMMA free from pigments and fillers.

During the experiments the heat of reaction was measured for the following reaction:

PMMA (293 K) ---> MMA (T K)

It's given by:

$$\Delta H_r = 660 + 0{,}336\ T + 1.8\ 10^{-3}\ T^2 - 0.46\ 10^{-6}\ T^3\ \ J/g$$

This was a major unknown factor until now.

In annexe E some useful information about the distillation of water-MMA mixtures is given.

2.3. Conclusions

Since the fluid bed technology gives the highest yield and has many other advantages this type of process was selected by SRRUC/UNIDO. The fluid bed must be operated at low temperatures (about 400°C) and be filled with fine sand, in order to minimize the steam requirements necessary to fluidize the bed.

3. PROCESS DEVELOPMENT AND DESIGN

After selection of a fluidized bed as the most suitable solution for the problem posed, a preliminary design and general instruction were prepared at V.U.B. The collaboration of Mr. SAMYN is gratefully acknowledged. These data can be found in Annexe C. The final drawing of the fluidized bed unit is found on the following page, detailed drawings in Annexe F.

Because a coal fire is to be used for heating much attention was paid to the form of the distributor. It was designed in such way that the reactor bottom would be cooled by numerous steam jets directed downwards. Without this special distributor the bottom of the reactor would be destroyed rapidly. It could also be protected by an external fire-proof liner but in this case the surface for heat transfer would be reduced by about 10 % and radiant heat would largely be lost. An ordinary distributor could be used if the reactor is heated

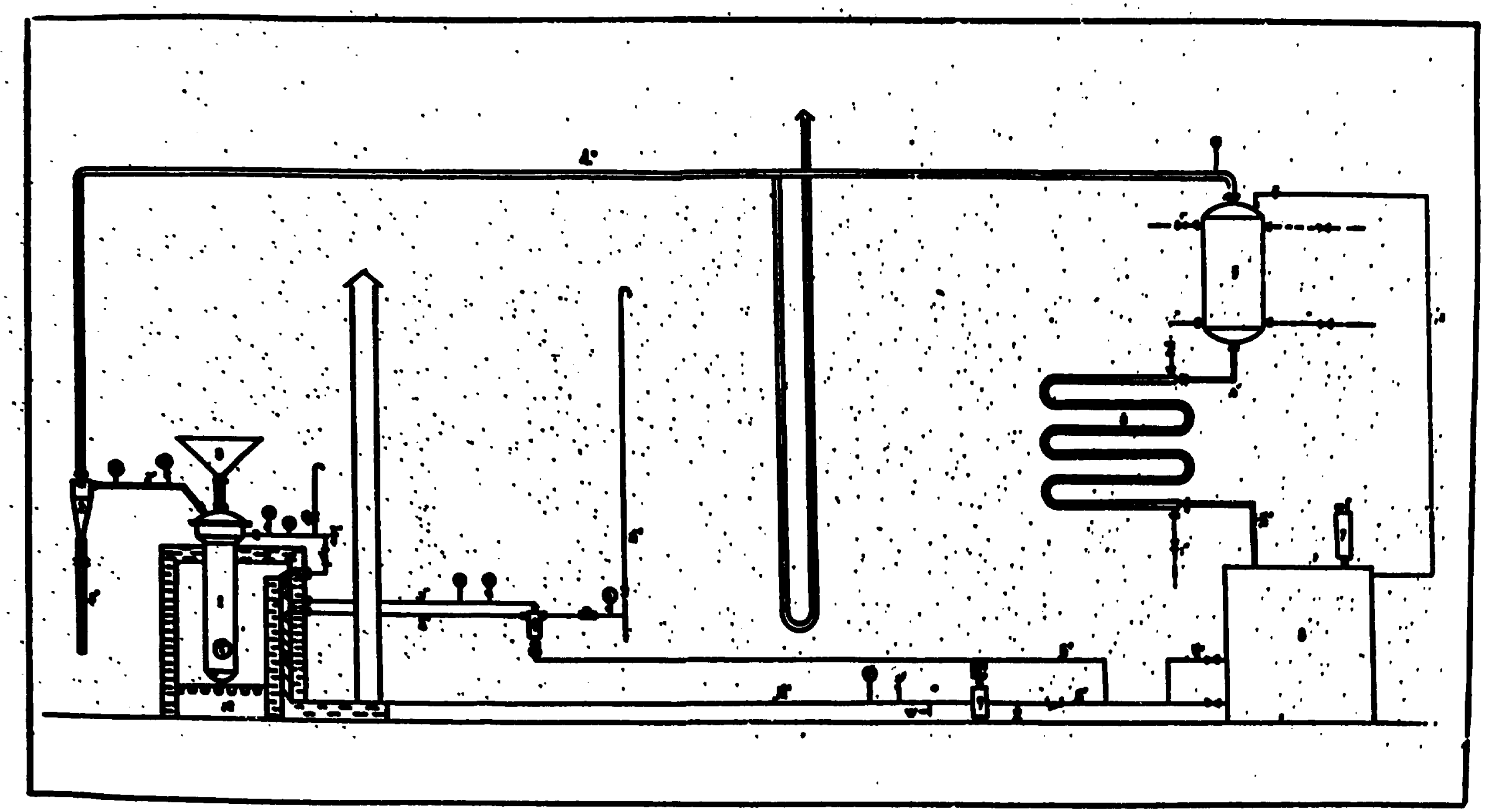


Figure 3: Lay-out of a PMMA Pyrolysis Plant

Another point of interest is the feeding system. The feeding of PMMA plates is uncomplicated but that of shavings is problematic. Originally, a system with two rocking valves was proposed. At SRRUC a completely new feeding system, approved by the UNIDO expert, was designed. This system still requires testing, but is expected to give less problems and can be found on the following page.

4. Safety and environmental aspects

4.1. Toxicity of MMA

The maximum allowable concentration (MAC) of MMA amounts to 100 ppm. The behaviour and body weight are unaffected for people poisoned repeatedly for several times (2 hours/day, continuing for 6 days) in air with MMA concentration of 10 mg/l. It is therefore concluded that MMA has no cumulative effect of toxicity.

Anesthesia can be found after at least 30 minutes of breathing in a large amount of MMA. Recovery is possible by breathing in fresh air.

A few people who have engaged in professional operation of MMA for more than 10 years suffer from insomnia and leucopenia.

It also causes local skin erythema and prurigo for some people, skin-sensitive to contact with MMA.

Contacting concentrated MMA vapor may immediately cause tearing, eyeache, throatache, cough, etc. and sometimes dizzyness and headache. But all the symptoms disappear quickly after the person is being removed from a MMA contaminated site into fresh air.

4.2. Safety aspects and environmental aspects

All process hazards have been reviewed methodically in annexe D. For further information we therefore refer to this annexe, in which also environmental aspects can be found. When the coal fire is replaced by electrical heating the emission of the coal fire is of course eliminated.

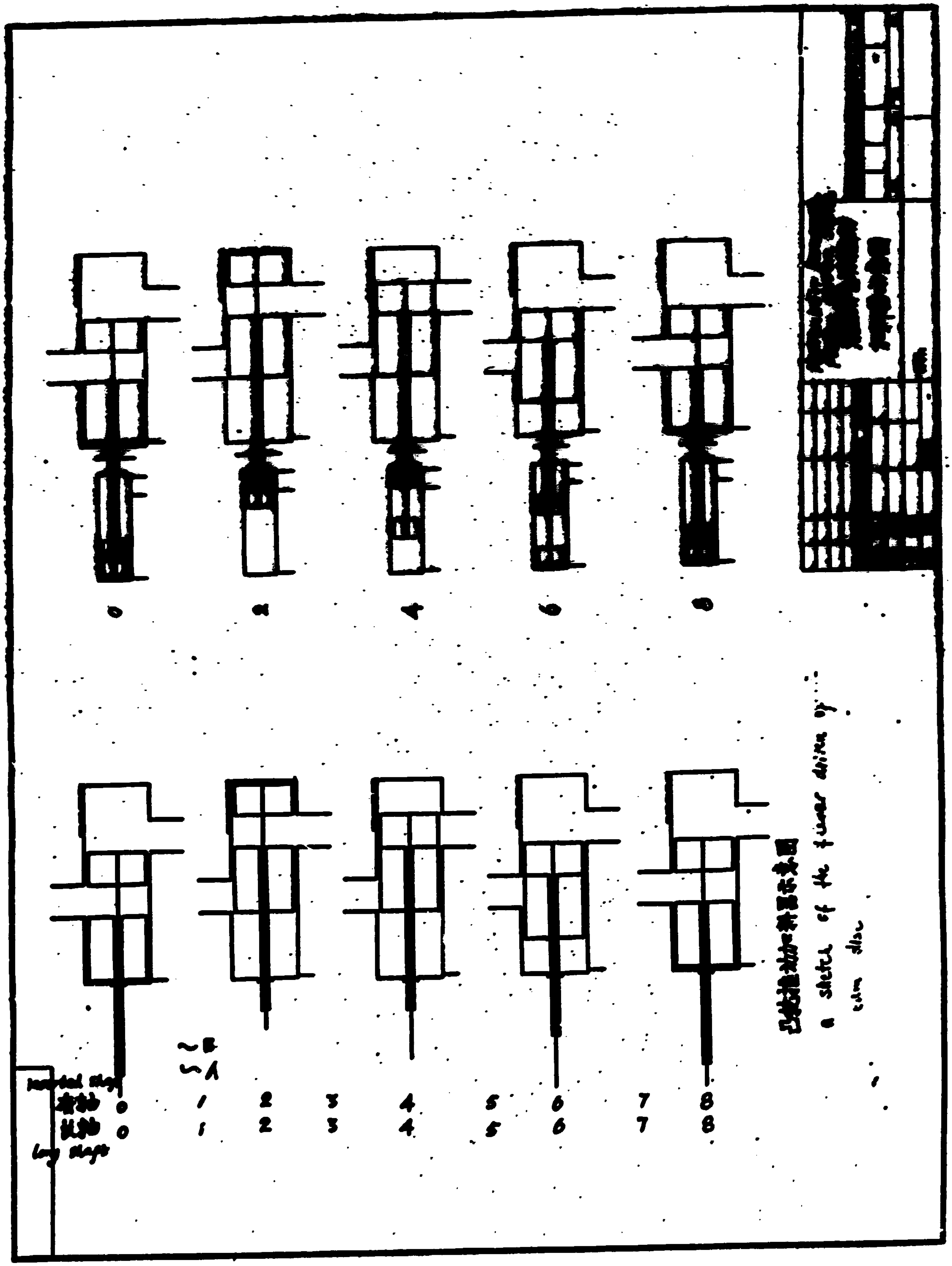


Figure 4: Feeding Mechanism

5. Results Achieved

Both the experimental and the design work have been concluded successfully.

The resulting constructive flow-sheet is shown in Figure 3, the proposed feeding mechanism in Figure 4.

The plant according to the UNIDO/VUB-design, as adopted and adapted by SRRUC will now be constructed at a new site.

6. Conclusions

Both the experimental work and the design phase have been concluded successfully. This opens the way to a new highly efficient and environmentally acceptable method of producing MMA.

Acknowledgements

The support of UNIDO and VUB is gratefully acknowledged. Mr. De Wolf was responsible for most of the experimental work. Dr. Ir. Schoeters (VUB) prepared material and thermal balances and Mr. Samyn (retired from Wanson) was actively engaged in the final design of the plant.

ANNEX 5

MISSION REPORT OF SEPTEMBER 12, 1985

RESTRICTED

12 September 1983
English

RECYCLING SYSTEM FOR PLASTICS WASTE

US/CPR/83/245/11-02/32.1.H.
PEOPLE'S REPUBLIC OF CHINA

Mission report :

Prepared for the Government of the
People's Republic of China
by the United Nations Industrial Development Organization,
acting as an executing agency for the United Nations
Development Programme

Based on the work of Georges Patfoort and
Alfons G. Buekens, experts in waste recycling

United Nations Industrial Development Organization
Vienna

This report has not been cleared with the United Nations Industrial Development Organization which does not, therefore, necessarily share the views presented.

EXPLANATORY NOTES

At the time of the visit U.S. dollars were exchanged at the following rate :

1 U.S. $ = 2.01 Yuan (¥)

The following abbreviations have been used throughout the text

Abbreviation	Plastic material
ABS	= Poly (acrylonitrile-butadiene -styrene)
EVA	= Ethylene-vinylacetate
HIPS	= High Impact Polystyrene
PA	= Polyamide
PE	= Polyethylene
PMMA	= Poly methyl metacrylate
POM	= Polyoxymethylene
PP	= Polypropylene
PS	= Polystyrene
PVC	= Polyvinylchloride

ABSTRACT

During a brief tour in China the two experts have studied the recovery and utilization of wastes in Shanghai, with a particular emphasis on the recycling of plastic wastes. Agreement was reached to implement a plastic processing line at SRRUC (Shanghai), which would serve as a pilot-plant for the whole of China, with the purpose of adapting the PW-processing technology to the Chinese raw materials and technical and economic conditions.

In the course of the discussions and plant visits the pyrolysis of PMMA was also singled out as an important topic for further action. A separate project proposal for tackling the PMMA-pyrolysis problem is added to this report in Annexe VI.

TABLE OF CONTENTS

INTRODUCTION

This report deal. with the data obtained, the observations made and the agreements reached during a 2 weeks mission in China of the two experts in Solid Waste Recovery.

The purpose of the project was to realize a recycling system for plastics waste adapted to the needs of the country integrated in a general programme of waste recovery.

Hence, a first task of the experts was to get acquainted with the local systems and customs in the field of waste recovery and recycling, including plastics and rubber. For that purpose the Chinese counterparts have organized a number of plant visits, the details of which are reported in a chronological order in one of the Annexes.

Secondly, a study was made of the technical requirements and needs in the field of plastics recycling. This task was greatly facilitated by the excellent technical knowledge of the Chinese counterparts and by the fact that the equipment they desired was originally invented by one of the experts.

Total agreement for the course to follow was reached during the discussion sessions scheduled towards the end of the visit. The results can be summarized as follows :

- the available budget would be used to
  (a) acquire the most essential parts of a FN mixed plastics processing-line. The non-essential parts of the line would be manufactured locally
  (b) send technical and commercial people to Belgium in order to obtain the necessary training for operating the equipment and to assess its financial benefits for the local (Chinese)operating conditions
- a R & D-agreement would be made between the Chinese counterparts and a Belgian public company, using a similar processing line for the recycling of mixed plastics
- further research would be initiated locally in order to adapt the line to the nature of the Chinese raw materials and market outlets. This would eventually lead to a more widespread use of the imported equipment throughout the whole nation on the basis of a suitable licensing agreement with the original manufacturer (FN)

In the course of the visit the Chinese counterparts put forward numerous questions regarding plastics recycling technology in general and the abatement of pollution in the processing plants in particular. The experts replied to these questions, but had to emphasize that the solution of most of the problems submitted would require important investments, which often would render unattractive the continuation of the present economic activity.

One of the most pressing questions of the Chinese counterparts was in the field of PMMA recycling, which at present is conducted with an exceptionally low yield.

Since this particular case could be solved by the experts on the basis of a limited amount of further study it is suggested that further work would be conducted in this field.

RECOMMENDATIONS.

1. Installation of a pilot recycling plant is recommended in view of the optimisation of the activities of the Shanghai company to increase the efficiency of the recycling of plastic Waste. Waste would be recycled to a much higher quality material and an increasing quantity of mixed waste would be processed which with present equipment is to be considered as useless material

2. Improvement of the operation of the PMMA plant would lead to an immediate and substantial increase of production an elimination of polluting side effects and a very important improvement in the quality of final products. The optimisation of the process is highly recommended.

PLASTIC WASTE RECYCLING PROBLEMS IN CHINA

1. Introduction

A large industrial city such as Shanghai(12,000,000 inhabitants) has great potentialities in the separate collection and recycling of waste containing all kinds of raw materials. The Shanghai Resource Recovery and Utilisation company (SRRUC)recovers at present sixteen categories of waste materials, including more than a thousand subgrades. This includes ferrous metals, non ferrous metals, rubber, paper, rags , cotton, chemical fibre, animal bones, human hair, broken glass, glass bottles, old machine parts and accessories, chemical residues, waste oil and of course plastics. The total amount of waste material collected in 1983 was 1,660,000 Ton in which industrial wastes accounted for 85 per cent and post consumer waste for 15 per cent. The fraction of plastics is 12,000 Ton and that of rubber 8,600 Ton.

One can easely imagine the future potentialities of this comprehensive system of recovery if it were extended to the whole country. In accordance with western standards public attitudes and cost factors, the method of recovery of this waste material may seem incredible. We have to take into account the very high sense of responsibility of the Chinese authorities combined with a very wide prospective view in the problem of exhaustion of some raw materials and the limits in the resources of the planet.

Moreover, the appalling conditions under which raw materials in most developing countries are recuperated from dumps and tipping sites by flocs of women and children are completely eliminated in the Chinese system. Finally, the system is a source of clean employment and may help in supporting some principles of [illegible] housekeeping and thrift in a society rapidly evolving to increased consumption levels.

2. Tasks and Activities of the Experts

2.1. Statement of the problem

The task of the experts was particularly focused on the recycling possibilities of plastics and polymers.

But it is obvious that recycling activities of one material are interconnected with those of other materials. Plastic scrap, originating in industry or in the household is being supplied to selective collection centres or collected by identical brigades. Especially in the smaller arisings problems of mixed waste already exist to a large extent. The problem of their separation, their recovery by physical or chemical processes or their use in composite materials is one that has to be solved in the very near future otherwise the present system of selective collection will loose several of its assets and potentialities in waste recycling. Indeed, even the best waste recuperation system becomes completely useless when there is no acceptable outlet for the recovered fractions. Conversely, the existence of suitable outlets will maintain and stimulate the demand for secondary raw materials, rise their value and thus intensify their recovery.

So if a plastics processing line treating this mixed kind of plastic waste with a good efficiency would be installed, the need of China with respect to this technology would be very important. For this reason, an agreement between the local Company SRRUC and an external Western partner would be desirable in view of an exchange of technology and the development and construction of a recycling line adapted to the local needs.

2.2. Organisation of activities

The stay of the two Unido Experts in Shanghai was very short. However, the organisation of activities by the management of the Shanghai Resource Recovery and Utilisation company (SRRUC) was remarkably efficient and flawless. So a maximum of information could be collected, lectures, meetings and discussions organised, and the required data gathered together to reach sound technological conclusions.

The material-labour ratio

It would be most inefficient to install a plastic recycling line in Shanghai that would be a true copy of those which are already operating in Europe at present.

Two determining arguments will be brought forward and illustrated with examples. One hour of labour in Western Europe represents the value of 15-20 kilogram of PVC. In China one kilogram of PVC represents nearly 4 hours of labour. So the ratio of the value of raw material to labour may very with a factor of 60 to 80. This modifies completely any concept based upon the efficiency and the output of a process for European conditions.

The value of waste

A second argument lies in the fact that in most cases waste material and especially household waste has no value in Europe. On the contrary one has to pay a steadily rising fee for its collection and ultimate disposal. Moreover, a large part of the waste is mixed so that expenses would be encurred to separate them. The Shanghai Resource Recycling and Utilization Company runs more than 400 collecting centers in the Shanghai area to which the population spontaneously brings in the waste material. The latter has already attained a high grade of preselection and is being paid for on the basis of its weight. Each center has a paper baling press to compress some of the materials. The later are transported to the factories, generally by simple means (cart, bicycle, ...). Further selection is of course much simplified by this pre-selection. Once more the ratio of the raw material to labour cost plays an important role in the profitability of the process.

Waste separation

As far as the plastics are concerned, the relatively straight-forward structure of the market facilitates the selection. In Europe composite and sophisticated articles, such as complex fibres, multiple extrusion items, multicolor products, fibre composites, multilayer synthetic leather, old shoes and copolymers makes a really comprehensive selection illusive.

Furthermore, because of the use of a variety of additives and fillers even the general purpose plastics are no more recognisable by simple inspection and are not separable by usual physical methods.

In China one can usually still separate the different families of plastics after visual inspection. However there remains a variable quantity that is mixed or polluted by small quantities of other materials. Separation of completely mixed domestic waste, an acute problem in Europe, will probably not be of immediate interest in China.

Pollution and working conditions

To understand the further development of the discussions we have to emphasize the very high sense of responsibility of the Chinese authorities and population regarding the problems of ecology, air and water pollution, occupational safety, and maintenance of the equipment in suitable working conditions.

The present situation in the recycling plants visited is such that no adequate solution can be given with relation to many of the problems which were submitted to the experts. The experts gave of course as much advise as possible but they know that the improvements they proposed are only temporary and inadequate having in mind the obsolete and out of date processes used. Most of the time the improvements would necessitate investments that are completely unjustified, because they are not in a harmonious proportion with the present value of the xisting assets.

Some of the processes used have been given up recently because of pollution or adverse working conditions. Other processes will undoubtedly follow in a very near future.

One can only approve of such decisions and admire the courage that is needed to take such humanitarian resolutions under difficult economic circumstances.

The pilot plant

In every case and especially under the present circumstances the decision not to install a ready to use plastic recycling line can only be ap voved of. This line, developed in Europe and exclusively taking into account Western living styles, social circumstances and economic situations is less suitable under Chinese economic and working conditions.

So the installation of a pilot plant to develop an adapted process, designed for local raw materials and operating conditions is certainly justified.

Furthermore, following arguments militate in favour of a prospective view for the development of an own specific technology adapted to the local requirements

- the extremely rapid development of the local economy and the subsequent changes in social conditions would render obsolete in a very short time a Western style line even if it could be adapted temporarily
- it is foreseen that the material/labour value ratio will evolve rapidly changing the conditions of efficient operation of any process
- the strictness of safety and sanitary regulations is augmenting rapidly
- air, water and soil pollution problems are increasing rapidly due to steady industrialisation so that some polluting processes will have to be eliminated.

All arguments are in favour of a pilot plant where local technology can develop and mature to an own appropriate process.

Once this obvious option is taken the next matter of discussion concerns the best adapted and most essential indispensable equipment needed for the pilot plant to allow a first research programme to be started. There is also the condition that the equipment is adapted as well to present needs as to future development.

In November '84 the Chinese Authorities organised an "International resource recovery and utilisation seminar" at Shanghai in order to be prepared for further discussion and study and to have at their disposal the necessary data and arguments regarding technology for future use. Companies all over the world that produce plastic recycling equipment have been consulted and study forums have been organised to test the efficiency of the different processes proposed. One of the delegation was visiting Belgium in '82, whereas one of the experts (Prof. Patfoort) was invited to demonstrate the Belgian realisations of industrial waste recycling in Andenne and the Intradel plant in preparation near Liege.

After this methodical preparation by the Chinese counterparts it is evident that the present discussions at Shanghai took place with full knowledge of the facts.

Industrial and domestic plastic waste

In Europe, as in China, one can divide plastic waste into two main categories : industrial and domestic waste. Normally the former category is not or only slightly mixed or contaminated. In case the latter category has been selected or separated it is assimilated to industrial waste. Two main problems are of fundamental importance in recycling :

- preparing the waste products of different form and shape (film, foam, big items), so that they can be accepted by a recycling machine. Often size reduction and densification and cleaning and drying are necessary
- plastifying and pelletising

The experts explained the different possible methods of separation, size reduction, plastification and pelletising.

Choice of equipment

Following the Chinese Technologist assisting to the meeting the two prevailing arguments determining the characteristics of the desirable equipment are the following :

- at present there is already a quantity of mixed plastic that is difficult or cannot be separated. This quantity will eventually augment in the future with the increased use of plastics in households and in packaging. These plastics generally present difficult separating problems and a method has to be found for reuse of these high value materials
- in the future items made of recycled material will come back a second or more times in the recycling cycle. Each time a plastic is processed the material is submitted to a thermal stress that depends on temperature and time. These stresses are additive and induce various degradation phenomena. It is essential that the residence time at high temperature of the plastics in the machine is reduced to a minimum.

The plastifying machine

To the opinion of the local technologist the only plastic recycling machine fullfilling these two conditions is the plastifying machine of the F.N. Company in Belgium. The Chinese delegation in Belgium (1982) was present during experiments to make polymer alloys with very high P.V.C. content mixed with other high melting point materials. These mixtures had never been accepted for testing with any other machine. The experts explained the scientific basis of this rather unusual behaviour of polymeric material in this equipment.

The second argument was also to the advantage of the F.N. plastifier the"hot"residence time in extruders of the order of the minute and even several minutes in other plastifier machines. In the F.N. machine this residence time is reduced to 10-20 seconds. It is immediately evident that the number of recycling cycles compatible with a good material quality is augmented in the same ratio.

So it was decided by the Chinese technologists that as well for present as for future development this equipment would fullfill the requirements of the pilot plant for the purpose of plastifying recycling.

Auxiliary equipment

As far as size reduction, cleaning and drying, transportation and packaging is concerned, local technology should prevail, It is the task of pilot plant to develop a complex line with auxiliary equipment, adopted to local needs but with lower investment costs. Chinese industry is already manufacturing similar equipment such as cutters, rotating separators, drying equipment, so that this solution is viable.

Micronising

Although the local counterparts are perfectly capable of providing a plastics cutter, it seems necessary to include in the project the acquisition of a microniser of a very new design. It has a rapid rotating action and a pulverising effect on hard materials such as glass and thermosets, which may be mixed with the plastics and incorporated in the final product, more or less like a filler. Hence this microniser is an essential and even inevitable tool in the recycling line; its action cannot be substituted by manual work or other mechanical equipment. This microniser also reduces the plastic material to very fine and dense particles and permits to

eliminate any contamination that could damage the plastifier screw. The plastifier is provided with a sieve and followed by a hot pelletiser that reduces the thermal stress on the material.

Conclusions

In anticipation, plans were developed for the completion of the line and investment funds are foreseen. For a final determination of the line and a more detailed analysis of materials to be processed and site plans are necessary and should be prepared by the counterparts, in collaboration with one of the experts. Still, testing with manual feeding can begin as soon as the machine would be installed at Shanghai. It is concluded that the selected plastics and also the high value engineering plastics can be processed on the FN-machine with the required efficiency and much shorter residence time , than is possible on classical or competing equipment.

The problem of PMMA (poly methyl metacrylate), that can be selected easily and has a high commercial value will be dealt with separately, the solution to this problem depending on a completely different process.

2.3. The PMMA Problem

Right from the beginning of the visit the Chinese counterparts had expressed keen interest in the experts' opinions, comments and advice on various practical topics, which are directly and indirectly related to the recycling of plastics.

A list of four important problems was presented on Friday, 23 August , and illustrated and commented upon during the various plant visits. The experts have replied to all the questions of the counterparts during the various discussion sessions.

One topic was singled out for further actions i.e. the PMMA pyrolysis.

The pyrolysis of PMMA is conducted according to a local process which for various reasons is highly inefficient and cumbersome. The extremely low yield of the process, currently about 48 %, in the opinion of the experts could at least be raised to the Western value of 80 % and possibly to an even higher yield.

In a view of further study a number of detailed data on plant engineering and operation as well as actual product samples were collected.

The local PMMA problem could be solved on the basis of the next programme for one of the experts

1. survey of relevant scientific and patent literature
2. experimental confirmation of the monomer yields at various operating temperatures, in the range of 350 to 550 °C, and for various addition rates of diluent
3. Preparation of a report on these findings
4. Preliminary design of a new pyrolysis plant, featuring continuous operation.
5. submitting the design data to SRRUC and help in finalising the new plant lay-out and construction.

The experts are confident that the problems experienced at SRRUC can be solved on the basis of the process flow sheet and operating procedure proposed by the Unido experts.

Please find a project proposal relative to this work in Annex VI.

Conclusions

The PMMA-unit described in Annex V attains a pyrolysis yield of only 48 %, against 80 % for even the simplest Western units. The development of a new continuous process based on the existing expertise would allow SRRUC to construct a new pyrolysis plant locally and attain much higher product yields.

The preparatory work required is described in a project proposal (Annex VI)

Acknowledgement

The experts like to express their deep gratitude to the Secretary and Manager and Staff of the Shanghai Resource Recovery and Utilization Company for the excellent preparation of the programme, the most pleasant atmosphere in which the mission took place and the exceptional hospitality they have shown.

Further aid is acknowledged from Mr. Sissingh, the S.I.D.F.A. at Beijing, and the Services of the Chinese Ministry , which took care of the organisation of the arrival, departure and accomodation at Beijing.

ANNEXE I

Background Information

Since 1971 intensive research has been performed in the CRIF laboratories in Liège, Belgium, on polymeric alloys. These alloys are essentially very finely divided emulsions obtained by intensive mixing of polymers in the molten state and stabilised by cooling.

To obtain a high quality mix of a very viscous polymeric liquid with a very short residence time in the heated state, a special device has to be used.

A theory of polymer mixing was worked out and a device invented by Prof. Patfoort and developed to a pilot machine in the CRIF laboratories.

Since the energy crisis, the study of the fabrication of polymeric alloys from mixed plastics waste was emphasized. Since 1977, the licence was taken over by the F.N. Industry in Herstal (Belgium), and the process was developed to a complete plastics recycling line also suitable for single component granulation with minimum residence time of the material in the machines, an absolute necessity for repeated recycling.

A Chinese delegation with a delegate from the Worldbank and Mr. Youssef from UNIDO visited Belgium on 13 May 1983. The study tour included a visit to the pilot plant of the F.N. Industry in Herstal, the municipal waste recovery plant in Liège that became fully operational in November 1983 (this plant is the EEC pilot unit), and the factory for industrial waste recovery in Andenne (all types of plastics waste).

Results of recent practical experiences are as follows:

- Polymer alloys can be obtained easily with the existing machines as well as from domestic and from industrial waste. Of course, the properties of the alloys are dependent from the composition and the origin of the components;

- A detailed study has to be made in relation with transport, selection, availability and quality of the plastics waste to determine the feasibility of the operation in each case;

- As an example, it takes two years for a factory like the visited Andenne type, to write itself off working with industrial waste. In the case of domestic waste a lot of non-technological operational factors have to be taken into account.

For this purpose, SCRUM (Shanghai Company of Recycling and Utilizing of Materials) requests the visit of two experts to discuss the problems regarding the establishment of a pilot plant for recycling and utilization of plastics waste.

ANNEX II

LIST OF THE MOST PROMINENT CHINESE COUNTERPARTS, WHO ASSISTED TO THE FINAL DISCUSSIONS ON THE PROJECT ON AUGUST 27

Li Bingzhang	Manager	SRRUC
Guo Yongkang	Deputy Section Chief	Foreign Economic Relations Shanghai Supplying & Marketing Cooperative
Zhang Dexing	Deputy Section Chief	SRRUC
Yuan Yong ling	Manager	Nashi District Branch, SRRUC
Guo Bangda	Technician	Nashi District Branch, SRRUC
Liu Paoping	Deputy Director Technician	Xinguang Plastic Factory, Nashi District Branch
Ye Liuying	Deputy Director Assistent Engineer Branch	Xinguang Plastic Factory, Nashi District
Lin Xuenong	Manager	Zhapei District Branch, SRRUC
Hu Deyu	Deputy Manager	Zhapei District Branch, SRRUC
Li Weigi	Technician	Zhapei District Branch, SRRUC
Huang Jianging	Chemical Engineer	SRRUC
Zhang Guochang	Interpreter	SRRUC
Chen Oiuying	Interpreter	SRRUC
Zhang Yiansiao	Interpreter	SRRUC

LIST OF THE PRINCIPAL CHINESE MANAGERS, WHO HOSTED VARIOUS PLANT VISITS

Yuang Yongling	Manager	Nashi District Branch SRRUC
Dai Oinghua	Manager	Nashi District Branch SRRUC
Guo Bangda	Technician	Nashi District Branch SRRUC
Liu Baoping	Deputy Director Technician	Xinguang Plastics Factory
Ye Liu ying	Deputy Director Assistant Engineer	Xinguang Plastics Factory
Jiang Fuging	Director	Xinlian Plastic Products Manufacturer
Liu Xuekong	Manager	Zhabei District Branch, SRRUC
Liu	Director	Huguang Plastic Products Manufacturer
Zhu Changsheng	Deputy Director	Ligong Plastic Products Manufacturer
Li Weigi	Technician	Zhabei District Branch SRRUC
Sun Yongsie	Manager	Recycling Center of Zhabei District
Hu Zhanhuei	Manager	Rubber, plastics & Miscellaneous Department, SRRUC

ANNEXE III

PROPOSED PROGRAMME FOR THE STUDY VISIT OF THE BELGIAN EXPERTS IN SHANGHAI

Aug. 23 Friday	
10:20	Experts arriving in Shanghai The leader of Shanghai Resource Recovery & Utilization Company meeting the experts at the airport.
12:00--13:30	Luncheon
16:00--17:00	The leader of SRRUC briefing on the recycling practice in Shanghai at the hotel Discussing the proposed programme
18:00	Welcome banquet
Aug. 24 Saturday	
8:30--11:30	Site-visit to Xinguang Plastics Factory
12:00--13:00	Working lunch
13:15--17:00	Visiting Xinlian Plastic Products Manufacturer Visiting the Nanshi Waste Plastics Supplying Station
Evening	Open
Aug. 25 Sunday	
8:30--11:30	Visiting Yan'an Dong Road & Sichuan Waste Purchasing Station
12:00--13:30	Lunch
13:30--16:30	Touring Shanghai's Town God's Temple--Yuyuan Garden & Jade-Buddha Temple
19:00	Performance
Aug. 26 Monday	
8:30--11:30	Visiting the Huguang Plastic Products Manufacturer
11:30--13:00	Working lunch
13:30--16:30	Visiting the Rubber, Plastics & Miscellaneous Scraps Business Department, SRRUC
Evening	Open
Aug. 27 Tuesday	
8:30--11:30	Prof. Patfoort [illegible]

	Plastics Factory Dr. Beukens visiting the Recycling Center of Zhabei District
12:00--13:00	Working lunch
13:30--16:30	Prof. Patfoort same as forenoon Dr. Beukens visiting the Nanshi Paper Stock Supplying Station
Evening	Open
Aug. 28 Wednesday	
8:30--11:30	Prof. Patfoort working in Xinguang Plastics Factory Dr. Beukens visiting the subordinate unit
11:30--13:00	Working lunch
13:30--16:30	Discussion with the leader of SRRUC on the existing problems in waste plastics recycling with suggestions for follow-up works to carry out the UNIDO Co-operating Project
Evening	Open

ANNEX IV

AGREEMENT PROPOSAL BETWEEN SRRUC, FN AND UNIDO (DRAFT)

Following agreement proposal was submitted to the management of the Shanghai Company, to the FN Company and to Unido.

The Shanghai Material Recovery and Utilisation Company wants to set up a pilot plant and laboratory to develop the technology of recycling and recovery of plastics.

In view of this development they want to install a short screw plastifier from the F.N. company in Belgium.

Materials and mixtures will be tested, technicians exchanged and an agreement would be important between the Chinese and Belgian pilot plant "Intradel" in Liège to exchange their experience and future developments.

However the Shanghai Material Recovery and Utilisation Company is aware of the intellectual property of the machine to the F.N company where the machine has been developed and agrees not to publish common results without previous agreement and not to copy, duplicate or sell machines of the F.N. type nor give information to other companies to facilitate their fabrication or commercialisation. A licence for realisation of machines and recycling lines in China would be desirable in the future and could be discussed later on between the two companies.

Unido would agree to provide the facilities of communication between the two companies and to assure the good working of their agreements.

Annexe V

CHRONOLOGICAL REPORT ON THE MISSION

Monday, 19 . August

- Arrival at UNIDO Headquarters in Vienna
- Briefing by Mr. May and Mr. Youssef. Contacts with Mr. Van Hellemont about the Belgian involvement in the project
- Consultation of Files on former projects in the People's Republic of China and on Operating Conditions and Practical Information regarding this country.

Tuesday, 20 August

- Discussion with Mr. Youssef regarding the available means alloted to the project and the possible uses of these funds, amongst other things, regarding
  1) the training of Chinese technicians in Belgium
  2) the economic evaluation of the process by Chinese experts
  3) the dispatching by air mail of Chinese samples to the Intradel processing plant
- Leave to Beijing

Wednesday, 21 August .

- Arrival at Beijing Airport. Experts welcomed by Representatives of the competent Chinese Ministry, the direct counterparts, Shanghai Resource Recovery and Utilization Company , further abridged to SRRUC not being represented in Beijing
- Installation at the Hua Du Hotel

Thursday, 22 . August

- Received at the UNDP offices by Mr. A. Slesingh, SIDFA, who confirmed the keen local interest in the project and the efficiency of local counterparts

Friday,23 August

- Flight to Shanghai-Welcomed by the Manager of SRRUC, Mr. Li Bingzhang, accompanied by technical staff and interpreters
- Installation at the Peace Hotel
- Luncheon together with the SRRUC-team
- Presentation of the proposed programme. After expression of their keen interest in a rapid realisation of the pilot-plant program and of some disappointment regarding the brevity of the experts' visit the following items were submitted for consideration by the experts :
  1) the low yields attained in the recovery of PPMA
  2) the quality problems (ageing, darkening of the colour) of recycled plastics
  3) the sorting of mixed plastics
  4) the environmental problems associated with the processing of nylon and phenol-formaldehyde resins.

The experts agreed to analyse these problems and propose a further course of action.

Welcome Banquet at the Friendship Shop

The original program, as prepared by the Chinese counterparts, is given in Annex III. This program was slightly adapted later, in order to introduce more room for group's work and discussion.

Saturday, 24 August

Visit to the Xingguang plastics recycling factory. Installed power : 420 kvA, but total requirements are higher. Two firetube boilers, generating low pressure steam with coal as a fuel.

Preliminary Discussion on the local production of plastics, the generation of waste plastics, the internal recycling in the factories and by plastics processors, as well as the recycling activities of SRRUC. Essentially all industrial plastic wastes and a sizeable amount of postconsumer wastes is being recycled, in part by SRRUC for industrial wastes and solely by them for postconsumer wastes. The main difficulties identified are :

- the characterization and manual sorting of the plastic wastes
- the recovery of relatively minor quantities of ill-known engineering plastics
- the recycling of thermosets (at present burnt in the open air).

Three sources of raw materials have been identified :

- plastic wastes, arising in factories
- plastic wastes, arising during conversion of plastics
- plastic wastes, delivered to the collection centres of SRRUC by private individuals, small shops and workshops

During the visit to the plant the following activities were observed :

1. PVC recycling

- the PVC-scrap processed was mainly of industrial origin and supplied in relatively modest unit quantities (in baskets, bags, sacks, etc), but to a minor extent also consisted of hand sorted, multi-coloured PVC-film, packaged in PVC-bags. The scrap was plasticized using three 400 mm double-roll mills, operating at 160 - 180 °C. Each unit is capable of plasticizing about 20 kg of waste in one quarter of an hour. A paste of additives, composed of plasticiser, lubricant, colorant and stabilizer is added in the process, which yields a strip of more or less even coloured soft PVC. The latter is cut to smaller strips (with a cross-section of 25 x 5 mm) by means of a rotating blade.

The latter are reprocessed by means of locally made extruders featuring a screw (L/D between 10:1 and 15:1) with an improved profile and a set of manually operated strainers. Finally the resulting strips are granulated by another set of extruders, yielding pellets of a relatively uneven shape after cutting to pieces of the air cooled extrudate.

Observations and comments

The experts have to recognize that considerable care is taken for the identification, sorting and grading of the material, part of which is washed with water or alkali solutions and dried. Moreover, aged material is also rejected.

On the other hand it seems that the technology used puts a considerable thermal strain on the product, which has to be reheated several times before its conversion to a granulate, which is still fairly uneven in form, the cooling and cutting provisions being far from adequate.

Especially in case of repeated recycling a number of side-effects, such as ageing, darkening and inefficient stabilization seems inevitable, mainly because of the nature of the process used.

2. PVC Flooring

- The conversion of the PVC to flooring tiles was not in operation during our visit.

3. Nylon Recycling

- The plant also featured a manual sorting operation, in which nylon textile cuttings were cleaned from impurities, such as cotton and other extraneous materials.

The material was then processed in 4 open-end extruders, yielding a flat lump of black, solidified nylon. The operation is accompanied by the liberation of fumes, which probably consist of evaporated moisture, together with minor amounts of decomposition products.

The nylon cuttings are extruded by means of two huge vertical preheating and melting vessels. The melted material is pressurised by means of a cogwheel pump delivering a single strand of extruded material. One line is watercooled, the other cooled by blowing air on the extrudate.

Observations

Here again the process used is ill-adapted to the necessity of limiting hydrolysis and degradation of the nylon. It seems desirable to dry the nylon, prior to its submission to a treatment at high temperature. This would not only reduce its loss in mechanical properties but also curtail the pollution of the working atmosphere by vapours.

4. PMMA pyrolysis and polymerisation

The plant converts the cast-quality of PMMA to monomer by a batch pyrolysis process. The PMMA of Chinese origin, or imported from the U.S.A., is chopped or cut to pieces and charged in a cauldron, lined up in a battery of eight. Each cauldron is heated by a separate coal fire. The temperature of the fire and inside the cauldron is not measured. The material is melted and heated, so that monomer vapours are distilled off and condensed by tubular coolers. The condensed product is collected in small, individual vessels for intermediate storage, from which they are discharged to a large, central vessel. Both are located, for safety reasons, outside the pyrolysis building.

The crude monomer is subsequently batch distilled in a steam jacketed boiler, fitted with a packed rectification column (∅ = 25 cm). Some low boiling impurities are removed. The monomer is agitated with saturated brine to coagulate some suspended material.

A second distillation takes place at a reduced pressure, so that the boiling point is lowered to 61 °C. After elimination of the residual moisture the monomer is distilled off and its quality is verified by means of gas chromatography.

As a next step the purified monomer is prepolymerized in a stirred tank reactor operating at about 90-94 °C, until the desired viscosity is attained. The reactant content is then cooled.

After colouring the material and removal of enclosed air bubbles the material is again polymerised in between two sheets of glass (moulds of 60 x 75 cm). A set of moulds is vibrated in a water cooling bath, until the polymerisation is complete.

Finally the plates of PMMA are stress relieved by reheating and released.

Observations

The engineering and operation of these locally made units show a good craftsmanship and ability, but still lead to utterly disappointing results. Hence, considerable emphasis was placed on the local desire to have these problems examined by the experts.

The main problem is the low yield, attained by the process. Charging
100 kg of PMMA
75 kg of pyrolysis oil
60 kg of crude monomer
48 kg of pure monomer are obtained.

In the opinion of the experts this yield could normally be doubled.

Moreover there are a number of operating problems, some of which are rather serious :

1) the cauldron is overheated by the coal fire in an uncontrollable way. Each month its bottom has to be replaced
2) part of the material is carbonized, forming a layer on the bottom of several cm. This further impairs heat transfer and leads to further overheating of the bottom and the charge
3) the temperature distribution and residence time in the cauldron are uneven and uncontrollable, which leads to the occurence of side reactions and lower yields
4) the excessively low yields render the distillation more complex than necessary and lower the final purity of the product
5) in case the operating temperature during prepolymerisation is not observed useless "blow material" is formed
6) the release of the PMMA plate from the glass mould is sometimes problematic
7) the intrusion of water or the appearance of bubbles is too frequent.

On the basis of their observations the experts have proposed a course of action, involving a redesign of the pyrolysis unit after collecting supplemental data on PMMA pyrolysis. The course of action was accepted by the local counterparts, who are prepared to finance all equipment provided the Unido experts deliver the necessary technology and know-how.

Since this topic completely deviates from the main object of this study a separate proposal will be submitted for approval to Unido and SRRUC.

Afternoon - Visit to Xinlian Plastic Products Manufacturer

This factory converts various raw materials, namely

PMMA	10-12 tonnes/month
PS	5 tonnes/month
ABS	3-5 tonnes/month
nylon	2-3 tonnes/month

to fashionable buttons for uniforms, dresses, etc. Part of the production is metallized elsewhere. The factory has an installed power capacity of 630 kVA and uses tap water for cooling (in closed circuit), with one cooling tower .

The PMMA-buttons are manufactured according to the following process :

1) punching of PMMA-plate
2) polishing the back-side
3) stamping of the design
4) polishing the front-side

The PA-buttons are made in the following sequence :

1) drying of the PA
2) injection moulding of sets of generally 6-8 buttons
3) drilling holes in the buttons
4) drying by means of appropriate solutions
5) inspection.

Observations

All buttons inspected had a very attractive appearance. The injection moulding of nylon, PS and ABS still makes use of plunger-type injection machines, made in China. This type of equipment is obsolete and fairly improductive. The amount of rejects is impressive, possible because of an inadequate design of the moulds or of insufficient post-pressing.

The machining of the buttons is extensive, and labourintensive.

Although this factory does not meet current Western standards of productivity there seems no urgent need for modifying operating methods or renewing equipment, because the over-all standards of quality and workmanship are excellent.

The working conditions were clean and fairly pleasant.

Nanshi Waste Plastics Supplying Station

This Waste Plastic Supplying Station started its operations in 1964. Originally it recovered only 500 tonnes/year but at present it would process 12,000 tonnes/year, a quantity which seems enormous indeed.

Of these materials 60 % originates in industry, 40 % domestically.

In 1964 only 3 types of plastics were treated : PVC, PE, PS. At present there are 10 types, namely the former + PP, HIPS, ABS, POM, PMMA , EVA, PA. Engineering plastics generally remain within the factories.

The activity of the station consists of

- the reception and grouping of plastics of industrial and domestic origin
- the storage of imported virgin plastics
- the manual sorting of industrial plastic waste (sprues and runners) according to their colour
- the manual sorting of mixed domestic waste plastics.

The material is regranulated in a separate, but nearby shop (not visited). Amongst the final outlets two applications were cited :

- foamed ceiling tiles from fire-proofed PE (?) (In the opinion of the experts the material resembled more to rubber)
- shuttles for weaving mills
- PVC drainage pipe.

The relative quantities of recovered materials are :

PVC (soft + rigid)	36 %
PE	20 %
PP	13 %
PS	7 %
ABS	7 %
PMMA	5 %
miscellaneous, including engineering plastics	12 %
	100 %

Observations

The hand sorting operations were observed and appeared to be relatively inefficient. According to the counterparts this operation is the most unpleasant and the least hygienic of all their activities. Advice was requested regarding the possibilities of mechanising these operations.

It is increasingly difficult to identify the various available qualities with the eye, touch and possibly flame tests. The plastic materials of domestic origin show a definite decrease in quality. Industrial wastes, on the contrary, have very good, steady properties.

Despite the relatively low capacity of each sorter (180 kg/sorter, 8 h-day) the operation is, according to the experts, economically justified. Some measures could be taken to increase productivity :

- avoid colour mixing at the source
- sorting of domestic plastic waste at a conveyor belt instead of around a working table. Other measures could be taken to make the working atmosphere more pleasant and hygienic, although over-all standards seemed quite acceptable already.

One of the experts (A. Buekens) promised to send data on the identification and grading methods, published in literature and from his own, earlier reports.

Sunday, 25 August - Morning

Visit to the Yan'an Dong Road Waste Purchasing Station

Visit to the Sichuan Road Waste Purchasing Station

Yan'an Dong Road Station

This waste purchasing station employs 19 people under the Direction of a Deputee Manager, Mr. Tsu. The shop opens every day from 8 a.m. to 5 p.m., only 4 days per year excepted! The total turn-over amounts to 270,000 ¥/year, which corresponds to a quantity of salvaged materials totalling 135 tonnes/year (1984 figures). Most supplies are delivered on Sundays and in the time period preceding the Festival, the moment Chinese housewives thoroughly clean up their premises.

The waste purchasing station serves a Residential Area of over 10,000 households. In their order of importance the recovered materials are : (1) paper, (2) scrap iron & steel, (3) rags & textiles (4) glass bottles.

The monthly amount of recovered plastics is 800 kg, which corresponds to a yearly salvage rate of about 1 kg per household.

The following contributions are paid per kg of accepted materials :

	¥/kg
Paper : newsprint	0.30
mixed paper	0.11
Plastics : average	0.20
PVC - industrial arisings	0.90
- household arisings	0.16
PE - white industrial trimmings	0.60
- mixed colours	0.40
PS - first class (mixed with ABS)	0.60
- second class	0.30
PMMA - industrial arisings	1.90
Rubber : 1st quality	0.467
2nd quality	0.36
3rd quality	0.20
Textiles : cotton	0.22
synthetic fibre	0.10
Animal bones	0.12
Glass bottles (reusable)	0.08
(broken)	0.04
Metals : raw iron	0.19
tin cans	0.22
steel plate	0.145
iron parts	0.05
copper (red)	4.7
(brass)	3.6
toothpaste tubes	0.01/tube
Clothes, dresses	according to the quality
Shoes	0.01/shoe

Furniture and wood can be supplied to a different company

Human hair is no longer accepted (although it probably is recuperated elsewhere).

The paper is baled in a double action press. Glass bottles, bones, metals, plastics are packed in various types of sacks. The iron & steel fraction is supplied to Shanghai steel plant number 1 and 10, the plastics to the Nanshi Waste Plastics centre. Clothes are sold to the villages. Most of the material being offered seemed in a good shape. Apparently actual Chinese youths have become fashion-conscious, a tendency which was actively discouraged in former times!

It was stated that 15 % of the turnover is handed over as a "cash-flow" for the collection station. On a basis of 270,000 ¥/year, this would amount to some 40,000 ¥/year. In view of the limited operating cost (renting of the premises, depreciation of the rather elementary equipment) and the low wages (order of magnitude of 1.000 ¥/person,year) this collection station looks like a high-profit operation!

<u>Sichuan Road Waste Purchasing Station</u>

This second waste purchasing station was smaller in size and not very busy at the time of our visit (late Sunday morning). On the other hand it had excellent records, as followed from a number of placards and trophies, obtained for excellent service. We were greeted by the Shop Manager, who was a lady and showed around. A prominent article, stored under cover because of its smell, were chicken plumes.

<u>Afternoon and evening Program</u> (organised by Tl SBr)

A visit was paid to two important local Buddhist temples and the famous Yuyuan garden.

The Evening Program consisted of a boat excursion on the River Huang-Pu, which allowed to get an impression of harbour activities and heavy industry, situated along the river.

<u>Monday, 26 August</u>

<u>Morning</u> : visit to the Huguang Plastic Products Manufacturer

This factory can be characterized by the following figures :

- fixed assets of 400.000 ¥
- surface of 7,260 m^2
- 150 staff members.

It has two activities :

- waste materials, arising in the manufacturing of synthetic leather are handsorted, crushed and hot pressed in a multi-storyed press, in which the colour sorted material is heated for 5 minutes, then cooled for 20 minutes. Apparently the heating and cooling medium is distributed by means of the same manifold. The final product is a handsome, multi-coloured square PVC-panel of 1 m x 1 m, used for decorative purposes and flooring No filler is added, but stearic acid is used as a releasing agent
- the production of a phenol-formaldehyde polycondensate, to be mixed with cotton cuttings and trimmings, collected by the waste purchasing stations.

The polycondensate is manufactured in the aqueous phase using a reaction vessel, fitted with a condenser. The impregnation takes place in a series of tumblers.

The following <u>problems</u> were submitted for the attention of the experts :

- the production of PVC plates heavily relies on hand sorting. No methods are available for eliminating the fibres. During the pressing there is evolution of gaseous HCl. Moreover the manufacture of 1.5 m^2 of sheet would require an incredibly high amount of 7-10 kg of coal!!
- the production of phenol-formaldehyde polycondensates give rise to minor quantities of phenol containing wastewaters, which are considered to be unfit for discharge
- the emission of fumes leads to condensation on the ceiling and the dripping of condensate onto the workpeople, causing skin irritation as well as troubles of the respiratory system.

<u>Observations of the experts</u>

The experts have replied that

- the evolution of HCl can be diminished by a more accurate control and (especially) a lowering of the pressing temperature. Other measures include a regular removal of small pieces of PVC, that lay on the pressing tables, without actually being pressed.
- a more sophisticated ventilation system of the workshop in principle would solve the problem of condensation. This method is being applied, int.al., above papermaking machines. The cost of such a system would, however, be prohibitive in this context!
- regarding the phenol-formaldehyde impregnation units (2, in separate buildings) it was concluded that this technology is obsolete. Nowadays, only solid resin powders (possibly under a pre-pelletized form) are used. The filling with wood flour or textiles is conducted in automated roll mills.
- the phenol could be removed from the wastewater using a liquid/liquid extraction unit with aromatics (toluene,e.g.) as an extraction agent. Such a unit would yield a purified effluent, together with a phenol-solution in toluene. As an alternative active carbon adsorption can be used, or the (relatively small amount of) wastewater evaporated.

<u>Afternoon program</u>

visit to the Rubber, plastics & miscellaneous scrap department

relevent figures :

workforce of 517 people
40,000 m^2 of surface available
5,560 m^2 of warehouse

chief activity : recycling of waste tyres and other rubber scrap, including old rubber boots

the amount of materials reworked would attain 70,000 tonnes, part of which is reprocessed elsewhere (e.g. the rethreading of tyres)

the scrap rubber is cleaned, finely crushed in double roll mills with a corrugated hard surface; after addition of plasticiser (oil), the rubber powder is thermally devulcanized in autoclaves and compressed to sheets of rubber reclaim. The yearly production of 30,000 tonnes/year is reused in rubber industry

tyres are skinned and peeled, yielding sheets of (vulcanized) rubber, which are measured and cut to pieces of standard size. The later are eventually converted to protective soles, fittings for spinning & weaving mills, rail gaskets, etc (4,000 tonnes/year)

another 9,000 tonnes/year is used as a raw material in mining and other industrial enterprises.

<u>other activities</u> collection of PVC fil (300 tonnes), trimmings (170 tonnes), thermoset plastics (100 tonnes). All figures relate to 1984, the first year of operation

2 lines of a Chinese design convert cotton-based materials to non-woven of a superior, white quality.

<u>late afternoon</u> : split Program

Prof. Patfoort gives a lecture on the technological aspects of the short screw extruder

Prof. Buekens paid a visit to the Recycling Centre of Zhabei District.

In this centre iron and steel scrap is gathered from about 500 factories, as well as from some 60,000 households.

The annual capacity attains 10,000 tonnes, which corresponds with a turn-over of 15 million ¥ . The annual operating profit amounts to 1/3 of this figure !

The activities consist of :

- manual sorting and simple mechanical processing (with small shears, by flame cutting, etc)
- mechanized baling of swarf, turnings, punchings, etc by means of hydraulic presses.

Handling was based on manual conveying (carts), cranes with a fixed magnet & mechanical discharge, conveyor belts, etc.

Observations

The only unusual features were :

- the cutting of structures with a flame torch, with the aim of recovering reusable profiles, tubes and parts. The latter are sold in a small local shop (or elsewhere)
- the treatment of relatively small arisings in a labour-intensive manner.

No particular problems were submitted for the attention of the experts. The baling presses were relatively highly mechanised. It was stated they were made locally and no longer up-to-date, but no indications of malfunctioning or loss of efficiency were apparent.

Tuesday 27 August

Group discussions on the Unido-project at the Recycling Centre of Zhabei District.

Wednesday 28 August

Group discussions on the Unido-project and the PMMA-pyrolysis proposal at the Xinlian plastic products factory.

End of the afternoon : Visit to the Nanshi Paper Stock Supply Station

During a fairly brief visit it was observed how the wastepaper was delivered, distributed over several parallel series of manual sorting lines, trommelled and baled. The main qualities set aside by manual sorting are books and comparable qualities of printing papers on one hand, contraries such as ribbons, plastic film and other extraneous matter on the other hand.

The trommel, used to screen off dirt and fines, may be regarded as a modern and technically efficient way to tackle this problem.

Some off-grade paper was reused on a basis of thorough manual control, combined with a subdivision using guillotine shears. The resulting piles of quality-sorted paper is bound together to notebooks and similar articles.

Thursday, 29 August

All important business being concluded .the last day in Shanghai had a more informal character, with a morning walk in a famous garden, a Farewell Banquet, followed by transfer to the Airport.

Flight back to Beijing, where no hotel accomodation was available. The experts were lodged at the UN Office, nearby the Great Wall Hotel.

Friday 30 August

Discussion of the results of the mission with Mr. Sissingh, who had taken arrangements for confirming the flight back. Mr. Sissingh showed interest in the addition of a PMMA-project as an Annex to the mission.

No further activities for the rest of the day.

Saturday, 31 August

Discussion with Mr. Sissingh on the working conditions in China and their evolution over the last few years. Further advice by Mr. Sissingh regarding future contacts, mail and other matters of practical interest.

Flight back to Vienna

Sunday 1 September

No activities

Monday 2 September

Visit to Unido Headquarters

Reporting to Mr. Yussef, Mr. May, and Mr. Van Helleputte.

Annexe VI

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

PROJECT PROPOSAL

PART A - BASIC DATA

COUNTRY: China	PROJECT TITLE: Development of an improved PMMA Pyrolysis system
PROJECT No:	UNIDO CONTRIBUTION: US$ 31,000
SCHEDULED START: as soon as possible	GOVERNMENT CONTRIBUTION US$ 300,000
SCHEDULED COMPLETION : 6 months later	CURRENCY REQUIRED FOR UNIDO INPUT:
ORIGIN AND DATE OF OFFICIAL REQUEST:	
GOVERNMENT COUNTERPART AGENCY: Shanghai Resource Recovery and Utilization	UNIDO SUBSTANTIVE BACKSTOPPING SECTION:
PROPOSAL SUBMITTED BY:	PROGRAMME COMPONENT CODE:
DATE OF SUBMISSION:	

PART B - NARRATIVE

1. Background and Justification.

The PMMA pyrolysis unit, described in Annexe V has a monomer yield of the order of 48% only, whereas in similar W.European plants 80% is attained.

If means were found to improve the technology and increase the yield to normal values SRRUC would finance all required plant modification and construction activities.

Without the intervention of the UNIDO-experts they would not be in a position to acquire the technology and know-how necessary to upgrade this plant. It is proposed that UNIDO provides the means for performing the required preliminary study. Since it is almost certain that this work would lead to success, the Chinese counterparts are most anxious to have this study started as soon as possible.

2. Special Consideration.

The expertise required for upgrading the proce[illegible], technical equipment for optimizing the PMMA pyrolysis and the design experience for converting the experimental results into the design of a small continuous plant are available at the V.U.B., Laboratorium voor Chemische Ingenieurstechniek en Industriele Scheikunde, Brussels.

Prof. Buekens, head of this department, was appointed as a UNIDO- expert for this mission.

3. Objectives.

Determine the optimum temperature, residence time and steam dilution factor in order to attain the highest yield in monomer and the lowest loss in by-products.

Propose a preliminary design for a continuous PMMA-pyrolysis plant, for approval by SRRUC.

Advice SRRUC in the detailed engineering and construction of the plant, according to the new design.

Help SRRUC in starting-up the plant and optimization procedures.

4. Project Outputs.

A new design for the present PMMA-pyrolysis plant, which will be replaced at the end of the project.

The new design will markedly increase product yield and quality. The unit will be more convenient ans economic to operate.

5. Project Activities.

- Survey of the few date (BIOS/FIAT reports) published in the literature
- Experimental optimization of the product yield at a bench-scale pyrolysis plant

  Operation temperatures: 400, 430, 500, 550°C

  partial pressure: 0,1, 0,3, 1 bar
- Preparation of a report on the experimental investigation
- Design of a new pyrolysis plant

  taking into account product yield and mass and heat transfer consideration
- Proposing the plant design to SRRUC
- Follow-up in construction , start-up and optimization

6. Project Inputs.

A. Government Contribution

The contribution of China (SRRUC) is in the detailed engineering, construction and erection of the full-scale plant

The required investment is difficult to evaluate by the experts, because of a lack of knowledge of Chinese cost factors. In Belgium the construction cost of the new plant would amount to some 30,000 U.S. $, excluding peripheral equipment and extraneous costs.

The Government of China will, in the opinion of the experts, be willing to bear this high cost because of

-a very short pay-off time of the required investment

-the possibility of locally constructing almost all of the equipment required.

B. UNIDO Contribution.

UNIDO will provide adequate funds for carrying out the necessary activities to study the present design, gather the necessary data, prepare the experimental work and prepare a new design for a PMMA plant.

This will involve

- 3 months of home-based work for one of the experts
- the necessary budget for renting the required experimental facil[illegible] , and obtained the product yields and composition under optimized conditions.
- 1 month of follow-up activities
- one visit to Shanghai

7. Proposed Evalution.

The results of the project will be easy to evaluate on the basis of the:

- bench-scale experimental results
- full-scale plant operating data

8. Envisaged Follow-up.

Although this project is self-contained and can be terminated within a reasonable time and budget it cannot be excluded that the Chinese counterparts would request to

- perform additional experimental work on other types of PMMA
- pay an additional visit to the new pyrolysis plant for further evaluation or expansion.

ANNEX I- PROJECT BUDGET.

UNIDO Constribution (Estimate)

(1)	Mission Cost to China	US $	4,000	
3	Months of expert	US $	18,000	(gross)
	Subcontract for the experimental work	US $	3,000	
1	Month of follow-up activities	US $	6,000	(gross)
		US $	31,000	

BIBLIOGRAPHY

The following references proved to be of value in the preparation of the mission:

Schenkel W., "Abfallwirtschaft in der Volksrepublik China",
Müll und Abfall 14(2), 29-36,1982

Kaufhold W., Lauer H., Koo Cheul Shin,
"Umwelthygiene in einer chinesischen Industriestadt, am Beispiel von Dalien/VR China",
Müll und Abfall 15 (12), 310-4, 1983

Tabasaran O., Shin Koo Cheul,
"Sanitärhygiene in der Volksrepublik CHina
-Eindrücke eines Kurzbesuches -
Müll und Abfall 13 (6), 142-51, 1981

Reference

Part of the relevant data were extracted from the Proceedings of the "International Resource Recovery and Utilization Seminar" Shanghai China, November 1984

ANNEXE A

MISSION REPORT OF AUGUST 1, 1986

RESTRICTED

August 1, 1986
English

PYROLYSIS SYSTEM FOR POLYMETHYLMETACRYLATE

SI/CPR/86/028/11-51/32.1.H.
PEOPLE'S REPUBLIC OF CHINA

Mission report :

Prepared for the Government of the
People's Republic of China
by the United Nations Industrial Development Organization,
acting as an executing agency for the United Nations
Development Programme

Based on the work of Alfons G. Buekens,
expert in waste recycling

United Nations Industrial Development Organization
Vienna

This report has not been cleared with the United Nations Industrial Development Organization which does not, therefore, necessarily share the views presented.

EXPLANATORY NOTES

<u>Exchange Rate</u> :

1.U.S.$ ≅ 3.5 Yuan

≅ 44 B.F. (Belgian Francs)

The following abbreviations have been used consistently throughout the text

Abbreviation	Entity or Material
MMA	methylmetacrylate monomer
PMMA	Polymethylmetacrylate
PE	Polyethylene
PS	Polystyrene
PVC	Polyvinylchloride
SRRUC	Shanghai Resource Recovery and Utilization Company
PRC	the People's Republic of China

ABSTRACT

During a brief stay in China the results of the expert's home work were presented to the Chinese counterparts of Shanghai Resource Recovery and Utilization Company (SRRUC) i.e.

- a literature and patent survey
- the preliminary experimental work performed on a bench scale pyrolysis plant
- the preliminary design of a tentative pyrolysis system and the establishment of a materials and energy balance.

During his visit to the Xingguang factory the expert was confronted with a number of environmental and production problems of this factory. Although the study of these problems was outside the scope of his mission the expert had to consider these problems carefully, as their continued presence could even compromit the very existence of PMMA pyrolysis process at the Xingguang factory, in which the proposed new PMMA pyrolysis system is to be installed.

For this reason most of the local time was devoted to these extraneous problems. Still, thanks to the excellent collaboration received from SRRUC, it was possible to achieve the results expected from this mission, i.e. to visit the PMMA workshop and collect the necessary data for the pyrolysis plant to be designed.

TABLE OF CONTENTS

Annexes

INTRODUCTION

This report deals succinctly with the preparation of the home-based work and more in detail with the results of our mission at SRRUC, Shanghai, People's Republic of China (PRC).

The purpose of the project is
- to conduct the necessary experimental work at a pyrolysis plant on a bench scale to determine and optimize of the product yield
- to design a continuous pyrolysis unit
- to prepare a report on the results
- to return visit to PRC with the proposed plant design and follow-up on the construction, start-up and optimization.

As usual, the Chinese counterparts have prepared the expert's visit in detail :
- Annexe I shows the "Outline of the Technical Discussion with the UNIDO-Expert"
- Annexe II lists the detailed programme of the UNIDO-Expert.

From Annexe I it follows that the Chinese counterparts desired to consult the expert on
(1) the Thermal Cracking Procedure
(2) the Purification Procedure
(3) the Polymerization Procedure.

Moreover, special attention was to be paid to the environmental and occupational safety aspects of the existing and future PMMA-plant.

Annexe III lists the main results of this mission, i.e. the design requirements of an improved PMMA Pyrolysis system, according to SRRUC specifications.

Although the present mission will basically be completed within the projected timing and budget, the possibility of extending this programme so that it also covers the purification, prepolymerization and polymerization of MMA, should be contemplated. A formal request for such an extension will probably be filed by SRRUC.

RECOMMENDATIONS

1.It is recommended, in a first phase, to improve the operating standards of the existing plant. In a second phase, SRRUC will construct a new plant according to the most modern technology and based on a design from the UNIDO-expert.

2.It is desirable that the collaboration between SRRUC and UNIDO would be continued. Several possibilities for such a further collaboration can already now be identified within the Xingguang factory.(These are listed in Annexe IV)

3.It is desirable that full attention be given to the environmental problems of the Xingguang factory, as well as to a gradual improvement of equipment and operating standards.
This could be a further objective of UNIDO-aid to SRRUC, with both short-term and long-range actions.

I. THE PMMA PYROLYSIS UNIT AT XINGGUANG FACTORY

A. Survey

The PMMA Pyrolysis Unit can be subdivided into :
(1) the raw materials' reception and sorting area
(2) the pyrolysis cauldrons battery
(3) the storage of crude MMA
(4) the distillation/rectification units
(5) the prepolymerization step
(6) the polymerization step
(7) the quality control and packaging department.

All of these operations are now briefly considered from the following viewpoints
- technical basis
- efficiency and yield of pyrolysis
- environmental aspects
- occupational safety and hazards.

More detailed consideration should be given to these points, during a future extension of the project according to the listing in Annexe IV.

B. Raw materials Reception and Sorting

The raw material of the pyrolysis plant can be subdivided into
a) shavings from a PMMA-button making factory at Shanghai (bulk density 80 kg/m^3)
b) trimmings from PMMA plates (bulk density 600 kg/m^3)
c) mixed PMMA-wastes acquired in the USA, Italy, etc.

In the new pyrolysis plant the feed material will mainly consist of (a) and (b) in a 60/40 relationship.
It follows that the bulk density is very much variable, but also that part (c) of the product is rather unpredictible in composition, size and quality.

For this reason the existing method of sorting material (c) was observed and found to be grossly inadequate. The following suggestions were made to improve the sorting procedure :

a) to sort the PMMA upon a long (3 to 4 m) sorting table with a convenient height and fixed with side walls to retain the product, rather than on a raw, concrete floor as done at present.

The table should be long enough to receive the contents of at least 2-3 jute sacks with PMMA, as well as to accomodate a series of containers receiving the PMMA and the various contaminants (PE, PVC, PS, acrylics,...). The table should also serve as a transfer station, to load the selected PMMA raw material into large, conical plastic buckets (100L or more), which would make furnace loading easier.

2) injection or extrusion types of PMMA have a higher market value than cast qualities. Hence, it should be verified whether the former can be sorted out and whether they effectively command a higher market price at Shanghai.

Moreover, extrusion types are relatively rich in copolymers, which form a source of by-products during pyrolysis and, hence, a problem in purification.

3) productivity would be much enhanced by providing better operating conditions for identification of unknown plastics. A small testing table, installed off-line, would allow to have doubtful products identified by the most experienced sorter, on a basis of sound, burning behaviour, hot soldering iron test, etc. A test procedure was explained to differentiate between PMMA and other plastics.

4) especially the plastics, acquired commercially, have a fairly uneven and unpredictable quality. A bag from Italy contained easily recognizable foreign plastics, e.g. PE-flasks, which do not contribute to the monomer yield and may cause obstructions in the ducting. Moreover, the dirt and dust which is obviously present may very well contribute to a decrease in product yield and quality and enhance carbonization.

As a general conclusion it can be stated that sorting should

1) take place in better working conditions, and allow to extract higher-value PMMA-types, and to eliminate dirt and unknown materials more systematically

2) be accompanied by a more thorough testing of unknown and extraneous materials, which decrease the product yield and purity.

It could be advantageous to wash some of the raw materials to eliminate dust, dirt and floating plastics. After washing, air drying is required, but storage time seems adequate to eliminate all adhering moisture.

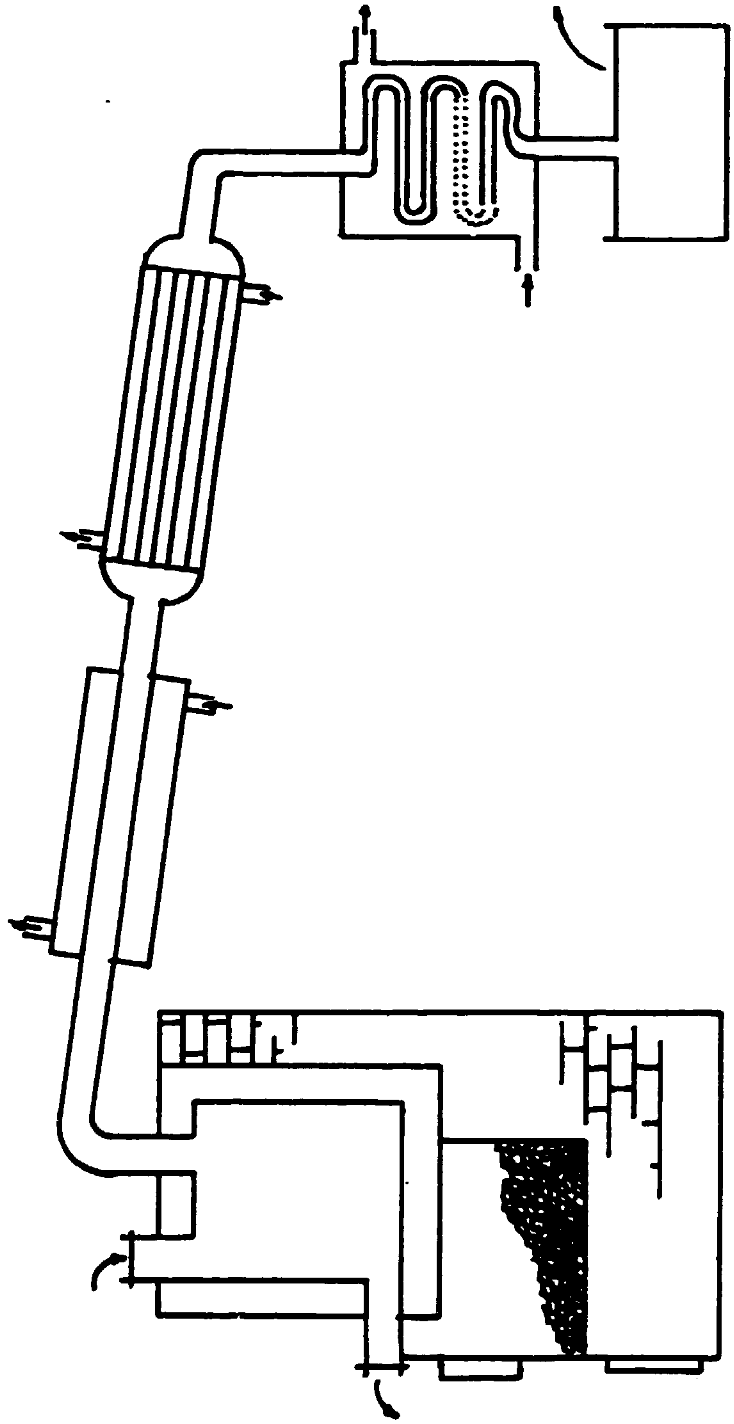
The sorting should be accompanied by a transfer of the raw materials into containers, which allow easier handling than the jute sacks used at present.

It is to be recommended that the product yield and raw monomer purity is determined for each batch separately, as a first step towards improved process and quality control.

The sorting operation is, at present, no source of air or water pollution. A more thorough sorting and cleaning, as recommended above, would result in a few wt. % of waste solids and sludge, which require disposal.

C. Pyrolysis furnaces

The battery of 8 pyrolysis furnaces and cauldrons is operated batchwise. The products emerge under the form of vapours, which are cooled in heat exchangers using ordinary (30°C) cooling water. At this temperature the vapour pressure of MMA is still sizeable, but the total emission remains limited in size, together with the total flow of pyrolysis gas. The latter, however, has not been monitored during actual plant operation and hence is unknown in size and composition (Figure I).



The main problem of the pyrolysis system is its extremely low yield, combined with various operating problems, such as

- low yield of crude monomer (about 70-77 wt.%)
- low grade of the crude monomer, which contains various impurities as shown in Table 1
- high consumption of coal
- constant damage of the equipment
- the heating by means of an open fire is a source of unsafety; it renders the quality uncontrollable and requires intensive labour
- serious environmental problems.

In fact, these are the problems to be solved by the UNIDO-Expert under the terms of the present contract.
The better yield, which seems attainable by means of the UNIDO-process holds the promise of

- lower raw materials losses
- less purification problems
- better product quality
- less environmental problems.

The yield of the SRRUC-system compared as follows to other yields :

Pyrolysis Technique	Yield of Crude Monomer Weight %	Refined Monomer Weight %
- SRRUC Cauldron	70-77	42-49
- Lead Bath	95	80
- Screw-type Pyrolyser	not available	85
- UNIDO-technique	not available yet	not available yet

Table 2 : experimental yield factors in PMMA-pyrolysis

	Batch	Screw Pyrolysis (*)
Methyl formiate	-	0.3
Methanol	11.08	1.83
Acetone	0.96	0.09
Methyl acrylate	0.38	0.49
Methyl propionate	1.4	2.25
Ethyl metacrylate	0.65	0.39
?	1.3	0.68
MMA	84.27	93.46
	100.04	99.49

<u>Table 1.a.</u> : Analysis of Crude Monomer

?	-	1.15
Methanol	0.06	0.046
Acetone	0.07	0.006
Ethylmetacrylate	0.32	0.23
?	2.255	0.35
Methyl acrylate	-	1.19
MMA	97.00	97.05
	99.70	100.00

<u>Table 1.b.</u> : Analysis of Distilled Monomer

<u>Table 1</u> : Composition of Crude MMA according to local GLC-analysis
(November 11, 1985)

(*) Experimental Screw Pyrolyzer of SRRUC

The low yield may be attributed to various sources, the effects of which probably combine and enhance each other :

- limited purity of the PMMA raw material (presence of foreign plastics and of charges) :
- poor quality of the raw materials (cf. 1)
- long residence times of the PMMA (6-7 hours) and of the MMA-vapours (probably of the order of 1 minute) in the cauldron. (The Cauldron diameter is 0.9 m, the height 1.0 m, the volume approximately 0.64 m^3, the charge 100-120 kg, with an apparent density 157-189 kg/m^3)
- formation of dimers or trimers in the liquid or the vapour phase
- autocatalytic carbonization, due to local overheating
- fugitive losses, distributed over the entire plant.

At present the relative importance or contribution of each of these causes is hard to estimate. It is evident, however, that the actual procedures have to be changed drastically.

There is no quality control at all during the pyrolysis; it is suggested that following quantities be monitored systematically

- weight and identity of the charge
- weight and composition of crude monomer
- weight of residue (on a carbon free basis)
- carbon content of the residue
- pyrolysis temperature in the plastic phase and in the vapour phase
- condensate flow.

At present the end of the pyrolysis process is derived from manual sensing of the wall temperature of the exhaust tube of the cauldron. There are no further controls regarding the operation of the process, the quality or yield of the monomer.

The <u>environmental problems</u> of the unit are related to

1) the operation of 8 coal fires in a cyclic mode : at the end of the operation the coal is covered with wet coal, to reduce the fire to low proportions. At that moment volatile products escape unabated, since there is no postcombustion of them.

A simple cyclone was installed recently in the flue to the chimney: under its actual, unattended operating conditions it can only serve as a coarse grit arrestor.

2) the loading of the hot cauldrons gives rise to fumes, which escape through the roof. The problem can be alleviated by the use of a simple, metal lock, grossly adjusted by means of a few, loose bolts onto the upper loading apertures of the cauldrons. Provisions will be required to aid in the compression of the charge.

3) in the cauldron the unloading of pyrolysis residue gives rise to a similar problem. Moreover, when the operation is halted the following aperture B is opened, then the discharge aperture A. When the pyrolysis is not fully completed yet, subsisting products of pyrolysis burn for a short while above B. Furthermore, the carbonized residue is burned relatively clean of carbon while it resides on the bottom of the cauldron.

This may result in a loss of about 1 kg of PMMA-residue, on a total charge of 100-120 kg charged, as well as in fairly considerable and uncontrolled emissions.

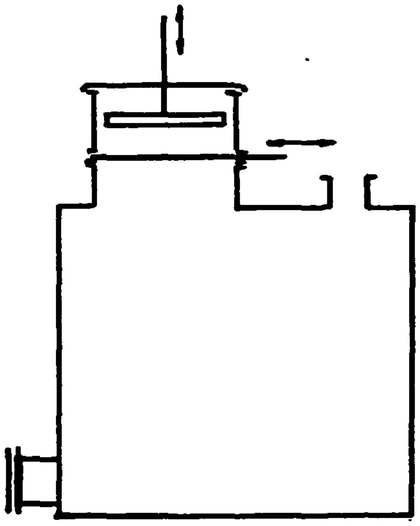


Figure 2 : Loading System for use on the Cauldrons

It is noteworthy that the 8 pyrolysis cauldrons, although they are well constructed, are completely devoid of any measuring instruments. When the pyrolysis vapour duct no longer attains 200°C (!) it is decided that product evolution is over and that the bottom of the plant has to be cleared ! In principle, the possibiliy is provided to measure oil productions of individual cauldrons, by means of a level indicating glass on 8 individual steel container. It is doubtful, however, that these 8 individual containers have been calibrated and that the volume contained is efficiently monitored as a function of pyrolysis time.

At present the major hazards of the pyrolysis process are associated with

1) the loading of the cauldrons, which is inefficient and cumbersome
2) the opening of the loading aperture, which many gives rise to a blaze of the exhaust gases
3) the operation of the coal fire
4) the open storage of the crude monomer, which is unacceptable from a safety and an environmental viewpoint.

D. Storage and Handling of Liquids

Crude Monomer (Figure 3)

The volatile products of pyrolysis are gradually condensed by means of an air cooler, a water jacket and a tubular condensor. The condensate flows through separate lines into individual receivers, probably of an average dimension of

0.4 x 0.4 x 1.2 m or about 200 liters

which is amply sufficient to receive the product from one cauldron (charges of 100-120 kg).

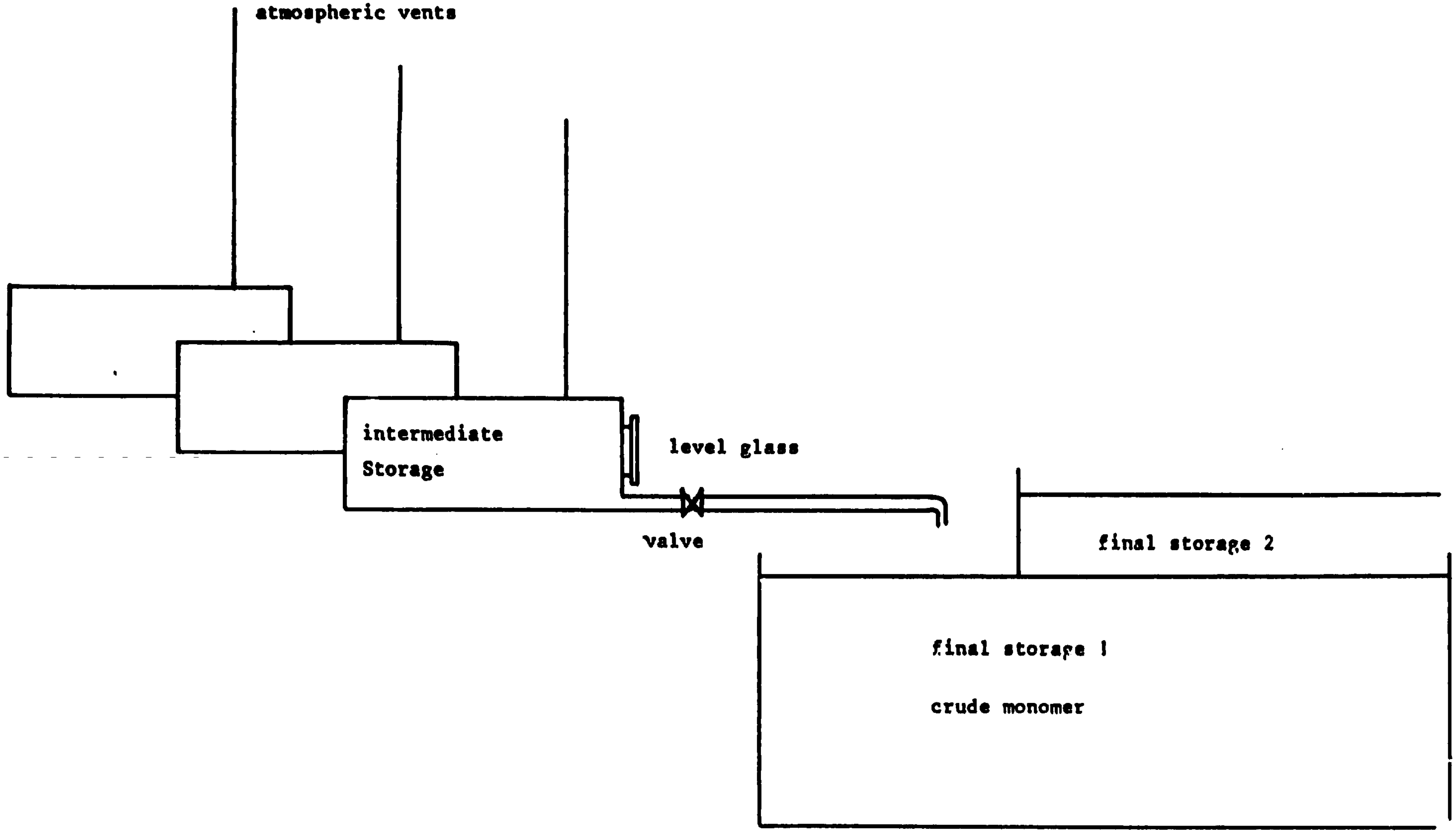
Each receiver is fitted with a level showing glass tube and with a vertical vent duct, used to eliminate non-condensible gases.

After each run it seems desirable to ascertain the amount and composition of the crude monomer. This can be obtained by :

- calibration of the receivers
- reading the level on the glass tube, fitted with mm-paper
- taking a sample for gas chromatographic analysis.

On the last day of our visit the gas chromatographic equipment became operational again. The column allowed to make the distinction between several light products. Another column should be made in order to distinguish between crude monomer and higher boiling dimers, trimers and heavies.

(As an alternative, distillation at a laboratory scale could be used to characterize the product, especially with respect to the heavies).


atmospheric vents
intermediate Storage
level glass
valve
final storage 2
final storage 1
crude monomer

The individual receivers are emptied over individual valves into two large plain steel vessels, fitted into a cave.
This method of storage is unacceptable, because of
- safety hazards
- evaporation losses and concomitant smells in the surroundings
- the occurrence of oxidation with formation of
  - (a) peroxides, which may initiate polymerization in an uncontrolled manner
  - (b) formaldehyde and other volatile organics with a pungent smell

Hence, the following corrective measures are proposed :
- calibration of the receiving vessels
- providing the receiving vessels with a convenient sampling aperture, which can be closed after use
- linking the existing vent lines of the various receivers to a single vent, which is connected to a central treatment system
- storing the crude monomer in one or more completely closed vessels, fitted with all safeties normally provided for storage of volatile liquids.

Monomer and Prepolymer

Several methods are in use for the handling and the intermediate storage of the liquid products (crude monomer, purified monomer, prepolymer, ...).
They are based on gravity discharge, direct, manual transfer and aspiration by vacuum into an evacuated vessel.

The handling and conveying of liquids in numerous storage vessels is a diffuse source of vapours and smells in the various workshops.
Hence, it is to be recommended that :

1) all containers used in the various workshops be fixed and closed from the air. At the design phase, the possibility of blanketing the system with nitrogen should be foreseen and eventually installed, in case the presence of oxygen would prove to deteriorate product quality. Since all containers are closed the origins of fugitive losses forcibly disappear. The addition of pigments, plasticizers, initiator, etc., can be handled over locks. Moreover, most of these compounds have a negligible vapour pressure or smell.

2) the various containers, mixers, reaction vessels should be linked by fixed, steel lines. The flexible tubing, which is sometimes used at present, should be banned, because of permeation losses, and especially because of the risk of cutting, rupturing, puncturing or loosening, which would lead to a dangerous spread of flammable liquids in the surroundings. Proper attention should be given to the quality of plumbing, which should use leakproof fittings.

E. Distillation, Salting Out and Rectification

Present Procedures

The crude monomer at present is purified in two steps :

1) batch distillation, to remove a bottom fraction of the product. The unit is schematically depicted in Figure 4; it basically consists of a steam heated, jacketed cauldron, a column packed with Berl-saddles, a set of condensors and a salting-out unit.
2) a batch rectification, under mild vacuum conditions, to remove lights as well as subsisting heavies (Figure 5). The "pure" monomer is obtained as a fraction with a boiling range of ± 1°C at a pressure of about 560 mm Hg.

Operating Conditions

The light fraction is obtained at a pressure below 560 mm Hg and below 61°C. The "pure" monomer boils at a set pressure of 560 mm Hg with a temperature level of 61 ± 1°C.
The heavies boil at a still higher temperature; also the pressure rises above 560 mm Hg.

The reflux ratio is given by a value
of 1 while driving off the light fraction
of 2 while distilling the purified monomer
of > while exhausting the heavies.

蒸馏系统流程图.

1986.7.19.

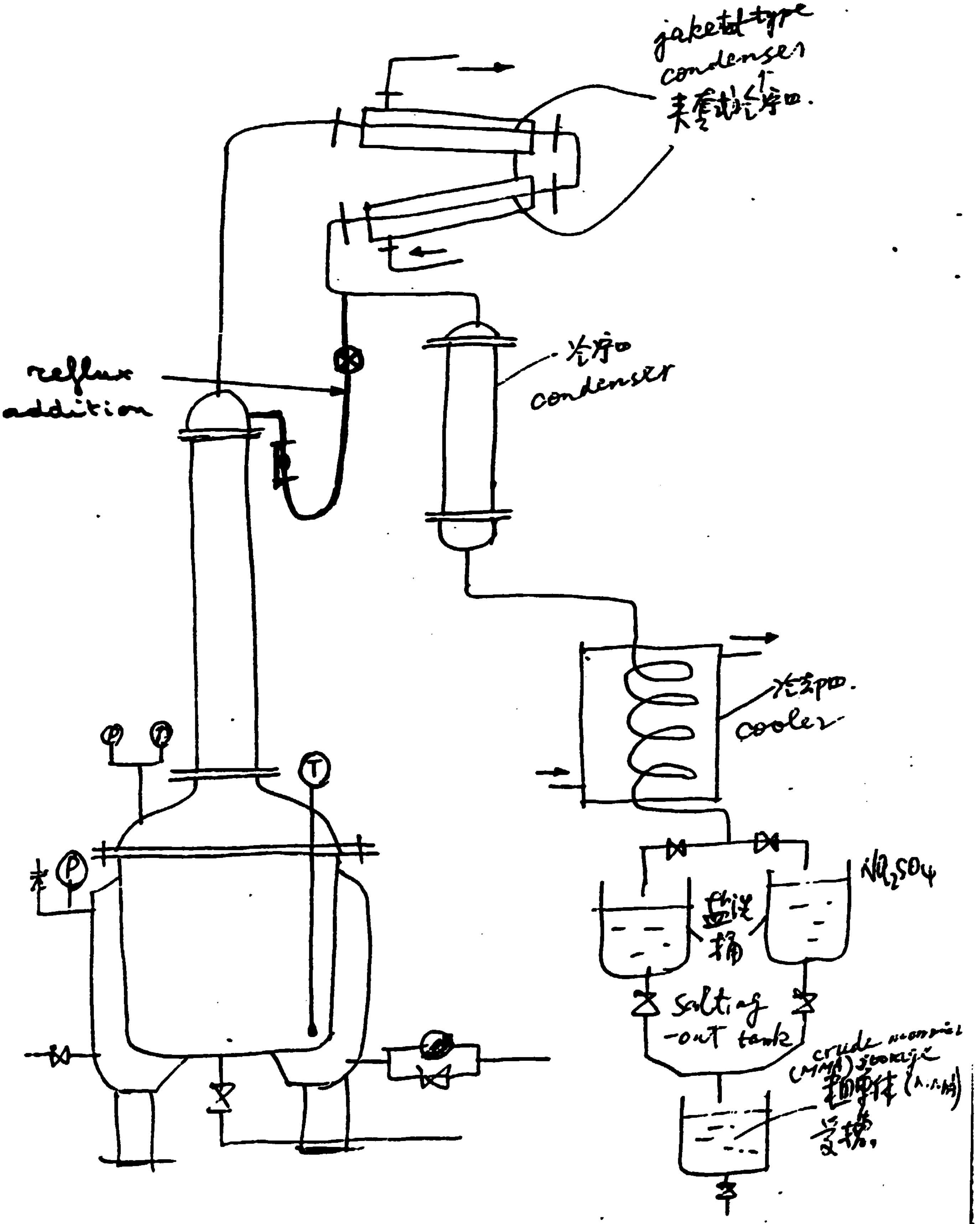


Fig.4 **Distillation Unit** (batch)
present situation + reflux added
charge = 650kg period of operation (7h)

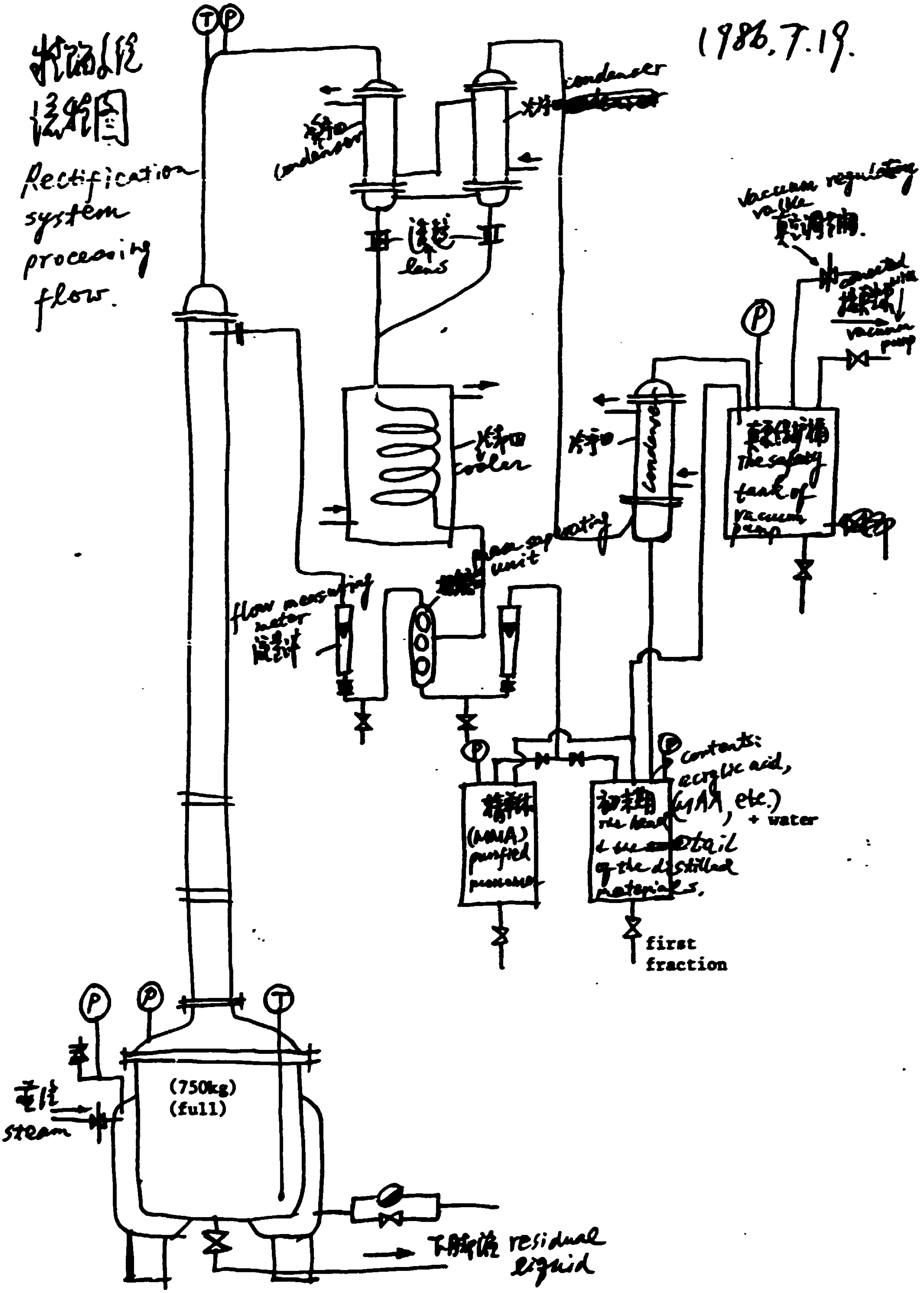


Fig.5 Rectification System Process Flow Diagram

Operating problems

- Possibly the distillation and rectification may be combined into a single operation
- The grade of the refined product is too low (about 96 %). A grade of 98 % or better is desirable
- There are serious losses under the form of
  - (a) vent streams
  - (b) lights
  - (c) heavies
- Salting out the distilled product yields a polluted wastewater with the following characteristics :

  generation rate : 250 Liters, every 5 h

  COD-value 6679 mg O_2/L.

Suggestions for further study

1) Since the present procedure of distillation is inefficient, it should be verified whether its operation is warranted at all. Alternatively, some reflux could be practised, using only minimal modifications, as seen in Figure 4.

   In W. Europe a first distillation uses live steam, which is simpler in use, but gives rise to a problem of aqueous condensates.
2) the salting-out operation at present is ill-documented. If an extension of the study is granted, various methods of salting-out will be compared and their effect on product purity studied.
3) the rectification unit seems to operate well. Moreover, once the new pyrolysis unit starts up, the raw material will probably be of better purity.
4) it can be studied whether the heavy fraction forms an acceptable feedstock for the fluid bed pyrolysis unit of UNIDO-Design.
5) for the new plant, a continuous mode of distillation is warranted (800 T/annum plant).

F. Prepolymerization

Present Procedures (Figure 6)

The crude monomer is mixed with the other ingredients, such as the initiator, ABN = azo bis iso butyronitrile, plasticisers, e.g. dibutylphosphate (DBP), and releasing agents, such as stearic acid.

The raw material is stored in the material blending vessel (Figure 6) and in the purified monomer storage vessel, both with the same composition.

A stirred tank reactor is filled with the content of the first vessel. The reactor is heated up to the temperature of reaction (91°C) bij means of a steam jacket.
The reactor is directly venting into the workshop.

Once the reaction is started the steam supply is replaced by cooling water. Moreover, in order to maintain the temperature at its initial value monomer is added from the second vessel.

Gradually the liquid becomes more viscous.

Finally the prepolymer is discharged through a cloth filter into a storage vessel. (This operation is also a source of acrid smell in the workshop).

The prepolymer is then aspired into the degassing vessel, which is connected to the vacuum pump. Degassing is continued for 40 minutes.

Finally the prepolymer is mixed with pigments in a vessel, which is only semi-covered.

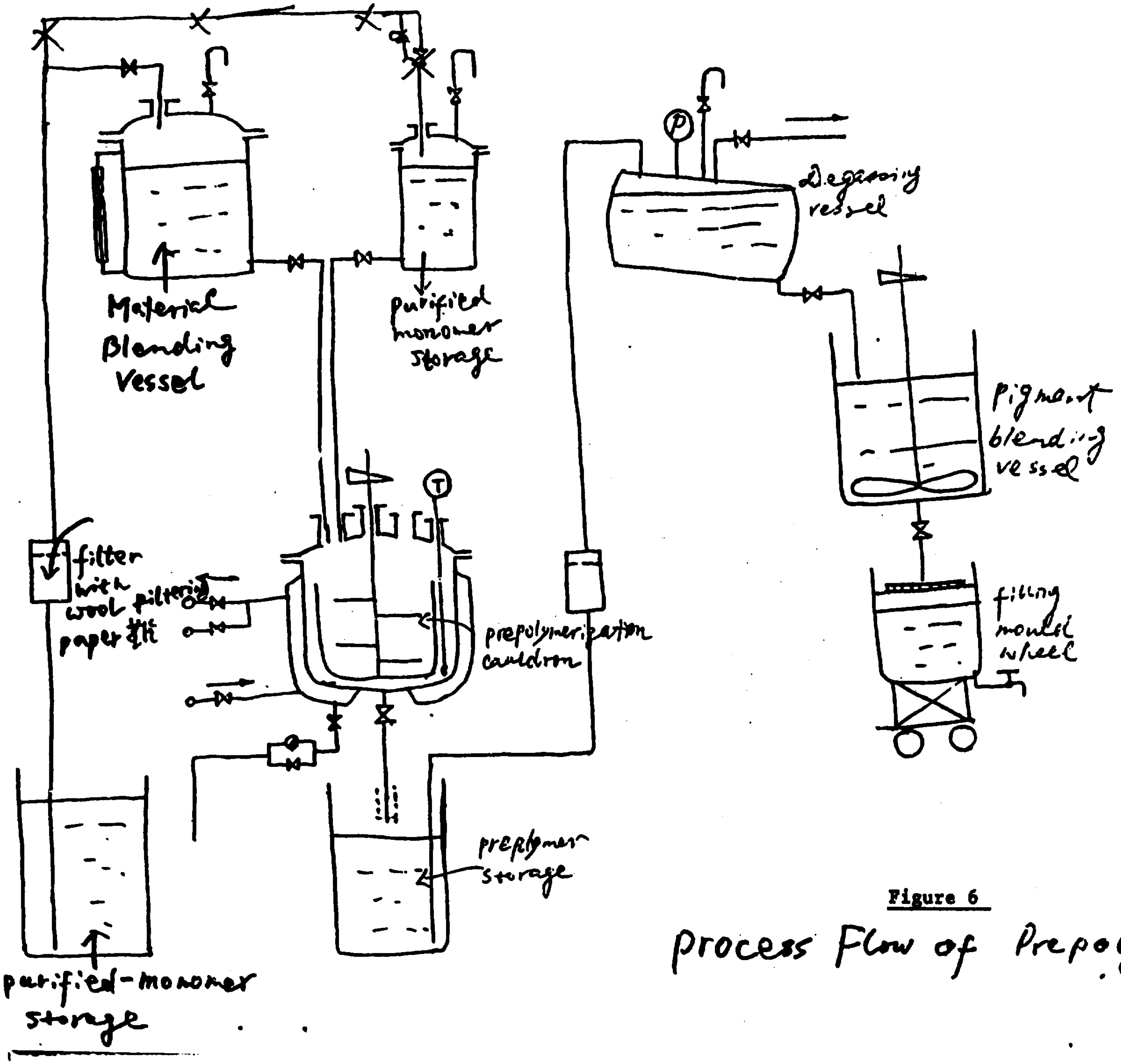


Figure 6

Process Flow of Prepolymerization.

Comments

1) A discussion of the composition of the reactor ingredients (initiator, release agent, plasticises) is out of the scope of the present study. Still, the procedure of prepolymerization can be critized from 2 different angles :

- the method of temperature control is entirely manual, an operator being required for continuous watching the glass thermometer plunged into the reacting bath
- the reactor is venting in the immediate vicinity of the operator, which has to be protected from this exhaust by a fan, blowing this exhaust throughout the workshop.

It would be much simpler to

- install a thermostatic or thermoprogrammable control, possibly after enhancing the cooling capabilities of the reactor.
- draw a vertical exhaust line to the roof and connect it to a general exhaust system for further treatment.

2) The operating conditions during the deaeration of the slightly viscous prepolymer are inefficient from a viewpoint of mass transfer rates.

It is proposed to increase the contact surface between liquid and vacuum, enhancing the elimination of air and other gases, so that a shorter degassing period may be used. This, in turn, reduces the amount of monomer losses to the vacuum system.

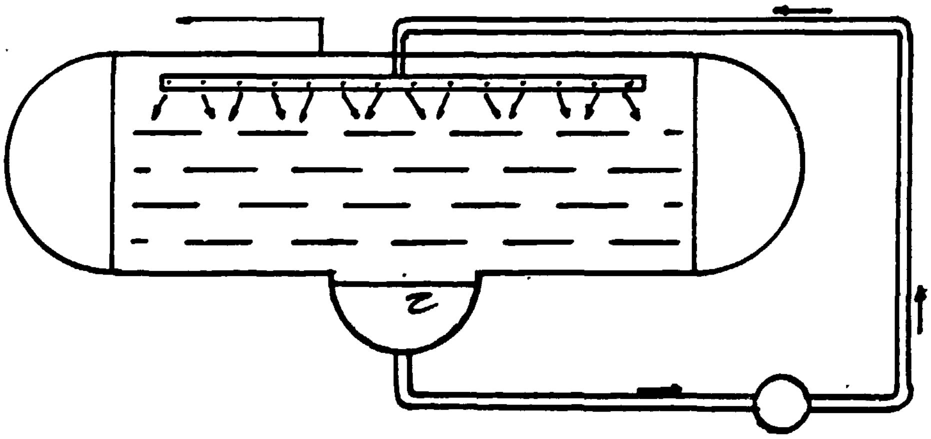


Figure 7 : Improved degassing system

It is curious to note that, after this degassing the prepolymer (a solution of some polymer in monomer) is again exposed to the air, while pigments are mixed into it and while filling the moulds.

This may lead to a dissolution of oxygen, a formation of peroxides and an erratic initiation of the final polymerization. Part of the poor quality of the PMMA-plates may be due to these circumstances.

Moreover, the storage of prepolymer in half-open or periodically opened containers is a source of smell.

The effect of pearlite and other pigments upon (pre-)polymerization should be investigated during an extension of this study.

6. Polymerization

Present Procedures

The polymerization process involves the following operations :

1) preparation of the mould
2) filling of the mould
3) polymerization of the prepolymer in the mould, while the latter is maintained in a thermostatic bath
4) demoulding
5) quality control
6) packaging the PMMA plate.

The mould plates are rubbed free from polymer or other adhering materials and cleaned with solvent.

Each mould consists of two glass plates, of a size of about 80 x 80 cm. The mould is completed by means of flexible rubber tubing, wrapped in a kind of cellophane film, to avoid the colouring of the PMMA by the (red) rubber tube. The tubing is curved in a U-form, following the 3 sides of the plate and (after filling) also the fourth side. It is maintained by means of spring loaded-clamps.

When the mould is filled, by means of a flat type of funnel, the top side is also closed, the entrapped air is eliminated and clamping is finalized.

Still, for a short while tiny bubbles are seen to mount to the surface.

The plates are lined and placed in a frame. A set of about 36 plates is suspended in a hot bath. The polymerization of the prepolymer is initiated by the rise in temperature; later the bath absorbs the heat of polymerization.

Demoulding is aided by means of a flat knife.

During quality control a fair fraction of the plates is discarded, because of the extensive occurrence of small bubbles and even of large inclusions of a suspension of PMMA in water. Sometimes, one of the glass plates breaks altogether, which yields irregular PMMA skins in the mould and spillage of PMMA to the waterbath.

Even the "normal" quality plates are but very rarely devoid of defects, such as a few bubbles. If these are small in number, the plates are sold as a second choice material.

Problems to be solved

1) The water bath is a source of technical problems. The mechanical agitation is possibly a source of breakage of mould plates and of intrusion of water into the moulds. The precise mechanisms have to be investigated further.
2) There is no method available to test the activity of the prepolymer. There is only a simple viscosimeter (measuring the time required for liquid to flow out from a vessel or for a ball to sink in the liquid).
3) some kind of pigments (pearlite = basic lead carbonate) are suspected from interfering with the initiator.
4) there is considerable deviation in the thickness of the plates.
5) the adherance of the plate to the glass is uncontrollable and leads to more breakage.
6) the effect of amplitude and frequency of the excentric vibration is unknown.
7) a remarkably large number of plates is spoiled by the presence of bubbles. For this reason an improved degassing vessel design was proposed.

Suggested Approach

1) investigate the present mould design from various viewpoints (occurrence of water leaks, shattering of the glass, labour requirements, control of the plate thickness, etc.)
2) establishing better quality standards for the prepolymer and adhering to them, especially with respect to the content of impurities and of MMA monomer
3) improving the control over the operating conditions during polymerization (temperature, time, agitation)
4) any other suggestions brought forward by SRRUC or by detailed study of the operating circumstances.

II. Environmental and Occupational Safety Problems

As explained in the introduction, the Management and Staff of SRRUC have urged the UNIDO-expert to prepare a preliminary assessment of the actual environmental problems of the PMMA-pyrolysis unit at the Xingguang-factory.

The following sources of environmental problems can be listed
1) dust and noise problems in the shredding of the PMMA. Explosion hazard.
   (Importance : secondary only)
2) PMMA-pyrolysis
   - emissions of dust, SO_2 and unburnt organics by 8 coal fires
     (To be replaced later by new pyrolysis technology)
   - emissions of fumes during charging and opening of the cauldron
     (SRRUC to construct a more or less gastight lock-system)
   - emission of non condensable gases from the condensate receiving vessels
     (to local or central exhaust cleaning system)
3) Crude MMA Storage
   - fugitive emissions and deterioration of monomer quality by oxidation
     (SRRUC to construct closed storage tanks provided with all necessary safety features)
4) Purified MMA and Prepolymer
   - numerous fugitive emissions
     (SRRUC to construct a closed system, which can be purged and blanketed where necessary)
5) Prepolymerization
   - vent exhaust should be sited out of the workshop and connected to the general exhaust system
6) De-gassing
   - vacuum pump exhaust should be fully treated; important loss of monomer to the environment, as well as safety-hazard
7) Polymerization
   - moulds should be filled at a fixed location, which is equipped with adequate ventilation.

The various fugitive emissions can be treated
- by recovery in a suitable scrubbing liquor
- by destruction in a flare system

In view of the importance of these problems a further and more detailed study seems warranted.

III. Suggestions to improve the Present Pyrolysis Equipment and Operating Procedures

1. Prepare mass balances on a regular basis for charges of different origin.

2. Improve the purity of the raw materials of foreign origin by more systematic testing and sorting.

3. Improve the environmental standards of the pyrolysis unit by

   1) short range :
      (a) loading through a lock
      (b) unloading only after pyrolysis is fully completed and the cauldron is completely outgassed. To avoid a lengthy overheating of the bottom a purge gas or steam could be used.
      (c) eliminating other sources of fugitive emissions in the reception and storage area.
   2) long range : adopt a technology, which promises a much higher yield of MMA.
   3) intermediate range : upgrade environmental and process monitoring conditions.
4. implement some method of analysis, such as :

   gas chromatography (*)
   refractometry
   density at a specified temperature
   ASTM-distillation (*)

   for improving the quality control of the crude monomer

(*) available already

5. store crude monomer in closed containers only with (a) a reception container and (b) a container for product the quality of which has been controlled by analysis. Off-grade crude monomer should be treated separately.

6. controls of operating temperature and product monomer flow rate are also essential in the pyrolysis unit.

7. since the filler/carbonized materials probably promote the formation of carbon and by-products it is wise to empty the content of the cauldrons frequently (= after each batch) and thoroughly. The "pearlite" material is more dangerous in this respect.

8. Tests may be initiated using a lead bath technology. Relevant patents are included in Annexe V.

Environmental pollution should not be a problem, as far as the bottom of the cauldron does not burn through. This is an unfrequent occurrence in Europe, but the charged material is harmful in this respect, because it builds up a layer of ash on top of the lead bath, and leads to superheating and excessive thermal and mechanical stress on the bottom of the cauldron.

The latter should be sufficiently strong to support the charge of lead : 1 cm of lead in a cauldron with diameter fo 0.9 m weighs 72 kg ! Local overheating would impose a heavy burden on this bottom!

In Europe the duration of pyrolysis in a lead bath cauldron is 2 1/2 to 6h, depending on the quality (amount of filler) of the product.

3. Storage of Various Grades of Product.

The various grades of product (crude monomer, distilled & rectified monomer, prepolymer, and distillation bottoms) are stored and handled in open containers to a large extent. It is essential to ban this occurrence completely, in order to minimize environmental pollution as well as evaporation losses. There are vents on the tanks for intermediate storage of pyrolysis product, which contain a large amount of volatiles. Since most of these are at least somewhat soluble in water it is suggested to replace a vent to the atmosphere by the following system.

Conclusions

The objective of our first mission to Shanghai was to
- visit the PMMA workshop in Shanghai and collect the necessary design data

Thanks to the preparatory work of the SRRUC-team, this objective was attained without any difficulty. The expert exposed some of the benefits to be attained from the new UNIDO-pyrolysis system, namely

The further activities, i.e.
- conduct the necessary experimental work at a pyrolysis plant on a bench-scale to determine optimizations of the product yield.
- design a continuous pyrolysis production unit
- prepare a report on the results

are now beind completed at a home basis. Afterwards the UNIDO-expert will return visit to PRC with results proposing the plant design and follow-up on the construction start up and optimization if desired.

The consultant will also prepare a final report on the findings of his mission.

Since various environmental problems and product quality issues remain more or less unsolved it seems plansible that SRRUC will

Acknowledgement

Despite the number of items on the technical programme the operating conditions at SRRUC werd extremely pleasant and the constant attention and help of the SRRUC-team is most gratefully acknowledged.

ANNEXES

OUTLINE OF THE TECHNICAL DISCUSSION WITH THE BELGIAN EXPERT

From Jul. 19, afternoon to Jul. 23, forenoon ,altogether 3 working days.Focusing on the status-quo and disadvantages of the existing PMMA purolysis system.

1. THERMAL CRACKING PROCEDURE
   EXISTING PROBLEMS:
   A. Low grade of cracked monomer with lower content of MMA and higher impurities;
   B. Low yield (about 70-77%);
   C. Open fire heating, unsafety, intensive labuur and quality uncontrollable;
   D. High consumption of energy and constant damage of the equipment;
   E. Serious environmental pollution.

2. PURIFICATION PROCEDURE
   EXISTING PROBLEMS:
   A. Low grade of purified monomer (most of it is less than 97%, the specification set by the factory)
   B. Low yield (after two steps of distillation,60-64% product can be attained);
   C. High energy consumption (in theoretically, these two steps can be combined into only one step, but it is difficult to realized in the practice);
   D. Serious atomosphere pollution :
      a. Vacuum ventilator is connected with air directly and the exhausted gas escapes to the air without treatment;
      b. Because of cleansing crude monomer with saturated brine, the COD index of the waste water will be up to 5000-10000 mg/l;
      c. The residual liquid after purified can not be treated efficiently, at present, we just use it as kiln fuell , which brings about environmental pollution seriously.

3. POLYMERIZATION PROCEDURE
   EXISTING PROBLEMS:
   A. During the prepolymerization , the monomeric activity can not be measured exactly, which leads to uncontrollable quality of the prepolymer;
   B. The product attained after the water-bath polymerization exists a great deviation in thickness and we still have great difficult to control the products' glossiness, we haven't find out the relationship between the amplitude, frequency, resident time and glossiness of products, stability of thinkness;
   C. Operating with high labour strungth.

From Jul.23, afternoon to jul.24, forenoon,Focusing on the new design of a pyrolysis system.

1. DETAILED REQUIREMENTS OF THE DESIGN
   A. We hope to receive a design chart covering the whole process flow (from thermal cracking to polymerizing);
   B. If it possible, we'll ask Dr. Buekens work in two periods:first,the design chart of the PMMA pyrolysis technological process (in two months), and then the others.The design will meet the needs of following:

      a. The capacity of the design will be 800T/Y;
      b. The specification of the final product gained from the mass production with new design process;
      c. Safe operating and labour protecting;
      d. Environmental protecting (the standard of the dischargedmaterial);
   C. Ask Dr. Buekens deliver the constracting chart as soun as finishing it, after 15 days when we receive the chart, we will invite Dr. Buekens to mission Shanghai again to confirm the final design;
   D. If we meet with difficulties during the construction , perhaps we will request Dr. Buekens to come to Shanghai to conduct the debugging and acceptance checking of the system;
   E. Inviting Dr. Buekens to introduce his designing idea, and negotiating with him if he will accept the requirements abuve,

2. DESIGN PLAN
   We want to know the data of the required power, fule water, steam for 800T/Y production line su as to prepare the new system starting-up sufficiently.

Annexe 1

PROPOSE PROGRAMME FOR THE STUDY VISIT OF DR. ALFONS, BUEKENS IN SHANGHAI(Jul. 1986)

July 18, Friday	
Forenoon:	Leaders of SRRUC and Nanshi District Branch meeting Dr. Buekens at the Shanghai airport; Installation at the Jingjiang Hotel.
Afternoon: 14:30-16:00	Manager of SRRUC,Mr. Li Bingzhang and relevant working staff meeting Dr. Buekens at SRRUC headquarters; Discussing the proposed programme.
Evening: 19:00	Welcome Banquet
July 19, Saturday	
Forenoon: 8:30-11:30	Leaders of Nanshi District Branch, SRRUC and Xingguang Plastics Factory holding a talk with Dr. Buekens at Xingguang Plastics Factory; Briefing by SRRUC-team; Introducing the purpose and requirements of this study visit by Dr. Buekens.
Afternoon: 13:30-16:30	Dr. Buekens working with the SRRUC-team; Discussion on the status-quo and disadvantages of the existing PMMA pyrolysis system; Discussing the thermal cracking procedure
July 20, Sunday 8:00	Touring activities
July 21, Monday	
Forenoon: 8:30-11:30	Continue the same subject as last Saturday Asking Dr. Buekens to introduce the up-to-date pyrolysis technologies; equipments, and their manufacturers and users abroad.
Afternoon: 13:30-15:30	Discussing the purification procedure
July 22, Tuesday	
Forenoon: 8:30-11:30	Continue the same subject as last afternoon; Inviting Dr. Buekens to introduce the state-of-the-art facilities and technologies in the field of purification abroad.
Afternoon: 13:30-16:30	Discussing the polymerization procedure.
July 23, Wednesday	
Forenoon : 8:30-11:30	Continue the same subject as last afternoon; Inviting Dr. Buekens to introduce the advanced means, and technique of the quality control in the field of polymerization abroad.
Afternoon: 13:30-16:30	SRRUC-team putting forward the detailed requirements and needs regarding the overall design of PMMA pyrolysis system Dr. Buekens presenting a preliminary design by request.
July 24, Thursday	
Forenoon: 8:30-11:30	The economic assessment of the recommended process analyzed by Dr. Buekens.
Afternoon: 13:30-16:30	Compiling the note and preparing the agreement separately.
July 25, Friday	
Forenoon: 8:30-11:30	Adopting the agreement.
Afternoon: 13:30-16:30	Winding up the study activities.
Evening: 19:00	Fairwell Banquet
July 26, Saturday --July 27, Sunday	Touring activities
July 28, Monday 8:30	Shopping, and preparing to depart Shanghai.

SHANGHAI RESOURCE RECOVERY
AND UTILIZATION COMPANY

Annexe II

THE DESIGN REQUIREMENTS OF AN IMPROVED PMMA PYROLYSIS SYSTEM

1. Owing to the present PMMA recycling production exists a series of problems, such as low yield, serious environmental pollution and imperfect quality of the end-product which affect the economic benefits and hazard the workers' health directly, it must be reformed systematically and completely to meet a crying need.

2. In accordance with the status-quo of Xingguang Plastics Factory, the PMMA technological reformation should be carried on in two steps: In the first step, preliminary improvement should be adopted to cope with the environmental polluting problem, which has to be concerned at a top priority, as well as the low production yield by improving the pyrolysis procedure suitably.
As the second step, a PMMA pyrolysis processing line covering the whole process flow , from thermal cracking, purification to polymerization, will be needed . The design will be economic and reasonable and will reach to the advanced world standards.

3. At the first step, namely the immediate objective, we have to focus our attention on how to eliminate the pollution and how to increase the PMMA recovery rate just on the basis of the present processing line. Detailed means recommended by Dr. Buekens will be helpful for us to implement the technology modification step by step.

4. At the second step, namely development objective, a PMMA pyrolysis processing line will be designed to meet the requirements as follows:
   - A. The capacity of the design will reach to 800 tons of PMMA wastes treated per year;
   - B. The production yield of PMMA ≥ 85%;
   - C. The quality index:
     - purity ≥ 98.5 %
     - acidity ≤ 0.08 %
     - α - methyl hydroxyisobutyrate ≤ 1.5 %
   - D. The maximum denity allowance of the exhaust gas effluented :
     - a. MMA (in the air) : 0.1mg/m^3
     - b. MMA (in the workshop atmosphere): 20 mg/m^3
   - E. The maximum concentration allowance of the waste water discharged :
     - a. PH value : 6-9
     - b. suspension ≤ 500mg/l
     - c. five day BOD ≤ 30mg/l
     - d. COD_{cr} ≤ 50mg/l
     - e. petroleum ≤ 10mg/l
     - f. lead ≤ 1mg/l
   - F. Noise (out of the factory)
     - a. in the day time ≤ 65 dB
     - b. at night ≤ 55dB
     - c. in the working area ≤ 85 dB

5. We hope the preliminary design scheme of an improved production process will be provided to us within three months and if possible , may be sent to us at expert's earliest convenience so that we can submit it to the environmental protecting government to clear and to confirm it . We expect Dr. Buekens to mission Shanghai in this coming autumn, better around October, we may discuss and finalize the further design chart and strive for finishing the construction drawing in this year.

Annexe III

Annexe IV.

POSSIBLE FOLLOW-UP ACTIVITIES AT THE XINGGUANG FACTORY.

1. Monitoring the sorting and grading of raw materials
2. Monitoring the testing of lead bath technology as an intermediate step to the implementation of UNIDO-pyrolysis technology
3. Advising on crude and refined monomer storage and handling
4. Advising on the collection and treatment of the existing fugitive losses of monomer.
5. Advising on the procedures for purifying the crude monomer based on (a) distillation (b) salting-out
6. Revamping the prepolymerization and degassing units in order to reduce fugitive emissions and improve the quality of the prepolymer
7. Advise on the procedures of production and the gradual improvement of quality and control of the PMMA-sheets
8. Help in identifying, monitoring and treating all environmental problems and safety hazards in the plant
9. Monitor the gradual improvement of new technology, operation procedures and environmental controls.

Annexe V

Patents related to PMMA Pyrolysis

RÉPUBLIQUE FRANÇAISE

MINISTÈRE
DE L'INDUSTRIE ET DU COMMERCE

SERVICE
de la PROPRIÉTÉ INDUSTRIELLE

BREVET D'INVENTION

Gr. 14. — Cl. 8.

N° 1.114.639

Classification internationale :

C 08 /

Procédé de transformation des déchets de polyméthacrylate de méthyle en produits industriellement utilisables.

Société dite : COMPAGNIE FRANÇAISE DES PLASTIQUES INDUSTRIELS résidant en France (Seine).

Demandé le 19 novembre 1954, à 16 heures, à Paris.
Délivré le 19 décembre 1955. — Publié le 16 avril 1956.
(Brevet d'invention dont la délivrance a été ajournée en exécution de l'article 11, § 7, de la loi du 5 juillet 1844 modifiée par la loi du 7 avril 1902.)

Le procédé qui fait l'objet de l'invention consiste à chauffer les déchets de polyméthacrylate de méthyle à une température de l'ordre de 250° à 400° de façon à les transformer par un procédé de pyrogénation en produits monomères volatils qu'on recueille par condensation dans une partie refroidie de l'appareillage.

Le produit brut ainsi obtenu peut être utilisé, soit tel quel, soit transformé en d'autres produits, par des réactions connues dans la chimie organique.

Ainsi on peut, en effectuant la transestérification dans des conditions déterminées, obtenir d'autres esters supérieurs méthacryliques.

Le procédé peut permettre d'aboutir à partir des déchets, dans un minimum de nombre d'étapes, à d'autres produits ayant une valeur industrielle.

On décrira ci-après à titre indicatif et non limitatif un cycle d'opérations :

On chauffe 1 kg de déchets de polyméthacrylate de méthyle à 370°, température extérieure, dans un ballon muni d'un réfrigérant descendant. Les déchets commencent à se décomposer et dans le récipient se condense un liquide jaune qu'on recueille dans un ballon.

A la fin de l'opération, on augmente la température vers 400°. Quand on effectue cette opération sur des quantités plus importantes, il est nécessaire d'ajouter une matière inerte telle que du sable ou de la terre d'infusoires, ou d'effectuer une agitation (30 tours par minute), pour mieux égaliser la température.

L'addition de terre d'infusoires peut servir non seulement pour une meilleure répartition de la chaleur, mais elle permet également de contrôler la température à laquelle s'effectue la dépolymérisation. En effet, quand on place un thermo-couple à l'intérieur de l'appareil sans aucune addition de terre d'infusoires ou de sable, la température mesurée est toujours celle de la vapeur formée, de l'ordre de 170°, quel que soit le chauffage extérieur. Par contre, si le déchet de polyméthacrylate contient du sable, il est possible de contrôler exactement la température de décomposition. Cette température ne doit pas dépasser 250°.

Dans ces conditions, on obtient 980 g d'un produit brut constitué principalement par le méthacrylate de méthyle et l'acide méthacrylique.

On sèche 775 g du mélange précédent sur du chlorure de calcium puis on y ajoute 310 g de butanol normal et 90 g d'acide sulfurique à 66 °Bé ainsi que des morceaux de cuivre pour empêcher une polymérisation au cours des opérations suivantes.

Ce mélange est chauffé dans un ballon muni d'une colonne de fractionnement et d'un réfrigérant descendant, de façon que la température en bout de colonne ne dépasse pas 70°. Au bout d'un certain temps, il commence à distiller un mélange de méthanol et de méthacrylate de méthyle. Quand la distillation ralentit trop, on augmente le chauffage et on distille ainsi tout ce qui passe jusqu'à 105°. L'opération dure environ 4 à 5 heures et on obtient ainsi 300 cm³ d'une solution constituée par un mélange de méthanol et de méthyl-méthacrylate (première fraction).

On continue la distillation et on obtient 130 cm³ d'une fraction passant de 105 à 140°. Et finalement on obtient 400 cm³ de méthacrylate de butyle passant de 140 à 160°. Cette fraction est suffisamment pure pour la plupart des opérations ultérieures.

La première fraction après lavage avec de l'eau saturée de sel, séchage sur chlorure de calcium, et distillation, donne 310 g de méthacrylate de méthyle pur, avec point d'ébullition de 99 à 101°.

La deuxième fraction, constituée principalement

par un mélange de butanol et d'esters méthacryliques, peut être employée dans une opération ultérieure.

Les monomères méthacryliques ainsi obtenus peuvent être polymérisés, soit en émulsion, soit en solution dans un solvant organique approprié.

Le méthacrylate brut provenant de la pyrogénation peut être transformé également en un sel d'acide polyméthacrylique, de la façon suivante :

On dissout 300 g de méthacrylate dans 700 cm³ d'une solution aqueuse contenant 120 g de soude. L'opération est effectuée dans un ballon muni d'un agitateur et d'un réfrigérant à reflux.

L'agitation est maintenue jusqu'à ce que le mélange devienne homogène. Pendant la dissolution, il y a un grand dégagement de chaleur.

On ajoute ensuite 3 g de persulfate de potassium et on maintient le mélange à 70° pendant 12 heures.

On obtient ainsi 1 kg de polyméthacrylate de sodium à 30 % qui se présente sous la forme d'une masse épaisse, qu'on peut diluer avant l'emploi à une concentration voulue.

RÉSUMÉ

1° Procédé de transformation des déchets
polyméthacrylate de méthyle en produits industr
lement utilisables, consistant à chauffer ces déch
à une température de l'ordre de 250° à 400°
façon à les transformer par un procédé de py
génation en produits monomères volatils q
recueille par condensation dans une partie ref
die de l'appareillage utilisé.

2° Application du procédé ci-dessus, consist
à soumettre le produit brut obtenu, additionné
butanol, à une distillation fractionnée pour l'ob
tention de divers monomères.

3° Application du même procédé suivie de sa
nification pour l'obtention directe de polymères
partir du produit brut obtenu, par des procé
divers de polymérisation.

Société dite : COMPAGNIE FRANÇAISE
DES PLASTIQUES INDUSTRIELS.

Par procuration :

P. CASANOVA.

Pour la vente des fascicules, s'adresser à l'Imprimerie Nationale, 27, rue de la Convention, Paris (15e).

RÉPUBLIQUE FRANÇAISE

MINISTÈRE
DE L'INDUSTRIE ET DU COMMERCE

SERVICE
de la PROPRIÉTÉ INDUSTRIELLE

BREVET D'INVENTION

Gr. 14. — Cl. 8.

N° 1.079.107

Procédé et dispositif de régénération des monomères à partir de polyméthacrylate, et, en particulier, de polyméthacrylate de méthyle.

MM. Estaban DOMINGO-SEGUI et Bienvenido CABANERO ALARCON résidant en Espagne.

Demandé le 23 mars 1953, à 14h 14m, à Paris.
Délivré le 19 mai 1954. — Publié le 25 novembre 1954.
(Brevet d'invention dont la délivrance a été ajournée en exécution de l'article 11, § 7, de la loi du 5 juillet 1844 modifiée par la loi du 7 avril 1902.)

Depuis un certain temps, on a cherché à récupérer le monomère en traitant des débris de polyméthacrylate.

Le procédé actuellement employé consiste à chauffer dans une cuve les débris ou copeaux de ce produit en mélange avec du sable.

Outre une pyrogénation importante, ce procédé qui est très long, ne fournit qu'un rendement médiocre.

La présente invention a pour objet un nouveau procédé de régénération du monomère donnant des résultats excellents et des dispositifs permettant la mise en œuvre du procédé.

Le procédé de régénération du monomère à partir du polyméthacrylate, de préférence en fragments, est, en principe, caractérisé par le fait que ces fragments sont chauffés dans une cuve contenant du plomb en fusion, les vapeurs de monomère étant ensuite récupérées et condensées.

Selon un mode de réalisation d'un dispositif permettant une mise en œuvre rationnelle de ce procédé, ce dispositif comprend une cuve contenant le plomb et pouvant être chauffée, un panier constitué par un cylindre devant enfermer les fragments du produit à traiter, ledit cylindre, de préférence, ouvert par sa base supérieure et dont la base inférieure et la surface latérale sont percées de trous, pouvant être partiellement immergé dans le plomb en fusion, une cloche chapeautant le panier perforé et en communication par sa partie supérieure avec un appareil condenseur de vapeurs.

D'autres particularités et avantages de l'invention apparaîtront au cours de la description qui va suivre, laquelle, faite en référence aux dessins annexés, donnés à titre d'exemples non limitatifs, fera bien comprendre comment la présente invention peut être mise en pratique, les particularités qui ressortent tant du texte que des dessins faisant, bien entendu, partie de celle-ci.

La figure 1 représente une cuve à bain de plomb;

La figure 2 montre le dispositif perfectionné permettant d'obtenir les résultats optima.

Comme il est dit dans le préambule, la régénération d'un polyméthacrylate est actuellement effectuée par chauffage du produit en mélange avec du sable.

Pour obvier à la pyrogénation importante produite, le demandeur préconise de remplacer le sable par du plomb fondu.

L'expérience a montré qu'une température de bain de plomb fondu comprise entre 450° et 500 °C permet l'obtention d'excellents résultats, pour le polyméthacrylate de méthyle.

Sur la figure 1, on peut voir une cuve 1 contenant du plomb fondu 2 et chapeautée d'une cloche 3 en communication par sa partie supérieure 3a avec un appareil condenseur de vapeurs (non représenté).

Les fragments ou déchets de polyméthacrylate sont placés dans la cuve contenant le plomb.

Le méthacrylate de méthyle fondant à 48 °C et bouillant à 100 °C, la dépolymérisation de son polymère s'obtient par apport de calories, les vapeurs qui s'échappent du bain liquide se rassemblent dans la cloche et s'acheminent vers le condenseur à la sortie duquel on obtient le monomère.

Sur la figure 2, le dispositif a été perfectionné pour éviter la calcination du polyméthacrylate. Celui-ci est enfermé dans un panier 4 constitué par un cylindre dont la base supérieure est ouverte, la base inférieure 4a et la surface latérale 4b étant réalisées en feuilles métalliques perforées.

Le fond 4a de ce panier est prolongé extérieurement de manière à former une rigole circonférentielle 4c dans laquelle vient s'engager la surface latérale de la cloche 3.

Comme précédemment, la partie supérieure 3a de cette cloche est en communication avec un condenseur, d'un type connu en lui-même tel, par exemple, le tube 5 à boules, le monomère étant récupéré presque pur à la sortie de celui-ci.

Prix du fascicule : 100 francs.

Une canne pyrométrique 6 et un galvanomètre 7 permettent de surveiller la température du bain de plomb.

Les opérations sont les mêmes que dans le cas de la figure 1; mais la distillation est facilitée par la possibilité qu'ont les vapeurs à s'échapper par les trous de la surface latérale du panier 4 dans l'espace annulaire ménagé entre le panier 4 et la cloche 3.

Des résultats très intéressants ont été obtenus grâce à ce procédé et à ce dispositif, le monomère a atteint une pureté de 98 %, avec une moyenne de 94 %.

Il va de soi que l'on peut, sans sortir du cadre de la présente invention, apporter toute modification aux formes de réalisation qui viennent d'être décrites, en particulier, appliquer le procédé et utiliser le dispositif à la régénération de tout polyméthacrylate : de méthyle, de propyle, d'éthyle, de butyle.

RÉSUMÉ

L'invention comprend notamment :

1° Un procédé de régénération du monomère à partir du polyméthacrylate de préférence en fragments caractérisé par le fait que ces fragments sont chauffés dans une cuve contenant du plom en fusion, les vapeurs de monomère étant ensui récupérées et condensées;

2° Un dispositif permettant une mise en œuvr rationnelle de ce procédé, comprenant une cu contenant le plomb et pouvant être chauffée, u panier constitué par un cylindre devant enferm les fragments du produit à traiter, ledit cylind de préférence ouvert par sa base supérieure dont la base inférieure et la surface latérale so percées de trous, pouvant être partiellement immer dans le plomb en fusion, une cloche chapeauta le panier perforé et en communication par sa part supérieure avec un appareil condenseur de vapeur

3° Des modes de réalisation du dispositif spéci sous 2°, présentant les caractéristiques suivant prises isolément ou en combinaisons :

a. Le fond inférieur du panier est prolongé ex rieurement de manière à former une rigole circo férentielle;

b. La cloche chapeautant le panier vient appuy contre le fond de cette rigole circonférentielle;

4° Les produits résultant de cette régénératio et de l'utilisation du monomère régénéré.

Estaban DOMINGO-SEGUI
et Bienvenido CABANERO ALARCON.

Par procuration :
René-G. Dupuy et Jean-M.-L. Loyer

Pour la vente des fascicules, s'adresser à l'Imprimerie Nationale, 27, rue de la Convention, Paris (15e).

N° 1.073.307 MM. Domingo-Segui et Cabanero Alarcon Pl. unique

Fig. 1

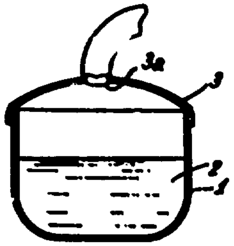
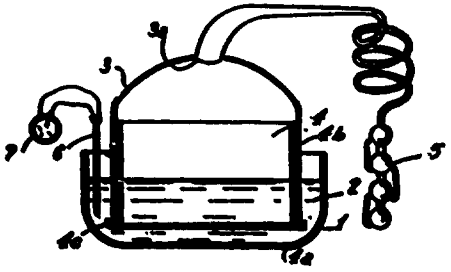


Fig. 2



United States Patent [19]

Tokushige et al.

[11] **3,959,357**

[45] **May 25, 1976**

[54] METHOD FOR CONTINUOUSLY THERMALLY DECOMPOSING SYNTHETIC MACRO-MOLECULE MATERIALS

[75] Inventors: Hiroyuki Tokushige; Akira Kouchi; Tadamoto Sakai, all of Hiroshima, Japan

[73] Assignee: Japan Steel Works, Ltd., Japan

[22] Filed: Dec. 12, 1974

[21] Appl. No.: 532,064

Related U.S. Application Data

[63] Continuation of Ser. No. 335,309, Feb. 23, 1973, abandoned.

[52] U.S. Cl. .... 260/686 R; 260/2.3; 260/683.9; 260/669 R; 260/676 R; 260/683 R

[51] Int. Cl.² C07C 69/34

[58] Field of Search .... 260/686 R, 683.9, 669 R, 260/676 R, 683 R

[56] References Cited

UNITED STATES PATENTS

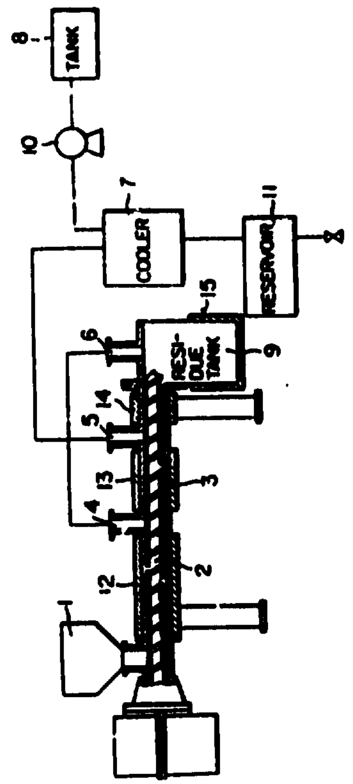
2,030,901	2/1936	Strom	260/686 R
2,341,282	3/1944	Marks	260/686 R
2,377,952	6/1945	Marks	260/686 R

Primary Examiner—Paul J. Killos
Attorney, Agent, or Firm—McGlew and Tuttle

[57] ABSTRACT

Synthetic macro-molecule materials are continuously supplied into the cylinder of an extruder so that said synthetic macro-molecule materials are internally heated by the shearing as well as kneading action of the screw to which they are subjected and externally heated by the heat transmitted through the wall of the cylinder of said extruder from an outside heat source so that said synthetic macro-molecule materials are continuously thermally decomposed within said cylinder, thereby vaporized thermally decomposed products are fed to the condensing means through one or more discharge orifices provided in said cylinder to be recovered there as thermally decomposed products having low molecular weight.

4 Claims, 2 Drawing Figures



METHOD FOR CONTINUOUSLY THERMALLY DECOMPOSING SYNTHETIC MACRO-MOLECULE MATERIALS

This is a continuation of application Ser. No. 335,309 filed Feb. 23, 1973 now abandoned.

BACKGROUND OF THE INVENTION

The present invention relates to a method for continuously thermally decomposing synthetic macro-molecule materials and more particularly to a method for continuously thermally decomposing synthetic macro-molecule materials to recover the separated thermally decomposed products having low molecular weights by heating said synthetic macro-molecule materials to their thermal decomposition temperature.

As systems for thermally decomposing the synthetic macro-molecule materials in order to obtain products having low molecular weights, there have hitherto been known a batch-type and a continuous-type systems, but both of them have the following problems as common phenomena.

1. Since the synthetic macro-molecule materials have a poor thermal conductivity, it requires a long time before reaching the thermal decomposition temperature, as the result of which the processing capacity for the thermal decomposition is small compared with the dimensions of the decomposition apparatus;

2. Most of the synthetic macro-molecule materials contain substances hard to be thermally decomposed such as inorganic fillers, etc. and moreover carbon compounds remain as the residue of the thermal decomposition. These carbon residues have a tendency to firmly adhere to the walls of the thermal decomposition apparatus and, in most cases, it is difficult to continuously discharge them from the apparatus;

3. Many of the synthetic macro-molecule materials become melts having high viscosity in the process of heating, so that their transportation becomes difficult.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a method for continuously thermally decomposing synthetic macro-molecule materials which can eliminate all of such difficulties as aforesaid, which are inherent to the conventional methods.

A method for continuously thermally decomposing synthetic macro-molecule materials according to the present invention is characterized to supply said synthetic macro-molecule materials into the cylinder of an extruder having a screw which functions to shear, knead and transport said synthetic macro-molecule materials so that they are continuously thermally decomposed by internal heat generated by the shearing and kneading action to which they are subjected as well as by the external heat transmitted through the wall of said cylinder which is heated by an external heat source, thereby the volatilized thermo-decomposed products are discharged through one or more discharge orifices provided in the cylinder of said extruder to the condensing means to recover the material there. As the extruder a single-screw type or a twin-screw type of any known construction may be used, either independently or in combination, such as using a single-screw type and a twin-screw type extruders in tandem, or in combination with any other apparatus.

BRIEF DESCRIPTION OF THE DRAWING

This and other objects of the present invention will become more readily apparent upon reading of the following specification and upon reference to the accompanying drawing, which shows diagrammatically a preferred apparatus for carrying out the method according to the present invention using a single screw type extruder independently as the extruder.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Reference is made to the drawing.

The synthetic macro-molecule materials to be treated are supplied into a hopper 1. The synthetic macro-molecule materials thus supplied are fed forwardly by a rotating screw 2 to be plasticized and thermally decomposed by internal heat generated by their subjection to the shearing and kneading action of said screw as well as by the external heat transmitted through the wall of the cylinder 3 of said extruder which is heated by any suitable heating means 12, 13, 14 such as electric heaters. A fear of fire due to the back flow of the thermally decomposed products towards the hopper side can be prevented by sealing action of the melt during its transportation. Accordingly the feeding of the synthetic macro-molecule materials into hopper 1 can be carried out by any known means. However, in the case where there occurs variation in supplying the synthetic macro-molecule materials due to such as the occurrence of bridging of the synthetic macro-molecule materials in hopper 1, the filling state of cylinder 3 with the melt may be insufficient, so it is preferable that hopper 1 is constructed so as to be replaced by nitrogen. The heating of cylinder 3 is preferable to be carried out separately at the melting zone and the thermal decomposition zone, making their temperatures, respectively, e.g. about 250°C and 300°–400°C.

Products having low molecular weights volatilized from the heated synthetic macro-molecule materials are led to a cooler 7 through discharge orifices 4–7 to be condensed there, the condensate being accumulated in a reservoir 11. The discharge orifices are appropriately provided in cylinder 3 over its whole length from the position at which the thermal decomposition starts to the forward end of cylinder 3. And when it is desired to return the product having high boiling points to cylinder 3 again for its further thermal decomposition, it is preferable to provide one of the discharge orifices at right angles to the thermal decomposition starting position. Further, in condensing the volatilized products, if the temperature of the cooler is adequately adjusted or a multi-stage distilling column or the like is used as the cooler, the refining of the thermal decomposition product can be accomplished at the same time with its thermal decomposition. Non-condensed ingredients of gases are stored in a tank 8.

Though the formation of the residue carbon may occur on the inner surface of the cylinder, its adhesion to the surface can be prevented by the thread of screw 2, but, in order that the residue formed is surely fed to a residue tank 9, it is necessary that screw 2 is provided with the thread extending to its forward end so that it projects into residue tank 9 which is directly connected to the extruder at its forward end.

Further, in this case, to further thermally decompose the material supplied in the incomplete decomposition

state as the result of externally heating the residue tank to high thermal temperatures is advantageous when the supply amount of the material has increased beyond the thermally decomposing capacity of the cylinder due to some cause or in the case when treating such a material as needing a comparatively long period of time for its thermal decomposition up to a given mean molecular weight.

In the case when part of the residual carbon is liable to adhere to the flow passage of the screw, such a tendency can be alleviated by externally supplying a little amount of air into the thermal decomposing zone while the system is under operation, whereby the residual carbon becomes comparatively active making such residual carbon adherence difficult. In this case, as part of the product burns, it contributes toward reducing the amount of the external heating. Further, as a mechanism for supplying the residual carbon completely, it is desired that the whole of the cylinder or the thermally decomposing zone is constructed to use a two-shaft-engaging screw.

Further, in this case, since the products produced partially burn, contributing to reduce the quantity of the outer heating.

It is preferable to use twin-type screw for the whole extruder or only for the thermal decomposition zone in order to perfectly feed the residue.

When the necessity has occurred to perfectly remove the residue carbon firmly adhered to the flow passage of the screw after the continuous operation, it can be achieved by stopping the supply of the synthetic macro-molecule materials and supplying air to the thermal decomposition zone so that the carbon firmly adhered is changed into carbon dioxide.

In the present invention, it is possible to control the mean molecular weight of the thermally decomposed products by regulating the degree of vacuum at the thermal decomposition zone by means of a vacuum pump 10 disposed at the end of the condensing part, this being especially advantageous in the treatment of the random decomposition type synthetic macro-molecule materials, e.g. polyethylene etc. The control of the mean molecular weight of the thermally decomposed products can also be carried out by changing the thermal decomposition temperature or the feed velocity, the former being possible by changing the external heating temperature of the cylinder by the control of heaters, 12, 13, 14, while the latter is possible by changing the number of rotation of the screw.

Thus, according to the continuously thermally decomposing method of the present invention, it is possible to melt and thermally decompose rapidly and uniformly even synthetic macro-molecule materials of poor thermal conductivity by the internal heat produced by the application of shearing and the external heating, as well as, at the same time, it is possible to discharge the residue continuously on the strength of the transporting ability of the screw.

With the synthetic macro-molecule materials of such a random type as polyethylene, too, it is possible, according to the present invention, to adjust the degree of their thermal decomposition by controlling the feed velocity for the material, the temperatures for thermal decomposition and the degree of vacuum; and it is also possible to obtain low-molecular products in liquid type or wax-like, depending on decomposing conditions.

On the other hand, with the synthetic macro-molecule materials which is easy to produce monomers by the thermal decomposition, the secondary reaction at the time of the thermal decomposition is less so that the monomers can be recovered with a large yield.

The following specific examples will serve to illustrate preferred embodiments of the invention, although it should be understood that these examples are not intended to limit the scope of the invention.

EXAMPLE 1

The experiment was made using a single-screw type extruder having an inner diameter of 40 mm.

The material was "polystyrene 525-51" (a trade name of Mitsui Toatsu Chemical Inc.) as the general polystyrene.

Thermal Decomposition Temperature (°C)	Degree of Vacuum (Gauge Pressure, mm Hg)	Number of Rotation of Screw (r.p.m.)	Yield Ratio of Liquid Products (%)	Amount of Styrene in the Liquid (%)
[illegible]°C	-30mm Hg	50rpm	[illegible]	[illegible]
"	-250	"	–	[illegible]
"	-500	"	[illegible]	[illegible]
[illegible]	Atmosphere	60	[illegible]	[illegible]
"	-30mm Hg	"	100.0	[illegible]
"	-250	"	[illegible]	[illegible]
"	-500	"	[illegible]	[illegible]

The most of the recovered liquid decomposed products was styrene together with dimer, trimer, toluene, benzene, α-methyl styrene.

In this case, the formation of the residue carbon was not recognized at all, but the gaseous decomposed products was about 0.5–4.0%.

EXAMPLE 2

The experiment was made using a single-screw extruder having an inner diameter of 40 mm.

The material was "High Impact Polystyrene 830-02" (a trade name of Mitsui Toatsu Chemical, Inc.) as high impact polystyrene.

Thermal Decomposition Temperature (°C)	Degree of Vacuum (Gauge Pressure, mm Hg)	Number of Rotation of Screw (r.p.m.)	Yield Ratio of Liquid Products (%)	Amount of Styrene in the Liquid (%)
[illegible]°C	-30mm Hg	50rpm	[illegible]	[illegible]
"	-300	"	[illegible]	[illegible]
"	-650	"	[illegible]	[illegible]
[illegible]	Atmosphere	60	[illegible]	[illegible]
"	-250	"	[illegible]	[illegible]
"	-500	"	[illegible]	[illegible]

The most of the liquid products was styrene. The gaseous products were somewhat more than the case of the general polystyrene and inflammable. The thermal decomposed residue carbon was about 1–2% and most of it was recovered from the residue tank, but a small amount of the carbon was recognized in the flow passage of the screw.

EXAMPLE 3

The experiment was made using a single-screw type extruder having an inner diameter of 40 mm

The material was "Cyco Lac T1100" (a trade name of Ube Cycon Co., Ltd.) as the copolymer of acrylonitrile, butadiene and styrene.

Thermal Decomposition Temperature (°C)	Degree of Vacuum (Gauge Pressure, mm Hg)	Number of Rotations of Screw (r.p.m.)	Yield Rate of Liquid Products (%)	Amount of Styrene in the Liquid (%)
500°C	~100mm Hg	30rpm	67.0%	51%
600	"	"	90.1	44

The liquid products included a relatively large quantity of styrene, but acrylonitrile, toluene, α-methyl styrene, etc. are also recognized. Further, in the gaseous products the existence of ammonia was not recognized. Though, when the thermal decomposition temperature was not equilibrated with the material supply velocity (i.e. r.p.m. of the screw), the thermal decomposition in the extruder did not completed so that incompletely thermally decomposed products were fed into the residue tank, the thermal decomposition was completed by heating the residue tank.

EXAMPLE 4

The experiment was made using a single-screw type extruder having an inner diameter of 40 mm.

The material was "Shinko Lac. ABS" (a trade name of Mitsubishi Rayon Co., Ltd.) as polymethylmethacrylate.

Thermal Decomposition Temperature (°C)	Degree of Vacuum (Gauge Pressure, mm Hg)	Number of Rotations of Screw (r.p.m.)	Yield Rate of Liquid Products (%)
500°C	~100mm Hg	30rpm	95.0%
"	~230	"	91.0

More than 95% of the liquid products was methyl methacrylate monomer.

Further, in this case, the formation of carbon after the thermal decomposition was not recognized at all.

EXAMPLE 5

The experiment was made using a single-screw type extruder having an inner diameter of 40 mm.

The material was "Poly Propylene P600" a trade name of Mitsui Petrochemical Industries, Ltd.) as polypropylene.

Thermal Decomposition Temperature (°C)	Degree of Vacuum (Gauge Pressure, mm Hg)	Number of Rotations of Screw (r.p.m.)	Yield Rate of Liquid Products (%)	Properties of Products
600°C	Atmosphere	40rpm	70.0%	Liquidous at a room temperature
"	~100mm Hg	"	68.5	"
"	~210	50	72.1	Greasy at a room temperature

The thermally decomposed products varied from a liquidous substance of low viscosity at a room temperature to a greasy one according to the decomposition condition.

The gaseous products were obtained in the amount of 20% or thereabout, and their property corresponded to that of LPG. Further no carbon produced by the thermal decomposition was recognized in this experiment.

EXAMPLE 6

The experiment was made using a single-screw type extruder having an inner diameter of 40 mm.

The material was "Mirason Neo 23H" (a trade name of Mitsui Petrochemical Industries, Ltd.) as polyethylene.

Thermal Decomposition Temperature (°C)	Degree of Vacuum (Gauge Pressure, mm Hg)	Number of Rotations of Screw (r.p.m.)	Yield Rate of Liquid Products (%)	Properties of Products
600°C	Atmosphere	30rpm	66.0%	Liquidous at a room temperature
"	"	40	74.0	"
"	~100mm Hg	"	80.0	Greasy at a room temperature

The thermally decomposed products obtained varied from a liquid-like substance with low viscosity at a room temperature to a greasy one or a wax-like one according to the decomposition condition.

As the result of the analysis of the thermally decomposed products by a gas chromatography, hydrocarbons having carbons in number ranging from 5 to about 35 were obtained.

The decomposition condition effected remarkably on the mean value of number of carbon rather than the range of the distribution of the carbon. The gaseous products were inflammable gases comprising principally ethylene and propylene.

What is claimed is:

1. Method for continuously thermally decomposing a synthetic macro-molecule composition consisting essentially of an organic polymer selected from the group consisting of polystyrene; copolymer of acrylonitrile, butadiene and styrene; polymethylmethacrylate; polypropylene; and polyethylene, comprising the steps of continuously supplying said synthetic macro-molecule composition in an extruder and having a cylinder with

means for heating said composition to a temperature of from 500°C to 600°C and discharge orifices for removing volatile products, said extruder being capable of subjecting said synthetic macro-molecule composition to shearing and kneading, transporting said synthetic macro-molecule composition within said extruder and continuously shearing and kneading said composition, continuously heating and thermally decomposing said synthetic macro-molecule composition in said cylinder of said extruder at a temperature from about 500°C to about 600°C, discharging low molecular weight volatilized products of not more than about 35 carbon atoms from thermally decomposing said composition through said discharge orifices in said cylinder of said extruder, conveying said low molecular weight volatilized products of not more than about 35 carbon atoms to condensing means directly connected to said discharge orifices, and condensing said low molecular weight volatilized products in said condensing means as products having from about 5 to about 35 carbon atoms per molecule.

2. Method for continuously thermally decomposing synthetic macro-molecule composition as claimed in claim 1, wherein said condensing means are provided with means for reducing pressure and providing a vacuum therein, whereby the mean molecular weight of said low molecular weight products to be recovered is controlled by controlling the degree of vacuum in said condensing means.

3. Method for continuously thermally decomposing synthetic macro-molecule composition as claimed in claim 1, wherein the residue of said synthetic macro-molecule materials having not been decomposed in the cylinder of said extruder is discharged at the discharge end of said extruder into a residue receiving means directly connected to said end by the screw of said extruder, said screw having one or more threads projecting into said residue receiving means.

4. Method for continuously thermally decomposing synthetic macro-molecule composition, according to claim 1, wherein the melting of the said synthetic macro-molecule composition is carried out in said cylinder in a melting zone at about 250°C.

* * * * *

(19) BUNDESREPUBLIK DEUTSCHLAND

DEUTSCHES PATENTAMT

(12) Offenlegungsschrift
(11) DE 3146194 A1

(51) Int. Cl.3:
C08F 8/50
C08F 20/10
C08J 11/04

(21) Aktenzeichen: P 31 46 194.8
(22) Anmeldetag: 21. 11. 81
(43) Offenlegungstag: 26. 5. 83

DE 3146194 A1

(71) Anmelder:
Röhm GmbH, 6100 Darmstadt, DE

(72) Erfinder:
Müller, Manfred, 6101 Roßdorf, DE; Wenzel, Franz, Dr., 6100 Darmstadt, DE

(54) Verfahren und Vorrichtung zur thermischen Depolymerisation von Polymeren

(57) Die Erfindung betrifft ein kontinuierliches Verfahren zur thermischen Depolymerisation von Polymeren in mehreren thermischen Behandlungsabschnitten, wobei das zu depolymerisierende Polymermaterial in einem Extruder zunächst in schmelzflüssigen Zustand überführt, dann in den zur thermischen Depolymerisation geeigneten Temperaturbereich gebracht und partiell thermisch abgebaut wird, dann das entstehende Gemisch aus geschmolzenem und gasförmigem Material unmittelbar anschließend in einen mit Rührvorrichtung ausgestatteten Pyrolysereaktor überführt und dort bei Depolymerisationstemperatur die thermische Depolymerisation unter Bildung gasförmiger Produkte fortgesetzt wird und abschließend die gasförmigen Produkte kondensiert werden.
(31 46 194)

DE 3146194 A1

Verfahren und Vorrichtung zur thermischen Depolymerisation von Polymeren

Patentansprüche

1. Kontinuierliches Verfahren zur thermischen Depolymerisation von Polymeren unter Verwendung eines Extruders und eines mit Rührvorrichtung versehenen Pyrolysereaktors,

dadurch gekennzeichnet,

daß das Verfahren mehrere thermische Behandlungsabschnitte umfaßt, wobei das zu depolymerisierende Polymermaterial im Extruder zunächst in schmelzflüssigen Zustand überführt, dann in den zur thermischen Depolymerisation geeigneten Temperaturbereich gebracht und partiell thermisch abgebaut wird, dann das entstehende Gemisch aus geschmolzenem und gasförmigem Material unmittelbar anschließend in den mit Rührvorrichtung versehenen Pyrolysereaktor überführt, und dort bei Depolymerisationstemperatur die thermische Depolymerisation unter Bildung gasförmiger Produkte fortgesetzt und abschließend die gasförmigen Produkte kondensiert werden.

2. Kontinuierliches Verfahren gemäß Anspruch 1, dadurch gekennzeichnet, daß die bei der Depolymerisation gebildeten, gasförmigen Produkte unter Ausnutzung ihrer Wärmeenergie direkt anschließend destillativ aufgearbeitet werden.

...

3. Kontinuierliches Verfahren gemäß den Ansprüchen 1 und 2, dadurch gekennzeichnet, daß das Verfahren zur thermischen Depolymerisation von Polymethylmethacrylat (PMMA) verwendet wird.

4. Kontinuierliches Verfahren gemäß Anspruch 3, dadurch gekennzeichnet, daß die Depolymerisation des PMMA im Temperaturbereich zwischen 200 und 800°C, vorzugsweise 400 bis 500°C, durchgeführt wird.

5. Vorrichtung zur Durchführung des Verfahrens gemäß den Ansprüchen 1 bis 4, bestehend aus einem Extruder (1) mit Transportschnecke (2), an dessen Austrittsöffnung (3) ein Pyrolysereaktor (4) direkt angeschlossen ist, der einen beheizbaren Rohrmantel (9) und eine Rührvorrichtung (5) aufweist.

6. Vorrichtung gemäß Anspruch 5, dadurch gekennzeichnet, daß sich im oberen Abschnitt des Pyrolysereaktors (4) eine Austrittsöffnung (7) für gasförmige Produkte und im unteren Abschnitt ein nach unten führender Auslaß (8) für die nicht pyrolysierbaren Anteile befinden.

7. Vorrichtung gemäß den Ansprüchen 5 und 6, dadurch gekennzeichnet, daß die Rührvorrichtung (5) des Pyrolysereaktors (4) aus einer Rührwelle, vorzugsweise mit Rührelementen besteht, die direkt an die Transportschnecke (2) des Extruders (1) angeschlossen ist.

8. Vorrichtung gemäß den Ansprüchen 5 bis 7, dadurch gekennzeichnet, daß der Pyrolysereaktor (4) teilweise mit einem, im wesentlichen inerten zur Wärmeübertragung geeigneten, nicht-gasförmigen Material (6), gefüllt ist.

9. Vorrichtung gemäß Anspruch 8, dadurch gekennzeichnet, daß der Pyrolysereaktor (4) mit Sand oder Metallspänen, vorzugsweise bis etwa zur Hälfte gefüllt ist.

10. Vorrichtung gemäß den Ansprüchen 8 und 9, dadurch gekennzeichnet, daß Anteile des zur Wärmeübertragung geeigneten, nicht-gasförmigen Materials (6) kontinuierlich dem Pyrolysereaktor entnommen und gegebenenfalls nach ihrer Regeneration dem Pyrolysereaktor wieder zugeführt werden können.

11. Vorrichtung gemäß den Ansprüchen 8 bis 10, dadurch gekennzeichnet, daß das im wesentlichen inerte, zur Wärmeübertragung geeignete Material (6) im Kreis geführt und mit Gas, Rauchgas u.ä. geheizt wird.

Verfahren und Vorrichtung zur thermischen Depolymerisation von Polymeren

Die Erfindung betrifft ein Verfahren zur Depolymerisation von Polymeren wie z.B. Acrylharzen, insbesondere von Polymethylmethacrylat.

Der Polymerisationsprozeß von Monomeren, der bei niederen Temperaturen in Richtung vom Monomeren zum Polymeren verläuft, kehrt sich in der Regel bei hohen Temperaturen um. Jeder Temperatur kommt eine bestimmte Gleichgewichtseinstellung zwischen Polymerradikalen und Monomeren zu. Die ceiling-Temperatur, bei der das Gleichgewicht völlig auf der Seite des Monomeren liegt, beträgt z.B. für Methylmethacrylat 220°C. Bildung, wie Zerfall der Polymeren vom Typ des Polymethacrylats verlaufen radikalisch.

Der Zerfall beginnt an den instabilsten Stellen des Makromoleküls (häufig an den Enden) und setzt sich bei entsprechenden Bedingungen fort bis zum völligen Abbau oder bis der Abbau bei einem Baustein angelangt ist, der thermisch keine Radikale bildet oder derart instabile, daß diese weiterreagieren, bevor es zur Abspaltung eines Monomeren kommt. Eine solche blockierende Funktion können z.B. Acrylsäureester als Comonomere in Methylmethacrylat-Copolymerisaten ausüben.

Die Aufgabe, aus Polymethylmethacrylat (PMMA), wie es beispielsweise bei der Be- und Verarbeitung zu Halbzeug und zu den Endprodukten anfällt, monomeres Methylmethacrylat (MMA) zurückzugewinnen, beschäftigt die Technik schon seit den Dreißiger-Jahren (DE-PS 642 289). Die Hauptprobleme waren dabei in der Wärmeübertragung und dem Auskreisen des der jeweiligen Gleichgewichtskonzentration entsprechenden Methylmethacrylats und dessen Aufreinigung gesehen worden.

Im allgemeinen wird bei Depolymerisationstemperaturen zwischen ca. 200 - 500°C gearbeitet, wobei u.a. versucht wurde, die Temperatur durch Anwendung von Vakuum herabzusetzen (DE-PS 729 730). In der Folge wurde die Reaktion in theoretischer und praktischer Hinsicht an vielen Stellen untersucht, wobei u.a. dem Einfluß bzw. der Abhängigkeit von Inhibitoren, Sauerstoff, Verunreinigungen, der Kettenlänge usw. nachgegangen wurde.

In der FR-PS 1 114 639 wird als indifferenter Wärmeüberträger Sand oder Infusorienerde empfohlen. Aus dem Gemisch des Trägers mit PMMA-Abfällen wird bei ca. 250°C ein Destillat erhalten, aus dem man nach Zusatz von n-Butanol und Schwefelsäure, MMA, Methanol und Butylmethacrylat destillativ gewinnen kann.

Aus der FR-PS 1 079 107 ist die Verwendung von geschmolzenem Blei bei einer Reaktionstemperatur von 450 - 500°C bekannt, und aus der Zusatzanmeldung FR-PS 64 464 die Anwendung von weiteren Metallen bzw. Metallegierungen und Verbindungen, die in diesem Bereich schmelzen (Bi, Cd, Sn, Rb, Se, Te, Th bzw. Gemischen und Legierungen).

Weiter ist der thermische Abbau unter Stickstoff bekannt.

Aus der DE-OS 23 10 463 und der US-PS 3 959 357 ist ein Verfahren zur kontinuierlichen thermischen Zersetzung synthetischer Makromoleküle im Extruder bekannt, wobei die

thermisch zersetzten, verflüchtigten Produkte in eine Kondensationsvorrichtung eingeleitet werden, welche direkt an die Austragsöffnungen im Zylinder des Extruders angeschlossen sind, um dort kondensiert zu werden. Beispielhaft wird auch die Zersetzung von PMMA zu MMA im Einschneckenextruder unter Vakuum bei einer thermischen Zersetzungstemperatur von 500°C angegeben, wobei über die Gewinnung von mehr als 95 % der flüssigen Produkte als MMA berichtet wird.
Kontinuierliche Pyrolyse von PMMA-Abfällen in einem Zwei-Schnecken-Pyrolysegerät bei 450 bzw. 500°C mit einem Durchsatz von 5 kg/Stunde läßt sich aus Chem.Abstr. 86, 73864, entnehmen. Die Ausbeute an MMA beträgt 90 %. Auch andere in technischem Maßstab für pyrolytische Reaktionen geeignete Aggregate, wie Röhrenöfen, Drehrohröfen, Wirbelschichtöfen, sind einschlägig verwendet worden. Sie erfordern das Arbeiten unter Schutzgas bzw. unter Sauerstoffausschluß (Pyrolysegas). Die Verfahren sind daher im allgemeinen zu aufwendig und zu teuer.

Die Verfahren des Standes der Technik konnten insgesamt nicht völlig befriedigen.
Bei der totalen Pyrolyse innerhalb des Extruders kann es sehr schnell zur Verstopfung der Extruderschnecke infolge Ablagerung von nicht-crackbaren Anteilen kommen. Eine nur teilweise durchgeführte Crackung führt zwangsläufig zu Verlusten. Das Austragen der nicht gecrackten Anteile belastet das Verfahren erheblich.

Es bestand daher die Aufgabe, ein kontinuierlich arbeitendes technisches Verfahren zur thermischen Depolymerisation von Polymeren, wie Polymethylmethacrylat bzw. anderen thermisch abbaubaren Homo- und Copolymerisaten von Methacrylsäureestern zu finden, das die genannten Nachteile vermeidet. Im Vordergrund steht die Gewinnung möglichst reinen Methylmethacrylats.
Weiter sollte das Verfahren in möglichst geringem Umfang zur Belastung mit Rückständen, verunreinigten flüssigen Trägern bzw. Lösungsmitteln, Abgasen usw. führen. Ferner war auf eine möglichst ökonomische Energiezuführung zu achten. Schließlich sollte auch auf die Verwendung von Schutzgasen nach Möglichkeit verzichtet werden.

Es wurde nun gefunden, daß die Forderungen der Technik weitgehend verwirklicht werden können, wenn man die zu depolymerisierenden, in der Regel als Festkörper vorliegenden polymeren Materialien unter Verwendung eines Extruders (1) und eines mit Rührvorrichtung versehenen Pyrolysereaktors (4) in mehreren thermischen Behandlungsabschnitten depolymerisiert, wobei die zu depolymerisierenden Materialien, vorzugsweise in zweckmäßig zerkleinerter Form, in den Extruder (1) eingeführt und dort zunächst aufgeschmolzen (Stufe 1), dann in einen, zur thermischen Depolymerisation geeigneten Temperaturbereich gebracht werden und eine partielle thermische Depolymerisation durchgeführt wird (Stufe 2), dann das entstehende Gemisch aus schmelzflüssigem und gasförmigem Material unmittelbar anschließend in den mit Rührvorrichtung versehenen Pyrolysereaktor (4) überführt und dort bei Depolymerisationstemperaturen die thermische Polymerisation unter Bildung gasförmiger Produkte fortgesetzt wird (Stufe 3) und diese anschließend kondensiert werden (Stufe 4). Zur näheren Erläuterung dient Fig. 1, auf die sich die Zahlenangaben in Klammern beziehen. Ein besonderer Vorteil des erfindungsgemäßen Verfahrens ist darin zu sehen, daß für die ersten beiden thermischen Behandlungsstufen handelsübliche, heizbare Vorrichtungen mit rotierender Schnecke (Transportschnecke (2)) zum Fördern und Aufschmelzen von Kunststoffen verwendet werden können, welche im Sinne der vorliegenden Erfindung unter dem Sammelbegriff "Extruder" zusammengefaßt werden. Der Prozeßablauf im Extruder umfaßt dabei Fördern und Verdichten, Aufschmelzen und Mischen, Druckaufbauen und Fördern (vgl. Kunststoff-Handbuch, Herausgeber R. Vieweg u. D. Braun, Bd. I, S. 1029 ff).

Die Temperaturbedingungen sollen in den infrage kommenden Abschnitten des Extruders (1) so gewählt werden, daß partielle Depolymerisation der eingebrachten Polymeren erfolgen kann. Im Falle des Polymethylmethacrylats liegt dieser Bereich bei 200 bis 800°C, vorzugsweise bei 400 bis 500°C.[*]
Zweckmäßigerweise werden Extruder (1) und Pyrolysereaktor (4) in unmittelbarer Kombination betrieben, z.B. indem das im Extruder gebildete Gemisch aus Schmelze und Pyrolysegasen durch die Austrittsöffnung (Schneckenkopf (3)) direkt in den Pyrolysereaktor (4) gedrückt wird.
Der Pyrolysereaktor (4) kann im Prinzip aus einem (von außen) beheizbaren Rohr, insbesondere einem metallischen Rohrmantel, beispielsweise in zylindrischer oder konischer Form bestehen,

---

[*] Unmittelbar nach dem Eintrag des Polymermaterials in den Extruder wird das Material von RT auf die Schmelztemperatur (ca. 250 - 400°C) aufgeheizt.

das eine Rührvorrichtung (5) besitzt, also beispielsweise mit einer Rührwelle mit Rührelementen ausgestattet ist. Die Rührwelle (5) kann zweckmäßigerweise direkt an die Transportschnecke (2) des Extruders (1) angeschlossen sein. Vorzugsweise ist der Pyrolysereaktor (4) teilweise, etwa zur Hälfte mit einem im wesentlichen inerten, zur Wärmeübertragung geeigneten, nicht gasförmigen Material (6) gefüllt, (im folgenden als "wärmeübertragendes Material" bezeichnet). Hierfür kommen z.B. die aus dem einschlägigen Stand der Technik als Wärmeüberträger bekannten, insbesondere aus leicht beweglichen Partikeln bestehenden Materialien, z.B. Sand, Metallspäne, Kieselgur, Quarz u.ä. in Frage. Gegebenenfalls können auch Materialien, welche die Depolymerisation katalysieren, (mit)verwendet werden.[*]
Vorteilhafterweise befindet sich die Austrittsöffnung (7) für die Pyrolysegase am oberen Teil des Pyrolysereaktors (2). Die Pyrolysegase können unmittelbar unter Ausnützung ihrer Wärmeenergie der destillativen Aufarbeitung zugeführt werden. Die nicht pyrolysierbaren Anteile werden vorteilhafterweise nach unten ausgetragen, z.B. über einen Auslaß (8) und beispielsweise über ein geeignetes Sieb in eine mit Sperrflüssigkeit (Wasser) versehene Wanne eingeführt.
Die Rührelemente der Rührvorrichtung (5) können so ausgeführt sein, daß das wärmeübertragende Material (6) umgewälzt wird.
Der Pyrolysereaktor (4) kann beispielsweise so gebaut sein, daß eine kontinuierliche Entnahme und Wiederzuführung einer gewissen Teilmenge des wärmeübertragenden Materials zwecks Regenerierung möglich ist.
Der Pyrolysereaktor (4) kann, aber braucht nicht direkt beheizbar zu sein. Die notwendige Energiezufuhr kann bei-

---

[*] Besonders vorteilhaft ist eine Ausführungsform, bei der das wärmeübertragende Material (6) im Kreis geführt und die Heizung des im Kreis laufenden Materials mittels Gas, Rauchgas o.ä. betrieben wird.

spielsweise auch durch Aufheizen (z.B. mit Rauchgas) des wärmeübertragenden Materials im Zuge des Umlaufens erfolgen. Zweckmäßigerweise können anschließend an die Austrittsöffnung (7) geeignete Staub- und Rußabscheider (10), z.B. Zyklonabscheider dem Pyrolysereaktor (4) nachgeschaltet werden.*

Das Verfahren der Erfindung eignet sich besonders zur thermischen Depolymerisation von Polymethylmethacrylat (PMMA) sowie thermisch depolymerisierbarer Copolymerisate desselben neben anderen Polymeren. Insbesondere bietet sich das Verfahren zur Verwertung von Abfallmaterial aus Produktion und Verarbeitung an. Ein Vorteil des erfindungsgemäßen Verfahrens liegt darin, daß es sich mit Extrudern konventioneller Bauart in Kombination mit einem einfach aufgebauten Pyrolysereaktor durchführen läßt. Die Verarbeitungsabläufe sind somit übersichtlich und die praktische Durchführung des Verfahrens gestaltet sich unerwartet einfach und problemlos.
Vorteilhafterweise werden die Acrylglas- oder Spritzgußabfälle vor dem Einbringen in den Extruder (1) in zweckmäßiger Weise zerkleinert. Besonders günstig sind die relativ kurzen Verweilzeiten, denen die zu unerwünschten Nebenreaktionen befähigten Substanzen bei dem Verfahren der Erfindung ausgesetzt sind. Dadurch erhält man ungewöhnlich reine Verfahrensprodukte, insbesondere sehr reines Methylmethacrylat (MMA). Die Bildung von hydrierten Nebenprodukten wird z.B. weitgehend unterdrückt.
Weiter läßt sich das Verfahren im allgemeinen ohne Schutzgas durchführen, da die Förder- und Aufschmelzzone gegen

---

* Die Temperaturbereiche im Extruder (1) lassen sich z.B. in a) eine Aufheizzone (mit 250 - 400°C) und b) eine Schmelz- und Crackzone (mit Richttemperatur von 450°C) unterteilen. Der Richtwert für den Pyrolysereaktor (4) liegt z.B. bei 450°C.

die Außenluft dicht abgeschlossen ist. Das Verfahren ist auch deshalb besonders fortschrittlich, weil es keine ins Gewicht fallenden ökologischen Probleme mit sich bringt.
Abgasprobleme treten in der Regel nicht auf, da die auftretenden Gase kondensiert werden, ebenso ist mit Abwasserproblemen nicht zu rechnen. Es tritt keine Verunreinigung der Luft auf. Die Gefahr der Verstopfung an den Förderelementen spielt praktisch keine Rolle. Die gesamte Vorrichtung ist servicefreundlich und einfach zu reinigen.

Die folgenden Beispiele dienen zur Erläuterung der Erfindung.

Je nach Verweilzeit tritt im Extruder (1) mehr oder weniger vollständige Crackung ein. Je kürzer die Verweilzeit, umso länger wird die Aufheiz- und Schmelzzone im Extruder und umso mehr wird der Pyrolysereaktor (4) belastet.
Die (geschätzten) Verweilzeiten, bezogen auf die Schmelze, liegen bei 0,1 bis 2 min im Extruder (1) und bei 0,5 - 8 min im Pyrolysereaktor (4).
Die Temperaturverteilung gestaltet sich für die Beispiele wie folgt.

Aufheizzone	:	250 - 400°C
Schmelz- und Crackzone	:	450°C
Pyrolysereaktor	:	450°C

Beispiel 1

In einem Einschneckenextruder mit einer Schnecke von 45 mm Durchmesser und 1,2 m Länge, Heizleistung 10 kW, mit nachgeschaltetem je zur Hälfte mit Bausand gefüllten Pyrolysereaktor (Nachkracker), Länge 46,8 cm, Durchmesser 45 mm und 4,750 kW Heizleistung wurden 1070 kg PMMA-Abfälle zugesetzt und 1068 kg MMA roh direkt kondensiert (98 % MMA). Stundenleistung 17,5 kg an Abfallmaterial.

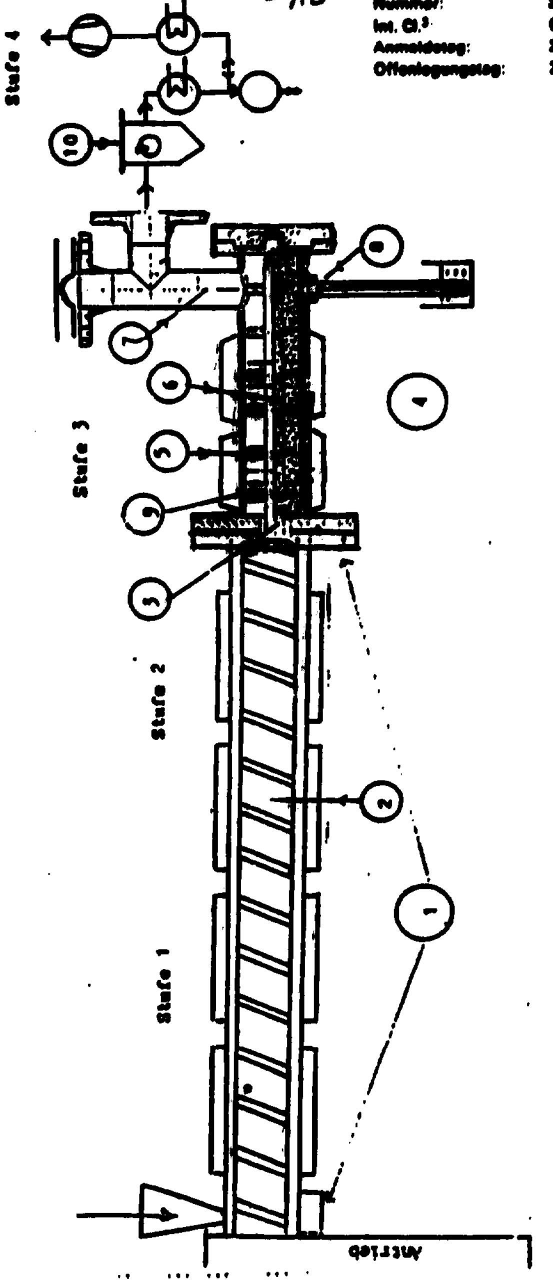
Beispiel 2

An dem Extruder von Beispiel 1 wurde ein auf 80 cm verlängerter Nachkracker mit 10 kW Heizleistung angeschlossen. Es wurden 1322 kg PMMA-Abfälle mit einer Stundenleistung von 21 kg/h durchgesetzt, wobei 1318 kg MMA-Kondensat und 4,0 kg Asche erhalten wurden (98,24 % MMA; 0,82 % H_2O).

Beispiel 3

Durch die Anlage von Beispiel 2 wurden 211 kg Spritzgußabfälle (PMMA, Polymethylmethacrylat) mit einer Stundenleistung von 11,3 kg durchgesetzt, wobei 210,9 kg Kondensat und 0,25 kg Ascha erhalten wurden (3,6 % Methylacrylat, 93,8 % MMA; 0,2 % H_2O).

Nummer: 3146194
Int. Cl.³: [illegible]
Anmeldetag: 21. November 1981
Offenlegungstag: 26. Mai 1983



Anlage zur thermischen Depolymerisation von Polymeren

Fig. 1

Annexe VI

Economic Parameters

The total workforce of the PMMA-factory, which operates in 2 shifts, is as follows

per shift	
8 cauldrons	5 operators
distill./rectification	2 "
prepolymerization + pigment harmonization	2 "
polymerization	12 "
mould preparation	6 "
water bath	6 "
maintenance	4 "
logistics	1 "
analysis	1 "
quality control	1 "
packing	1 "
	41 "

This number seems very high. Due to the summer period activity was low. Most work seemed to take place on a part-time basis.

Other economic data

Utilities

Power	0.1 Yuan/kWh
Coal	0.12 Yuan/kg
Steam	0.05 Yuan/kg (low pressure)
Cooling Water	0.20 Yuan/kg (32°C)
	0.30 Yuan/kg (about 10°C)

Raw Materials and Products

PMMA-waste	3.0 Yuan/kg
Monomer	8.0 Yuan/kg (Purity 98 %)

Manpower

Operators	1.5 Yuan/man-hour

Equipment

Raw material cost of plain steel
2000 Yuan/tonne

Equipment cost, simple equipment in stainless steel
20000 Yuan/tonne

Annexe VII

The SRRUC-team

Mr. Yuang Yongling, Manager	Nashi District Branch SRRUC
Mr. Zhang Dexing, section chiefa	SRRUC
Miss Sun Xiao Lu, asst. engineer	"
Mr. Guo Bangda, technician	Nashi Branch
Mr. Hu Zhongging, vice Director of Xingguang Factory	" "
Mr. Liu Paoping " "	"
Mr. Zhang Yanxias, interpreter	SRRUC
Miss. Cheng Qiuying, "	"
Mr. Xu Ruitian, engineer	"

ANNEXE B

MISSION REPORT OF NOVEMBER 15,1986

RESTRICTED

November 15, 1986
English

DEVELOPMENT OF AN IMPROVED PMMA PYROLYSIS SYSTEM

SI/CPR/86/028/11-51/32.1.H.
PEOPLE'S REPUBLIC OF CHINA

Mission report :

Prepared for the Government of the
People's Republic of China
by the United Nations Industrial Development Organization,
acting as an executing agency for the United Nations
Development Programme

Based on the work of Alfons G. Buekens,
expert in waste recycling

United Nations Industrial Development Organization
Vienna

This report has not been cleared with the United Nations Industrial Development Organization which does not, therefore, necessarily share the views presented.

TABLE OF CONTENTS.

1. SCOPE OF THIS REPORT.

The aim of this study is to develop an improved PMMA Pyrolysis system. The presently used technology has the following disadvantages :
- low yield of the MMA product
- low purity of the MMA product
- pollution hazards
- safety hazards

In the course of this study experimental work is being conducted to test a proposed new technology and optimize its operating conditions.

Design computations are being conducted in order to assist the Chinese counterparts in the dimensioning, construction and testing of the unit.

This report is only concerned with the second part of this study. The experimental study will be discussed in a separate report, the production of which has been delayed by the occurrence of a mechanical problem in the experimental unit.

Still, it can be claimed at present that the new technology is capable of generating a higher yield and a much better product quality than the one in use at present.

2. SELECTION OF AN IMPROVED PMMA PYROLYSIS METHOD.

Pyrolysis processes may be conducted in various types of reactors and modes, e.g.

1. as a batch process, or 2. as a continuous process	OPTION (A)
1. in an indirectly heated reaction 2. in a directly heated reactor 3. in a reactor with circulating heat carrier	OPTION (B)
1. in a vertical shaft reactor 2. in a rotary kiln reactor 3. in a fluidized bed reactor	OPTION (C)

At present, the PMMA pyrolysis is conducted in a batch mode, in an indirectly heated pyrolysis retort. This productionmethod is described in detail in our previous report dd August 1, 1986.

After consideration of various factors a continuous fluidized bed type of reactor has been selected as an optimal means of conducting the process.
A batch process will necessarily have a lower yield as well as less convincing safety and pollution records than a continuous plant.
Moreover, at the scale desired by SRRUC (100-300 kg/h) a continuous operation becomes desirable.
Option B3, featuring a circulating heat carrier, may be considered to be too complicated for this scale of capacity. Moreover, it would require very extensive development work, which cannot be completed within the scope of this project.
A vertical shaft reactor is unsuitable for the pyrolysis of shavings of PMMA (button factory). Moreover, a rotary kiln reactor presents a difficult sealing problem, which entails supplemental environmental and safety precautions.
By elimination, a fluidized bed reaction, either directly or indirectly heated, has been selected. Its main advantages are : high yield, high selectivity, fast heat transfer and continuous elimination of the filler materials.
As a transition measure, cauldrons with some molten lead on the bottom can be tested and used at a scale determined by mechanical constraints. This method can only be used as an interim solution because of the poor heat transfer characteristics which arise when treating pearlite filled PMMA.

3. PRELIMINARY DESIGN COMPUTATIONS.

The required performances of the improved unit are given in Annexe III of our previous report.
Capacity : 800 tonnes/year
This capacity can be realized in several ways :

- unit capacity : 100 kg/h
A fully continuous operation (during 7 days/week) yields a weekly production of 16.8 tonnes/week.
The required capacity is obtained, by operating 47.6 weeks a year, leaving a meagre 4.4 weeks for maintenance (8.5% excess capacity)

- unit capacity : 200 kg/h
Continuous operation for 6 days/week (136 hours at operating temperature) gives a weekly production of 27.2 tonnes/week, which leaves 76.8% excess capacity, which is extremely ample.

- unit capacity : 300 kg/h
daily operation in 2 shifts of 8 hours limits the effective daily operation period to some 10 hours at the desired temperature. The weekly production (6 working days) amounts to 18 tonnes/week, which leaves only 11.7% excess capacity.
The desired capacity of the unit can be selected by SRRUC on the basis of the previous considerations.

Fluidized Bed Units

An indirectly heated unit may either use steam or pyrolysis gas as a fluidizing medium.
During start-up an external supply of steam is required. Our computations are based on steam of 110°C. The minimum steam quality requirements are determined by the pressure loss over the plant.

A directly heated unit is simpler from a conceptual viewpoint, but also more delicate with respect to safety and environmental considerations. The fluidizing medium consists of (a) gas obtained by (slightly sub-) stoichiometric combustion of gas mixed with (b) recycle gas to adjust the operating temperature. An afterburner should be foreseen to complete the combustion of the purge gas to the atmosphere.
The preliminary design computations are based on a fluidizing gas, resulting from stoichiometric combustion.
The recovery of MMA is simpler in an indirectly heated unit. For large units, however, the available heat transfer surface becomes rate limiting, so that the latter should be extended by suitable means.

Preliminary Design Computations were conducted on a basis of mass and heat balances; only kinetic data have not been incorporated yet. Hence, it is assumed that pyrolysis proceeds sufficiently fast at the selected reaction temperature. The equations are given in Annexe.

The following basic assumptions have been used :

Bed Height = 1 m

Bed material density = 2 400 kg/m^3 (in case of indirect heating)
diameter = 500 µ

The minimum velocity of fluidization (U_{mF} heating) is computed from a correlation given in Reference (1)

The fluidized bed(s) is (are) operated at a value of the superficial velocity u, which equals $3u_{mf}$. This value is optimal from a viewpoint of heat transfer and also ensures a thorough mixing of the bed.

The heat of reaction is supposed to be 2 430 kJ/kg PMMA converted (2); this value has to be confirmed in actual practice.

The over-all heat transfer rate coefficient is supposed to be 0.5 kW/m^2,h, which is a high value. A lower real value could lead to capacity limitations in the case of indirect heating.

The pyrolysis temperature in most computations is selected to be 500 °C.

The pyrolysis rate is supposed to correspond with a heat consumption rate of 4.10^6 kJ/m^3, h. The definition of this rate is given in Annexe.

4. Discussion.

The actual design data computations are given in Annexe II.

In direct heating the resulting data can be summarized as follow.

capacity	100	200	300	kg/h
Reactor Diameter	465	657	805	mm
Gas velocity	249	249	249	mm/s
Fuel consumption (natural gas)	17.9	35.9	53.8	kg/h
Flow rate cooling water	5.0	10.0	15.0	m^3/h
Condensor Area	5.3	10.6	15.9	m^2

In the hypothesis that the rate of reaction would be adequate at 400°C the reactor diameter of the 100 kg/h plant becomes slightly smaller (432 mm), along with the gas velocity (217 mm/s) and the fuel consumption rate (15.5 kg/h).

It can be concluded that the reactor volume is essentially determined by the rate of heat generation by combustion. which based on losses of 10% deducted in this example amount to 4 million kJ/m^3, h. This is equivalent to the sensible heat, delivered by the fluidizing gas to the bed, a value which can easily be controlled by varying the inlet temperature. The distributor of the fluid bed should be constructed from a heat resistant material.
The major unknown factor, i.e. the bed temperature, does not have a large influence upon the individual design parameters.

For indirect heating the corresponding data become (same basic assumptions) 500°C.

Capacity	100	200	300	kg/h
Reactor Diameter	383	542	664	mm
Steam velocity	381	381	381	mm/S
Fuel Consumption (coal)	30.0	65.9	106;9	kg/h
Steam consumption	45.2	90.4	135.5	kg/h
Heating bed temp.	713	801	869	°C
Shell diameter	660	960	1210	mm
Flow rate cooling	3.8	7.6	11.4	m^3/h
Condensor Area	4.1	8.1	12.2	m^2

In this case the heat release rate corresponds to the amount of heat, transferred into the bed from an other furnace. In this computation the latter is supposed to be an external fluid bed, in which either coal or gas is fired.
In the hypothesis that a sufficient production can be realized at 400°C the corresponding data become :

Capacity	100	200	300	kg/h
Reactor Diameter	368	520	637	mm
Gas Velocity	381	381	381	mm/s
Fuel Consumption (coal)	24.9	54.0	86.5	kg/h
Steam Consumption	47.8	95.6	143.4	kg/h
Heating Bed temp.	604.4	689	754	°C
Shell diameter	610	890	1110	mm
Flow rate cooling water	3.45	6.9	10.4	m^3/h
Condensor Area	4.4	8.7	13.1	m^2

This results is in somewhat lower furnace temperature and fuel consumption values.

In the last few computations the effect was studied of
(a) using natural gas as a fuel instead of bituminous coal
(b) halving the heat transfer rate at the fluid bed/wall interphase
(c) using a finer sand particle size (0.25 mm)
(d) using a much lower value for the heat of PMMA pyrolysis

Variation (a) has no effect upon the pyrolysis bed and only a small effect on the shell diameter (0.71 instead of 0.66 m)
Variation (b) leads to an unacceptably high temperature of combustion (926 °C instead of 713 °C) in the heating bed.
Variation (c) reduces the steam velocity from 381 to 96 mm/s, leading to a reduced consumption of steam (10.6 instead of 45.2 kg of steam/h). The inner and outer shell diameter remain about the same, since they are determined by the heat balance.
Variation (d) has a favourable effect upon : the reactor diameter, the combustion temperature and the consumption of coal.

5. Advantages and disadvantages of the Proposed System.

Two versions of the PMMA pyrolysis system can be postulated :

1. **Internal heating** by means of
(a) a very hot fluidizing gas, generated by combustion of gaseous fuel and admixture of cold pyrolysis gas, or
(b) immersed electric resistance, or
(c) immersed internally heated tubes

2. **External heating** by means of
(a) an external radiant furnace
(b) an external fluid bed, heated by combustion of coal or gas

In the first version (1a) a neutral hot pyrolysis atmosphere is generated using an auxiliary furnace. The bed is fluidized by means of a hot, non oxidizing gas. Furnace and pyrolysis reactor may be constructed from plain steel, with an internal lining of refractory and insulating material. The flue gas is cleaned from sand and filler using a battery of hot cyclones (temperature above 100°C).
The MMA is condensed from the clean gas.

After completing condensation a droplet removal and demisting unit may be required. Part of the gas is recycled to control the temperature of the fluidizing medium, another part is bleeded and led to a flare or a postcombustion unit.
In the design due attention should be paid to :

- the design and control of the combustion furnace
- the quality of the MMA recovery

In all other versions steam is used as a fluidizing medium and the required heat is externally supplied, either by combustion of a fuel or by means of electric heating.
Conceptually, indirect heating is much simpler and holds the promise of better control and yields. The reactor material, however, should be of a superior quality, especially in case the fuel contains sulphur. A plausible choice may be a chromium alloyed steel.

The prefered design option, at present, is (in our opinion) solution 1b,1c, 2a or 2b.
A capacity of 100 kg/h can normally be attained using
a bed diameter of 400 mm
a steam flow of 10 to 100 kg/h (depending on the diameter of the sand particles)
a relatively small condensor
a stream of cooling water of the order or 2.5 to 5 m^3/h

Some other points of interest include

1) the total flow rate from the pyrolysis reactor (basis = 100 kg/h capacity)

	Direct heating	indirect heating dp = 0.5 mm	dp = 0.25 mm
PMMA, kg/h	100	100	100
steam, kg/h	-	45.2	10.6
flue gas, kg/h	254.6	-	-
	------	------	------
	354.6	145.2	110.6

The flow is much smaller in indirect heating, especially in case a fine bed material is used.
2) the heat balance (100 kg/h capacity)

Direct heating

<u>Heat of combustion</u>	651 000	kJ/h	(400°C)
of which	37.0%	heat of pyrolysis	
	33.8%	sensible heat	
	19.1%	latent heat	
	753 000	kJ/h	(500°C)
of which	31.9%	heat of pyrolysis	
	39.9%	sensible heat	
	18.1%	latent heat	

Indirect heating

<u>Heat supplied by furnace</u>	461 000	kJ/h	(500°C)
Total heat steam	<u>110 000</u>	kJ/h	(500°c)
	571 000		
of which	42.1%	heat of pyrolysis	
	31.8%	sensible heat	
	26.1%	latent heat	

The latent heat in the steam is an acceptable burden for the process.

Conclusions

From preliminary design computations it follows that an externally heated reactor, constructed from a suitably alloyed steel may be a good solution to the design problem at hand.

Acknowledgement

All design computations were performed by Dr. Ir. J. Schoeters, who also has supervised the experimental part of the programme.

Annexe I

HEAT BALANCES

1. Case of External or Electric Internal Heating

Thermal capacity =

(Heat of Pyrolysis of PMMA) x (Feeding rate of PMMA) x (Conversion of PMMA)

+ (Gas flow. Specific Heat gas
  + Steam flow. Specific Heat steam + oil flow. x Specific Heat oil
  + Ash flow. Specific Heat ash) x (Temp. of Pyrolysis - 20)

+ (Latent heat of evaporation of steam x flow rate of steam + latent heat of evaporation of oil x flow rate of oil)

- (Feeding rate of PMMA. Specific Heat of PMMA) x (T_{feed} - 20)
- (Feeding rate of Steam. Specific Heat of Steam) x (110-20)
- (Feeding rate of Steam. Latent Heat of Evaporation)

Reference temperature = 20°C.

Note : The steam term is slightly inaccurate.
Steam flow. Specific Heat Steam
Oil flow. Specific Heat Oil

2. Case of Heating by combustion gases

Thermal capacity =

(Heat of Pyrolysis of PMMA) x (Feeding rate of PMMA) x (Conversion of PMMA)

+ (Gas flow. Specific Heat gas
  + Steam flow. Specific Heat oil
  + Ash flow. Specific Heat ash) x (Temp. of Pyrolysis - 20)

+ (Latent heat of evaporation of steam x flow rate of steam + latent heat of evaporation of oil x flow rate of oil)

- (Feeding rate of PMMA. Specific Heat of PMMA) x (T_{feed} - 20)

REFERENCE LIST

[1] D. Kunii, O. Levenspiel, "Fluidization Engineering", J. Wiley & Sons Inc., New York, 1969

[2] W. Kaminsky and H. Sinn, "Verwertung von Kunststofabfällen durch Pyrolytischen Abbau", Final Report to the Verband Kunststoferzeugender Industrie e.v., Frankfurt am Main, 1981

ANNEXE C

MISSION REPORT OF JANUARY 5, 1987

RESTRICTED

January 5 , 1987

English

DEVELOPMENT OF AN IMPROVED PMMA PYROLYSIS SYSTEM

SI/CPR/86/028/11-51/32.1.H.
PEOPLE'S REPUBLIC OF CHINA

Mission report :

Prepared for the Government of the
People's Republic of China
by the United Nations Industrial Development Organization,
acting as an executing agency for the United Nations
Development Programme

Based on the work of Alfons G. Buekens,
expert in waste recycling

United Nations Industrial Development Organization
Vienna

This report has not been cleared with the United Nations Industrial Development Organization which does not, therefore, necessarily share the views presented.

ABSTRACT.

During the two week visit to the PRC the UNIDO-expert has presented to SRRUC the results of his design computations regarding a new PMMA pyrolysis plant, featuring modern UNIDO-Technology.

The SRRUC-team, on their hand, related their preliminary experience using a small, externally heated cauldron in which a certain amount of tin acts as an internal, molten heat carrier. During this visit this work was continued and amplified and can now be used to further support the system selection and reactor design work by the UNIDO expert.
Moreover, a full-scale test was performed on one of the large cauldrons under normal production circumstances.
The results of these experiments are analysed is this report, together with the feasibility, economics and required investment of such systems.
On the basis of the available experimental results and of the design computations performed by Dr. Schoeters (VUB), the UNIDO-expert also investigated the possibilities for a prompt implementation of the UNIDO pyrolysis technology at the Xingguang factory of SRRUC.
It was concluded from this analysis that a demonstration plant can be built almost immediately, with construction of almost all new parts of this plant in Shangai,but also that further support of UNIDO to this demonstration is a justified and necessary requirement. On the basis of these considerations SRRUC will propose a Protocol to UNIDO, which has the full support of Dr. Buekens.

TABLE OF CONTENTS

INTRODUCTION

This report deals mainly with the results of the experimental work, conducted during the stay of the UNIDO-expert in Shanghai, and with the conclusions that can be reached on their basis regarding the future PMMA Pyrolysis Demonstration plant, operating according to the process developed by UNIDO and VUB.

The Chinese counterparts have prepared the expert's visit on the basis of the Programme in Annexe I. There was one major addition to this programme : on 27, 29 and 31 December experiments were conducted by the SRRUC-Team, according to the desires of the UNIDO-Expert. In this respect, a word of praise should be granted to the SRRUC-Team for their promptness and diligence in conducting such work at a very short notice.

In the course of this visit, little attention was paid to the downstream operations (distillation, salting out, purification, prepolymerization, ...), which received considerable attention during the first visit, although they are not within the scope of the present UNIDO-Project.

On the basis of the information available at present it is possible to design a PMMA-Pyrolysis Plant, featuring the UNIDO-developed technology.
This technology will provide a higher product yield and purity, a lower consumption of coal, as well as better environmental and safety standards. After the successful conclusion of the demonstration project a renewed attention should be given to the downstream operations, which will amply benefit from the upgrading of the pyrolysis systems. This could form the basis of a further extension of this programme.

RECOMMENDATIONS.

1. After the comprehensive and dedicated efforts of the SRRUC-team throughout the experimental programme of technology development and design it seems fair to continue the UNIDO-support to this programme at the inception of its second phase, i.e. the construction, start-up, operation and optimization of a full scale demonstration plant. The latter will be based on UNIDO-developed technology. The requested financial support seems relatively limited in comparison to the pursued results and to the own financial effort made by SRRUC.

2. The help from UNIDO could take three forms :

- to finance the training of SRRUC technicians in Europe
- to provide further expert help during the second phase of the project
- to buy some measurement and control equipment, which at present is scarcely available in the PRC.

I. IMPROVEMENTS AT THE XINGGUANG FACTORY.

On the basis of the recommendations of the UNIDO-Expert several improvements were implemented at various levels of production.

- the sorting of raw PMMA
- the construction of an environmentally acceptable loading system
- the closing of the crude PMMA-tanks by means of removable covers
- the closing of the salting out unit, to avoid evaporation, oxidation, and air pollution.

The expert concludes that the proposed measures form a step forward in a direction of gradual improvement ; further progress is still possible in :

- the amplification of local PMMA testing facilities at the sorting stage
- the extension of the new loading system to a system for feeding the PMMA to the demonstration plant
- the redesign of all MMA and prepolymer handling facilities

The latter activity is warranted especially after the succesful completion of the pyrolysis unit demonstration project.

II. EXPERIMENTS USING THE SRRUC TIN BATH TECHNOLOGY

The experimental reactor cauldron has the following caracteristics :

internal diameter :	150 mm
internal height :	200 mm
wall thickness :	5 mm
weight cauldron (vessel) :	14.33 kg
(Top lid) :	6.33 kg
(Total) :	20.66 kg
cross-section of cauldron :	1.767 dm^2
volume of cauldron :	3.53 dm^3

The amount of material charged was either 500 g or 250 g. The amount of tin was 500 g or some 69 ml (at room temperature).

The cauldron was heated by means of a small fire, combusting egg-shaped coal agglomerates.

Three experiments were performed :

A : using 500 g of pearlite-filled PMMA plate punchings
B : using 500 gr of PMMA-plate (clear, coloured or filled)
C : using 250 g of pearlite-filled and other shavings

The temperature was monitored as follows :

Tw = wall temperature measured by a thermocouple at the level of the tin bath. The temperature is presumed to correspond to the temperature of this bath but in reality may be somewhat lower, due to cooling along the thermocouple protection tube.

Texh = temperature read by means of a mercury thermometer located in an insert into the exhaust line

Occassionally, the wall temperature of the cauldron was investigated and found to vary rather erratically with location and time.
The production of condensated crude MMA was monitored as a function of time, along with the various temperatures.

During experiment A, the temperature Tw first rose rapidly to 238°C (first drops), then continuously rose until the end of the experiment to a final temperature of 321°C (50 minutes later). The outside temperature of the cauldron varied in the top section of the vessel in a range, which was 30-60°C lower at the start, and afterwards remained constant at a temperature below 200°C.

III. RESULTS AND DISCUSSION.

When the coal fire was burning well the cauldron, filled with the PMMA sample, was installed on top of the fire. First the bottom and gradually the complete cauldron were heated. A characteristic point in this heating procedure is the time elapsed between the start of the experiment and the production of the first drop of crude MMA. This time can be reduced considerably by animating the fire with the aid of a forced draft fan.

After the initial drop of crude monomer is observed the rise of the 'tin bath temperature' Tw may continue, halt, or even reverse. This depends on the relative value of the two following entities :

'heat transferred from the coal fire to the charge'
and
'heat consumption by pyrolysis'

In early experiments the temperature generally continued increasing, which means that the first term remains higher than the second. In experiment C the metal became considerably overheated, before the loose shavings would report to the bath for pyrolysis.
At that moment the temperature of the bath started decreasing dramatically.

The rate of the crude MMA production may depend on :

- the temperature of the tin bath
- the quality of the PMMA supply to the surface of this bath (density, melting or flow behaviour).

In the course of each experiment the production rate can be computed on the basis of :
r = crude MMA generated/minute
After an initial period of rising rates, this production rate remains fairly constant throughout the major part of the experiment. By the end of the experiment the rate again falls off and eventually drops to zero.
The gas flow from the reactor could not be measured, no flow meter being available. For future experiments, the use of a simple gas bubble flow meter or of a capillary flow meter is recommended.
The amount of residue was remarkably small after experiment A, with very little filler material or carbon visible. The latter is loosely present on the wall more or less up to the height of the original load but especially occurs on some tin flakes on the metal bath.

In experiment B the final amount of carbon was definitely higher; experiment C showed a large amount of filler (pearlite) as well as a relatively high amount of carbon. The latter may be associated with the large overheating of the metal bath prior to the start of the reaction.
The quality of crude monomer, for the first time, was monitored in experiment A, B and C, by means of gas chromatography.

It can be concluded that the quality is determined by three factors :

- the best product is generated during steady-state production, initial and final product being of a lower quality
- the decomposition of material, generating light products rises from the start up to the end of the experiment and even further, during the next experiments (B and C)

This could be associated with a rise in the amount of carbon available in the reactor.

IV. CONCLUSIONS REGARDING THE FUTURE OF THE TIN BATH TECHNOLOGY.

From the experiments it is concluded that tin bath (or lead bath) technology is feasible for the PMMA pyrolysis.
The molten metal homogenizes the bottom temperature of the cauldron and improves the heat transfer to the charge, especially when agitated by falling pieces of PMMA (in continuous feeding) or by mechanical agitators (cf. theRohm & Haas patent in Annexe IV).

On the other hand the technology shows the following limitations, with respect to the proposed UNIDO-technology :

1) the carbon and filler materials are not eliminated from the reactor and accumulate, enhancing the formation of more carbon and leading to overheating of the metal.

2) the charge has only limited contact with the heating medium. In UNIDO technology this contact is very intimate and does not decrease with time.

3) the tin bath is relatively costly; some losses will occur (say 0.5 % per charge) and after a certain period of time the tin will have to rerefined.

The requirements of a full-scale cauldron amount to :

$$\left[\frac{0.90}{0.15}\right]^2 \times 500 \text{ g} = 18 \text{ kg}$$

at 'usual' tin values of 10-12 $/kg (*)
this leads to an inventry of 180-216 $/cauldron and a loss at every charge of 1$/charge

---

* the present price is unusually depressed.

V. EXPERIMENTAL TESTING OF THE HOT CAULDRON TECHNOLOGY.

The test of the large cauldron was conducted in a similar fashion with, however, a few differences :

1) the temperature of the charge could not be monitored.
Hence, special attention was paid to the temperature of the top of the cauldron and of the exhaust line. The figures are given in Table 5.

2) the rate of crude monomer production could not be monitored with precision. Still, the time of the initial production as well as the total quantity produced could be followed up.

3) for the first time the rate of gas production at this plant could be determined with suitable precision.

VI. RESULTS AND DISCUSSION.

Experimental data

Heating period : 17 minutes (first appearance of oil)
Production period : 78 minutes
Production rate (average) : 20.4 kg/h (without) 16.7 (with start/ and stop included)
Continuing gas production, without visible oil condensation : about 10 minutes.
The analytical data of the various samples show :

1) definitely higher quantities of by-products, lights as well as heavies

2) increase of the lightest products as a function of time

NOTE : On the basis of the temperatures recorded and on previous measurements it can be concluded that the attained yields were idealized by (a) larger heating rates and (b) shorter production periods than usual !

VII. CONCLUSIONS

From experiments and observations it can be concluded that:

1) a batch system gives rise to much idle time (heating up, cooling down, burning out, reactivating the fire). This leads to a loss of capacity of 25 % in extremely optimized conditions, of 35 % in more realistic conditions.

2)a batch system yields sub-standard product, both initially and by the end of the batch production. Moreover, there is a continuous deterioration with time.

3)a large-scale system yields a product , which is very much inferior to that of a small scale system.

For these reasons the use of continuous technology, featuring a reasonably fast heating of the raw material and a limited residence time of the volatile products is strongly advocated. These desirable features can be obtained using -lead or thin bath technology
-fluidized bed technology.

The latter presents superior characteristics with respect to a rapid heating and mixing of the charge and the automatic removal of char and fillers from the reactor, ensuring a superior continuity of heat transfer rates and operation in general. Moreover, its operation is simple and safe.

If UNIDO continues to support this project throughout its second, demonstration phase, the following aspects should receive further consideration:

1) enhancing the capacity of the actual coal-fired furnaces by providing a more modern coal feeding system, enhancing the temperature of combustion and the quality of radiant heat transfer. Also the grate and flue gas system should be revamped, to improve combustion efficiency, enhance furnace capacity, and reduce coal consumption and environmental emissions

2) an evaluation of the operation of the demonstration plant and its optimization to obtain maximum yield and purity minimum coal requirements, and a larger throughput than will be available with the existing coal-fired furnaces

3) a critical appraisal of the downstream operations with respect to occupational hazards and safety, emissions and other environmental hazards.

ANNEXE I

Proposed Programme for Prof. Alfons Buekens
Mission to Shanghai

Dec. 23, Tuesday	
21:30	Leaders of SRRUC and Nanshi District Branch meeting Prof. A. Buekens at the Shanghai airport
Dec. 24, Wednesday	
Forenoon 9:00	Departure for Xingguan Plastics Factory Discussing the proposed programme
12:00-13:30	Luncheon
Afternoon 13:30-15:30	Site-visit to the PMMA workshops, SRRUC-team summarizing necessary works made for improving the existing technology and equipment
Evening 18:30	Welcome banquet
Dec. 25, Thursday	Touring activities
Dec. 26, Friday	
Forenoon 8:30-12:00	SRRUC-team briefing on the experimental data about lead-bath and tin-bath
12:00-13:30	Luncheon
Afternoon 13:30-17:00	Prof. A. Buekens recommending the PMMA pyrolysis tests at home
Dec. 27, Saturday	
Forenoon 8:30-12:00	Prof. A. Buekens analysing the pyrolysis experiment
Afternoon 13:30-17:00	Requesting Prof. A. Buekens to put forward the preliminary design of an improved PMMA pyrolysis system and make a study of the recommended proposal about the feasibility, economic benifit and estimated investment of the system
Dec. 28, Sunday	Touring activities
Dec. 29, Monday	
8:30-17:00	Exchange ideas on the system
Dec.30, Tuesday	Discussion going on as yesterday

Dec. 31, Wednesday	
8:30-17:00	Consulting with Prof.A.Buekens on improving the existing PMMA recycling technology and the operational facilities
Jan. 1, Thursday	Touring activities
Jan.2, Friday	
8:30-17:00	Discussion on the general aspects of the project Drafting the protocol
Jan.3, Saturday	
Forenoon 8:30-12:00	Requesting Prof. A.Buekens to design the complete flow-chart of the recommended pyrolysis system
12:00-13:30	Luncheon
Afternoon13:30-17:00	Open

ANNEXE II

FLUIDIZED BED PYROLYSIS UNIT ACCORDING TO THE UNIDO TECHNOLOGY DEVELOPED BY THE FREE UNIVERSITY OF BRUSSELS

Basic Principles of Operation

The PMMA is pyrolysed in a fluidized bed reactor featuring :

- the use of fine sand (average particle size of 0.25 mm or smaller), in order to attain smooth fluidization with a minimum of fluidizing vapour. Entrainment of bed particles is minimized by the use of a disengagement section.
- the use of a special distributor, blowing out downwards the fluidizing medium to ensure a proper cooling of the reactor bottom, which is exposed to intense radiation from the furnace.

The bed is fluidized by means of

- external steam (during start-up or emergency)
- evaporated process water (normal operation)
- distillation heavies (when desirable)

or a suitable combination of these media. After minor modifications pyrolysis gas can also be used as a fluidizing medium, but its intermediate storage would require the erection of a fairly large gas holder.

The PMMA feeding system can be based on a combination of rocking valves (as in the Figure), or of one sliding and one motorized metering valve.
It is essential that it remains airtight.

The pyrolysis products are freed from entrained sand by means of a wide disengagement section on top of the bed. A cyclone takes care of the accidental entrainment of bed particles and of the removal of coarse dust particles.

The exhaust line is slightly inclined, in order to allow for the evacuation of high-boiling condensate. The balance of the condensate is condensed in two steps. The first condensate, containing most of the high boiling material, can be recycled into the reactor. The balance flows into a condensate storage container, in which it separates into two layers (crude MMA and aqueous condensate).

The permanent gas leaving the plant is cooled by means of an ice trap, in order to minimize the spreading of MMA into the environment.

The aqueous condensate is normally selected for recycling as a fluidizing agent by means of a valve

A volumetric pump presses the liquid through an evaporator bundle. The resulting mixture of steam and water is separated and allowed to flow back over a condense pot. The steam, after droplet removal, is superheated in a second bundle, situated in the convection section.

During start-up and in case of failure of the feedwater pump external steam from the steam grid of the factory is provided.

The superheated steam is injected through a three ring distributor, fitted with downward-directed holes.

Technical Specifications

Reactor : pipe of 16" or similar size

Distributor : composed of (Figure 1)

- a central steam duct
- three feeder headers
- three circular distributors, fitted with 120 holes

Each hole is directed downwards under an angle of 45°. The evolving steam jets should be equally distributed over the entire bottom of the cauldron, in order to ensure adequate cooling.

Diameter of the holes : 1 mm

Evaporation Section :

14 m of 1/2" tube (21.3 x 3 mm)

Superheating Section :

5.8 m of 1/2" tube (21.3 x 3 mm)
2.3 m of 3/4" tube (26.9 x 3.5 mm)

In case the steam superheat temperature is excessively high a by-pass should be created between the outlet of the furnace and the chimney.

Feedwater Pump

metering pump with cogwheels or piston with variable speed and/or stroke length
gaskets in PTFE
flow rate : 10-20 L/h
pressure : at least 50 m Water Column

Steam Droplet Separator

see drawing (Figure 2)
Scale 1/4
hydrostatic removal of condensate (type Sarco FT 1/2")

Hearth

The hearth should be upgraded so that the capacity rises to 28.4 kg of coal. This should be possible using a grate of 1 m^2.

Height of the Unit (Figure 3)

- grate and ash compartment		0.3 m
- flaming coal		0.4 m
- fluidized bed (expanded state)	max	1.4 m
- empty tube + disengagement section)		0.75 m
		2.85 m

+ feeding system

Bridgewall : height 15 cm
length at least 40 cm

Convection Section

weight 10 cm
length 100 m

The convection section should be accessible for cleaning.

Chimney : transition of 600 cm^2

Construction materials :

refractory masonry or concrete, with external insulation in order to reduce heat losses and maximize the wall temperature

Condensor : first section (condensation)

cooling and condensing to 100°C
required heat exchange surface : 5 m^2
on a basis of 1200 L/h of cooling water, with a temperature rise from 23 to 53°C.

second section (cooling)

further cooling to 30°C
required surface : 0.5 m^2
10 m tube of 1/2" (21.3 x 3)
or 1" (33.7 x 4).

Storage 7

disengagement of non-condensables, which are evacuated through an externally insulated ice-basket.

Piping (in 1/2" tubes) and Instrumentation

(a) between storage 7 and positive displacement pump
two feed points, one in the water fraction, a second (normally closed) in the MMA fraction
before the pump : coarse and fine strainer and a drain

(b) between pump and evaporator section: manometer and thermometer fitting
safety valve for water pressure lines

(c) separator is fitted with a tangential inlet and a condensate purger

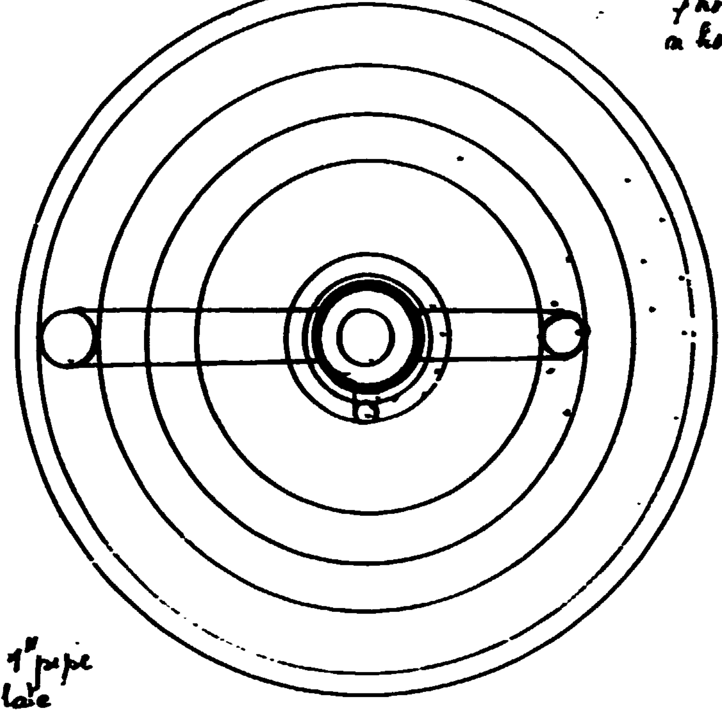
(d) for starting up a steam line with condensate removal is provided. Fitted with manometer, suitable for steam grid and an adjustable expander, adjustable in between 0.1 and 3 bar overpressure.

- the line towards the superheater contains a manometer of 0-3 bar overpressure and optionally a thermometer 50-200°C
- the outlet of the superheater has (a) a fitting for a safety valve (steam) opening at 3 bar overpressure, (b) a thermowell 100 to 600°C, (c) a manometer 0-3 bar overpressure
  connection to fluidized bed : see drawings.
- in the fluidized bed and above the bed : thermowells for the range 50-600°C.
- before the condensor a safety water slot with a height of 3 m and a pressure indicator in a range from -0.5 to +0.5 bar.

VUF, 22/1/87 ES

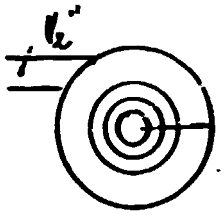
INJECTOR SCALE 1/4

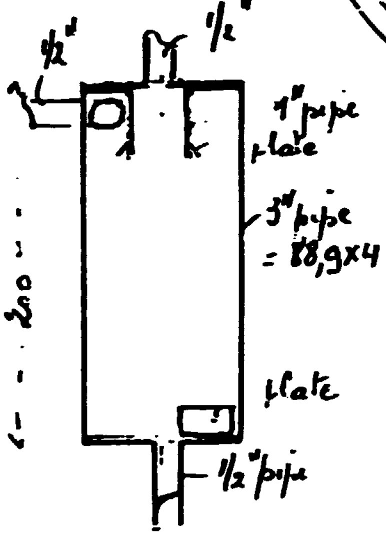
Θϕ = 201 ϕ = 33,2 pipe 3/4"
ϕ holes = 191 − 211
n holes = 19+19
5ϕ = 324 mm pipe 1"
ϕ holes = 336 − 312 mm
n holes = 33 + 33
ϕ = Θ 31 mm
ϕ holes = 1 mm

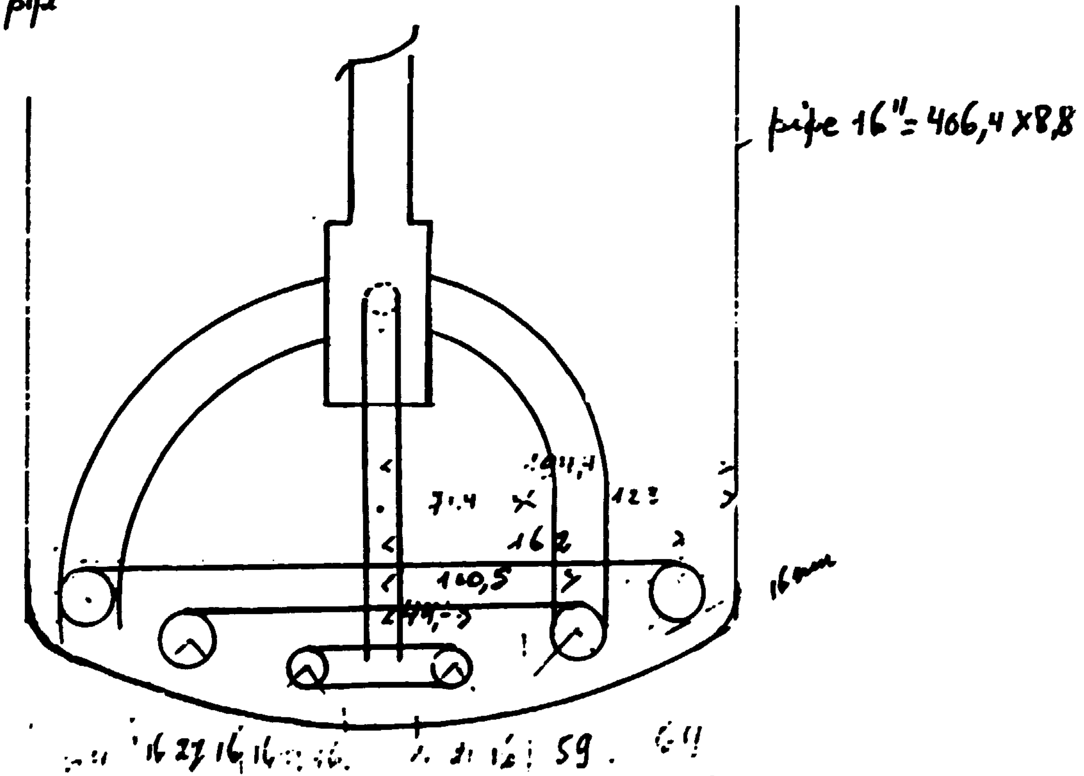


3ϕ = 88 pipe 1/2"
ϕ holes = 81 − 95
n holes = 8 + 8

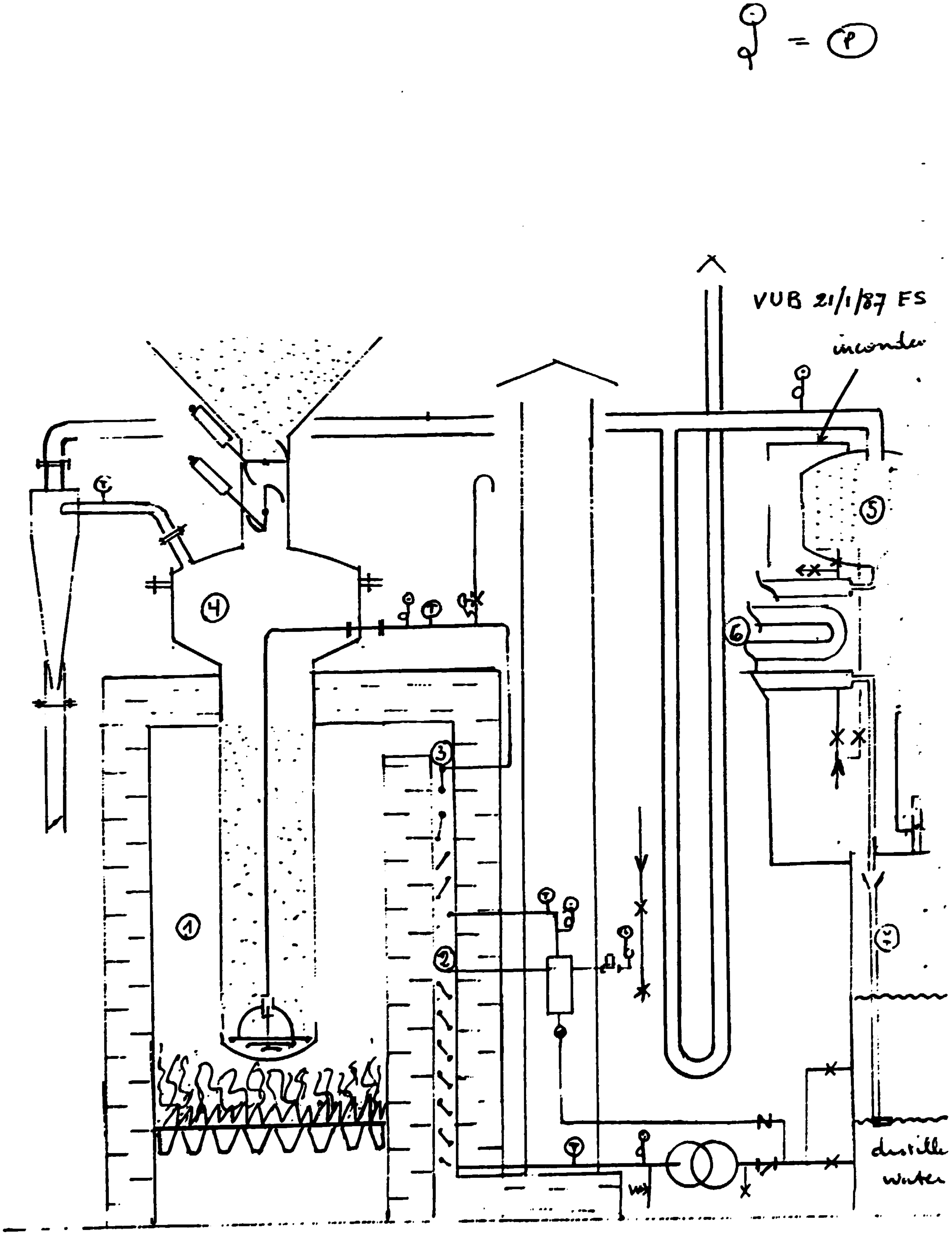
SEPARATOR







120h = 16h + 38h + 66h


= (P)
VUB 21/1/87 FS
inconder
④
①
②
③
⑤
⑥
T
P
distille
water

GENERAL INSTRUCTIONS: TABLE OF CONTENTS

1. Fittings
1.1. Fluidised bed
1.2. Pressure drop
1.3. Pressure readings - and pressure Dials specifications
1.4. Safety valves
1.5. Strainers
1.6. Steam trap
1.7. Feed pump
1.8. Monitoring valves
1.9. Temperature controls

2. Piping

3. Heat exchangers
3.1. Vaporizer
3.2. Superheater
3.3. Condenser
3.4. Cooler
3.5. Wild vapors condenser

4. Shells
4.1. Reactor
4.2. Separator
4.3. Cyclone
4.4. Injector

5. Oven
5.1. Combustion grate
5.2. Firing
5.3. Firebox
5.4. Economiser
5.5. Chimney
5.6. Frame

6. Starting the plant
6.1. Checks
6.2. Heating up
6.3. Normal process
6.4. Normal process using MPPA vapors
6.5. To stop normal process

1. GENERAL INSTRUCTIONS : FITTINGS

1.1. Fluidized bed

Filling with sand : density 2 400 kg/m^3
particle size 0.250 mm
volume 152 liter - weight 370 kg

1.2. Pressure drop

1.2.1. through bed 0.34 bar = sand weight /cm^2

	at 100°C outlet bed	at 450°C outlet bed
1.2.2. through orifice	0.05 bar	0.1 bar
1.2.3. through superheater	0.08 bar	0.12 bar
1.2.4. sub total	0.47 bar	0.56 bar
1.2.5. through vaporiser	0.1 bar	0.1 bar
1.2.6. total	0.57 bar	0.66 bar
1.2.7. through cyclone	0.1 bar	0.1 bar
1.2.8. through condenser	0.0 bar	0.0 bar

1.3. Pressure readings and pressure Dials specifications

1.3.1. inlet condenser 0.0 bar up to 0.01 bar
1 mano-depressometer -0.1 up to +0.1
1.3.2. inlet cyclone = 1.3.1 + 1.2.7 = 0.1 bar
1.3.3. outlet superheater
1 manometer 0 to 5 bar (1.3.2. + 1.2.2. + 1.2.1.)
1.3.4. outlet steam separator
and inlet additive steam 1.3.3 + 1.2.3. = 0.66 bar
1 manometer 0 to 5 bar
1.3.5. outlet pomp 1.3.4 + 1.2.5. = 0.76 bar
1 manometer 0 to 5 bar
1.3.6. inlet pressure reducing device = Plant boiler pressure
1 manometer 0 to boiler pressure

1.4. Safety valves

1.4.1. superheated steam
opening pressure 3 to 5 bar
ATT : make sure that escaping MMA vapor cannot hurt people or explode
(Pressure is set that high too avoid opening of this safety item).
1.4.2. pump outlet
Because pump is of a positive displacement type a safety valve set at 5 bar is necessary this valve can be inside the pump or outside on the outlet pipe.
In that case bring the escaping fluid back to the pump feed.
1.4.3. U-tube safety on vapor before condenser.
Give this tube a height of 3 to 5 meter to ensure a pressure lower than 0.5 bar and avoid air introduction by vacuum up to -0.3 bar.
ATT : be sure that escaping vapors and or fluids cannot hurt people or damage materials (temperature up to 450°C).

1.5. Strainers

1.5.1. the positive displacement pump has to be protected with a strainer on the feed line, gauge following pump manufacture instructions.

1.5.2. it is recommended to protect the steamtrap inlet with a strainer, but this is not compulsory.
1.5.3. just before the inlet of steam in the reactor place a filter with max. diameter 0.5 mm.

1.6. Steam trap

The fluids separated from steam in the separator are evacuated by a steam trap.
This must be fully hydrostatic, that means only influenced by fluid level and not by temperature. Only float ball type with closed ball is suitable.
Thermodynamic, thermostatic, inverse bucket, open bucket or labyrinth types are not acceptable.
If maximum level in the condensate tank is higher than steam trap level, steam trap outlet must be fitted with a check valve (avoiding return flow).
The fluid from the steam trap goes to the pump inlet.

1.7. Feed pump.

Positive displacements pump - this means or piston pump or gear pump.
feed flow : adjustable manually from 10 up to 20 liter/hour
feed pressure : up to 5 bar.

1.8. Monitoring valves.

1.8.1. the settling and storage tank has three valves :
1.8.1.1. drain valve in the bottom
1.8.1.2. water tapping valve 0.1 m above bottom
1.8.1.3. PMMA tapping valve 0.1 m above water/PMMA separating level
1.8.2. feed pump inlet drain valve
1.8.3. steam feed from plant boiler
Diameter for all of the above discribed valves is 1/2 "
1.8.4. cooling water system needs 5 valves :
1.8.4.1. drain valves emptying the system ø = 1/2 "
1.8.4.2.
1.8.4.3.
1.8.4.4. 4 valves authorising both either serial or parallel feed
1.8.4.5. towards cooler and condenser ø = 1 1/2 "

1.8.5. PMMA feed
2 butterfly type valve from which the lower
1.8.5.1. is fitted with a hard seat and the upper with
1.8.5.2. soft seat ø = 4 "
monitored by power pistons (air, oil, steam) or manually
1.8.6. ash remover from cyclone
1 butterfly type valve hard seat ø 4 "
1.8.7. uncondensable drain valve ø = 1/2 "
Progressive opening type (e.g. needle valve or ball valve with triangular grove)
1.8.8. Pressure reducing device on plant boiler steam line (automatic-membrane type)
ø 1/2 " inlet pressure = boiler pressure
outlet pressure = from 0.3 up to 3 bar
flow = from 0 up to 30 Kg steam/hour (max 15 Kg at 0.3 bar - 20 Kg at 1 bar)

1.9. Temperature controls

1.9.1. feed temperature - outlet feed pump range 10 to 70°C
1.9.2. steam temperature from separator range 100 to 200°C
1.9.3. steam temperature from superheater range 100 to 600°C
1.9.4. vapors temperature inlet cyclone range 100 to 600°C
1.9.5. condensate temperature outlet cooler range 10 to 70°C

2.GENERAL INSTRUCTIONS PIPING

2.1. from tank to feed pump 1/2 "
2.2. from pump to separator 1/2 "
2.3. from separator to pump 1/2 "
2.4. from boiler to separator 1/2 "
2.5. from separator to superheater 1/2 "
2.6. from superheater to injectors 3/4 "
    a dubbel set of flanges on both sides of reactor wall are necessary for disconnecting
2.7.1. from reactor to cyclone 2 "
2.7.2. from cyclone to dust (ash) collector 4" min 1 m
2.8. from cyclone to storage tank
    2.8.1. from cyclone to condenser 4"
    2.8.2. safety U-tube 4"
    2.8.3. from condenser to cooler 1"
    2.8.4. from cooler to tank 1"
    2.8.5. cooling water pipes 1 1/2 "
    2.8.6. uncondensables from top condenser to tank 1/2 "
All tubes following DIN 17175 or ASME 106B or simular.

3. GENERAL INSTRUCTION HEAT EXCHANGERS

3.1. vaporizer surface 0.8 m^2
ø tube 1/2 " (21,3 x 3 mm)
lenght 14 m

3.2. superheater surface 0.5 m^2
of which 2/3 ø 1/2" tube = 5.8 m lenght
of which 1/3 ø 3/4" tube = 2.3 m lenght
3/4" = 26,9 x 3,5 mm

Vaporizer and superheater are installed in a space, 0.1 m width and 1 m length between two insulating refractory brick walls.

3.3. condenser.
- one or more concentric coils total surface 5 m2 cooling water in tubes - vapors in Shell-
- water flow 1 200 l/h from 23 to 53 °C
- minimum water speed in tubes 0,5 m/sec

3.4. cooler
- one 1/2" inside a 1 1/4" pipe
- total surface 0.5 m^2 (32 x 4 mm)
lenght 7.6 m
condensate in 1/2" pipe

cooling water in 1/4" pipe

3.5. wild vapors condenser
tube ø 200 mm length 600 mm filled with ice
with tube inside tank down to separation level PMMA/water
see filling on top

4. GENERAL INSTRUCTION SHELLS ALL DIMENSIONS IN MM

4.1. reactor : DIN 17175 KL1 or equivalent

4.1.1. bottom
16" CAPS thickness 0,375"
ø 406.4 thickness 9,5 mm
height 177,8 mm — weight 20.5 kg

4.1.2. tube
ø 406.4 thickness 8.8 (DIN 17175)
or thickness 9.5 (ASTM 106 B)
height 1 700 - 177.8 = 1 522 mm — weight 131 kg

4.1.3. cone plate following DIN 17155 or equivalent
thickness 9 or 9.5 mm
ø 406.4 ≥ ø 609.6
angle 45°
height 102 — weight 16.5 kg
length 143 mm

4.1.4. two DIN 2632 Welding neck flanges
ø norm 609,6 ø out 780 h = 2 x 80 = 160
20 bolts ø 27 — weight 42.2 kg x 2 =84.4 kg

4.1.5. top - 24" cap thickness 0.375"
609.6 mm thickness 9.5 mm
weight 46 Kg
height 267 mm

Total height 177.8 + 1 522 + 102 + 160 +267 + (4x2) + 4 = 2 241 mm
inside oven = 1 420 mm
= bed heigth
Total weight 20.5 + 131 + 16.5 + 84.4 + 46 + 5.4 = 300 kg

4.2. separator. (see drawing)
0.2 m 3" pipe 88.9 x 4 mm
2 x caps 3" or two plates ø 80 mm x 4 mm thick with central bore ø 20 mm
- do not forget anti vortex plate or cross
- inside tube 1" is 50 mm long and fitted with conical plate 8 mm wide on the lower end of this tube

4.3. cyclone

- 4.3.1. vapor inlet 2"pipe welded tangentially in ø 200 pipe
- 4.3.2. body
  - ø 200 I.D. pipe length 200 mm
  - come from ø 200 > ø 50 ID
    length 600 mm (mi thickness 2 mm)
  - top plate ø 200 with 4" pipe fitted in center from which 120 mm length inside body for vapor outlet
  - 4" pipe lenght 2 m (min 1 m) with butterfly valve on bottom
- 4.3.3. 2 x flange DIN 2631
  ø norm 50 4 bolts ø 12
  2 flange DIN 2631
  ø norm 100 4 bolts ø 16

4.4. injector (see drawing)

- 4.4.1. steam inlet ø 3/4"pipe 27 x 3 mm with 90° bend and 2 x flanges DIN 2631 ø nom 20. 4 bolts ø 10.
  length to be adjusted.
- 4.4.2. distribution box ø 2" pipe 60 x 5 mm
  length 120 mm
  - one end closed by plate 4 mm thick ø 50 (bottom)
  - upper end welded on 3/4"pipe (steaminlet)
- 4.4.3. three pipes with bend 90° are welded radially on to the 2"box on one end
  one ø 1" 33.2 x 4 mm
  one ø 3/4" 27 x 3 mm
  one ø 1/2" 21 x 3 mm
  and on to the three distribution torus of same ø on the other end
- 4.4.4. torus
  - 4.4.4.1. torus ø 1" primitive ø 324
    holes are bored radially on the underside with a 45° to the vertical on ø 336 and on ø 312 - On both circles 33 bores ø 1 mm means that, on each - circle bores are distant of approxim, 31 mm from each circle. The max distance between two bore is approxim 28 mm.
  - 4.4.4.2. torus ø 3/4" primitive ø 201 - ø bore are 211 and 191
    number of bores are 19 + 19.
  - 4.4.4.3. torus ø 1/2 primitive ø 88 ø bore are 95 and 81 mm
    number of ore are 8 + 8.
    total number of bores ø 1 mm = 120 bore
- 4.4.5. foot
  on to each torus three rounded up prices of wire ø 6 to 8 mm lenght 16 mm will be welded to check that each torus is distant of 16 mm from bottom plate.
  length of the three 4.4.3. pipes will be adjusted to obtain this.
  for the same reason length of 4.4.1. will be adjusted, once the upper horizontal part of it is welded through the conical part of the reaction shell (4.1.3.)

5. GENERAL INSTRUCTIONS OVEN

5.1. Combustion grate.

The Combustion grate will be placed between 30 and 40 cm under the bottom of the reactor.
Coal consumption is approxumatively 30 Kg/h grate surface will be 1 m2.
It is advisable but not compulsdry to use a grate with thin airgass and high pressure drop, combined with a draft inducer (fan).

5.2. Firing.

If underfeed stokers are not used, one shall attentively charge the grate to obtain a continuous red hot radiant surface.

5.3. Firebox.

Firebox with inside dimensions of 1 x 1 m and height above grate of 1,7 meter is build from hight alumina content stone to obtain a quickly heated surface.
Where necessary (firing zone) refractory stones will be used, to resist the coal handling.
This firebox will be enclosed in any material suitable for support and insulation; gas outlet through a lateral gap on the upper part of the fire box, with a section of 600 to 700 cm^2 as for example with gratings height 150 mm length 1 m and 50% open bringing the gases in the economiser zone - with a good distribution all along the economiser.

5.4. Economiser.

The economiser is installed between two walls of aluminia rich stones distant 0.1 m = 100 mm from each other with a width of 1 m = 1 000 mm over the full heigth.

5.5. Chimney.

From bottom of economiser section, gases are evacuated to the chimmey.

5.6. Frame.

The weigth of the reactor (without loading mechanism) being 300 Kg steel and 370 Kg sand = 670 Kg
it cannot rest on the brickwork and must be sustained by a steel frame - with facilities to lift the reactor cover and sustain the piping.

6. STARTING THE PLANT

6.1. Checks.

6.1.1. Check, and refill if necessary the level of sand in the reactor
6.1.2. Check, filter, cleanlines of steam line, inlet of the reactor
6.1.3. Empty the ashtray from cyclone
6.1.4. Close the two feeding butterfly valves
6.1.5 Check the levels of PMMA and of water in the settling and storage tank. (water must be boiler quality feed water : distilled, condensate or

demineralised. Sodium/chloride ion exchanger treatment is not acceptable).

6.1.6. Check the filling of ice in wild vapor condenser

6.1.7. Check water filling to half height of the U tube

6.1.8. Check if cooling water, plant steam and electricity are available

6.1.9. Check if feed pump runs in right direction.

6.2. Heating up.

6.2.1. open the plant steam valve - check wether the pressure is normal

6.2.2. check the pressure on manometer 1.3.4. and adapt pressure reducing valve setting if necessary.
[during the first start-up and before this value is known please check if the pressure is high enough to move slightly the sand bed, before the fire is ignited].

6.2.3. Light the coal fire make sure that the fire remains about 5 cm below the reactor - and avoid black spots on the surface.

6.2.4. regulate the feed pump speed to obtain a flow of 14 l/h but don't start the feeding

6.2.5. when steam temperature reaches 200 °C at reactor inlet, open valve 1.8.1.2. (water valve) check with 1.8.2 if pump is fed with water and start the pump.

6.2.6. When the vapor inlet of the condenser becomes hot or when manometer dial indicates positive pressure open the 1.8.4.2 and 1.8.4. valves, close 1.8.4.1 valve and open 1.8.7 valve.

6.2.7. When reactor outlet temperature reaches 450°C the process may begin.

6.3. Normal process.

6.3.1. check again pressure on dial 1.3.4.
This pressure must be slightly higher compared with the setting point of the pressure reducing valve.
If not (adjusting will be necessary by first start) reduce the setting pressure of reducing device to stop flow from plant boiler. Proceed slowly.
If now, for any reason, steam flow to the bed is reduced, plant steam will compensate the lack of steam flow.
Pipe 2.2. must become warm.

6.3.2. Fill up the feeding cone with PMMA ground to a particle dimension of 1 to 2 mm (*) open and close again 1.8.5.2 to fill the 1.2 liter lock between the valves.

6.3.2.1. open and close again 1.8.5.1. to discharge it in reactor

6.3.2.2. open and close 1.8.5.2. to fill the lock and avoid escape vapors

6.3.2.3. Check if temperature vapor stop rising.
If not repeat 6.3.2.1 and 6.3.2.2.
And do it again any time temperature exceeds 450°C.

6.3.2.4. A temperature of vapor of 500°C may not be reached safely without damaging the reactor.
If necessary reduce the fire.

(*) larger dimensions are not acceptable with this particular feeding system, because of smooth valve lining

6.3.3. Setting of the uncondensable drain valve

There is approximatily 5% uncondensable gasses in vapors. The valve 1.8.7. must be set to drain all the non-condensables plus some of condensables.

This is right when dial 1.3.1. indicates pressure between 0.0 and 0.01 bar.

6.3.4. If cooling is not sufficient, increase the water flow in both condenser and cooler by closing 1.8.4.4. and open 1.8.4.5. and 1.8.4.4.

6.3.5. Steam trap from separator must deliver 2 or 3 liter per hour of condensate at least.

If not, the steam lines and injectors will block up by salt deposits.

If necessary increase feed of pump to be sure the thermometer 1.9.1 authorises the check, because if there is a normal excess of 15% temperature on 1.9.1. will be about 15°C higher than in the storage tank.

6.3.6. Adjusting the fire.

Because reactor is mostly heated by radiation fire intensity will have more influence on economiser than on reactor.

Fire may be increased (eventually with help of a fan) as far as the steam temperature on the thermometer 1.9.3. does not exceed 475°C.

6.4. Normal process using MPPA vapors (*)

6.4.1. close 1.8.1.2. valve and open 1.8.1.3. when plant is in normal process with steam from water

6.4.2. Check feed pump flow as explained in 6.3.5.

6.4.3. Check carefully vapor temperature 1.9.3. (This temperature may not exceed 280°C) and regulate fire accordingly. There is namely a danger to block the superheater by carbon deposits which may be detected by increased pressure on 1..4. and possibly leaking on 1.4.2. with as a consequence that 1.9.2. will indicate a temperature of superheated vapors not in accordance with the pressure.

6.5. To stop normal process.

6.5.1. stop the fire

6.5.2. when temperature stays below 450°C stop feeding of PMMA

6.5.3. stop the feed pump and close feeding valve 1.8.1.

6.5.4. stop plant steam by closing 1.8.3. when 1.9.4. indicates 120°C max.

Open again 1.8.3. at intervals to check if 1.9.3. and 1.9.4. does not overheat because of the heat storage in the brickwork

6.5.5. remove ash from cyclone

6.5.6. Close cooling water 1.8.4.2.

(*) after approval by UNIDO-expert only.

ANNEXE III

PROTOCOL

According to the UNIDO Project SI/CPR/86/028 for the development of an improveu PMMA pyrolysis system, Dr. A. Buekens visited Shanghai in July and December, 1986 to study the problems and disadvantages of the existing PMMA thermo-cracking process in Xingguang Plastics Factory, a subsidiary of SRRUC.

In the implementation of the UNIDO Project Dr. Buekens has dedicated himself to the improvement of the current thermo-cracking technology at the factory. His contribution to the revamping of the present unsatisfactory recycling practice can be briefly summarized as follows:

1. Making a complete study of the existing technology and equipment for thermo-crackingthe PMMA scrap in the factory;
2. Recommending the current advanced technologies of recovering PMMA monomers from the scrap in foreign countries, which comprise chiefly the fluidized bed system, lead bath and further processing. Top priority is, however, placed on the employment of fluidized bed technology;
3. Providing a detailed report for SRRUC on the results of his investigation on the PMMA thermo-cracking process presently adopted by Xingguang Plastics Factory;
4. Proposing the improved technology and devices to meet the crying need of technical reform at the factory;
5. During his second mission to Shanghai, Dr. Buekens collaborated with the SRRUC technical staff on the experiment of PMMA pyrolysis on the fluidized bed and suggested to further the experiment with the utilization of the existing pyrolysis equipment at the factory.

With the direction of Dr. Buekens the technical staff of the factory have performed their tasks with required regularities, such as:

1. Sorting and classifying the PMMA scrap into different grades and categories;
2. Improving the feeding system to meet the operational

requirement;

3. Sealing up all the containers for PMMA monomers in order to eliminate the fugitive loss of the products and avoid oxidation;
4. In consideration of the possible generation of pollutants from lead bath fumes, tin bath has been adopted instead.

In contrast to the original processing method with the improved technology the recovery rate is upgraded to 85%, and the content of MMA monomers increased by 90%. But due to the long residence of material in the processing device a deterioration of product quality, and due to the batch operation pollution of environment still exist.

SRRUC highly appreciates the consistant effort Dr. Buekens has rendered to the development of an improved PMMA pyrolysis technology. And now by the end of Dr. Buekens' second visit we would like to discuss with him about the follow-up activities. In order to carry the reform task through to an end the following suggestions might be considered as vital:

1. It is expected that Dr. Buekens would finalize experiments on PMMA pyrolysis on the fluidized bed, and, see if it is possible, to send the experiment report to SRRUC at the end of February, 1987;
2. SRRUC requests Dr. Buekens to complete the design of a continuous PMMA pyrolysis system and provide us with technical documentation which includes:
   - A. Specifications of the design;
   - B. The technological flow chart of the design;
   - C. A detailed location plan for the installation of equipment and distribution of conduits;
   - D. Design for measurement devices and eventual automatic control;
   - E. Schemes for treatment of the resulting waste water and residue.

SRRUC expresses its deep gratitude to UNIDO for its support in completing the experimental part of the projest, which was required to obtain all the necessary data for a final design of the PMMA pyrolysis system according to modern UNIDO technology. SRRUC is fully aware that the improved PMMA pyrolysis system will not only eliminate the environmental pollution at Xingguang Plastics Factory but will be extended to the entire Third World to solve the same contamination problem it is now facing. With this in view, SRRUC earnestly wishes that this project would be continued and finalized and that UNIDO would continue its support to the necessary follow-up activities of the project, which include:

1. Providing training to the qualified technical staff of SRRUC at the University of Brussels in Belgium;
2. Ensuring the assistance of Dr. Buekens to help in the second stage of the project, i.e. the demonstration of the fluidized bed pyrolysis technology at Xingguang Plastics Factory;
3. Providing some extra equipment required in monitoring the operation and environmental aspects of the factory.

SRRUC will proceed to carry on experiments on the fluidized bed pyrolysis technology with the existing equipment at Xingguang Plastics Factory on the basis of further supply of design for equipment installation by Dr. Buekens and training of its technical staff.

This protocol is signed on January 2, 1987 in Shanghai by

Dr. Alfons Buekens

Shanghai Resource Recovery &
Utilization Co.

ANNEXE IV

PATENT SPECIFICATION

(11) 1 350 612

1 350 612

(21) Application No. 33326/71 (22) Filed 15 July 1971
(31) Convention Application No. 55224 (32) Filed 15 July 1970 in
(33) United States of America (US)
(44) Complete Specification published 18 April 1974
(51) International Classification C07C 69/54
(52) Index at acceptance
C2C 200 20Y 30Y 366 358 37X 43X 628 CD

(19) THE PATENT OFFICE LONDON

(54) DEPOLYMERISATION OF ACRYLIC POLYMERS

(71) We, ROHM AND HAAS COMPANY, a corporation organised under the laws of the State of Delaware, United States of America, of Independence Mall West, Philadelphia, Pennsylvania 19105, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to a process of producing monomeric esters of substituted or unsubstituted acrylic acids by depolymerization of the corresponding polymeric ester.

Acrylic polymer resins range from soft elastomers to hard plastics which can be sawed and machined on a lathe. The materials generally have excellent initial color and they are stable to light since they do not discolor on ageing, or degrade on outdoor exposure. They have relatively good heat resistance, since they show little or no color change at temperatures up to about 50°F. and tend to decompose at about 500°F. Even though they are thermoplastic materials and therefore sensitive to some solvents, they have good resistance to acids, alkalies, water, and alcohol. Generally they have low acid numbers and they are not reactive with pigments or fillers and have good resistance to vegetable and mineral oils and greases.

Elastomeric acrylic resins can be used as base coats in textile, leather, and paper finishing. Some are also compatible with cellulosic polymers, and vinyl resins to which they impart an improved stability to heat and light. Because of their exceptional properties, some of the harder resins are used as the entire film-forming material in heat-resistant white baking enamels.

Generally, acrylic polymers, because of their outstanding clarity and transparency, find use in windows, lenses, instrument panels, optical parts, such as contact lenses, reinforced plastics; protective coatings, including lacquers, paints, and other finishes; adhesives; plasticizers and modifiers for various other resins, lubricating oil additives and textile and leather finishes and coatings.

Economically, it would be tremendously beneficial to be able to use any wasted, or contaminated, acrylate monomers from polymerization processes, along with any polymer scraps and formed polymeric articles in such a way as to enable the depolymerization of such material so it can be repolymerized and reused in subsequent articles.

Acrylic polymers have been in use for some years and find considerable application in the molding of various articles, by numerous molding methods. In the course of such manufacture, there is a considerable amount of waste polymer which is an important factor in determining the cost of the molded article. Various methods have been employed in an attempt to recover the monomeric material, among these are included treatment of the acrylic polymer with heat to decompose and depolymerize the resin to form the starting monomer.

In one known depolymerization process, a batch of the polymeric material is put in a reaction vessel containing lead, the vessel is heated externally to the depolymerization temperature, about 400°C., and the monomer vapor is passed to a condenser wherein the vapor is condensed to a crude liquid monomer. In this system, carbonaceous particulate deposits are formed on the inside walls of the vessel and also float on the surface of the lead. The monomer vapors progressively deteriorate in quality and the vessel must be cleaned frequently, such as every six to eight hours, to prevent complete fouling and/or stoppage of the process.

In accordance with the present invention, there is provided a process in which an acrylic polymer containing two or more mers of one or more alkyl esters of acrylic acid and/or an alpha alkyl-substituted acrylic acid is depolymerized to form the corresponding monomeric ester(s) in an inert atmosphere by con-

[*Price 25p*]

tact with a hot molten metal surface, characterised in that the surface of said molten metal is constantly renewed.

The depolymerization process of the invention is simple, effective and economically feasible, adapted to either batch or continuous operation, utilizing a minimum of labor and apparatus and yielding a high quality monomer which can be used in further polymerization reactions. The use of a molten metal for the heating of the polymeric material in contact therewith has the advantage over the use of a rigid heating surface, such as the rigid internal surface of a heated metal vessel, of being adapted to be readily changed or renewed constantly by mechanically disturbing the surface of the molten metal. This disturbance may be effected in some instances by the falling of the polymeric material onto the surface as it is continuously or continually fed into the reaction vessel or it may be accomplished by a skimming or raking of the surface, or most preferably by simple agitation of the molten metal. [illegible]

The vapors formed by contacting the polymeric material with the molten metal surface can be passed through suitable conduits or vapor-conducting lines into a liquid-vapor contact type condenser to be condensed and recovered. The vapors are maintained at an elevated temperature, preferably above 250°C, more preferably in the range 300°—400°C, in the vapor-conducting lines to reduce dust accumulation and undesirable deposits in various sections of these lines.

In the present process the liquid metal with which the acrylic polymer is contacted, may be lead, tin, cadmium, or various alloys, maintained at above the depolymerization temperature of the acrylic polymeric material. This contacting step is usually followed by condensing the vapors formed thereby and recovering the monomeric ester.

Any metal which melts from 400°C. to 450°C. is a preferred metal for use in the practice of this invention with due consideration given to economics, ease of handling, and availability. Metals particularly suitable for the process disclosed herein include lead which melts at 327.4°C., cadmium which melts at 320°C., and tin which melts at 251.9°C. Metal alloys melting up to about 400°C. are also within the purview of the instant invention. Examples of such alloys include:

Soft solders (Sn and Pb in range of 40—60% each, and especially that of 50:50 weight ratio)

Cerrobend (50% Bi, 26.7% Pb, 13.3% Sn, 10% Cd)

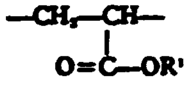
Cerrotru (58% Bi, 42% Sn)

(Cerrobend and Cerrotru are Registered Trade Marks).

In view of the criteria noted above, lead is the preferered metal for the practice of this invention.

Generally, the polymeric material fed into the reactor to be depolymerized can be in any conveniently workable form, including shavings, pieces, granules, powder, chips, sheets; singularly or in combination, or with liquid monomer, either contaminated or uncontaminated. The apparatus used to carry out the process of the invention will generally employ a hopper-feeder in combination with a conveyor belt to the reaction vessel. Large scraps, such as sheets or original molded articles can be broken up into smaller, more usable pieces to facilitate charging into the depolymerization vessel. This, of course, depends upon the size and design of the apparatus used to supply the reaction vessel with polymeric material. Many different types of polymer scrap may be fed into a cracking vessel simultaneously, provided an appropriate feed mechanism is available for the different types.

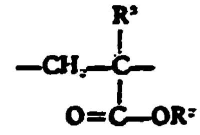
The preferred acrylic polymers for carrying out the process of the invention contain mers and more preferably consist substantially entirely of mers of Formula I or II below:



$$-CH_2-\underset{\substack{|\\ O=C-OR^1}}{CH}-$$

Formula I

or



$$-CH_2-\overset{\substack{R^2\\ |}}{\underset{\substack{|\\ O=C-OR^3}}{C}}-$$

Formula II

In Formula I and Formula II above, R^1, R^2 and R^3 are lower alkyl groups having from 1 to 6 carbon atoms, preferably from 1 to 4 carbon atoms.

Representative polymers having mers of the above formulae include polymethyl acrylate, polyethyl acrylate, polymethyl methacrylate, polypropyl acrylate, polybutyl acrylate, polypropyl methacrylate, and polybutyl methacrylate; the first four polymers named being preferred in the practice of the instant invention.

The most common impurities encountered in polymeric material of this nature include plasticizers, fillers, dyes, pigments, polymerization inhibitors, and other polymers used in molding processes or those which may be used to extend or modify the polymeric acrylates. Generally, these contaminants or impurities will not greatly affect the process since upon contact with the heated metal surface the polymeric material vaporizes and the vapors are subsequently condensed while the solid or certain liquid contaminants remain behind on the liquid metal surface as residue. This may result in a need to remove these impurities from the liquid metal surface periodically.

The rate of the feed will, of course, be a function of the size of the scrap, the size of the apparatus used to depolymerize the scrap, and the temperature maintained on the heated liquid metal surface.

The reaction vessel may be practically any size vessel made of a suitable material which will be able to withstand the temperatures required to maintain the liquid metal in a molten state. Examples include various steels (including stainless steels) which are resistant to corrosion under the conditions within the reaction vessel and especially those which are resistant to cracking at the temperatures encountered herein. The types of steel used for making furnace fireboxes are quite useful, one example thereof being No. 285 Grade C firebox steel.

The reaction is conducted in a non-oxidizing atmosphere, i.e., an inert atmosphere, generally of nitrogen gas, however, other inert gases may be used, for example, argon, helium, or neon gas would serve the same purpose.

Decomposition of some of the acrylic polymer forms solid carbonaceous materials including carbon dust which materials deposit on the surface of the molten metal. These deposits may also result from impurities in the starting polymer. While the mechanical disturbance of the molten metal surface by the introduction of the acrylic polymer into the reaction vessel may serve to renew the surface in some instances (for example when the acrylic polymeric material by virtue of heavy pigmentation is relatively dense or when the polymeric material is deposited on the molten metal with great force) the renewal of the surface is preferably effected by agitation of the molten metal at or near the surface. The renewal maintains a high rate of heat transfer from the molten metal to the polymeric material deposited therein and thereby assures maintenance of a rapid rate of depolymerization for considerable periods of time in spite of the accumulation of carbonaceous or other impurities on top of the molten metal.

An important aspect of the instant invention resides in the fact that the molten metal, and especially the upper layer thereof, is constantly agitated by a mechanical stirrer located in the vessel or by some other suitable form of agitation. Agitation of the molten metal serves many purposes, including constantly renewing the metallic surface and maintaining a high rate of heat transfer between the heated liquid metal and the polymeric material. The heat conductivity from the agitated liquid metal surface to the polymeric material is increased and the polymer residence time is decreased, resulting in a considerably reduced deposit on the surface of the liquid metal for a given volume of crude monomer produced as compared to such a system without agitation. Furthermore, with agitation, some of the dust deposits within the reactor leave with the vapors and can easily be removed at a later stage in the process. When any of the liquid condensate is recirculated to the condenser as is preferred, it may be passed through an appropriate filter. That portion of the condensate that is not recirculated may also be filtered before distillation.

The molten metal surface may be maintained at a temperature of from 350°C. to 700°C., more specifically the temperature can be maintained at from 400°C. to 650°C., preferably from 450°C. to 550°C., and most preferably from 500°C. to 530°C. No appreciable depolymerization usually takes place below 400°C. Above 700°C, the decomposition produces excessive amounts of undesirable products which have low condensing temperatures and some of these products do not condense at normal condensed conditions. The production of these undesirable products lower the yield and quality of recovered monomer.

The deposits of carbon and impurities on the surface of the molten metal generally have to be removed periodically. A plant reactor of an average size, for example a steel vessel 12 feet in diameter having a 10-foot diameter agitator operating at 10—12 rpm in a molten lead bath of 18 inches depth operating at a feed rate of 3000 pounds of poly(methyl methacrylate) per hour may be operated for a period of 5 days before it becomes necessary to shut down the apparatus to skim the lead surface to remove the residue of impurities deposited thereon.

A carbonaceous residue is almost always produced, regardless of the method of heat application. The residue generally forms and/or is deposited at the heat transfer surface and without agitation of the molten metal the carbonaceous residue accumulated on the metal surface rapidly reduces the efficiency of the heat transfer process. Furthermore, in the absence of agitation, the production of carbonaceous residue makes it necessary to shut down the apparatus and clean the equipment quite frequently, such as every 6 to 8 hours.

The molten metal may be maintained at the desired temperature by any commonly known method of heating, including direct gas or fuel oil flame impinging on the bottom of the reactor, or electric heaters employing Nichrome (a registered trademark of the Driver-Harris Company, Harrison, New Jersey, U.S.A.) wires and voltage regulators. It has been discovered that electric heaters are particularly suitable since they maintain a more uniform heat distribution and increase the usable life of the reactor since there is no direct flame impinging on the reaction vessel itself.

The polymer residence time in the reactor depends on the depolymerization rate which is a function of the temperature of the molten metal, the higher the temperature above the minimum depolymerization temperature the more rapid the depolymerization. If the input rate, i.e., the feed rate of the polymeric material, is equivalent to the cracking rate, as determined by the molten metal temperature, the residence time would be a minimum and the production of carbonaceous residue would also be a minimum. The rate of depolymerization is essentially independent of the intensity of agitation provided the agitation is sufficient to continuously or continually provide a fresh, exposed molten metal surface to the polymeric material by disrupting the layer of solid particulate impurities that gradually builds up on the molten metal surface.

Condensation of the vapor after contact of the polymeric material with the heated metal can be effected in any appropriate manner. Care should be taken to minimize or avoid the formation of undesirable deposits, for example, carbonaceous deposits, which tend to build up in the distillation equipment.

The increase of the depolymerization capacity by agitation may be attributable to the improvement in the rate of heat transfer. One of the by-products of the depolymerization reaction is the carbonaceous residue which forms a layer, scum or film on the molten metal surface between the polymer and the metal. The build-up of this layer gradually reduces the rate of heat transfer from the molten metal to the polymer. With agitation, the motion of the molten metal surface destroys this layer and largely restores the heat-transfer rate that originally prevails before formation of the layer.

Preferably the intensity of agitation is sufficient to provide the maximum capacity of the particular depolymerization equipment under the conditions of operation, such as rate of feed, temperature of the molten metal, and rate of vaporization.

Without agitation substantially all of the carbonaceous residue remains inside the reaction vessel. When moderate agitation is applied, the carbonaceous residue in the form of dust is discharged with the vapors. With such low intensity of agitation that the layer of impurities on the molten metal is not disrupted to expose fresh surface to the polymeric material, no dust is discharged and in that respect operation is similar to that with no agitation. As the intensity of agitation is increased beyond that of [illegible]ion of the layer of impurities and exposure of fresh molten metal surface, the carry-over of carbonaceous dusts progressively increases until a point is reached where more than 60% of the carbonaceous residue formed during the depolymerization is discharged with the vapors into the condensing portion of the apparatus. The removal of residue from the reactor in this manner is quite desirable since less frequent cleaning of the molten metal surface is required.

Best results have been obtained by operating with vigorous agitation of the molten metal and maintaining a minimum polymer residence time inside the reactor by feeding the polymeric scrap continuously at a rate which equals the depolymerization rate at the particular temperature of the molten metal employed in the reactor.

Generally, any means of condensing the vapor formed is suitable for the practice of this invention. A liquid-vapor contact-type condenser has been found to be exceptionally suitable since the design eliminates dry spots where high boiling fractions would tend to condense. In addition, vapor lines are usually heated to help prevent condensation of the high-boiling fraction of the distillate in the vapor lines around particles of the carbonaceous residue which would cause gummy particulate deposits to form on the inside walls of the vapour conduits.

Since some carbonaceous residue formed in the reactor passes through the vapor lines to the condenser when the molten lead is agitated, the resulting monomeric ester will contain a small percentage of carbonaceous solids having small particle size. It is desirable to remove these solids before transferring the monomer to a distillation column for further purification if such purification is desired. Ordinary filtration commonly employed in known distillation processes is generally effective in removing this particulate material.

The following table gives a comparison of the compositions of two representative samples (Sample A and B) of crude methyl methacrylate monomer obtained by the depolymerization process of the present invention with the crude monomer obtained in a typical commercial batch process depolymerization wherein there is no continuous feed and no agitation of the molten metal. The analyses were performed by gas-liquid chromatography, the two crude monomer samples obtained by the process of the invention being the result of filtration of the condensed monomer vapors.

TABLE I

Component	Conventional Crude .Methyl Methacrylate %	Sample A %	Sample B %
Methyl Methacrylate	87.34	90.62	92.54
Ethyl Acrylate	0.97	1.18	0.03
Ethyl Methacrylate	0.26	0.12	0.06
MethacrylicAcid	0.38	0.44	0.24
Methyl Acrylate	0.18	0.09	0.03
Water	1.72	0.51	0.54
Acetone	2.11	0.04	0.01
Methyl Isobutyrate	0.28	0.23	0.14
Methanol	—	0.02	0.09
High Boilers	6.20	6.17	6.03
Others	0.61	0.47	0.27
Total	100.05	99.89	99.98

It can be seen from this table that a crude, depolymerized monomer of greater than 90% purity is readily obtained utilizing the process of the instant invention.

Furthermore, depending on the product requirements, additional steps employing various methods of purification may be used although the purity of the product obtained by the instant process closely approaches that of monomer produced from original reactants by conventional processes.

This invention is further illustrated by the following examples in which all parts and percentages are by weight unless otherwise indicated. These non-limiting examples are illustrative of certain embodiments designed to teach those skilled in the art how to practice the invention and to represent the best mode contemplated for carrying out the invention.

EXAMPLES.

Introduction

All of the following examples were conducted in an inert atmosphere in a laboratory size reaction vessel with heated vapor lines directing the vapors to a liquid-vapor contact-type condensing device of the countercurrent or concurrent variety having a product recycle stream to limit the carbonaceous residue which normally deposits on the walls thereof.

The reactor was a flat-bottomed closed vessel 12 inches in diameter made of stainless steel with 6-inch high steel side walls and a flanged, dished top also made of stainless steel. The unit was equipped with an agitator blade which runs parallel to the reactor bottom and is somewhat smaller in diameter having rectangular teeth projecting upward at regular intervals along the two arms of the agitating device extending from the center shaft which shaft extends along the center axis of the steel reactor. The molten metal used in the reactor was molten lead, maintained at a depth of about 1½ inches.

The dished stainless steel top of the reaction vessel was provided with an input coupling for the polymeric feed, and a coupling for the vapor outlet, i.e., the monomer. A nitrogen supply tank was connected to the input coupling and nitrogen was metered into this coupling at a rate sufficient to prevent the monomer vapor from entering the coupling. Both the side walls and the top of the reactor were appropriately insulated.

All heat supplied to the reaction vessel was supplied by external electric heaters controlled by voltage regulators. Heating tapes were used on the top of the reaction vessel to reduce heat loss therefrom and also in the vapor output line to the condenser to reduce premature vapor condensation and deposit formation.

The composite granular feed comprised polymeric methyl methacrylate in various forms including molding powder (colored and un-colored), smallpieces of scrap sheet and various other types of polymer scrap made into a granular feed suitable for use in the apparatus described.

EXAMPLE I.

In this example a composite granular feed of polymerized methyl methacrylate was fed continuously over a 44.5 hour period at the rate of 53 grams per minute to the reaction vessel. Nitrogen was also fed into the same conduit as the polymer at a rate of about 1.5 liters/min. to prevent monomer from escaping through this conduit and to provide an inert component in the vapor content in the vessel. The nitrogen content of the vapors in the reaction vessel was about 4% by volume. The molten lead was maintained at a temperature of 500°C. to 530°C. and the agitator maintained at a speed of 80 revolutions per minute. The monomer is condensed, filtered and distilled.

EXAMPLE II.

Slabs of poly(methyl methacrylate) in sheet form, 1.5 inches by 3 inches in size and 1/8 inch to ¼ inch in thickness, were fed continuously over a 47.5 hours period to the reactor at a rate of 45.5 grams per minute with the agitation and other reactor conditions essentially the same as those in Example I. The monomer vapor is condensed, filtered to remove carbonaceous dust, and distilled.

The results of Examples I and II are given below in Table II.

TABLE II

Example	Type Feed	Distillate Percentage of Feed	Percentage of MMA in Distillate	Total Carbon % of Feed
I	Granular Composite	97.25	85.7	0.67
II	1.5 -x 3 in. sheet 1/8 to ¼ in. thick	99.1	90.6	0.06

EXAMPLE III.

a) As in Example I a composite granular feed of poly(methyl methacrylate) was fed continuously to the reactor described above but at an agitator speed of 117 revolutions per minute. The average lead temperature during this run was 556°C. The cracking rate of the reactor under these conditions was 160 grams per minute. The monomer vapor was condensed, filtered, and distilled. The yield and quality of distillate was comparable to those of Example I. The equipment operated efficiently for about five days before a shut-down.

b) Under the same conditions as in part a) but without agitation, the maximum cracking rate was 75 grams per minute and it was necessary to shut down to clean the molten lead after 8 hours operation.

EXAMPLES IV—VII.

The same equipment was used as in the preceding examples with various agitator speeds. The material fed was the same as in Example I. In Table III, the effect of varying the intensity of agitation on the residence time of polymeric material in the reactor and on the residue distribution between the reaction vessel and the condensing section of the apparatus is shown.

TABLE III

	IV	V	VI	VII
Agitation r.p.m.	60	80	96	117
Feed Rate, Grams per Minute	74.5	53	66.8	75.0
Temperature of the Molten Lead (°C.)	513—540	500—535	595—608	515—532
Carbon in Reactor, Percentage of Feed	0.55	0.61	0.39	0.22
Carbon in Distillate, Percentage of Feed	0.06	0.06	0.17	0.38
Total Carbon, Percentage of Feed	0.61	0.67	0.56	0.60

EXAMPLES VIII—XIV.

In these examples, a composite granular feed of poly(methyl methacrylate) is fed to the same reactor in which the agitator is operated at 117 r.p.m. Various feed rates and lead bath temperatures are shown in the following table IV. It is noteworthy that the vapor in the reactor has a fairly constant temperature in the neighborhood of 400°C., i.e., the cracking temperature.

TABLE IV

Example	Temp. Lead	Feed Rate gm/min.	°C. Vapor	Production Rate of Monomer in lbs/hr/sq. ft. of Lead Surface Area
VIII	451	10.1	386	1.7
IX	457	29.9	400	5.0
X	466	49.8	400	8.4
XI	471	69.9	402	11.7
XII	495	90.0	396	15.1
XIII	526	115.0	403	19.3
XIV	552	160.0	394	26.9

The condensed monomer (the production rate of which is given in the last column of the table) is filtered and distilled, providing a yield of high purity monomer comparable to that of the preceding examples.

WHAT WE CLAIM IS:—

1. A process in which an acrylic polymer containing two or more mers of one or more alkyl esters of acrylic acid and/or an alpha-alkyl-substituted acrylic acid is depolymerized to form the corresponding monomeric ester(s) is in an inert atmosphere by contact with a hot molten metal, characterized in that the surface of said molten metal is constantly renewed.

2. A process according to Claim 1, wherein the molten metal is lead, tin or cadmium maintained at a minimum temperature of about 400°C.

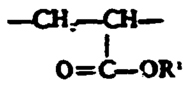
3. A process according to Claim 1 or 2, wherein the surface of the molten metal is constantly renewed by mechanical agitation.

4. A process according to any one of the preceding claims, wherein the vapours are condensed in a contact-type countercurrent or concurrent condenser and wherein a portion of the condensate is recycled back through the condenser to decrease the formation of undesirable deposits therein.

5. A process according to Claim 4, wherein the vapor output of the depolymerization reactor is conducted through heated vapour lines to said condenser.

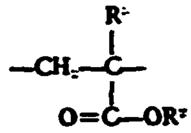
6. A process according to Claim 5, wherein the temperature of the vapour line is maintained at above 250° C. and a portion of the condensate from the condenser is recycled back through the condenser to reduce the build-up of undesirable deposits therein.

7. A process according to Claim 1, wherein the acrylic polymer consists substantially exclusively of mers of the formula:



$$-CH_2-\underset{\substack{|\\O=C-OR^1}}{CH}-$$

or



$$-CH_2-\overset{\substack{R^2\\|}}{\underset{\substack{|\\O=C-OR^3}}{C}}-$$

where, in the above formulae, R^1, R^2, and R^3 are C_1—C_4 alkyl groups.

8. A process according to Claim 1, wherein the acrylic polymer is poly(methyl methacrylate).

9. A process according to Claim 1 for producing monomeric methyl methacrylate from polymeric methyl methacrylate comprising adding the polymeric material in the form of fragments to a reaction vessel containing a molten metal selected from the group consisting of lead, tin and cadmium; said molten metal having a relatively large surface area which is constantly renewed by agitation and said molten metal being maintained at a temperature of from 400° C. to 650° C. in an inert atmosphere of nitrogen, argon, helium, or neon.

10. A process according to Claim 9, wherein the molten metal is lead.

11. A process according to Claim 10, wherein the temperature of the liquid lead is from 450° C. to 550° C.

12. A process according to Claim 10 or 11, wherein the vapours are condensed in a contact-type concurrent or countercurrent condenser and wherein a portion of the condensate is recycled back through the condenser to decrease the formation of undesirable deposits therein.

13. A process according to Claim 12, wherein the vapour lines to the condenser are maintained at a minimum temperature of 300° C. to prevent the formation of undesirable deposits therein.

14. A process according to Claim 13, wherein the vapour lines to the condenser are maintained at a temperature of up to 400° C.

15. A process according to any of Claims 10—14, wherein the temperature of the liquid lead is from 500° C. to 530° C. and the inert atmosphere is nitrogen.

For the Applicants,
D. YOUNG & CO.,
Chartered Patent Agents,
9 Staple Inn London, W.C.1.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1974.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

ANNEXE D

MISSION REPORT OF AUGUST 1, 1987

RESTRICTED

August 1, 1987
English

DEVELOPMENT OF AN IMPROVED PMMA PYROLYSIS SYSTEM

SI/CPR/86/028/11-51/32.1.H.
PEOPLE'S REPUBLIC OF CHINA

Mission report :

Prepared for the Government of the
People's Republic of China
by the United Nations Industrial Development Organization,
acting as an executing agency for the United Nations
Development Programme

Based on the work of Alfons G. Buekens,
expert in waste recycling

United Nations Industrial Development Organization
Vienna

This report has not been cleared with the United Nations Industrial Development Organization which does not, therefore, necessarily share the views presented.

EXPLANATORY NOTES

The following abbreviations have been used consistently throughout the text

Abbreviation	Entity or Material
MMA	methylmetacrylate monomer
PMMA	Polymethylmetacrylate
SRRUC	Shanghai Resource Recovery and Utilization Company
PRC	the People's Republic of China

TABLE OF CONTENTS

Annexes

I. The UNIDO/VUB process for PMMA pyrolysis

After completing the experimental development at VUB a preliminary design and general instructions were sent to Shanghai Resource Recovery & Utilization Co (SRRUC). The technical staff of SRRUC has studied these data most thoroughly and prepared numerous questions regarding design. construction, operation and safety procedures. These points were discussed methodically during the visit of Dr. Buekens, on the basis of a new design, prepared by the SRRUC technical staff in accordance with the principles of the original design and incorporating local materials specifications and schedules.

The most important questions raised were:

- the testing of the feeding system. An innovative system was locally designed and will be conctructed and tested. The feeding of PMMA plates is uncomplicated, but that of shavings is problematic, taking into account the required absence of jamming, bridging, or leakage of gas. Also the ambient air has to be excluded, possibly with the aid of inert gas (nitrogen)
- the monitoring of fluidization by measuring the pressure drop of the bed
- the testing of the distributor. The outlet velocity of the fluidizing gas is extremely high. Hence, it is necessary to test a cold model and possibly even to use larger holes. Since the coal fire would be replaced by electric (induction) heating, an ordinary distributor design would also be suitable
- the possible premature condensation of MMA in cyclones and other equipment. (The ducts have to be maintained above 100°C to prevent this occurrence)
- the distillation of MMA/water mixtures allows a drastic reduction of residual MMA-content in the wastewater.
- the plant lay-out has to be adapted to new surroundings (the riverside potch factory)
- the purification of MMA from fillers

Safety Aspects

PMMA is flammable
MMA is most inflammable. Toxicity data have been collected by SRRUC.

The process hazards have been reviewed methodically:

1) in case of overpressure the feedwater discharges over a safety valve. It is filtered or at least strained prior to feeding in order to avoid deposition of dirt, which may cause obstructions and overpressure.

2) underpressure can only occur in the condensor, which is constructed vacuum proof.

3) obstructions may form in the ducts, the strainer or the bed. No water (only steam) should be fed to the bed. The water should be filtered prior to feeding.

4) low levels can occur in the water reservoir or when the sand is blown out of the bed.

5) high levels can occur in the cyclone (sand collection)

6) low bed temperature. No steam should be fed as long as it could condense in the bed.

7) high bed temperature. Feed more PMMA, decrease heating
high tube temperature. Select suitable heat resistant material.

8) high flow rate of water. Leads to low flow rate of steam. When steam pressure drops, external steam is delivered automatically.

9) high flow rate of steam. Sand carry-over. Decrease water flow.

10) power failure. The bed continues to be fluidized by external steam.

Environmental Aspects.

The coal fire will be replaced by electric heating. This leads essentially to zero emission, provided the charging system is closed and the vent gas, after condensation, is led to an afterburner.

To avoid all smells measures are to be taken to control the vent of

- the MMA storage
- the distillation column
- the prepolymerisation reactors
- the vacuum compressor

and to use a closed system for prepolymerization, good quality fittings. etc.

The production of by-products is much lower than in the cauldron technology.

Fillers may have to be filtered from the MMA produced, since the residue no langer remains in the reactor.

II. Economic and Ecological Context

Historically, the Xingguang factory has been a source of small problems. Recently, new residential quarters, recreational units and young plant nurseries have been established in the vicinity. For this reason part of the production, including PMMA pyrolysis, had to be halted at this factory.

During our stay, two visits were paid to the new site, selected for the erection of the PMMA pyrolysis plant.

Also economic problems have made themselves felt:

1) the evolution in planified economy has stimulated parallel collection of PMMA-wastes by individuals, collection stations and private enterprise.

2) the changes in exchange rates have made the importation of foreign PMMA-wastes more problematic.

3) the sale of PMMA pearlite buttons has been slack.

The ecological and economic factors, on one hand, have delayed the realization of the pyrolysis plant. On the other hand, they have made the new technology even more valuable by increasing the competitivity of this new pyrolysis method.

The environmental requirements are:

- ambient air 20 mg/m^3. If the volume of the workshop is 1000 m^3 and the air is renewed X times/h, the "allowable" leak stream amounts to 20 X g/h.

- pH-value of 6. suspended solids below 500 mg/L.

BOD_5	≤ 30 mg/L
COD_{Cr}	≤ 50 mg/L
Extract. Oil	≤ 10 mg/L
lead	≤ 1 mg/L

In view of the small generation rate of wastewater, these limits seem excessively strict.

III. Miscellaneous

In agreement with the mission to study recycling opportunities in Shanghai several visits were paid to other units. namely:

1) The Shanghai Environmental Sanitation Administration Bureau

Responsible for the collection & transportation of refuse, generated by about 7,000,000 people.

Daily about 6,000 tonnes of household refuse
3,000 tonnes of demolition & construction waste
7,000 tonnes of nightsoil

are collected. Industrial wastes are taken care of by another Agency.

There are about 30,000 employees working in collection and transportation (by barges mainly). Studies are conducted regarding composting and incineration by the New York Office of Klockner.

The Bureau serves 12 District Stations and 50 Barge Stations. The total capacity of barges are 40,000 tonnes. with a medium sized barge taking 15 tonnes! Land is acquired for use as a landfill sites. Some scavenging takes place. In Huzhou (Zhejiang province) sorting is aided by trommelling. The fine fraction, after composting, is given away. The agricultural station at Shanghai has declared compost quality to be good.

As another test, transfer stations have been built, which store fresh refuse for about 1 week in a closed hall. Leachates are recycled over the refuse. After this pretreatment, smells are supposed to have diminished. During our visit there was on oversupply of refuse and the result of the operation was unconvincing.

3) Shanghai Food Co.

Basic data

3 slaughterhouses for pigs
1 slaughterhouse for cattle
cooled storage
yearly capacity: 4 million units/ employment : 10,000 people.

The company kills the animals and prepares meat products for the Shanghai market.

The cutting part uses a modern line imported from Denmark.

Porc products consist of ham, sausages, smoked and salted meat, salami, "hot dogs", etc.
Capacity: 8,000 tonnes/yr (?)

Glands are collected for pharmaceutical industry.

Present use of by-products

Blood is converted to powder. The use of the "hollow knife" technique allows plasma and haemoglobin to be separated.

Bone is converted to "peptin" and fertilizer; the vesicles are used as sausage skin.

Quest

other methods for using inside organs

ANNEXE I

PROPOSED PROGRAMME FOR DR. A. BUEKENS' PROJECT STUDY MISSION IN SHANGHAI

July 14, Tuesday	
Evening	SRRUC leadership meeting Dr. A. Buekens at the airport and accompanying him to the guesthouse
July 15, Wednesday	
Afternoon 1:30-4:00	In an interview with Dr. Buekens at the Headquarters SRRUC leadership briefly recommending the general plan for enforcing the UNIDO project
Evening	Supper
July 16, Thursday	
Forenoon 9:30-11:30	Visiting Xingguang Plastics Plant. SRRUC Nanshi District Branch Manager, Mr. Yuan Yongling, briefing on the existing status of PMMA production and the plan for near future realization of the technological reform of PMMA pyrolysis according to Dr. Buekens' process design
11:30-12:30	Lunch
Afternoon 1:30-4:00	Discussion continued
Evening	Open
July 17, Friday	
Forenoon 9:00-11:30	In SRRUC Nanshi District Branch office, Mr. Liu Baoping, Deputy Director of Xingguang Plastics Plant,recommending the preliminary design on the establishment of the improved PMMA pyrolysis system in the plant
11:30-12:30	Lunch
Afternoon 1:30-4:00	Discussion continued
Evening	Open

July 18, 19 Saturday & Sunday: Touring activities

July 20, Monday	
Forenoon 9:00-11:30	In SRRUC Nanshi District Branch office, Deputy Director, Mr. Liu Baoping, explicating his limited modification of Dr. Buekens' initiative process design and asking for Dr. Buekens' comment
11:30-12:30	Lunch
Afternoon 1:30-4:00	Discussion continued
Evening	Open
July 21, Tuesday	
Forenoon 9:00-11:30	In SRRUC Nanshi District Branch office, DR. Buekens proposing effective enforcement of his latest process design
11:30-12:30	Lunch
Afternoon 1:30-4:00	Discussion and making decision on adopting most appropriate procedures for carrying out the technological reform in the nearest future
Evening	Open
July 22, Wednesday	
Forenoon 9:30-11:30	Meeting in Xingguang Plastics Plant, general evaluation of the environmental impact after technological reform of PMMA pyrolysis according to Dr. Buekens' idea (with the participation of relevant technicians from the environment department)
11:30-12:30	Lunch
Afternoon 1:30-4:30	Discussion continued
Evening	Open
July 23, Thursday	
Forenoon 9:00-11:30	In SRRUC Nanshi District Branch office, exchange of ideas on implementation of the project
11:30-12:30	Lunch
Afternoon 1:30-4:00	Discussion continued
Evening	Open

July 24, Friday	
Forenoon 9:00-11:30	In SRRUC Nanshi District Branch office, Dr. Buekens winding up the project study mission in Shanghai
11:30-12:30	Lunch
Afternoon 1:30-4:00	Discussion on Dr. Buskens' summarizing statement
Evening	Dinner
July 25, 26, 27 Saturday, Sunday and Monday	Touring activities and shopping in downtown
July 28, Tuesday	Dr. A. Buekens leaving Shanghai

Modifications and Additions of the programme

Location : July 16 Xinglian button factory

17 Xingguang plastics plant

18 Shanghai Riverside Potch Factory

21 Xingguang plastics plant, Meeting with environmental authorities

22 Visit to the Shanghai Environmental Sanitation Administrative Bureau

23 Shanghai Riverside Potch Factory

24 Leaving for Nanking. Meeting with the local resource recovery company

25 Idem

26 Return to Shanghai

27 Visit by Shanghai Food Co.

ANNEXE II

Shanghai Environmental Sanitation Administration Bureau

Xu Zhengu	Chief Engineer
Fen Baosheng	Secretariat of the Bureau
Song Xingxin	Scientific & technology Dep.
Shen Xinfen	Scientific & technology Dep. Engeneer
Miao Guangyao	Production & Equipment Dep. Director
Gu Zeyi	Shanghai Design & Research Institute of Environmental Sanitation
Gu Yuxiang	(same as the above)
Chen Fangjing	(same as the above, Engineer)
Zhang Ming	Interpreter
Chen Oiuying	Interpreter of SRRUC

ANNEXE E

EXPERIMENTAL STUDY AT V.U.B.

TABLE OF CONTENTS

Annexes

1. Experimental set-up and conditions

The pyrolysis experiments were performed using the fluid-bed unit in Figure 1.

The reactor (1 + 2) is made of an Inconel 600 alloy; it has a diameter of 15 cm in the bed (1) and 30 cm in the freeboard zone (2). It is heated by two separate electrical heating blankets (3).

The fluidizing gas, i.e. steam, is preheated in a tubular furnace (4). The PMMA is fed by means of a variable speed screw convegor (9) from a locked feed hopper (5). The latter is swept by nitrogen.

The gases are cleaned from fly-ash in a cyclone (6) and the liquid phases are condensed in a shell and tube heat exchanger (7).

The temperatures are measured at different heights in the bed and the freeboard zone (T1-T7).

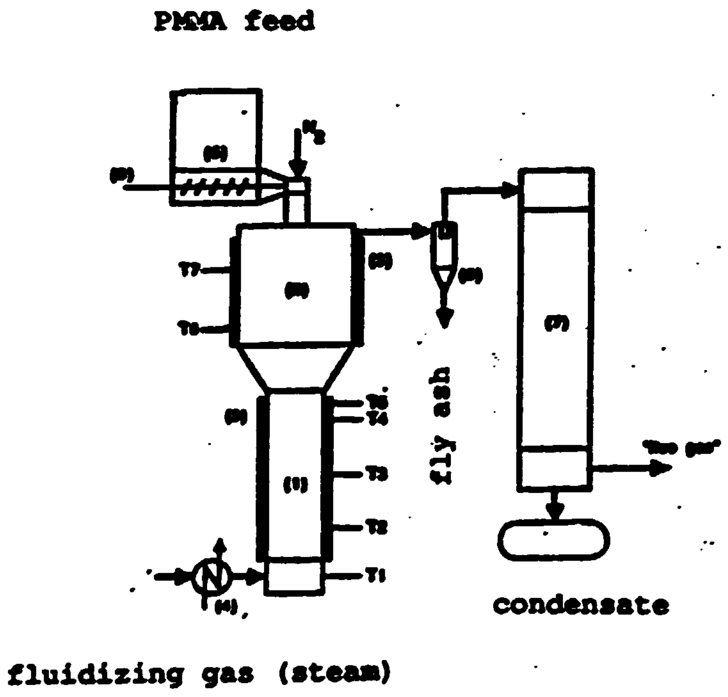


Figure 1: continuous fluid-bed unit

Liquid and solid flowrates are measured gravimetically. The flowrate of added gas (N_2) is measured by a calibrated rotameter. To determine the flowrate of non condensable reaction products (flue gas) the gas composition is determined gas chromatographically, using the added N_2 as an internal standard.

The PMMA used was free from pigments and filters. The reactor was filled with 4 liters of sand mesh 50 . In each experiment this charge was fluidized with a flow of approximately 4.5 kg/h of steam (of 360°C and 1 atm). This flow rate is about three times the minimum fluidization velocity and consequently the optimum flowrate for mixing the bed.

Since the monomer and water are almost insoluble in each other the condensate separates into two phases: an organic (oily) and watery one. These phases separate very well. Still, in case the aqueous condensate is to be discharged, its further purification may be required.

2. Results of the experiments

A summary of the experiments performed is given in Table 1.

Hence, the purity of the organic phase (wt% MMA) was determined by means of gas chromatography. For these analysis a packed OV-101 column was used. Using a flame ionization detector (FID) water is not detectable. The peaks were evaluated on the basis of an absolute calibration.

The MMA production in the organic phase was calculated as follows:

$$\frac{\text{purity of the organic phase (wt\%)} \times \text{flowrate of the organic phase}}{\text{flowrate PMMA}}$$

The aqueous phase is obviously saturated with nonomer. The solubility of MMA in water being 1.5 wt %, the total amount of MMA produced is given by:

$$\frac{\text{MMA in the organic phase (wt\%)} \times \text{flowrate of the organic phase} + \text{flowrate watery phase} \times 0.015}{\text{flowrate PMMA}}$$

Experiment number	$T_{reactor}$ (°C)	PMMA flowrate (g/h)	flowrate of the organic phase (g/h)	gas evolution (g/h)	purity of the organic phase (wt% MMA)	MMA production in the organic phase (% of feed)	total MMA production (% of feed)
A	387	990	900	3	99.0	90.0	98.1
B1	438	990	880	2	98.2	87.3	95.6
B2	432	990	890	2	98.4	88.5	96.4
C	472	990	850	4	98.6	84.7	92.8
D1	529	990	870	13	96.0	84.4	92.3
D2	529	990	820	10	96.5	79.9	87.6
E	557	990	820	28	94.0	77.9	85.5
F	577	990	820	32	92.9	76.9	84.8
G1	410	1470	1410	2	97.0	93.0	97.7
G2	416	1470	1410	3	97.6	93.6	98.4
H	422	1470	1380	20	95.9	90.0	94.8

Table 1: summary of the performed experiments

The results of the experiments A-F (flowrate PMMA = 990 g/h) is given in Figure 2 to 5.

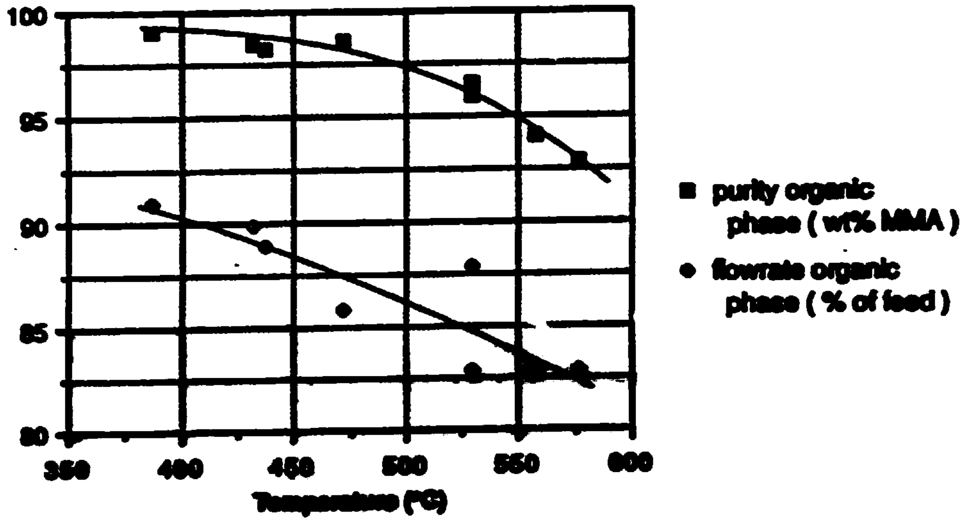


Figure 2: yield and MMA concentration of the organic phase

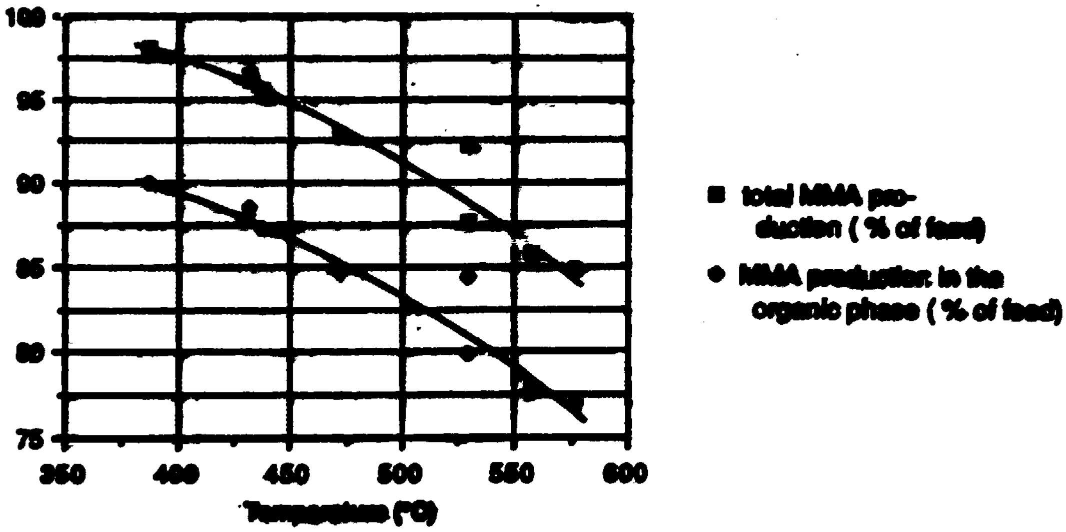


Figure 3: amount of MMA produced

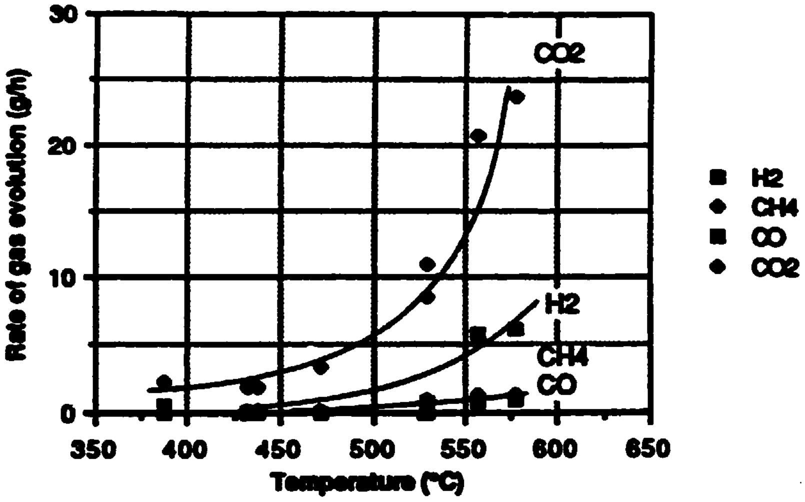


Figure 4: gas evolution (per compound) as a function of temperature

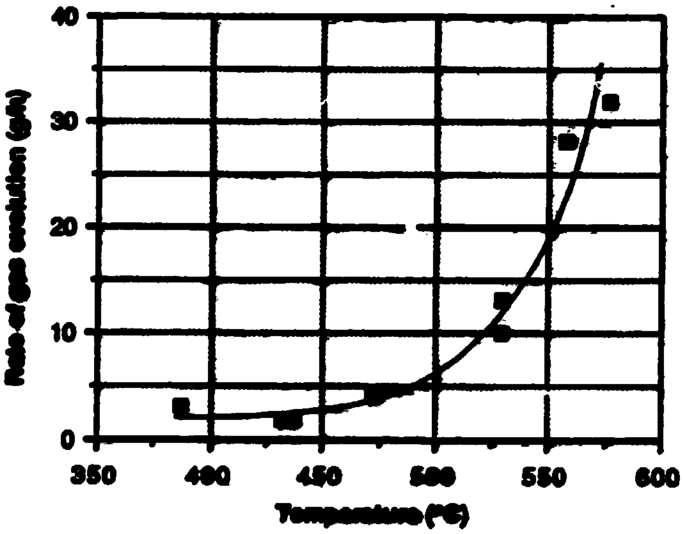


Figure 5: total gas evolution as a function of temperature

When the temperature is increased:

- less liquid fraction is produced
- the MMA yield in the organic phase decreases
- more waste gas is produced.

As result the yield of monomer decreases with increasing temperature. Hence, the reaction should be carried out at a temperature as low as possible. On the other hand, however, a low temperature leads to low reaction rates. As a consequence PMMA may accumulate in the reactor. This was the case, for example, at a temperature of less then 370°C and a flowrate of 990 PMMA g/h (volumetric yield of 248 g/h PMMA/l bed volume at rest).

From the gas chromatographic analysis it follows that: at low temperatures the impurities in the liquid fraction are mainly high boiling condensation components, whereas at high temperatures more low boiling, decomposition products are formed. This result is illustrated in Figure 6. In this figure the summated area of the peaks form the compounds with a smaller retention time than MMA (lower boiling point) are given as a percentage of the area of the MMA peak, analogous for the compounds with a longer retention time (higher boiling point).

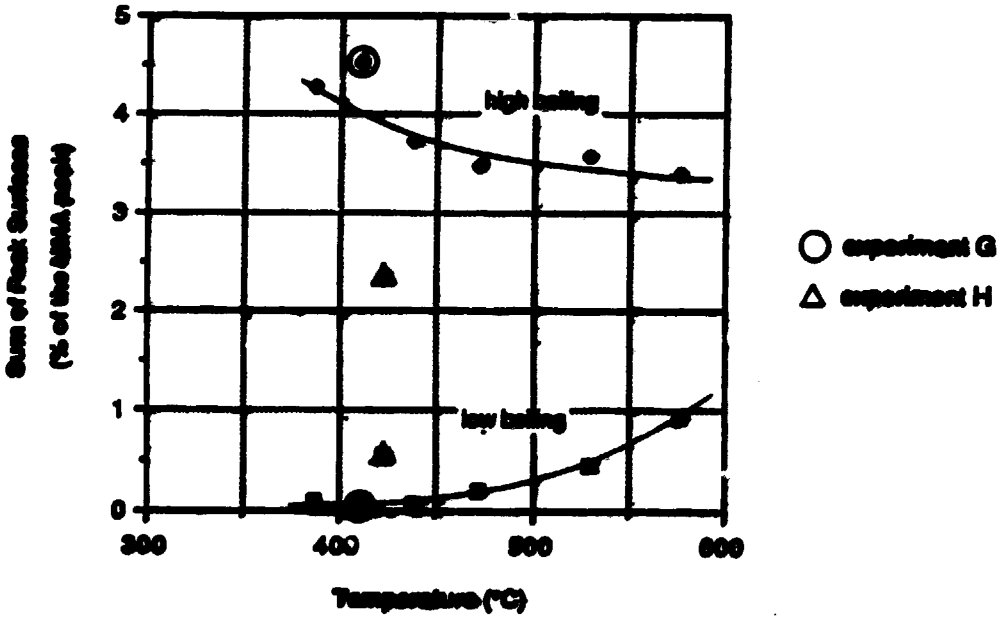


Figure 6: kind of compounds formed at different temperatures

In experiments G1-G2 the feed ratio of PMMA to steam is increased by a factor of 1.5. In these experiments more MMA was recuperated via the watery phase. This is quite logical, cause the amount of MMA in the watery phase (being saturated with MMA) is the same in all experiments. For this reason in an industrial plant the feed ratio of PMMA to steam should be as high as possible. Moreover, the production of steam is an important factor with respect to the economic evaluation of the process. In order to have a high ratio of PMMA to steam the reactor must be filled with a fine sand, so that the bed may be well mixed at low flowrates of steam. Another measure to keep the MMA losses low, is the recycling of the watery phase as a fluidizing medium.

The total MMA yield was, within the experimental errors, the same as in the experiments with a PMMA flowrate of 990 g/h and about the same temperature. It is also seen that more high boiling inpurities are formed (Figure 6). This may be due to:

- the higher partial pressure of MMA, so more condensation products (dimers,trimers, ...) are formed

- the shorter residence time, so less secondary decomposition products are formed.

3. Influence of the freeboard temperature

Experiment H was carried out with the heating blanket in the freeboard zone swithched on. Hence, the temperature in the freeboard zone was higher in experiment H than for exemple in experiment G2:

	H	G2
Bed temperature	422	416
Freeboard temperature	480	360

With the heating blanket in the freeboard zone swithched on:

- the flue gas evolution is larger (Table 1)

- the yield of MMA is lower (Table 1)

- there is a shift from high to low boiling inpurities in the pyrolysis oil (figure 6)

In order to have a high efficiency, the reaction products, hence, must be cooled as quickly as possible. The residence time of the reaction products should be minimized. As a matter of fact, a low residence time is one of the features why a fluid bed reactor is preferable to a cauldron.

4. Heat of reaction

By means of an energy balance over the reactor it was possible to calculate the heat of reaction (900 J/g of PMMA). This is the value of ΔH_r (293 K, 1 atm.). The heat of reaction ΔH_r of the following reaction

$$\text{PMMA (293 K)} \rightarrow \text{MMA (T)}$$

It's given by:

$$\Delta H_r = 900 + \int_{293}^{T} c_p(\text{MMA}).dT$$

For the heat capacity of MMA the following equation is used :

$$c_p = 0.336 + 3.6\ 10^{-3}\ T - 1.38\ 10^{-6}\ T^2\ \text{J/g.K}$$

The heat of reaction ΔH_r is thus given by :

$$\Delta H_r = 660 + 0.336\ T + 1.8\ 10^{-3}\ T^2 - 0.46\ 10^{-6}\ T^3\ \text{J/g}$$

At 450°C (723K) this gives 1670 J/g.

This relatively high endothermicity of the reactor enables controlling the temperature in a reactor by adjusting the flowrate of the feed.

5. Distillation of MMA-water mixtures

The vapour-liquid equilibrium of MMA with water has some interesting features in view of the distillation of the pyrolysis product and the treatment of any residual wastes. When a mixture of 164 g water and 165 g MMA was distilled an azeotrope with a minimum boiling point (80°C) was obtained. The quantity of the azeotrope distilled was 189 g. When it was cooled to room temperature (20°C) it separated in 2 phases : 25 g (13.3 wt%) watery and 164 g (86.7 wt%) organic phase. Hence, the vapour-liquid equilibrium of MMA-water is an equilibrium with a heteroazeotrope of the form tentatively presented in Figure 7.

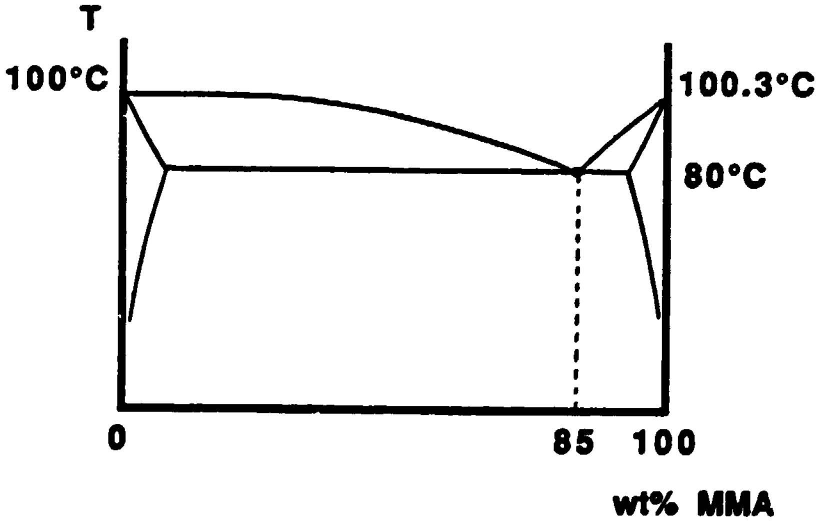


Figure 7: vapour-liquid equilibrium of MMA-water

When the organic phase obtained at the pyrolysis experiments was distilled, the following fractions were obtained :

- first, having the lowest boiling point, the azeotrope
- afterwards, at 100°C, MMA
- a residue, containing the heavy compounds.

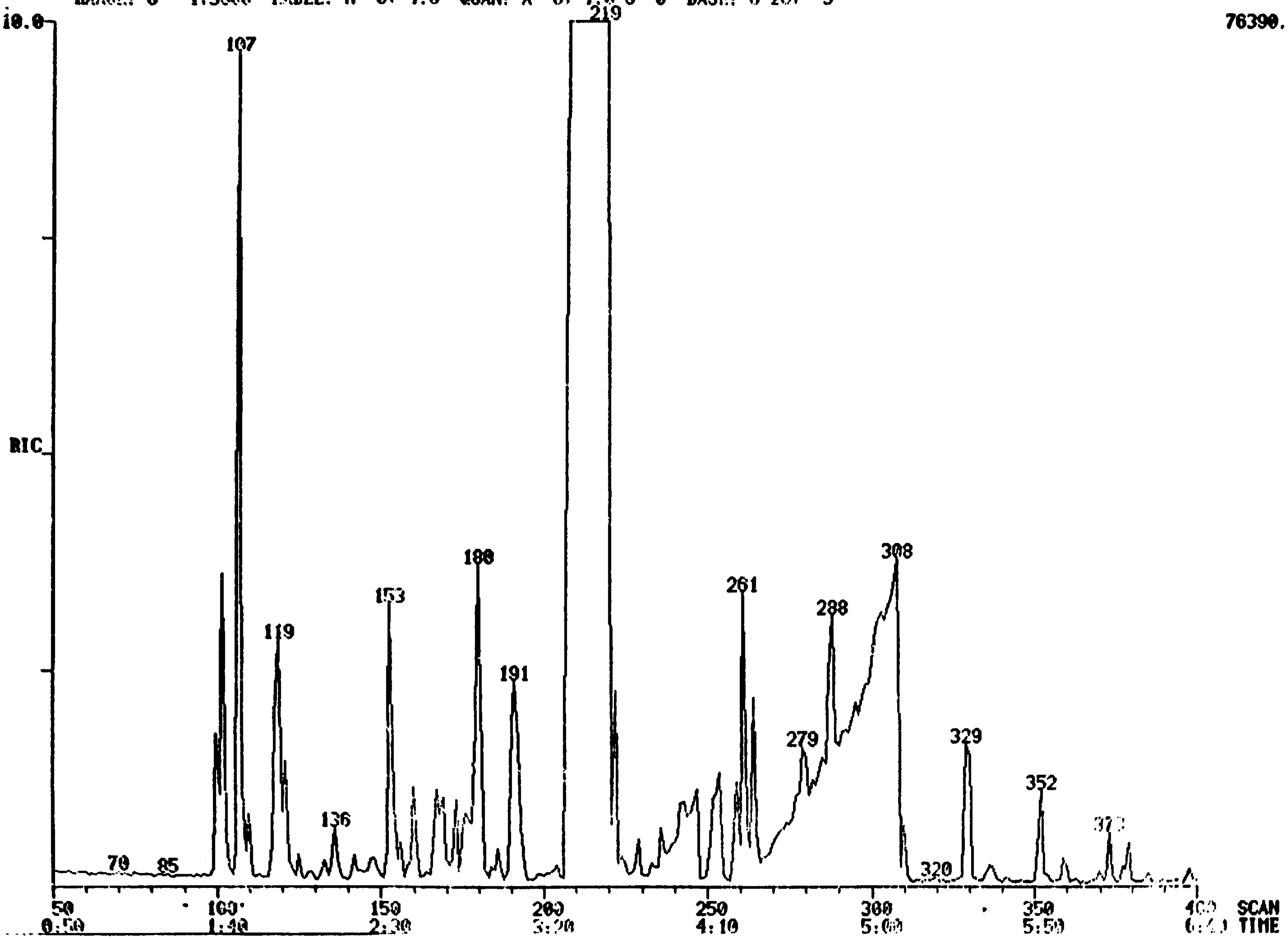
For a Belgian PMMA pyrolysis plant, using lead bath technology, the best quality MMA is obtained by steam distillation, rather than with a vacuum or atmospheric distillation. For this reason, when distilling the oily phase, it's of interest to add some (or all of the) watery phase. Enough water must be added, so that a (heterogeneous) mixture with more than 15% water is obtained. In this case distillation gives :

- as a top product, the azeotrope. After cooling it separates in a watery and a MMA-rich phase. The watery phase can be recycled, while the monomer rich phase is free of heavy components because the boiling point of the azeotrope is only 80°C.
- as a bottom product, a residue consisting of two phases : a phase containing the heavy pyrolysis products and a watery phase. The watery phase can also be recycled, while the organic phase should be removed or recycled in the process.

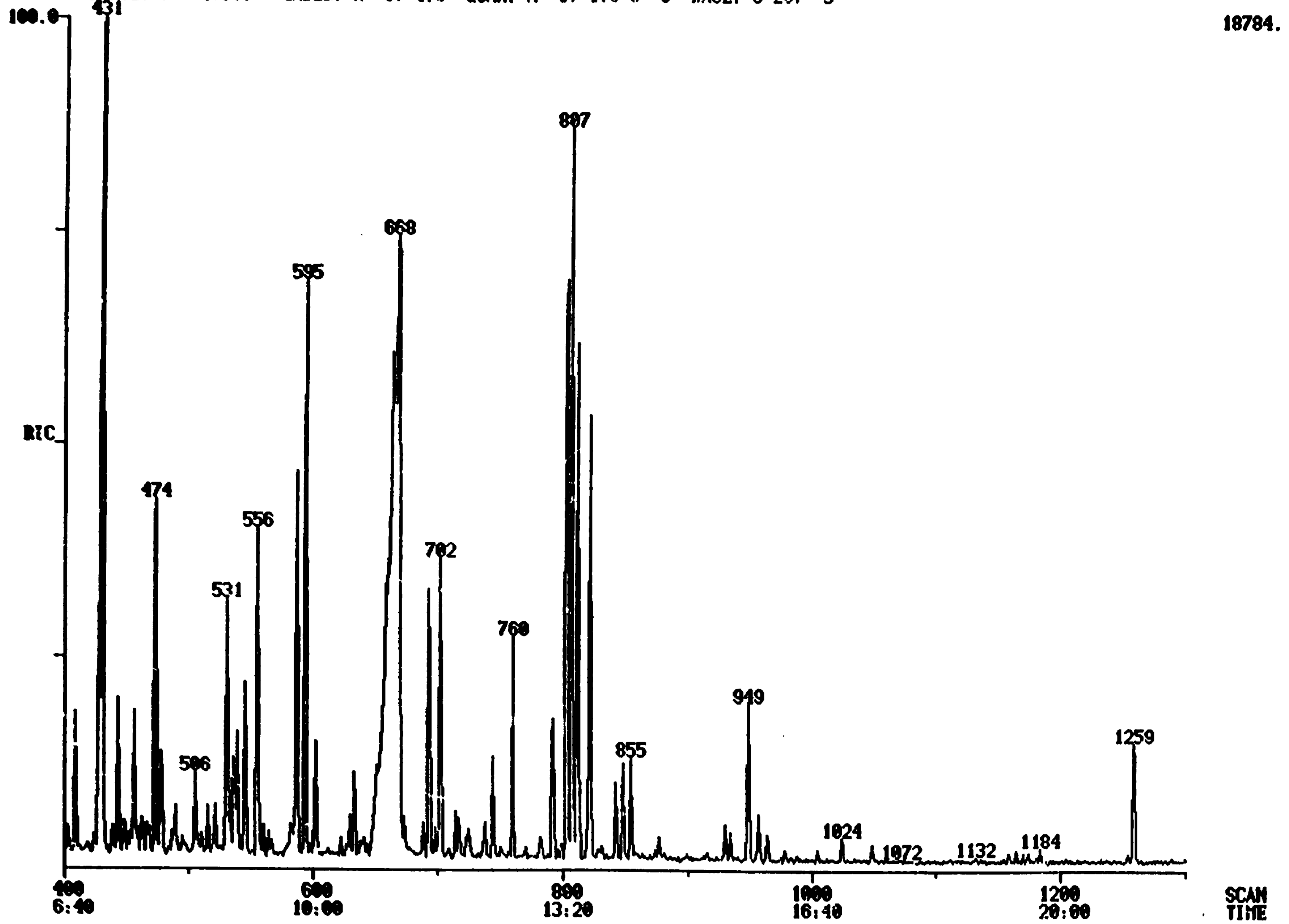
ANNEXE I

GAS CHROMATOGRAPHY-MASS SPECTROMETRY OF THE PYROLYSIS OIL

```
RIC                                    DATA: LUCL 01            SCANS  50 TO  400
09/11/87 11:41:00                      CALI: MARIA87D 02
SAMPLE: METHACR
CONDS.: ULTRA 2
RANGE: G   1,5000  LABEL: N  0, 4.0  QUAN: A  0, 1.0 J  0  BASE: U 20,  3
```

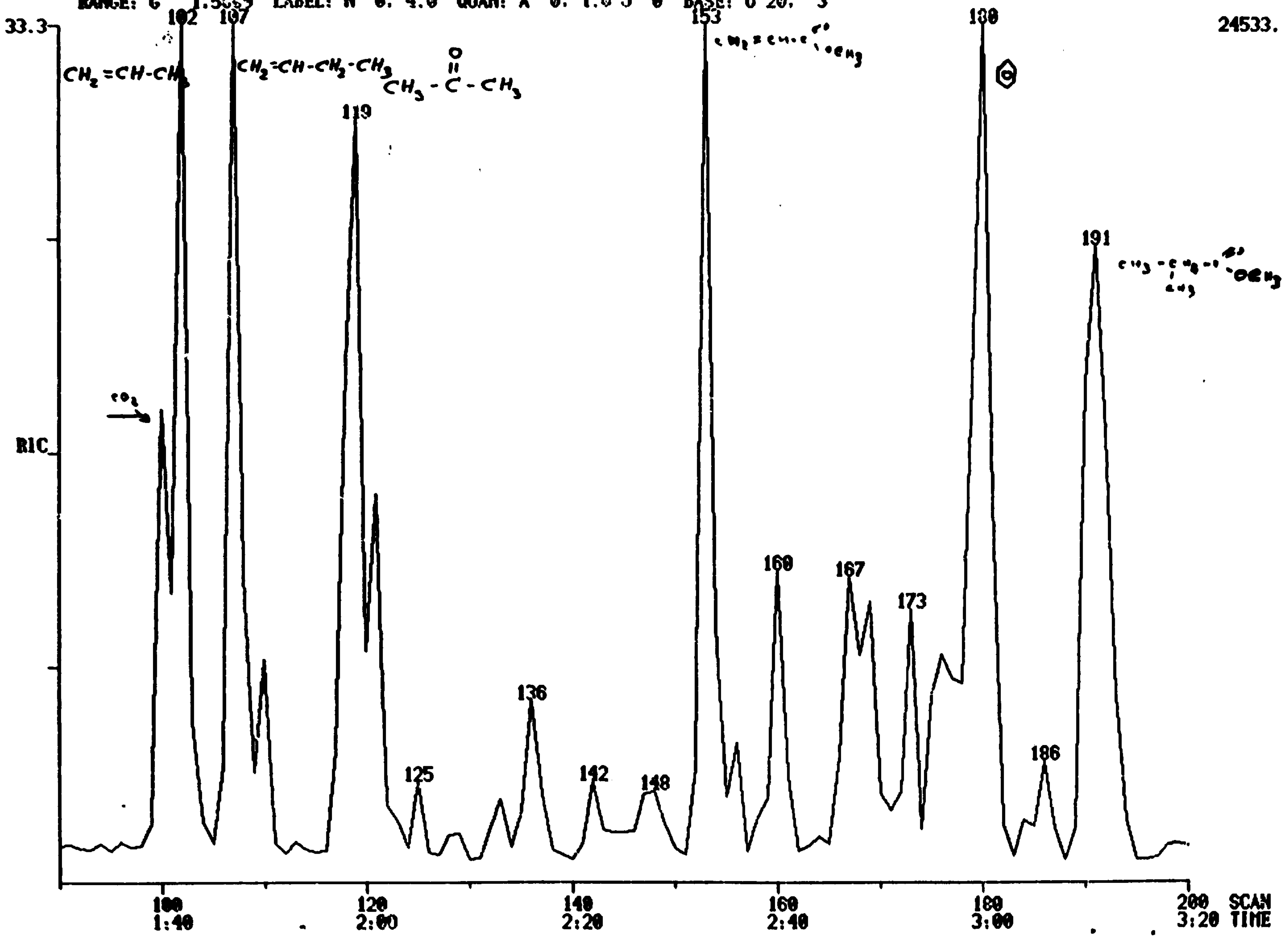


```
RIC
09/11/87 11:41:00                        DATA: LU L 01              SCANS  400 TO 1300
SAMPLE: METHACR                          CALI: MARIA37D 02
CONDS.: ULTRA 2
RANGE: G   1.5030  LABEL: N  0. 4.0  QUAN: A  0. 1.0 J  0  BASE: U 20,  3
```



```
REFERENCE RETENTION TIME (MIN:SEC)    3:39
NO. LOW MASS  HIGH  SCAN  TIME  METH     AREA    HEIGHT   NAME NUM
 :   0.80     0.90  182   1:42  A BB     58972.  35544.   --   0
```

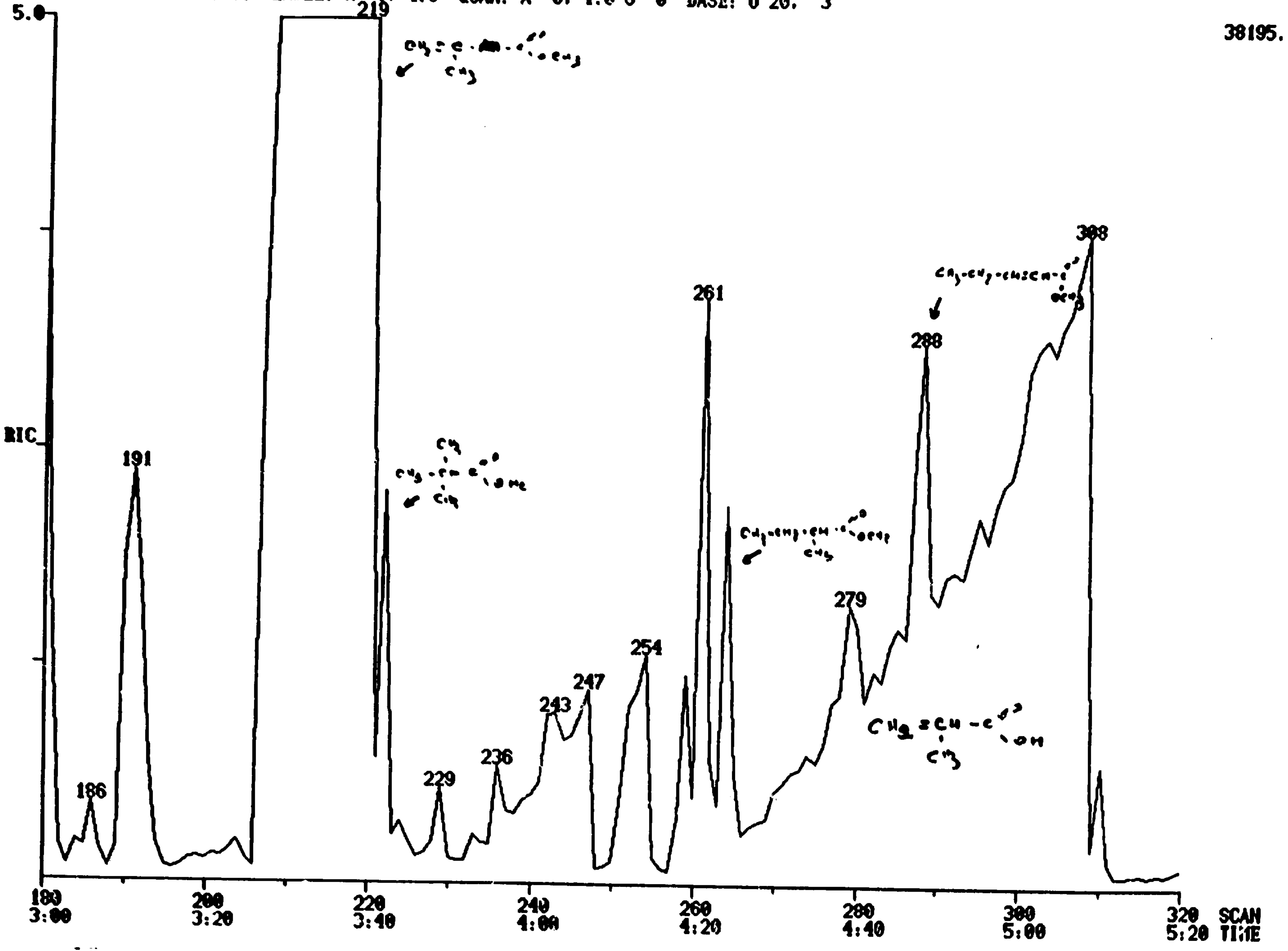
```
RIC                                 DATA: LUCL #102          SCANS   90 TO  20
09/11/87 11:41:00                   CALI: MARIA87D #2
SAMPLE: METHACR
CONDS.: ULTRA 2
RANGE: G   1.5089  LABEL: N  0. 4.0  QUAN: A  0. 1.0 J  0  BASE: U 20,  3
```



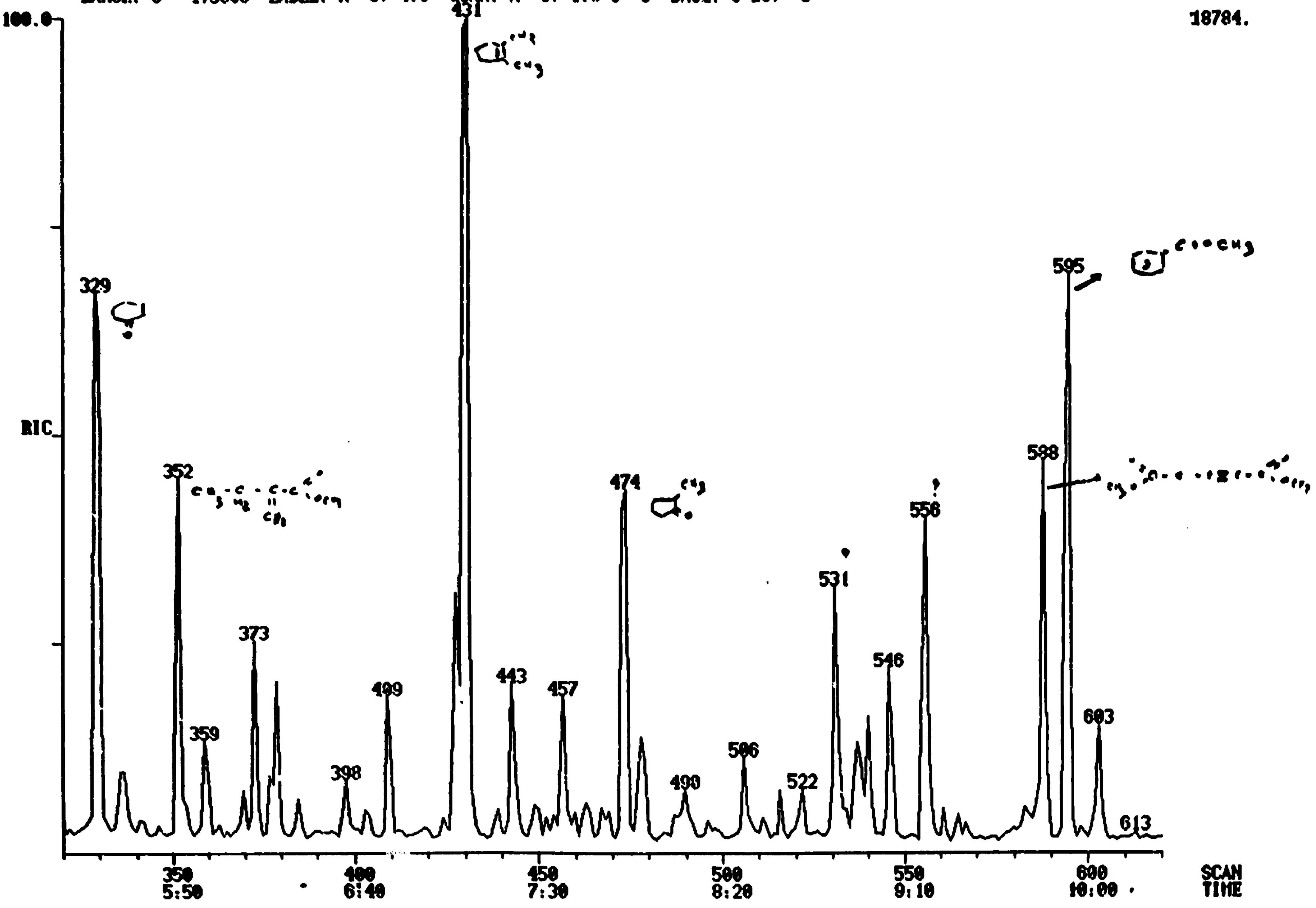
RIC
09/11/87 11:41:00
SAMPLE: METHACR
CONDS.: ULTRA 2
RANGE: G 1.5000 LABEL: N 0. 4.0 QUAN: A 0. 1.0 J 0 BASE: U 20. 3

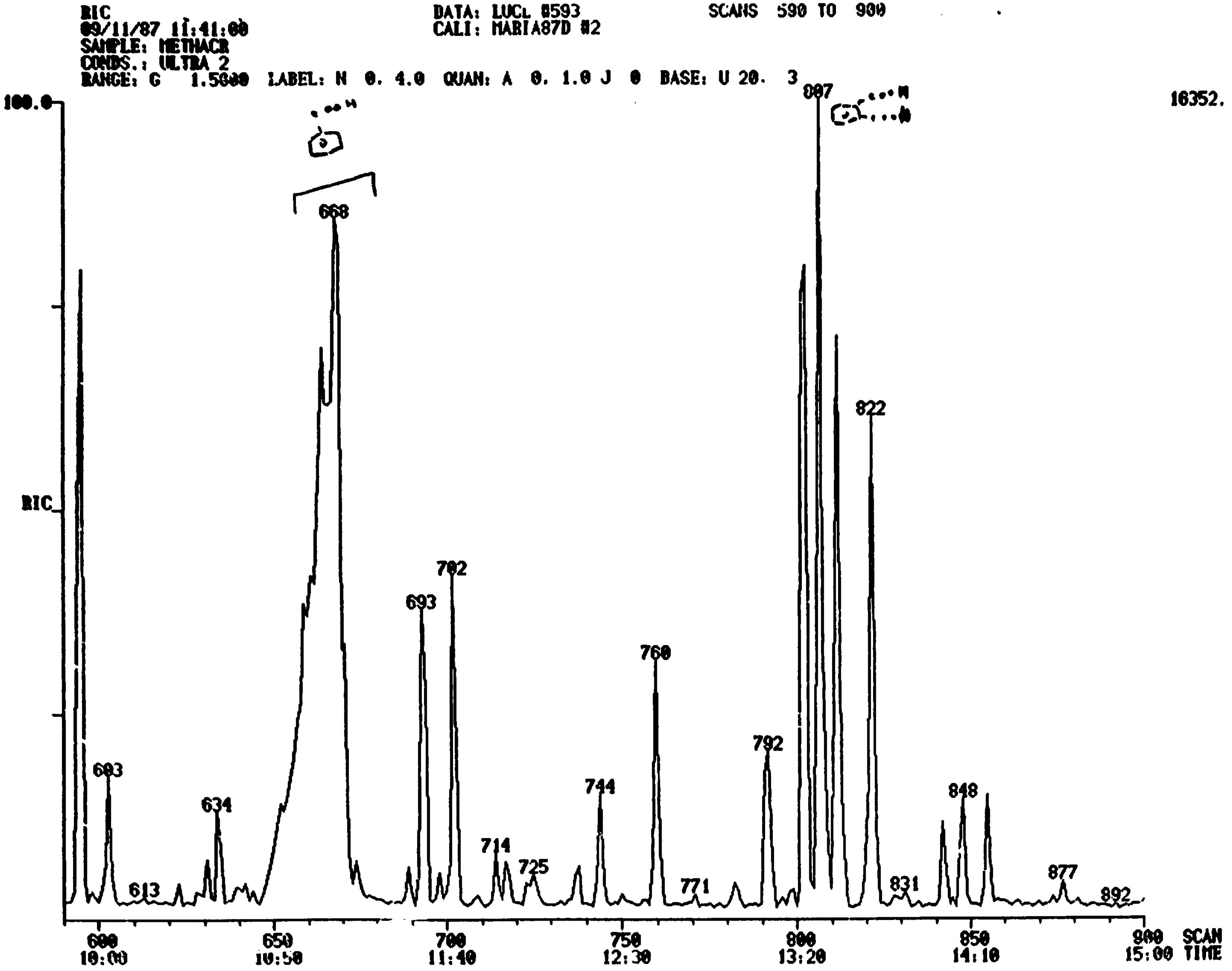
DATA: LL L #191
CALI: MARIA87D #2

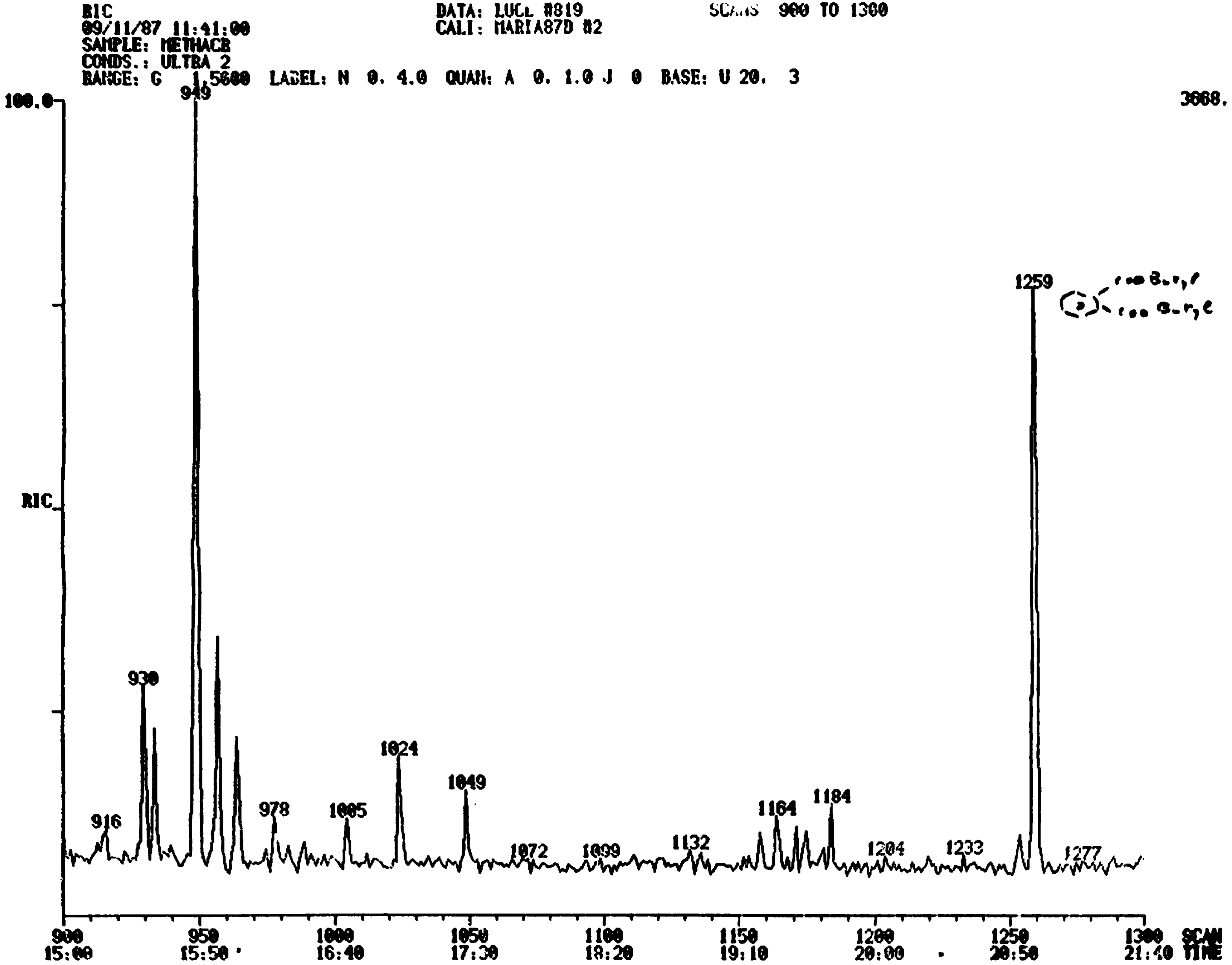
SCANS 180 TO 320



```
RIC                                 DATA: LUCL #288           SCANS  320 TO  626
09/11/87 11:41:00                   CALI: MARIA87D #2
SAMPLE: METHACR
CONDS.: ULTRA 2
RANGE: G   1.5300  LABEL: N  0. 4.0  QUAN: A  0. 1.0 J  0  BASE: U 20.  3
```







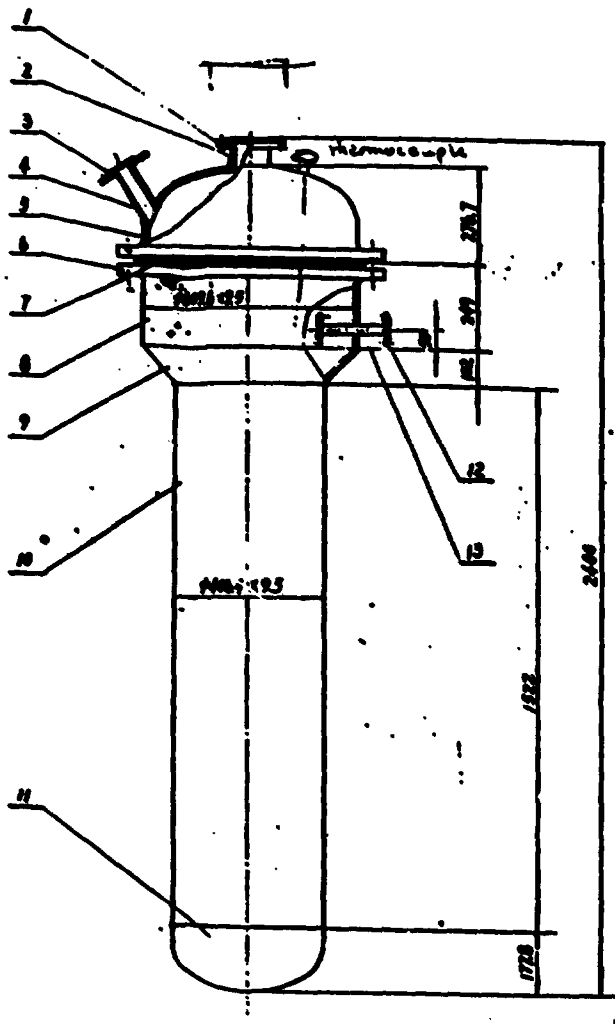
RIC
09/11/87 11:41:00
SAMPLE: METHACR
CONDS.: ULTRA 2
RANGE: G 1,5600 LABEL: N 0. 4.0 QUAN: A 0. 1.0 J 0 BASE: U 20. 3

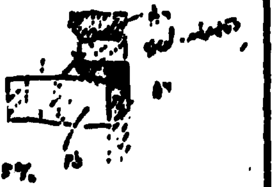
DATA: LUCL #819
CALI: MARIA87D #2

SCANS 900 TO 1300

ANNEXE F

FINAL DRAWINGS OF THE FLUIDIZED BED PYROLYSIS UNIT



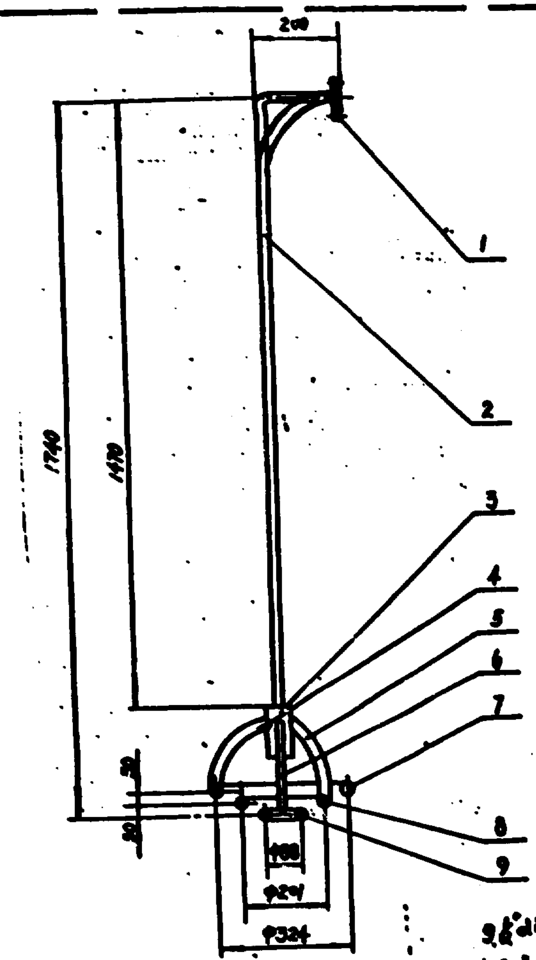


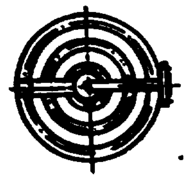
45"

	Name		Number	weight	material	specification	remarks
13. steam adapting pipe	13	蒸汽接管	1	[illegible]	1Cr18Ni9Ti	[illegible]	
12. steam adapting pipe flange	12	蒸汽接管法兰	1	0.748	45#	[illegible]	
11. under seal	11	底封头	1	[illegible]	1Cr18Ni9Ti	[illegible]	[illegible]
10. column	10	筒体	1	131	〃	[illegible]	[illegible]
9. conical plate	9	锥体平板	1	16.5	〃	[illegible]	[illegible]
8. straight body	8	直管	1	36	〃	[illegible]	
7. winding pad	7	缠绕式垫片	1		[illegible]	[illegible] (45)	
6. neck flange	6	颈法兰	1付	86.4	45#	[illegible]	[illegible]-59
5. top cap	5	顶封头	1	46	1Cr18Ni9Ti	[illegible]	[illegible]
4. MMA outlet adapting pipe	4	MMA出口接管	1	[illegible]	〃	[illegible]	
3. MMA outlet flange	3	MMA出口法兰	1	[illegible]	45#	[illegible]	[illegible]-59
2. PMMA inlet adapting pipe	2	PMMA浆料口接管	1	[illegible]	1Cr18Ni9Ti	[illegible]	
1. PMMA inlet flange	1	PMMA浆料口法兰	1	[illegible]	45#	[illegible]	[illegible]
	序号	名称	数量	重量	材料	规格	备注

[illegible] reactor

[illegible]



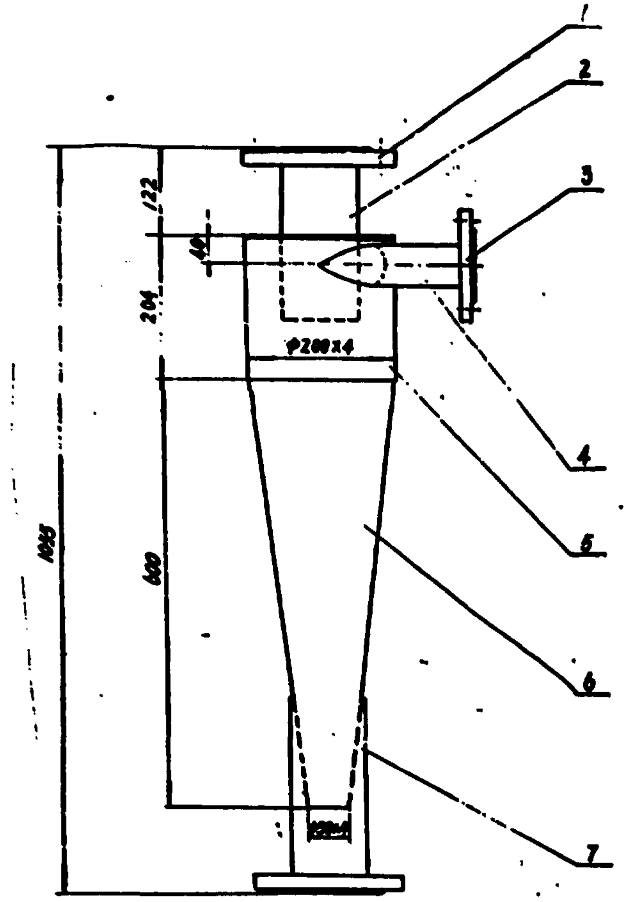


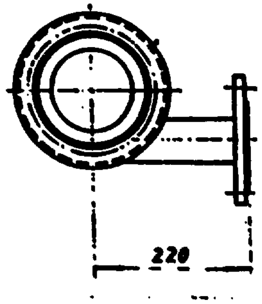
9. ½" distributing tore
8. ¾" distributing tore
7. 1" distributing tore
6. ½" radiation tube
5. ¾" radiation tube
4. 1" radiation tube
3. distributing box
2. gas inlet tube
1. flange

序号	Name 名称	Number 数量	Weight 重量	Material 材料	Specification 规格	[illegible] 备注
9	½"分布环	1	[illegible]	1Cr18Ni9Ti	[illegible]	[illegible]
8	¾"分布环	1	1.028	〃	〃 φ241	[illegible]
7	1"分布环	1	2.18	〃	〃 [illegible]	[illegible]
6	½"辐射管	1	0.278	〃	[illegible]	
5	¾"辐射管	1	0.448	〃	[illegible]	
4	1"辐射管	1	1.506	〃	[illegible]	two caps
3	分配盒	1	0.66	〃	[illegible]	[illegible]
2	进气管	1	2.73	〃	[illegible]	
1	法兰	1		[illegible]	[illegible] 20	[illegible]-59

Gas distributor

气体分布器





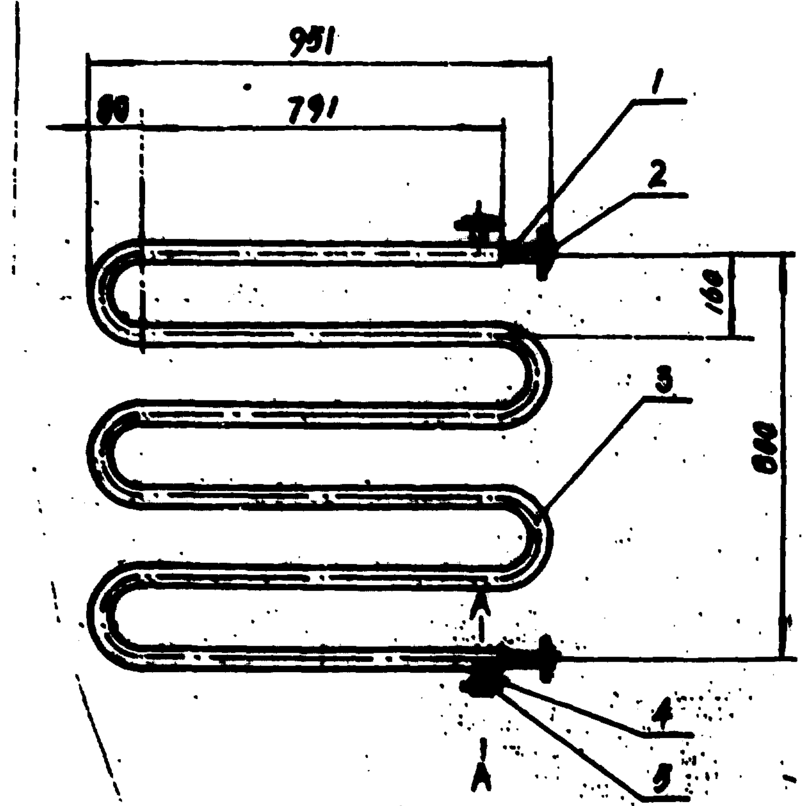
7. ash outlet adapting pipe
6. cone column
5. column
4. gas-inlet adapting pipe
3. flange
2. gas-outlet adapting pipe
1. flange

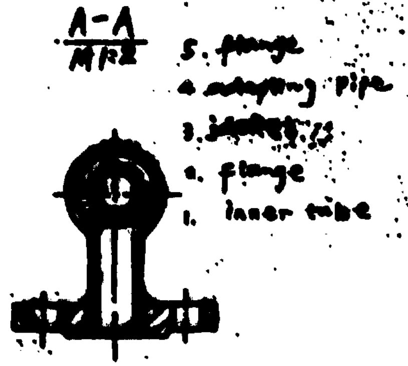
	Name	Number	weight	material	[illegible]	[illegible]
7	排灰口接管	1.	3.66	[illegible]	[illegible]	
6	锥形筒体	1	7.89	″	[illegible]	[illegible]
5	筒体	1	[illegible]	″	[illegible]	
4	进气口接管	1	[illegible]	″	[illegible]	
3	法兰	1	[illegible]	45#	[illegible]	JB81-59
2	出气口接管	1.	[illegible]	[illegible]	[illegible]	
1	法兰	2	[illegible]	45#	[illegible]	JB81-59
序号	名称	数量	重量	材料	规格	备注

cyclone

旋风分离器

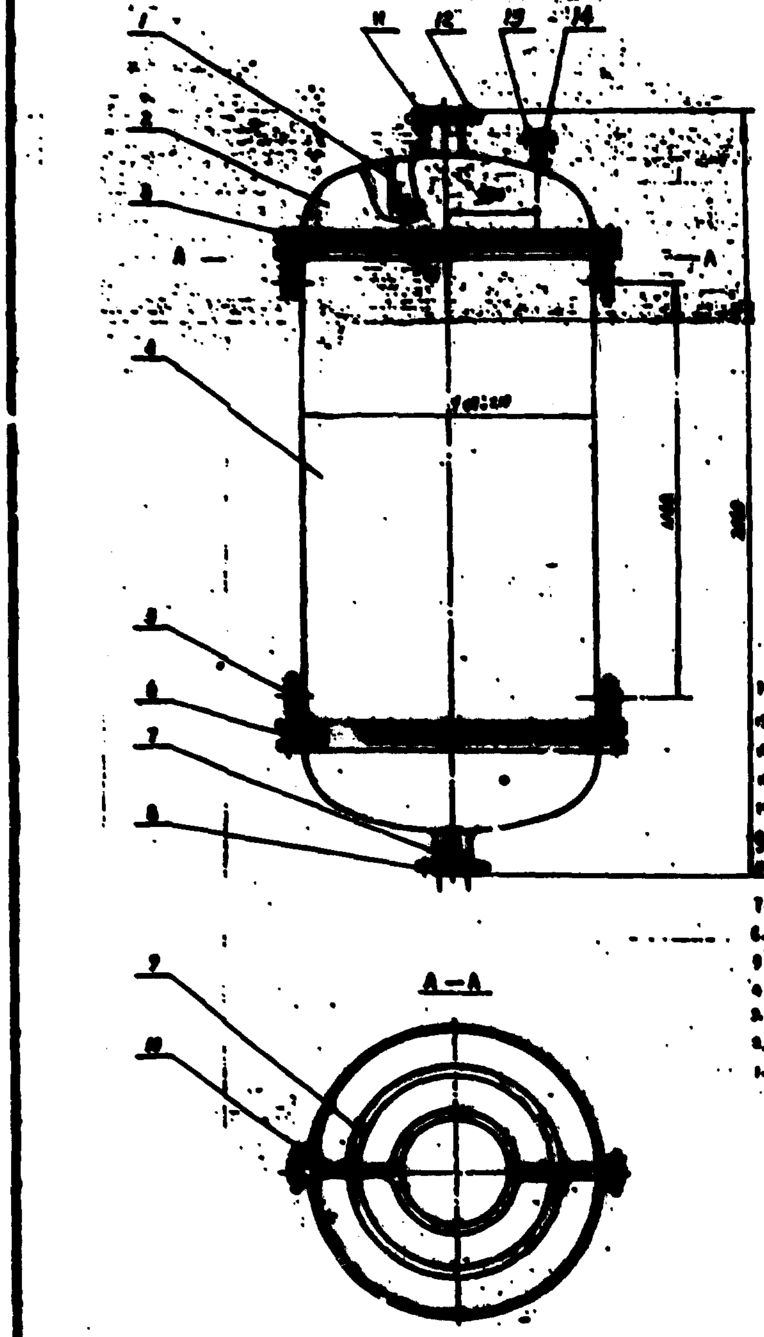
115





	Name	Number	Weight	Material	Specification	other
5	法兰	2	1.022	20#	Pg10 Dg15	JB81-59
4	接管	2	0.11	〃	Dg15×3 l=50	
3	套管	1	16.56	〃	Dg32×4 l=[illegible]	
2	法兰	2	1.022	45#	Pg10 Dg15	JB81-59
1	内管	1	6.84	1Cr18Ni9Ti	Dg15×3	l=6162
序号	名称	数量	重量	材料	规格	备注

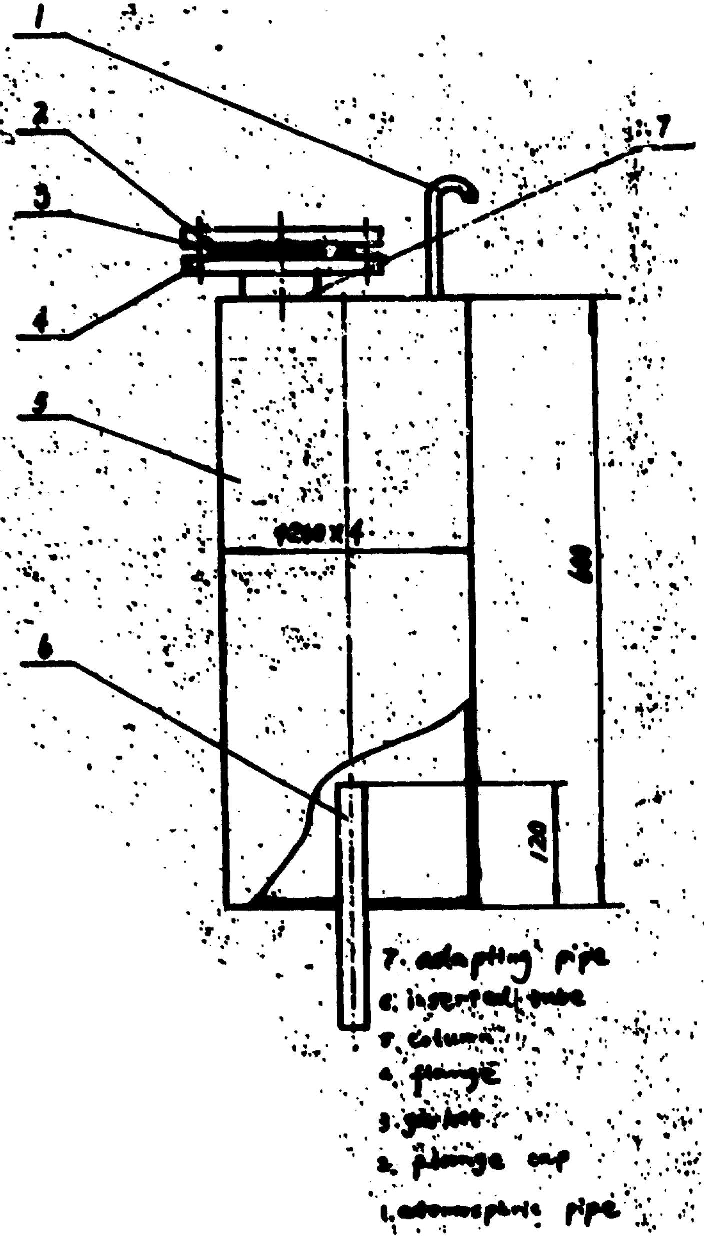
Cooler
冷却器



14. flange
13. [illegible] adapting pipe
12. flange
11. MMA inlet adapting pipe
10. inner oil tube
9. external oil tube
8. flange
7. MMA outlet adapting pipe
6. gasket
5. flange
4. column
3. flange
2. top cap
1. gas distributor

	Name	Number	Weight	Material	Specification	other
14	法 兰	1	0.511	45°	Pg10 Dg15	JB81-59.
13	[illegible]	1	0.111	1Cr18Ni9Ti	Dg [illegible] H=100	
12	法 兰	1	4.01	45°	Pg10 Dg100	JB81-59
11	MMA进口接管	1	[illegible]	1Cr18Ni9Ti	Dg100×4 H=100	
10	内盘管	1	[illegible]	1Cr18Ni9Ti	Dg32×3.5 H=1150	ℓ=19640
9	外盘管	1	[illegible]	〃	Dg32×3.5 H=1150	ℓ=35840
8	法 兰	1	[illegible]	45°	Pg10 Dg15	JB81-59
7.	MMA出口接管	1	[illegible]	1Cr18Ni9Ti	Dg15×3.5 H=100	
6	垫 片	2		[illegible]	[illegible]	
5	法 兰	4	[illegible]	45°	Pg10 Dg32	JB81-59
4	筒 体	1	[illegible]	1Cr18Ni9Ti	[illegible]	
3	法 兰	4	[illegible]	45°	Pg10 Dg600	JB81-59
2	椭封头	1		1Cr18Ni9Ti	[illegible]	[illegible]
1	气体分布器	1	[illegible]	〃	[illegible]	
序号	名 称	数量	重量	材料	规格	备注

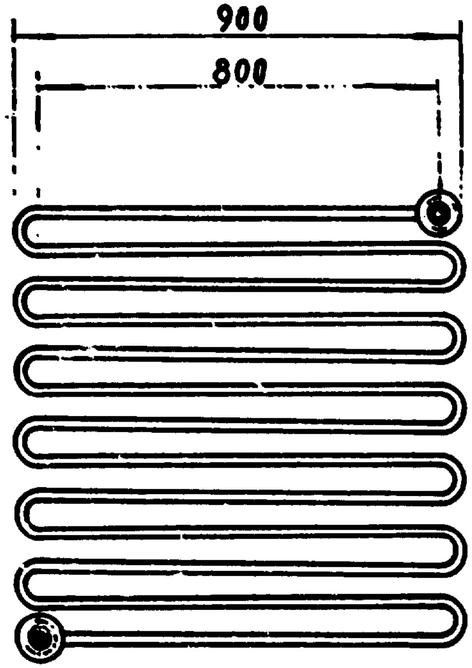
condenser
冷凝器

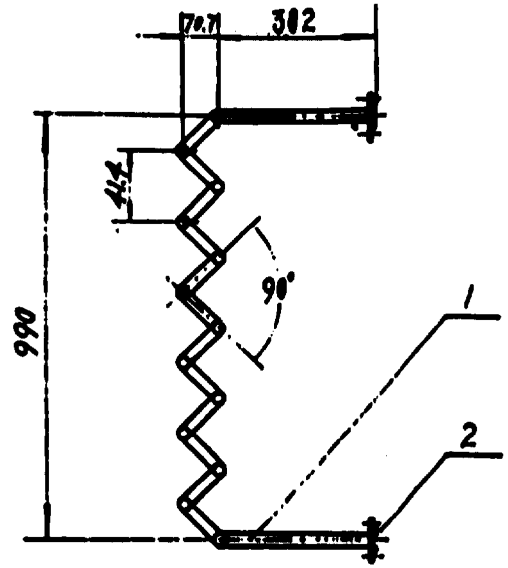


	Name	Number	Weight	Material	Specification	other item
7	接管	1	0.316	1Cr18Ni9Ti	Dg80×4	H=40
6	插管	1	0.59	1Cr18Ni9Ti	Dg25×3.5	H=240
5	筒体	1	11.68	〃	φ200×4 H=600	
4	法兰	1	3.24	45#	Pg10 Dg80	JB81-59
3	垫片	1		asbestos 石棉		
2	法兰盖	1	2.86	1Cr18Ni9Ti	Pg10 Dg80	HG5028-58
1	放气管	1	0.166	〃	Dg15×3	ℓ=150
序号	名称	数量	重量	材料	规格	备注

Ice-basket
冰篮

1:5



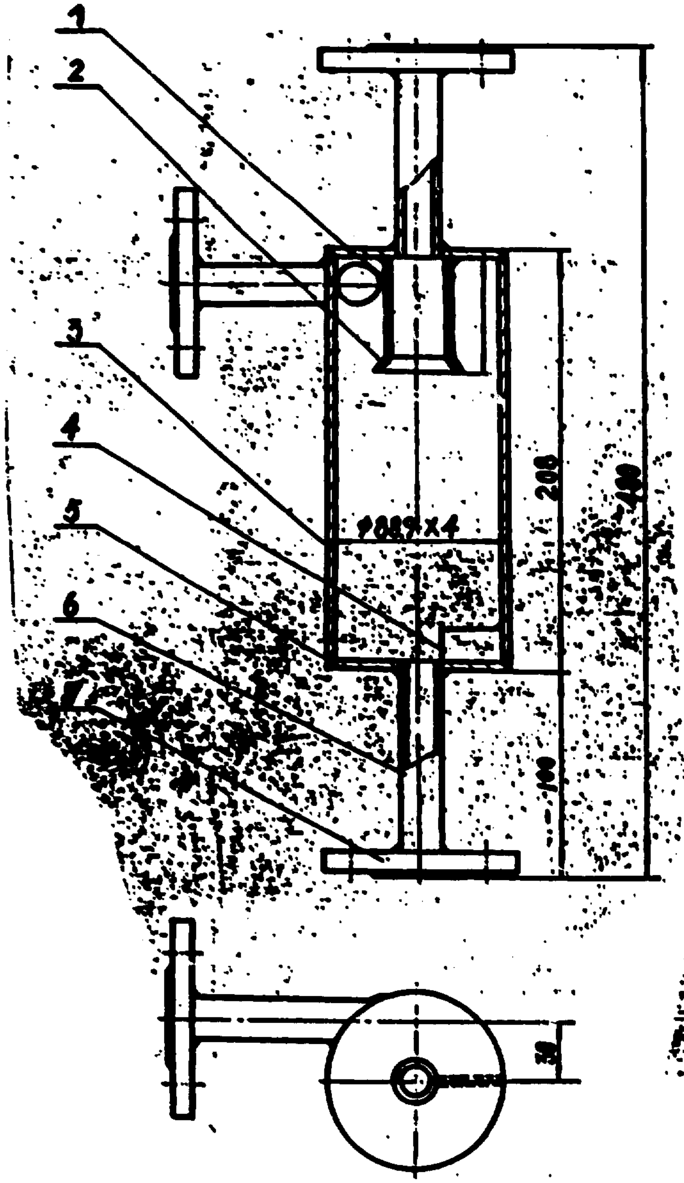


2. flange
1. coil tube

	Name	Number	Weight	Material	Specification	other item
2	法兰	2	1.022	45#	Pg10 Dg15	JB81-59
1	盘管	1	15.76	1Cr18Ni9Ti	Dj15×3 L=1490	α=90° H=990
序号	名称	數量	重量	材料	规格	备注

热交换器
Heat exchanger

1:10

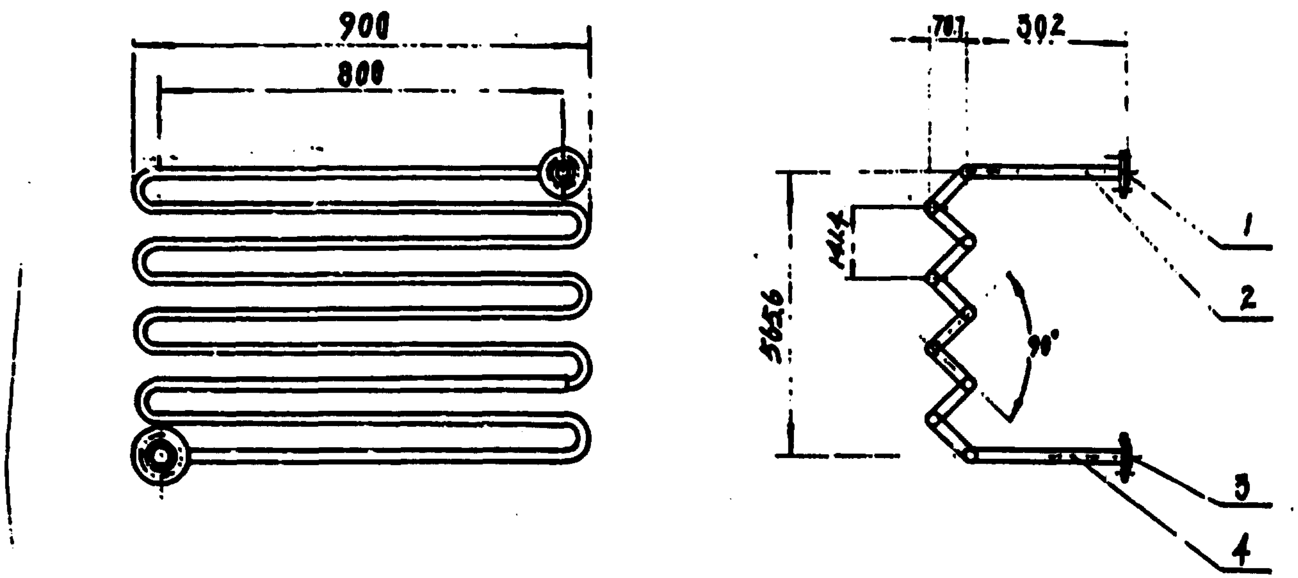


7. Flange
6. External adapting pipe
5. Top, bottom cap
4. Baffle-stopping block
3. Column
2. Cone pipe
1. Inner adapting pipe

	Name	Number	Weight	Material	Specification	remarks
7	法兰	3	1.850	45°	Pg10 Dg15	JB81-59
6	外接管	3	0.355	10[illegible]	[illegible]	
5	顶底盖	2	0.59	[illegible]	φ89X4	
4	[illegible]	[illegible]	0.065	[illegible]	80X10X3	
3	筒体	1	1.5[illegible]	[illegible]	φ89X4 [illegible]	
2	[illegible]	1	0.02	[illegible]	[illegible] H=8	[illegible]
1	内接管	1	0.128	[illegible]	[illegible]	
序号	名称	数量	重量	材料	规格	备注

疏水器
Steam trap

112



4. coil tube
3. flange
2. coil tube
1. flange

	Name	Number	weight	Material	specification	[illegible]
4	盘　管	1	4.278	1Cr18Ni9Ti	Dg20×3.5	l=2500
3	法　兰	1	0.748	45#	Pg10 Dg20	JB81-59
2	盘　管	1	6.458	1Cr18Ni9Ti	Dg15×3	l=5800
1	法　兰	1	0.511	45#	Pg10 Dg15	JB81-59
序号	名　称	数量	重量	材料	规格	备注

过热器
Superheater

NH.

1:10