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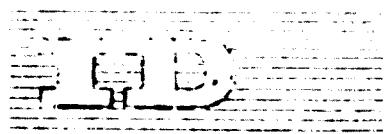
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The International Petrochemical Symposium on the
Development of the Petrochemical Industries in
Developing Countries

IET. SYMP. B/3

Vienna, USSR, 29 - 31 October 1969

D00347

THE SMALL-SCALE PRODUCTION OF ETHYLENE WITH SPECIAL
REFERENCE TO THE DISPOSAL OF CO-PRODUCTS^{1/}

by

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SUMMARY

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THE SMALL SCALE PRODUCTION OF ETHYLENE
WITH SPECIAL REFERENCE TO THE DISPOSAL OF CO-PRODUCTS 1/

by

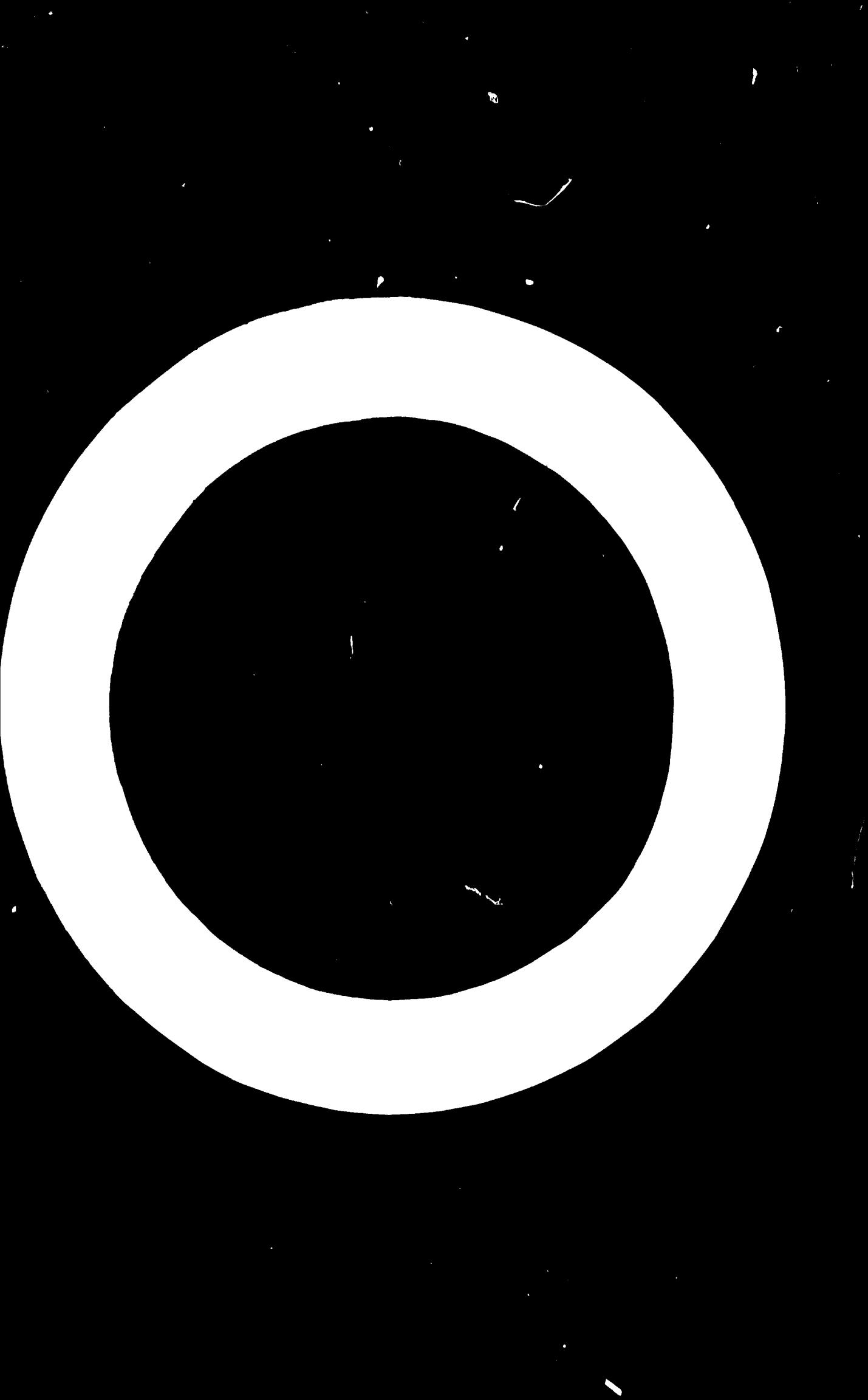
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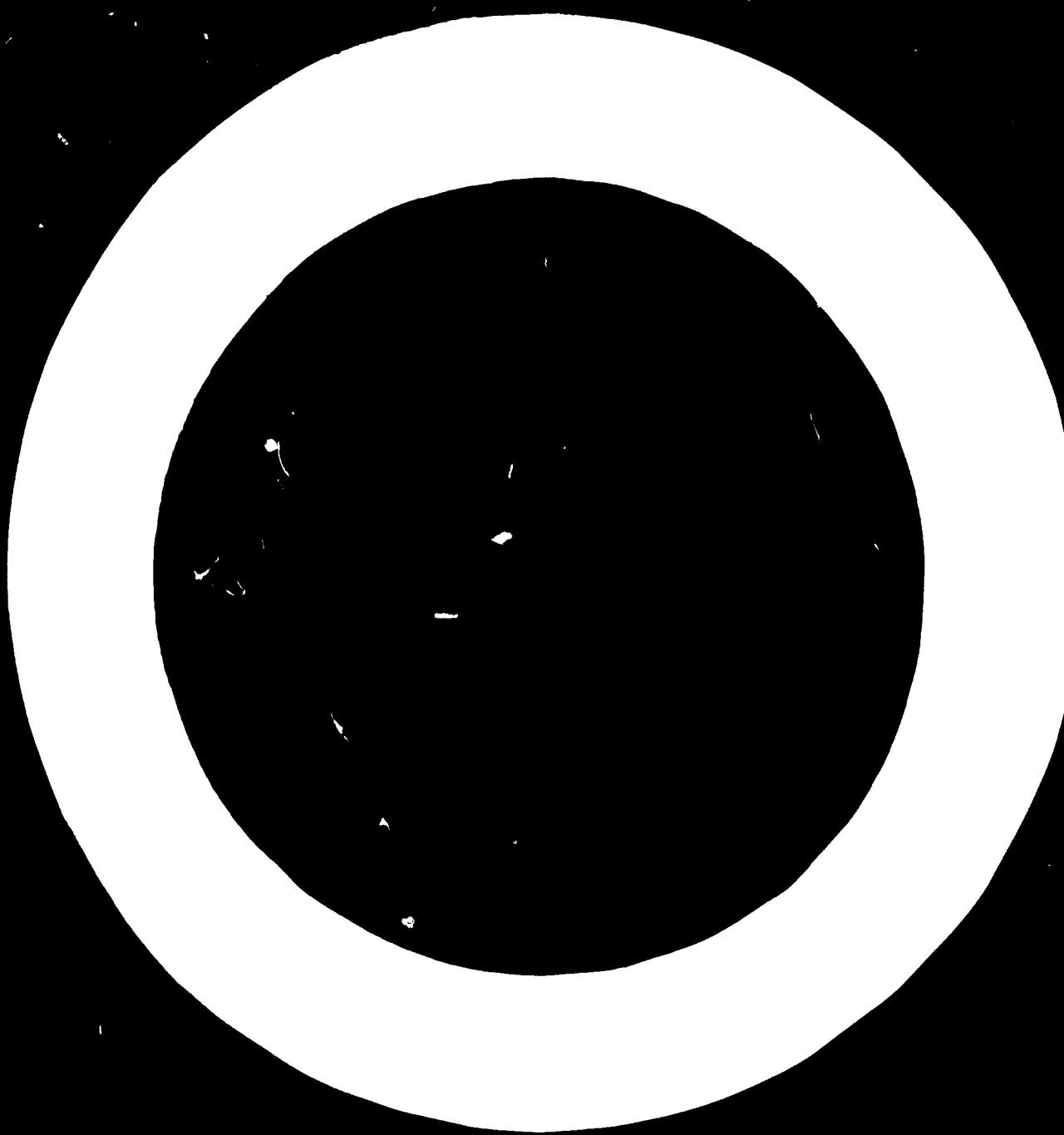
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The processing of liquid and gaseous hydrocarbons has not only developed very rapidly after the war from the technical point of view but the amount of processed materials has also increased very substantially. At present already the order of magnitude of hydrocarbons processing equals some million tons per year of base material for pyrolysis in the largest plants. This order of magnitude also determines the processing of the various products, since - because of the large quantities produced offer many more disposal possibilities than low-volume production. It should be remembered that even the largest plants cooperate with relation to some products. Evidently the level of technological development is very high in large plants.

However, in many places there is a demand for building pyrolysis

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plants of smaller size for various reasons, chiefly in small or in less developed countries. They wish to satisfy their national demands from their own raw materials sources and to raise their industrial level and in many cases these reasons are supported also by geographic conditions. However their economic resources do not permit them to build gigantic enterprises or plants. It would be hopeless for a small plant to compete with the large ones; not only because of the advantages inherent in the difference of size, but also because it does not possess a special process technology adapted to the processing of a small volume of materials. In possession of such a technology, on the other hand, the burden on a small company would be easier, even if it could not be competitive.

In low-volume pyrolysis plants the chief problem consists in the fact that beside ethylene and propylene - which are regarded as chief products - the rest of the products, amounting to 50 to 65 per cent in gasoline pyrolysis, can be sold only at very low prices, usually on fuel basis.

None of the components present in the C₄ fraction can be extracted economically in the pure state under current working conditions, if they are present only in amounts of a few thousand tons. Thus they cannot be regarded as base materials for rubber production, unless the geographic conditions permit their transport into large plants. The situation is different, however, if the components of the C₄ fraction can be copolymerized without any separation or special refining.

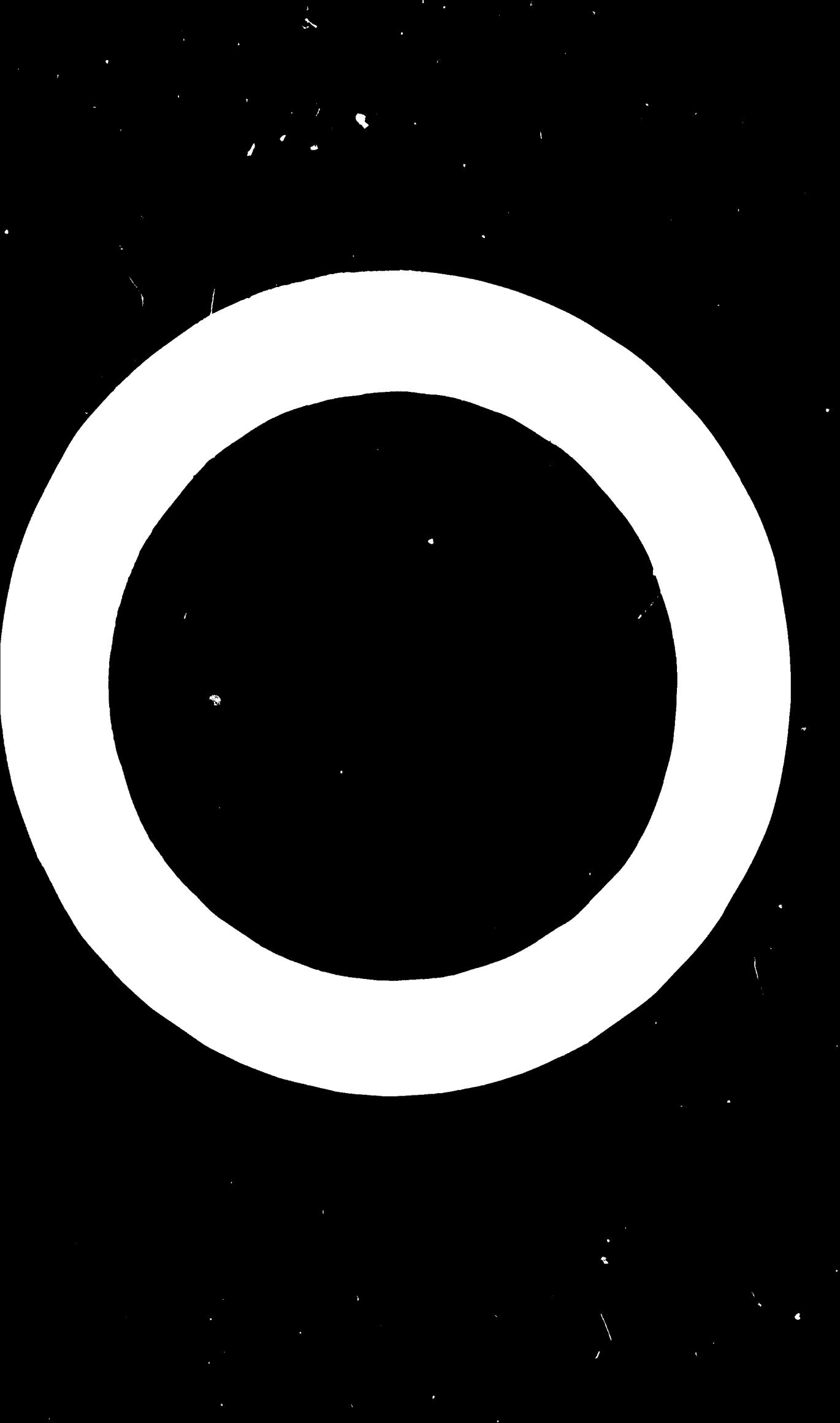
5000 - 10000 tons of special copolymer is a considerable quantity and one on which a production process may be based and if we succeed in sufficiently reducing the production costs this may have a significant influence on the economy of the whole pyrolysis process.

The value of such a copolymer depends naturally on its applicability. Since its composition is rather special, naturally its properties will also be rather special. Thus we have to find the field of application where the given special properties may be utilized with success.

A similar situation exists also with regard to the higher fractions. The fraction C₈-C₁₄, is a good example with its high content of aromatic

monomers. In the case of low quantities the isolation of these products is equally unreasonable. However, this does not necessarily mean that a less valuable plastic may be produced from this fraction than from the pure components.

The Institute which I am directing has been working on these problems for some time and has obtained results in connexion with the above-mentioned examples.



Competition in the production and consumption is forcing industry to set up larger and larger plants and at the same time to develop more and more advanced technologies (1-3). Even in 1953 plants with an annual output of 150,000 metric tons had been set up and at the present time even bigger ones may be designed. It has been estimated that the average capacity of an ethylene plant in 1970 will be 500,000 metric tons per annum (4-5). Using liquid feedstock, it involves the pyrolysis of some 2 million metric tons of naphtha per year in a single plant. Limitations of size only exist for short periods since developments in technology coupled with the need for more and more economical production always demand larger and larger plants. At the same time costs of investment are obviously increasing, so that only the most powerful nations or several smaller but economically well developed countries joining together are capable of setting up such large plants.

In fact this is very reasonable as it leads to the development of technology and to the low cost production of products. But in spite of this, many small or less developed countries endeavour to set up small-scale but individual polyolefin plants, the output of which corresponds to the requirements of the country. There may be various reasons for this; national consumption has to be provided from indigenous sources of basic materials, it is desired to raise the level of industrial production, political or geographical conditions may have an effect etc. All these reasons favour a trend in the setting up of such plants at a surprisingly rapid rate.

Such plants could not have entered into competition with the giant plants on the world market. Generally, they aim at more or less satisfying the national demand rather than supplying foreign markets. The term "more or less" refers to the fact that production is "temporarily" sufficient, in fact in the initial stages there is a danger of over production. These countries are however, at a disadvantage in that product exchange is not always practicable.

Advantages of bigger plants compared with the smaller units are generally shown in their profitability, the use of energy and labour is more efficient, the degree of automation is higher etc. On the other hand, there is a special point of view for polyolefin plants and that is the extent and possibility of utilization of the co-products. The amount of products from typical naphtha pyrolysis is shown in table 1.

Table 1.

The amounts of products from the biggest and the smallest
naphtha pyrolysis trains

	For cent W/W	Pyrolysis of C ₆ -naphtha tons	Pyrolysis of 100,000 tons of naphtha tons
H ₂ +CH ₄	14 - 18	200-360	14 - 18
C ₂ H ₄	22 - 29	440-560	22 - 29
C ₂ H ₆ +C ₂ H ₆	5 - 7	120-140	5 - 7
C ₃ H ₆	10 - 18	200-360	10 - 18
C ₃ H ₄ +C ₃ H ₆	1	20	1
C ₄ -fraction	9 - 12	180-240	9 - 12
gasoline	20 - 25	400-500	20 - 25
fuel oil	2 - 8	40-160	2 - 8

Let it be assumed that, besides ethylene, propylene is also to be considered as a principal product and utilized chemically in a plant of small capacity (which is often not practicable). In this case, between 20 - 25 and 10 - 18 % respectively of the products can be fully utilized. An additional 10 - 14 % (the C₄-fraction and the lower saturated hydrocarbons) is presumably used as fuel. Its value as such will be one third to one fifth its value as a chemical. The use as fuel of the residual quantity is even less favourable. Transporting these products to a larger plant is generally impossible because of the geographical situation or of the small quantity involved. The present technological knowledge does not permit more favourable utilization of these products even though they consist of very valuable components. Since their amounts are too small, the costs of isolation with the degree of purity necessary for chemical processing is far outside the limit of profitability. Isolation of 2000-3000 metric tons of butadiene, 4000-5000 metric tons of isobutane as well as 2000-3000 metric tons of styrene can not be viable.

On the other hand, in a plant consuming 2 million tons per annum of feedstock, 40 - 50,000 metric tons of butadiene, 20-140,000 metric tons of isobutene are formed annually, besides the large quantity of ethylene and propylene. These can be used as the raw material for a valuable polymerization unit since their extraction costs are reasonable that can be considered as main products. The difference between the largest and the smallest plant is further emphasized by the fact that the large production of saturated compounds can be recycled hence leading to a high yield of olefins on the feedstock. Thus a plant pyrolyzing 2 million metric tons of naphtha annually produces 90% of the feedstock as main products.

Small plants have also the disadvantage in that they have usually been designed to operate on a type of feedstock (the difference is about 40%). The proportion of co-products increases with the average number of carbon atoms in the feedstock, i.e. the production is shifted towards the more useless products.

In this connection, according to the literature, the total production cost of ethylene is two to three times higher when co-products are utilized only for their fuel value (5).

It is evident that the viability of a small plant is lower than that of a big unit but the difference can be minimized if chemical utilization of the co-products, or at least a part of them, were realized by using a special technology for processing small amounts of these products. In other words, a small unit can neither utilize its co-products in the same way as a big plant nor give them up completely. But solutions to this problem are not readily available.

In a specific problem, consider the C₄-fraction produced by a small plant. As mentioned, none of its components are present in sufficient quantity to be worthwhile separation in the past sense. However, they amount together to some 7-9000 metric tons, and what is more, in view of the known techniques of the separation of gases, their composition allows some kind of polymerization process to be used (they normally have to be freed from sulphur, water and possibly acetylenic compounds before polymerization). 60 - 80% of the fraction is theoretically polymerizable, i.e. contains an unsaturated bond.

Our attempts up till now to utilize this fraction were directed in two different ways:

- polymerization or copolymerization of all the unsaturated compounds to the greatest possible extent, and
- utilization of the individual components of this fraction without a previous preparation of them in a pure state by special or selective reactions.

As regards to the polymerization process, 85% of the olefin content of the C₄-fraction could be polymerized in one step without any pretreatment of the fraction. Obviously a co-polymer is formed, the composition of which depends on several variables. The amount of the C₄-fraction (4 - 10%) is influenced by the severity of cracking but its composition is almost unaffected by the temperature and the contact time of the pyrolysis in the range of 720 to 785° (6).

Table 2

Relation between the temperature of the cracking and the composition of the C₄-fraction

Temperature °C	Yield referring to the feedstock in %						Total %
	Butene-1	Isobutene	Butene-2	1,3-butadiene	Butane	Others	
690	3.0	2.6	0.7	1.0	0.35	8.55	
705	3.05	2.7	0.6	2.35	0.4	9.1	
720	3.1	2.75	0.6	2.75	0.4	9.6	
735	2.9	2.6	0.6	3.0	0.4	9.5	
750	2.75	2.55	0.5	3.2	0.4	9.4	
765	2.7	2.4	0.5	3.35	0.35	9.3	
785	2.6	2.35	0.45	3.4	0.3	9.1	

The consistency is more marked in view of these small-scale plants being usually operated at a higher severity or, in some cases, in such a way as to increase slightly the production of propylene. It is advantageous because, within the C_4 -fraction, the butadiene content is high while the cis and trans butene-2 content is low. It is desirable also since the molecular weight of the copolymer formed can be increased by decreasing the butene-2 content.

Several methods were tested for polymerization of this fraction. As it was expected, anionic co-ordination catalysts proved to be the most satisfactory. The individual olefinic components of the C_4 -fraction were incorporated into the polymer in the following proportion (based on the analysis of the residual gas).

Table 3

Incorporation of olefinic components of the C_4 -fraction

into the polymer

butadiene	65
cis-butene-2	31
trans-butene-2	36
isobutene	100
propylene	5

Since the C_4 -fraction contains only butadiene and isobutene in considerable amount, only the butadiene content of the polymerization residue is essential with respect to the yield of polymer. The structure of the product is, however, affected by the minor monomers too when they are incorporated.

The technique of polymerization is not very different from that of the low-pressure polymerization of olefins: the polymerization proceeds at 30 to 50° C for several hours. The pressure is about at 10 atmospheres.

It was mentioned before that the C_4 -fraction is capable of polymerization without any special pretreatment. It should be noted, however, that this is only a general statement, there are some exceptions to it. Since the pyrolytic

unit is now being built in my country, samples of the δ_1 -fraction from several neighbouring countries were analysed. Although compositions of the samples were roughly the same - approximately 80% ethene, 10% propene and small amounts of other alkenes - it will not be expected that it will even be possible to purify them completely. It would be necessary to use some kind of purification of the impurities would be needed depending on the individual samples. After all, the gases available at present are often capable of polymerization to give major technical difficulties. It was however, unnecessary to do this because we are convinced that special purification is avoided with a correct and careful operation in the separation of the fraction.

Various diethylaluminum salts like the diethylaluminim chloride + titanium tetrachloride system are suitable for the preparation of a copolymer with the composition described above. It is noteworthy, however, that by using several modified catalyst systems including the variations in the molar ratio of their components, the composition of the copolymer can be varied over a wide range. It is possible to produce liquid, solid or semisolid polymers without any isobutane content or pure polyisobutene from a fraction. These experiences may show the many possibilities of a potential successive polymerization. Experiments in this field are now in progress and I will come back briefly to this question later on.

The catalyst system containing acrylonitrile vanishes to remarkable degree because it results in utilization of olefins of a type (D). The incorporation of butene-1 and isobutene-2 into this polymer also takes place to a considerable extent.

Removal of the residual catalyst is an important part of the process know-how. This also leads to major technical difficulties in the low-pressure polymerization. According to experiments up till now the removal of catalyst is not more difficult with our copolymers than during the polymerization of the pure components. In fact, the processes may actually be simplified when dealing with the liquid product.

Profitability of the procedure is obviously determined by the applicability of the products. As it was mentioned, the composition as well as the molecular weight of the products can be varied over a wide range by means of the catalyst.

Referring to the above example where the highest possible portion of the olefin content is converted to polymer, the composition is shown in table 4.

Table 4
Composition of the polymer produced from the C₄-fraction

butadiene	25 - 27
cis-butene-2	1 - 4
trans-butene-2	4 - 7
isobutylene	53 - 64
propylene	1 - 4

Depending on the components of the catalyst and their concentration, both light liquids and viscous greasy products can be obtained at will with a molecular weight between 300 and 2400. On the other hand, a solid polymer could only be obtained with catalysts containing vanadium. The structure of these polymers is rather complicated since they consist of many kinds of monomers. Investigations indicated that predominantly copolymers were formed and not the mixtures of the individual homo-polymers. It is characteristic of the polymer that it contains considerable amounts of double bonds and the ratio of the incorporated butadiene to isobutylene is 1/2.

It was detected by infrared spectroscopy (Fig. 1) that principally geminal methyl groups (a doublet at 1375 and 1340 cm⁻¹), unsymmetrical methyl groups (1450 cm⁻¹) and double bonds in 1,4-trans positions (970 cm⁻¹) exist in the copolymer.

These facts alone can explain the instability of the polymer which was observed in practice when the snow-white product obtained after decomposition of the catalyst soon turned yellow in air. This resin is evidently not useful unless it can be stabilized. By adding in various conventional stabilizers, some improvement was attained but it was not sufficient even with extremely high amounts of stabilizer. Another possibility of stabilization was, therefore, tried out i.e. the double bonds of the polymer were used for chemical reactions. Moreover, favourable modifications of the resin can result in this

way.

The following reactions are considered:

- curing;
- grafting by styrene and acrylonitrile;
- emulsion;
- halogenation;
- sulphochlorination;
- hydrogenation;
- precipitation etc.

It means that the original copolymer is considered as a basic resin and its instability is exploited. In this manner U.S.-type resins, lubricants, plasticizers, hardeners, impregnants etc. may be obtained.

Some of these reactions such as chlorination of the polymer were studied in detail. The resin is chlorinated very easily up to the chlorine content near to that of PVC. A special interest of this procedure is the determination of the chlorination - hydrochlorination reactions but it can not be detailed now (1).

Chlorination is carried out in chlorinated hydrocarbon solution by a technology similar to the chlorination of PVC or polyethylene. Chlorine and hydrochloric acid are removed from the solution of the polymer, the solution is neutralized and the polymer is precipitated by means of a non-solvent. The viscous terephthalic (its molecular weight is 1200 to 1300) is converted into a fine, white, easily filterable powder.

Other preparation techniques used in polymer technology are also suitable such as spray-drying, precipitation or coagulation polymer etc.

The chlorinated polymer can be used for many purposes depending on its chlorine content. A product having low chlorine content improves markedly the impact strength of PVC when blended with it in proper amounts. The polymers of high chlorine content are very compatible with some kinds of polyester resins. They are applicable for manufacturing self-extinguishing polyester products.

Polyisobutylene modified with phosphorus and barium compounds or related materials is well known as an excellent addition for engine oil. The viscous resin from the C_4 -fraction can be used advantageously for this purpose.

According to our investigations, it is equivalent to additives from polyisobutene for this purpose.

By catalytic hydrogenation, unsaturation of the polymer disappears almost completely, thus the product can be regarded as a paraffin.

It is interesting that crosslinking of the polymer is rather difficult to carry out by curing in spite of its considerable number of double bonds and the product obtained in this way does not seem to be of any value. On the other hand, crosslinking may be brought about with tetrafunctional monomers. Such products are applicable to structural materials.

Many other examples could be mentioned in order to illustrate the possibilities of converting this basic material into products similar or equivalent to other known plastics, with apart from polymers regarded as new plastics.

I will also discuss in detail another coproduct of the pyrolysis of hydrocarbons, namely, the light liquid fraction which is collected in practice between 70 and 100°. Up till now, it has been utilized by the major concerns as a minor辛烷 component for gasoline after its partial or full hydrogenation.

Sometimes its aromatic compounds were separated which is, of course, a chemical application, but, in my opinion, not the best one. It is evident that the optimum is markedly influenced by the basic material situation e.g. the latter is reasonably solvable by all means when shortage of aromatic compounds exists. It should be noted that none of the methods for economical utilization of this fraction are really valid for the smallest ethylene crackers because of their high investment costs. As far as the composition of this fraction is concerned, it includes some very volatile components such as styrene, methyl styrene and benzene. The components of the light liquid fraction from the pyrolysis of Canadian heavy crudestock present in a concentration higher than 1 per cent are listed in Table 5.

Table 2Components of the light liquid fraction present in concentration higher than 1%

pentene	1.4
2-methyl-butadiene-1,3	2.7
cyclopentadiene-1,3	5.4
benzene	27.6
toluene	17.7
styrene	3.9
o,m,p-methyl styrene	1.5
indene	1.2
others	32.4
	100.0

The total amount of this fraction is approximately equal to the yield of ethylene, it is about 25 to 30% of the liquid feedstock. Considering again the smallest plants having an annual capacity of about 10,000 metric tons of feedstock, 25 to 27,000 metric tons per year are estimated to be produced. Some 20 to 30%, i.e. about 5000 metric tons are available as monomers.

Efforts have been made to use this fraction for considerable time (8-11) but as far as I know without much success. Investigations in this direction showed that, in spite of their relatively low concentrations, the polymerizable compounds of this liquid fraction can be concentrated properly (up to 45-50%) by not too complicated fractionation procedures. There are two ways for carrying out this procedure:

- all the polymerizable components are included in a single fraction (about 125 to 190°, cf. bl. 6), or
- two fractions are separated, namely, a styrene fraction from 125 to 150° (table 1) and an indene fraction in the range of 150 to 170° (table 2).

Table 6

Composition of the fraction collected from 125 to 190°

styrene	36.1 / w/v
methyl styrenes	2.4 / w/v
indene	0.9 / w/v
aromatics	54.2 / w/v
	100.0 /

Table I

Composition of the fraction collected from 125 to 150°:

	% w/w
ethyl benzene	5.7
m,p-xylene	23.1
o-xylene	6.4
styrene	21.3
a-propyl benzene	3.6
1-methyl-4-propyl benzene	1.2
1,3,5-trimethyl benzene	2.5
1-methyl-1-ethyl benzene	0.4
1,1-diphenyl ethylene	3.7
2,4,4,6-tetramethyl benzene	1.9
2,6-dimethyl benzene	1.7
indane	13.1
1-methyl-1,4-dimethyl benzene	1.6
2-ethyl benzene	0.5
1-methyl-1-tert-butyl benzene	1.1
1,2,4-trimethyl benzene	1.6
1,2,4-trimethyl-2-propyl benzene	0.2
	100.0 % w/w

Table 2
Composition of the fraction collected from 150 to 190°

	w/w
isopropyl benzene	1.6
1-methyl-4-ethyl benzene	5.4
1,3,5-trimethyl benzene	1.4
1-methyl-2-ethyl benzene	1.2
alpha-methyl styrene	2.3
o,p-dimethyl styrene	30.4
beta-methyl styrene	4.8
inden	36.4
1-methyl-3-isopropyl benzene	4.3
n-butyl benzene	1.4
1-methyl-4-isopropyl benzene	3.9
1,2-dimethyl benzene	4.4
1-methyl-1-isopropyl benzene	2.3
others	0.2
	100.0 w/w

Of course, this analysis is only an example of a particular case, the actual data may differ markedly depending on the feedstock and the method of separation. From these fractions, the monomers can be polymerized by three relatively simple methods:

- a) thermal polymerization,
- b) free radical polymerization, and
- c) cationic polymerization.

The technology of the thermal polymerization is simple and inexpensive. The molecular weight can be regulated quite well by the temperature. But products having molecular weights lower than 5000 can not be produced in this way since, at the higher temperatures required for a low molecular weight, the polymer decomposes. The highest molecular weight obtained was 5000. There are further drawbacks to this procedure compared with the other ones, namely it is

carried out at an elevated pressure, the rate of polymerization is relatively low and the yield from the monomers is only 60 - 70 %.

The product of the free radical polymerization is similar to that of the former procedure and the yield is scarcely higher (when the concentration of the peroxide initiator is maintained at a reasonable level). The temperature of polymerization is determined by the decomposition temperature of the peroxide used and it permits a control of the molecular weight. The upper limit of the molecular weight is 10,000. The method is advantages since it is carried out at atmospheric pressure but the expense of the initiator is a disadvantage.

The cationic polymerization is very rapid, its rate is limited only by the polymerization heat transfer. The polymerization rate is satisfactory at ambient temperature, the reaction takes place within one or two at atmospheric pressure. Only limited control of the molecular weight is possible in the range of 1500 to 2000. Advantages of this technique are the following:

high volumetric efficiency

relatively cheap catalyst, and

> 100 per cent yield based on monomer content.

The main disadvantage is the molecular weight is low and also that the removal of the catalyst is required in most cases.

In all three types of polymerization, the polymer is formed in solution so that it must be separated. It is economically solved but only the most suitable procedure should be selected.

It has been pointed out that the various methods lead to different products from the fraction between 125 and 150°, whether or not it has been split into two fractions, a resin containing mostly, paraffin is formed by thermal and/or radical initiation. By cationic polymerization, composition of the product from the side reaction is up to 1 to the monomer content of the reaction as a whole whereas a resin with high indene content is obtained from the middle fraction.

Keeping in mind that the resins formed are of different quality and different properties, a production pattern was developed including both of these main types. For example, the side reaction is subjected to thermal polymerization

In order to polymerize 60 - 70 % of the monomer content. The residual monomers along with the inert medium are separated by distillation then they are reacted by a secondary ionic polymerization. A schematic production pattern is shown in the next chart.

Finally, the value of the resin is determined by the use that can be found for it. Mechanical properties of a low molecular weight (up to 10,000), branched polymer are very poor thus it is of no value by itself as a structural material. However several combinations can be used to advantage. Thus resins of this type improve the physical properties of bitumen. Ductility of the bitumen can be doubled by mixing in a small quantity of the polymer.

The other interesting application is as a filler with epoxy resins. It is well known that the epoxy resin is one of the most expensive resins. It can be combined with 30-40 % of a type of these polymers. Mechanical properties of these combinations are equal to those of the pure epoxy resin, the electrical properties and the resistance to acids, bases and water are slightly improved though the translucence properties are not so good. The polymer can be coupled with low cold-cracked and heat-cracked types of epoxy resins, consequently, the resin produced from the liquid pyrolysis fraction can replace a portion of the epoxy resin at least in certain applications.

The special characteristics of these resins are derived from the fact that combinations of the pure polystyrene with the epoxy resin has not taken place.

The above instances served only as illustrations of the various fields where utilization of these resins is possible. Similar examples are their applications in form of emulsions and solutions. This are of particular interest because the relatively expensive separation of the resin has not to be carried out.

Applications of these resins are limited by their poor solubilities in aliphatic solvents. There is however, a possibility to copolymerize them with aliphatic compounds in order to alter their solubilities. A very useful resin is obtained by co-polymerization with the α -fraction which does not affect markedly the economy of the procedure.

Only about 6.0% of the fraction can be converted into resin. The utilization of the residue is obviously of crucial importance. This bulk is the fraction collected from 70° to 125° in the first stage and the aromatic and alkyl-aromatic solvent up to 100° remaining after the polymerization. A convenient use of these materials is not provided by the procedures mentioned above.

The principal problem is, therefore, whether the production of these resins compensates for the necessary additional expenses when the amount is only 1/12 to 1/14 part of the liquid liquid fraction. It does appear that, using the simple techniques outlined above and using the resins in a way that produces maximum return, viable process does exist. In small units where the liquid fraction can only be credited to fuel value, the economy of the whole production line may be influenced if the polymerization process is put in stand.

Converting to the general question of utilization of the co-products, there is another aspect of the problem outlined in this paper which may also be of importance sometimes in some of the largest ethylene crackers. All the present-day technologies are based on separation of the components in as pure as state as possible and then they are mostly intended in desirable proportions. The possibilities discussed demonstrate the existence of catalysts polarizing specifically one or more desired components from a given mixture. Such a development gives rise to countless possibilities even reforming the whole concept of olefin separation. At the moment the principle seems of limited application but if it develops it could yet see the disappearance of the characteristic olefin separation lines with resulting substantial reduction in investment.

Perhaps this is a long-drawn-out sounding conclusion, but believe that development and application of these technologies is useful and necessary for the rational operation of the small plants.

Another current problem should be touched on in this respect. According to well-founded estimates, the demand for ethylene in the next decade will exceed many times the requirements for its coproducts (based on the optimum applications known to-day) (2). Consequently, the new application possibilities of using the co-products may also affect the technologies of the largest plants.

Works referred to in the present paper were carried out in the Department for the Olefin Polymerization at the Research Institute for the Elastics Industry (Budapest). The head of the Department is Dr. J. Simai. The investigations were carried out by Dr. J. Jaradi and G. Grimes.

Literature cited

1. G. Grimes and J. Jaradi, "Elastics" 31/347-45. (1960).
2. Hungarian Chemical News ("Kémia") 1963. III. 1.3
3. Chemical Engg. 2585. (1960).
4. Hungarian Chemical News' 1963. 14. 34. (1963. Oct.).
5. Hungarian Chemical News ("Kémia") 1963. 4. (1963. Oct.).
6. K. Danekovici and C. Strameti, "Neftekhim." 5.6. (1955).
7. G. Polanyi, L. Jaradi, J. Kerec and J. Minor
paper presented in the International Symposium on Macromolecular
Chemistry, Budapest, 1960.
8. Chemical Engineering News 1963, 24 June, p. 34.
9. Biuletyn Polymerycielskiej Syntezy Organicznej 4/5.411. (1963).
10. Skifon-Olef-etyl-ol. 23/15.333. (1967).
11. Verteufelvormige Polyätherzusammensetzung bei $\text{C}_1/\text{C}_2 = 1/10$ -
- Leaflet.

34/18

Light tar separation

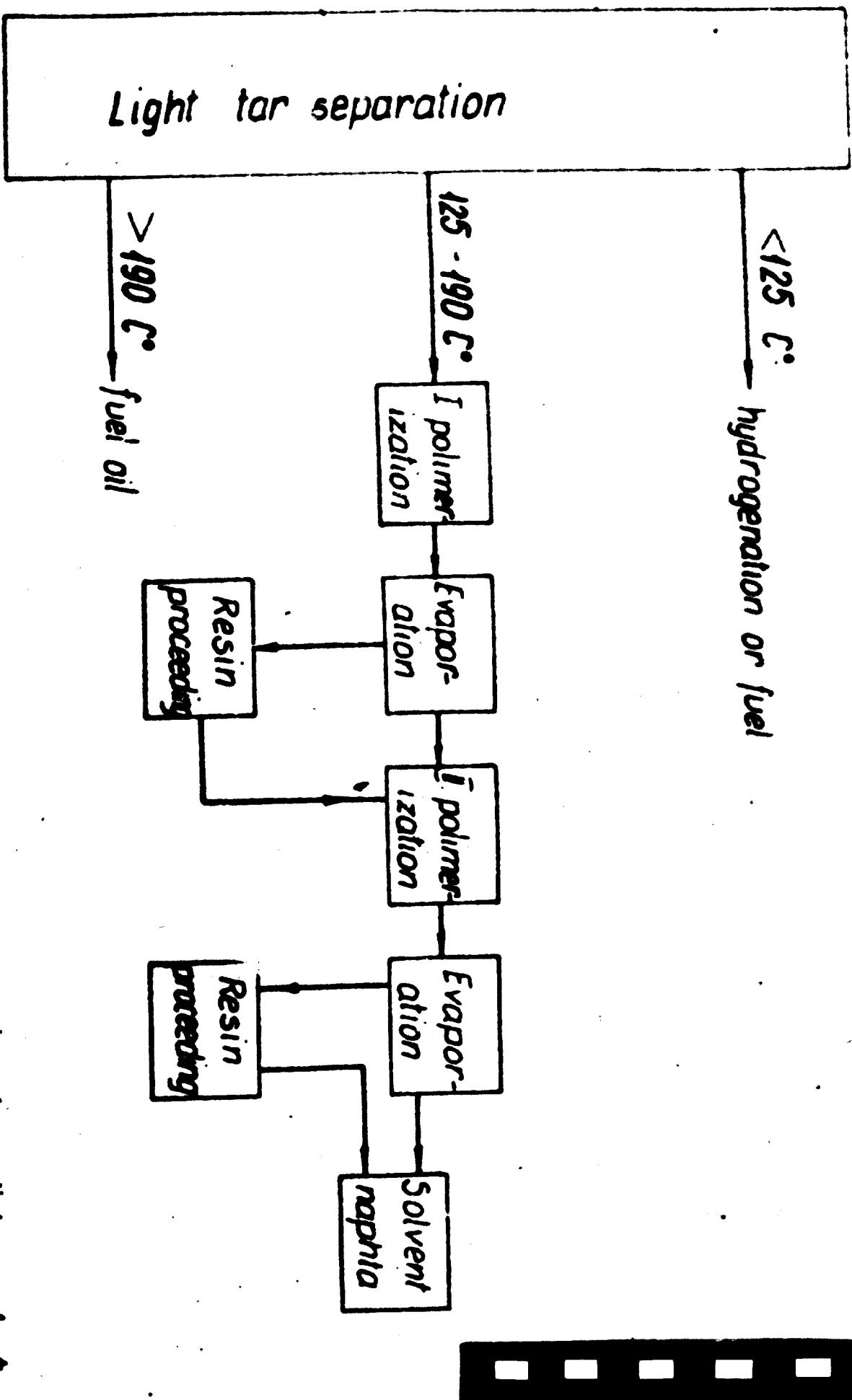


Fig. 1. A possible processing scheme of the liquid pyrolysis products.



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