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December 1988

ORGANIC TOXIC POLLUTANTS

DP/YUG/87/019

11-51

The Socialist Federal  
Republic of Yugoslavia

Expert Report\* (19 September - 5 October 1988)

Prepared for the Government of Yugoslavia  
by the United Nations Industrial Development Organization  
acting as executing agency for the United Nations Development Programme

Based on the work of Mr. S.C. WALLIN,  
Expert in the use of gas chromatography  
(19 September - 5 October 1988) to  
YUGOSLAVIA

Backstopping Officer: R.O. Williams, Chemical Industries Branch

United Nations Industrial Development Organization  
Vienna

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## CONTENTS

	<u>Page No.</u>
1. INTRODUCTION	3
2. DIARY OF VISITS AND MEETINGS	4
3. DISCUSSION	8
4. APPARATUS AND EQUIPMENT, FELLOWSHIPS, TRAINING, VISITS AND ACTIVITY	10
4.1 Apparatus and Equipment	10
4.1.1 Apparatus for the Determination of Volatile Organic Components	10
4.1.2 Apparatus for the Analysis of Polycyclic Aromatic Hydrocarbons (PAHs)	11
4.1.3 Particulate and Organic Vapour Sampler	11
4.2 Fellowships, Training and Activity	11
4.2.1 Key to Bar Chart Activity	12
4.2.2 Fellowships and Training	12
5. SAMPLING PROGRAMME	13
6. MONITORING DATA IN TERMS OF ENVIRONMENTAL IMPACT AND OCCUPATIONAL HYGIENE	14
6.1 Assessment of Risk from the Recurring Emissions	15
7. CONCLUSIONS AND RECOMMENDATIONS	15
8. REFERENCES	17
APPENDIX A. United Nations Industrial Development Organisation Job Description	A1
APPENDIX B. Lurgi-Based Coal Gasification Plant - Kosovo	B1

## 1. INTRODUCTION

In the autonomous province of Kosovo there is a large open cast lignite mining operation at Obilić near the capital city of Pristina. Associated with this source of fossil fuel are two electricity generating stations, a gasification plant and a fertilizer factory. To provide scientific and technical support for the Electric Power industry of Kosovo the Institute for Research and Development (INKOS), which is located adjacent to one of the power plants, has been functioning in its present form since 1979. INKOS is a small institute (about 100 total staff) and covers a wide range of disciplines including mining and mineral processing, chemical engineering, electric power generation and environmental science.

One of the two projects set up by UNIDO to strengthen the facilities and expertise of INKOS is described in Appendix A, and its objectives for the present mission given as follows:

The expert will execute the following tasks in co-operation with the Institute for Research and Development (INKOS), in the Socialist Autonomous Province of Kosovo:

1. Assist INKOS staff prepare neutral technical specifications for analytical instrumentation to be used in the detection and quantification of organic pollutants. This may include gas chromatograph ancillary detection and sampling equipment.
2. Suggest potential host institutions and content of training for the proposed fellowships and study tours concerning the use of gas chromatography in the detection and quantification of organic pollutants.
3. Advise on the sampling programme to be undertaken by INKOS to enable them monitor effectively the extent of pollution, by toxic organic compounds, of the immediate environment around the Kosovo gasifier plant.
4. Prepare a report in English for the concerned National Authorities, UNDP and UNIDO, setting out the mission findings and recommendations.

At this stage in the report it should be appreciated that although the present study and DP/YUG/87/020 have separate objectives in certain areas such as the environment, Figure 1, and also in the laboratory facilities, there is a commonality of interest. Furthermore, both missions were undertaken during the same time period and at some meetings the two projects were both under discussion. However, it is essential to report the two missions separately, but where appropriate cross references will be made to items relevant for both projects.

## 2. DIARY OF VISITS AND MEETINGS

As already pointed out there are some common features to the two projects therefore for the two reports paragraph 1 (except for the objectives) and paragraph 2 are identical. The subsequent paragraphs in the report will be specific to each project.

19.9.88

DAY 1 Briefing session at UNIDO Vienna. Owing to the postal strike in the UK it was necessary to visit Ms Ann Emery, Ms L Taylor and Ms Draxler to complete the administrative procedures. Full technical briefing was received from Mr R C Williams.

DAY 2 Flight to Belgrade

DAY 3 Briefing session at UNDP Belgrade. Background information to the work in Kosovo was given by the Programme Officer - Caroline Heider. Administrative requirements were also dealt with by Ms Heider.

I was given a copy of the general description of the gasification plant at Obilic, which I promised to return after completion of the mission. Ms Heider asked me to forward some general articles on important environmental issues which I agreed to do.

The flight from Belgrade to Pristina was delayed and being met at the airport by Mr B Jonuzi and Mr M G Jockie very much appreciated.

DAY 3 Visited INKOS. Meeting with Dr Slobodan Djekie (engineer business board), Dr Januz Zeqa (chief chemist?), Mr Basri Jonuzi (department of environmental protection), Mr Milan Jockie (Department of environmental protection) and Prof Alajdin Abazi (president of business board). Prof Abazi was introduced but owing to another concurrent meeting could not stay.

A general review of the Institute's activities was presented and I indicated areas of my own and other research and development work relevant to the situation at Obilic.

Following the meeting to prepare an itinerary of visits a short presentation on the significance of emissions and immissions (the concentrations at receptors in the ambient atmosphere) was made. Options were considered on the way to determine emissions from stationary sources.

DAY 4 Dialogue with Mr Januzi and Mr Jockie covered INKOS activities at the power stations, gasification and fertilizer plants. The facilities relevant to the projects were examined and included:

A mobile laboratory for the measurement of ambient concentrations of gases viz O<sub>3</sub> (Bendix 8002); SO<sub>2</sub> (Monitor Labs 8450) - 2 modules; NO<sub>x</sub> (Bendix 8440) - 2 modules; CO (Bendix 8501); Environmental Chromatograph (Bendix 8270); Dynamic Calibration System (Bendix 8852) and Air Purification System (Bendix 8833). The Laboratory was not in operational condition owing to no span gases being available (but are on order).

Equipment for measuring particulate emissions at source by an extractive method included a Ströhlein dust collection system and an 'in-stack' Andersen impactor.

The analytical facilities within INKOS are rather limited, but cover basic instruments and equipment such as atomic absorption, reflux and extraction units, calorimeters and spectrographs.

In addition one Andersen (General Metal Works Inc) Hi-Vol sampler for determining ambient particle concentrations is available.

26.10.88

DAY 5 Visits to Kosovo 'A' and Kosovo 'B' Power Plants.

Figure 2 indicates the location of the two power plants and Figure 3 the local topography and river Sitnica.

The director of 'A' station is Mr Janakovic and the total complement of his staff numbers about 1700. There are five steam boilers burning lignite as a fuel and generating the following nominal outputs:

A1	65 MW	Installed	1962
A2	125 MW	"	1965
A3	200 MW	"	1969
A4	200 MW	"	1971
A5	200 MW	"	1975

Each boiler has its own stack with discharge heights of A1-A5 of 90, 96, 106, 106 and 120 metres respectively. A general inspection of the plant covered the combustion systems, boilers, steam turbines, electrostatic precipitators and ash/clinker disposal. Facilities for sampling emissions and general instrumentation were also inspected.

The annual consumption of lignite is of the order of 3.8 Mte at the 'A' station.

The 'B' station employs a staff of about 1000 and the director is Mr F Nahi. There are two steam boilers, burning lignite as a fuel, each unit with a nominal output of 339 MW (boiler B1 installed in 1983 and B2 in 1984). The flue gas from the two boilers feeds into a common stack with a discharge height of 200 metres. Sampling positions were examined as well as the general instrumentation of the boiler plant.

DAY 6 Visit to Gasification and Fertilizer Plant

The first discussion was with the director of the fertilizer plant (Mr Mitat) and directors of the gasification plant (Mr Djerlek and Mr Restelica). Unfortunately the two plants were not working owing to problems

with the steam plant supplying process steam for the gasifier and other technical difficulties.

Production of gas has an installed capacity of  $400 \times 10^6 \text{ Nm}^3/\text{year}$  and present production is about  $120,000 \text{ Nm}^3/\text{year}$ . The targetted capacity of the fertilizer plant is 250,000 tonnes/year and 120,000 tonnes/year achieved. It is necessary to receive ammonia from another source to keep fertilizer production at its present level owing to difficulty with the  $\text{NH}_3$  synthesis plant.

Problem areas were identified as the gasification and fertilizer plants together with suitable sampling points for potential pollutants. Although the gasification plant was not operational, at certain locations on the site residual  $\text{H}_2\text{S}$  and mercaptans were evident. Methodologies for sampling at the sites were also considered.

DAY 7 Discussion with technical staff at INKOS on the plant visited and the questions posed in my mind. Reports of interest to the technology<sup>1-6</sup> were presented and those produced by INKOS<sup>7</sup> studied.

DAY 8 The requirements for equipment, fellowships and training were established and where possible specified. Work programmes were identified and a timetable for activity prepared.

DAY 9 A review of all the INKOS activities was held at the institute and I prepared network and activity charts. A visit was made to the Pristina University library to obtain information on local topography and sites of interest to the project.

DAY 10 Visited gasification plant because one gasifier unit was coming on stream.

Returned to INKOS and presented network and activity charts.

DAY 11 Obtained further combustion information from the chief engineer of Kosovo 'A' power station. Presented a verbal and outline written report to the Director and staff of the Institute.



DAY 12 Flight from Pristina to Belgrade and Belgrade to Vienna.

DAY 13 Debriefing session with Mr R O Williams.

DAY 14 Completed debriefing in the morning and returned to the UK in the afternoon.

### 3. DISCUSSION

In meeting the tasks of the present mission, reference has been made to the work previously carried out at the Gasification Plant by the United States Environmental Protection Agency (USEPA). The USEPA study involved three sampling campaigns in 1977, 1978 and 1979 to cover three different seasons in total. A description of the plant and the process flow diagrams are given in Appendix B. Data are also given on concentrations/emission rates for solid, liquid and gaseous pollutants. Application of these data provide a starting point and it is then possible to plan future campaigns using more up-to-date sampling and analytical equipment for monitoring and chemically characterising emissions. A knowledge of the locating rate and composition of the emissions can then be used with meteorological data for atmospheric dispersion estimates as well as validating a model using measured ambient concentrations. A range of tentative gaseous and particulate organic concentrations near the gasifier is given in Table 1, but other information is essential, i.e. averaging times and meteorological data, used for assessing their significance is not available. Nevertheless, the organic pollutants, some of which are included in the USEPA (Method 610) priority pollutants, can serve as indicators and will also provide an input for field studies where a 'fingerprinting' approach to modelling is used.

Bearing in mind the multiplicity of sources, pathways, physical and chemical composition the next chapter will deal with apparatus and equipment, fellowships, training and visits. During the mission relevant publications were given to INKCS staff in preparation for the proposed future activities.

**TABLE 1. - Tentative Identification and Range of Concentrations of  
Vapour and Particulate Phase Constituents in Samples Collected  
Near Yugoslavian Gasifier**

Vapour Phase		Particulate Phase	
Tentative Identification	Range of Concentrations, $\mu\text{g}/\text{m}^3$	Tentative Identification	Range of Concentrations, $\mu\text{g}/\text{m}^3$
Benzene	0.33-1.8	Biphenyl	0.29-4.2
n-C <sub>9</sub> H <sub>20</sub>	0.16-1.0	n-C <sub>19</sub> H <sub>40</sub>	1.8-11
Toluene	0.74-9.0	Phenanthrene	-b
n-C <sub>10</sub> H <sub>22</sub>	0.16-0.60	n-C <sub>20</sub> H <sub>42</sub>	0.44-2.0
Ethyl Benzene	0.46-1.3	C <sub>14</sub> -Benzene	-c
m-Xylene	0.20-1.3	n-C <sub>21</sub> H <sub>44</sub>	1.0-1.7
p-Xylene	0.38-3.2	C <sub>14</sub> -Benzene	-c
o-Xylene	0.24-1.6	n-C <sub>22</sub> H <sub>46</sub>	8.5-28
Cumene	0.02-0.38	Floranthene (+ Hydrocarbon)	0.93-1.1
C <sub>3</sub> -Benzene	0.11-0.52	n-C <sub>23</sub> H <sub>48</sub>	5.4-13
C <sub>3</sub> -Benzene	0.25-2.0	n-C <sub>24</sub> H <sub>50</sub>	1.6-3.8
Mesitylene	0.06-0.58	MW 256 + 274	-
C <sub>3</sub> -Benzene	ND-0.51	n-C <sub>25</sub> H <sub>52</sub>	6.2-18
C <sub>3</sub> -Benzene	0.21-2.2	n-C <sub>26</sub> H <sub>54</sub>	3.9-16
C <sub>3</sub> -Benzene	0.10-0.81	Bis(2 Ethyl Hexyl) Phthalate	43-120
o-Methyl Styrene	ND-0.11	MW 226 <sup>d</sup>	-
Benzaldehyde	1.1-2.8	n-C <sub>27</sub> H <sub>56</sub>	19-10
Acetophenone	1.3-3.0	n-C <sub>28</sub> H <sub>58</sub>	13-12
Naphthalene	0.02-1.5	C <sub>4</sub> -Guinoline	-d
2-Methyl Naphthalene	0.03-0.25	n-C <sub>29</sub> H <sub>60</sub>	11-21
1-Methyl Naphthalene	0.01-0.15	n-C <sub>30</sub> H <sub>62</sub>	2.2-7.9
Phenol	0.16-2.3	Benzo(bj or k)Fluoranthene	2.3-6.2
o-Cresol	ND-1.0	n-C <sub>31</sub> H <sub>64</sub>	7.1-13
Biphenyl	0.04-0.09	n-C <sub>32</sub> H <sub>66</sub>	1.4-7.2
Indole	0.02-0.13	n-C <sub>33</sub> H <sub>68</sub>	2.2-6.5
p-Cresol	ND-0.24	n-C <sub>34</sub> H <sub>70</sub>	1.1-3.6
m-Cresol	ND-0.36	n-C <sub>35</sub> H <sub>72</sub>	0.8-2.9
p-Ethyl Phenol	ND-0.16		

a ND = Not Detected

b Incomplete resolution prevents quantitation

c Standard not available for quantitation

d Not Benzo

#### 4. APPARATUS AND EQUIPMENT\*, FELLOWSHIPS, TRAINING, VISITS AND ACTIVITY

##### 4.1 Apparatus and Equipment

The major items of apparatus and equipment are specified below. Smaller items such as chromatographic columns and general laboratory equipment will follow when the major equipment suppliers are identified. It should be noted that INKOS already has a General Metal Works' Hi Volume particulate Sampler and therefore I have specified and identified a sampler for particulate and vapour phase organics manufactured by the same company.

##### 4.1.1 Apparatus for the Determination of Volatile Organic Components

- One multi-shot thermal desorption apparatus suitable for stainless steel tubes containing Tenax or similar absorbents. The dimensions of the tubes to be specified by the supplier.
- One gas chromatograph integrated with the thermal desorption apparatus (as specified) and with oven dimensions and programming suited to determination of trace levels of volatile organics.
- The GC (as specified) should be fitted as standard with a FID and the necessary gas controls
- The specified thermal desorption apparatus and gas chromatograph should be controlled from a micro-computer keyboard, and the micro-computer should have installed as standard:
  - A. A comprehensive chromatography data analysis facility
  - B. Floppy disk drives
  - C. Winchester disk drive

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\* A flame Photometric Detector (FPD) will be purchased if allocated funds permit. If not INKOS should consider purchasing one from its own budget.

- Separate to the items already specified, but with demonstrated compatibility, a detector capable of discriminating between analyte molecules by mass fragmentation is required.

#### 4.1.2 Apparatus for the Analysis of Polyaromatic Hydrocarbons (PAHs)

- One high performance liquid chromatograph (HPLC) providing rheodyne or similar injection port, isocratic and gradient solvent programming, thermo-controlled column enclosure and UV detector.
- Variable wavelength fluorescence detector with a flow cell suitable for HPLC effluent measurements.
- Two chromatographic columns suitable for the determination of the 16 priority pollutants for PAHs specified by the United States EPA (Method 610).

#### 4.1.3 Particulate and Organic Vapour Sampler

- One Andersen (manufactured by General Metal Works) Model PS-1 PUF (Polyurethane Foam) sampler.
- One GMW Calibration Kit with NBS curve.
- One additional glass cartridge.

The sampler to operate from a 115V 50 cycle electrical supply.  
Estimated cost \$4200.

#### 4.2 Fellowships, Training and Activity

Figure 4 is a 'Bar Chart' indicating the proposed activity plan. The plan has taken into account the requirements given by INKOS and seeks to present activity in a logical way leading to an adequately equipped and trained staff. Clearly there will be variations from the plan caused by problems such as INKOS staff availability and the organisation of host institutions but in my view the overall timescale is realistic.

#### 4.2.1 Key to Bar Chart Activity

- (1) Circulation of tenders for instruments and equipment.
- (2) Assessment of tenders and placing orders for instruments and equipment. At this stage additional items, depending on major items of equipment selected can be ordered. Also a check will be made of conformity to the budget ceiling of \$128K.
- (3) Receive, check and bench test where appropriate. In the case of the gas chromatograph and high performance chromatograph a visual check only.
- (4) Set up laboratory at INKOS to accommodate GC, HPLC, FPD, Extraction, Desorption and laboratory support facilities.
- (5) Evaluate analytical procedures for samples of known composition.
- (6) Check sampling procedures and analytical methods for source emissions, workplace and/or ambient atmospheres.
- (7) Carry out 'pilot' sampling and measurement campaign for emissions, workplace and ambient atmospheres.
- (8) Assess the environmental significance of the pilot study.
- (9) Plan 'full-scale' sampling campaign.
- (10) Commence sampling and measurement campaign.

#### 4.2.2 Fellowships and Training

- (11) Methods of desorption/extraction of organics from substrates and/or tenax or similar absorbents.

Identification and quantification of the desorbed/extracted organics.

Although not essential it is preferable for the fellowship candidate to cover the two areas of specialisation at an institute with similar

instruments/equipment to those specified under 4.1.1.

A period of 4 months is proposed by INKOS and in my view is the minimum required. The following candidate host institutions are suggested:

- (i) Warren Spring Laboratory (WSL), Stevenage, Herts
- (ii) Health and Safety Executive (HSE) Laboratory, Cricklewood
- (iii) M-T-TNO, Apeldoorn, Netherlands
- (iv) Argonne National Laboratory, Argonne, Illinois 60439, USA

If institutions (i) and (ii) are used they are within 30 km of each other, HSE specialising in occupational hygiene and WSL in source emissions and the ambient atmosphere.

- (12) Methods for sampling organics. The proposed host organisations for item (11) are suitable candidates. If a fellowship is arranged in the UK I suggest British Gas, Westfield Development Centre in addition to HSE and WSL. For the period of 2 months proposed by INKOS approximately 3 weeks at each location should provide a full insight into organic sampling.
- (13) The Lurgi Process for the Conversion of Coal into Gas. This area of specialisation is outside my terms of reference but INKOS state that a fellowship of one month is required.
- (14) Methods for Qualitative and Quantitative Analysis of PAHs. The proposed host organisations for item (11) are suitable. A one month fellowship is required.

## 5. SAMPLING PROGRAMME

The sampling positions on the gasification plant are shown in Figs A1-A7 of Appendix A. In addition Fig. 5 shows the proposed location of three ambient sampling sites for the determination of organics in the particulate and vapour phase.

The sections of the gasification plant to be studied include: generators, phenosolvan, tar separation and storage, CO<sub>2</sub> vent, rectisol section, waste gas flare, slag and waste water emissions.

Organic compounds in the following groups after capture will be measured by:

GC - Aliphatic HC	
GC/FID Aromatic HC	
GC with Nitrogen Detector	- N Aromatic Compounds
GC/FPD	- S Aromatic Compounds
HPLC/GC	- PAHs
HPLC/GC	- N Heterocyclic HC
GC	- Phenols
GC	- Mercaptan

Organic compounds in the liquid phase will measure 'head space' analysis where applicable. In all cases of sampling, work-up, fractionation, final analysis and data reduction validation methods will be used. The validated methods include US NIOSH/UK HSE/US EPA/other appropriate National standards.

The emission of  $\text{NO}_2$  from the gasification and fertilizer plant together with the  $\text{NO}_x$  emissions from the power plants indicate that ambient monitoring for  $\text{NO}_2$  should be considered within a radius of about 5 km. A useful low-cost method<sup>8</sup> is to use passive diffusion tube samplers for monitoring  $\text{NO}_2$  concentrations in the ambient atmosphere.

#### 6. MONITORING DATA IN TERMS OF ENVIRONMENTAL IMPACT AND OCCUPATIONAL HYGIENE

The monitoring and measurement of pollutants at the gasification plant will have three main outputs:

- (i) to provide information on features of the plant operation;
- (ii) to enable a pollutant emission inventory to be produced in terms of concentration/mass/physical and chemical composition/rate;
- (iii) to determine 'worker' exposure to pollutants in the working environment and provide data on fugitive (adventitious) emissions from the plant.

## 6.1 Assessment of Risk from the Recurring Emissions

There are two principal areas of risk from the emissions, the first being to human health and the second of environmental damage. The second risk will not be considered.

The risk assessment from the study should include the following steps:

- (i) Identify the health effects of the constituents of concern as a function of concentration level.
- (ii) Predict and/or measure the concentrations to which the general public may be exposed and determine 'worker' exposure by measurement (personal sampling or fixed point sampling).
- (iii) Estimate the health impact of such concentration exposures.

A comprehensive publication<sup>9</sup> on exposure methodologies has been prepared for the United States Federal Register and covers the requirements of the present study. Using these methodologies it is possible to apply published models in conjunction with meteorological and topographical conditions. Figure 3 indicates the local topography and Figure 6 a wind rose.

## 7. CONCLUSIONS AND RECOMMENDATIONS

- Within the financial constraints of the programme technical specifications have been prepared for sampling and analytical equipment. Further supportive laboratory/analytical apparatus of second order cost will be specified following selection of the main equipment.
- The expertise required for the characterisation and quantification of toxic and/or carcinogenic compounds is demanding and the proposed training periods should be regarded as a minimum. It is recommended that an expert from the host organisation visit INKOS for a short period (2 weeks) following the completion of the analytical laboratory and installation of the equipment. Preferably the visit should be after a 'pilot scale' monitoring exercise so that selected samples of organic



particles and vapours can be analysed both at INKOS and subsequently at the host institution for checking.

- Sampling locations at the gasification plant follow those previously selected (Appendix A) by a USEPA study, but will include additional areas of potentially high risk e.g. PAH concentrations at the tar pumping station.
- In the ambient atmosphere sampling positions have been selected at three locations. It is strongly recommended that these locations are at least 75 metres from external sources that could vitiate the results. These sources include road traffic (particularly diesel engines), houses where fossil fuel is used and small commercial activities all of which can emit organic compounds in particulate and/or gaseous form.
- It is recommended that in addition to measuring the emissions in the slag and wastewater, bench-scale leachability tests are carried out on the slag.
- As a follow-up to the gasification plant monitoring campaign a feasibility study should be undertaken on remedial abatement measures with reference to the cost effectiveness of achieving pollutant reduction viz cost per unit of pollutant abated.
- Consideration should be given to using a percentage of the gas produced to improve combustion at Power Plant A. It is possible that a gas-line already installed could be utilised. If this is practicable and economically viable the possibility of directing some of the vent gases should also be explored.
- Improvement in the Lurgi Generator operating conditions could result in lower pollutant emissions as well as a higher conversion efficiency. Such a programme of test work could be incorporated in a sampling campaign.
- A reiterated complaint for this mission is the highly variable quality of the lignite. Rapid and simplified analytical procedures should be considered so that sudden variations in lignite quality can be avoided

and the operating conditions for gasification optimised to suit the fuel composition.

- It is recommended that where possible simplified sampling and analytical procedures should be employed as developed. In particular the analysis of organics can be extremely time consuming and expensive and such techniques as 'fingerprinting' can be helpful in providing useful information at lower costs. The use of passive sampling for NO<sub>2</sub> is another technique which can provide data in the ambient atmosphere at relatively low cost and staff involvement.

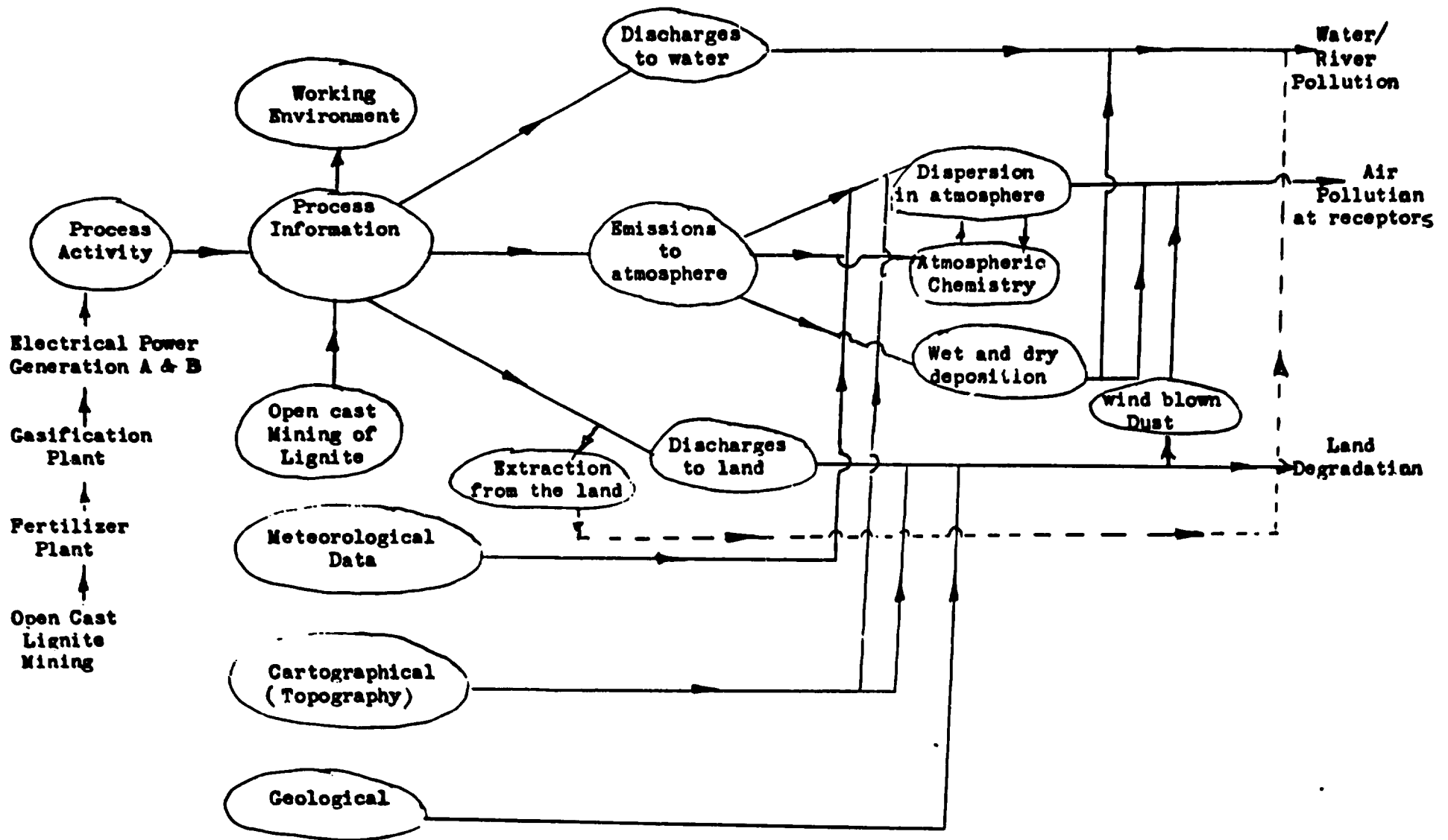
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Reports given to INKOS mark thus \* and:

- A Bibliography covering the adsorption of Sulphur Oxides on Alkaline Particles - Unpublished.
- A number of publications covering Acid Deposition, Source Emission Measurement and Occupational Exposure Limits for the Working Environment.



**Fig. 1** Network for the Environment



Key: Kosovo A power plant  
Kosovo B power plant  
Fertilizer plant F  
Gasification plant G  
Institute I

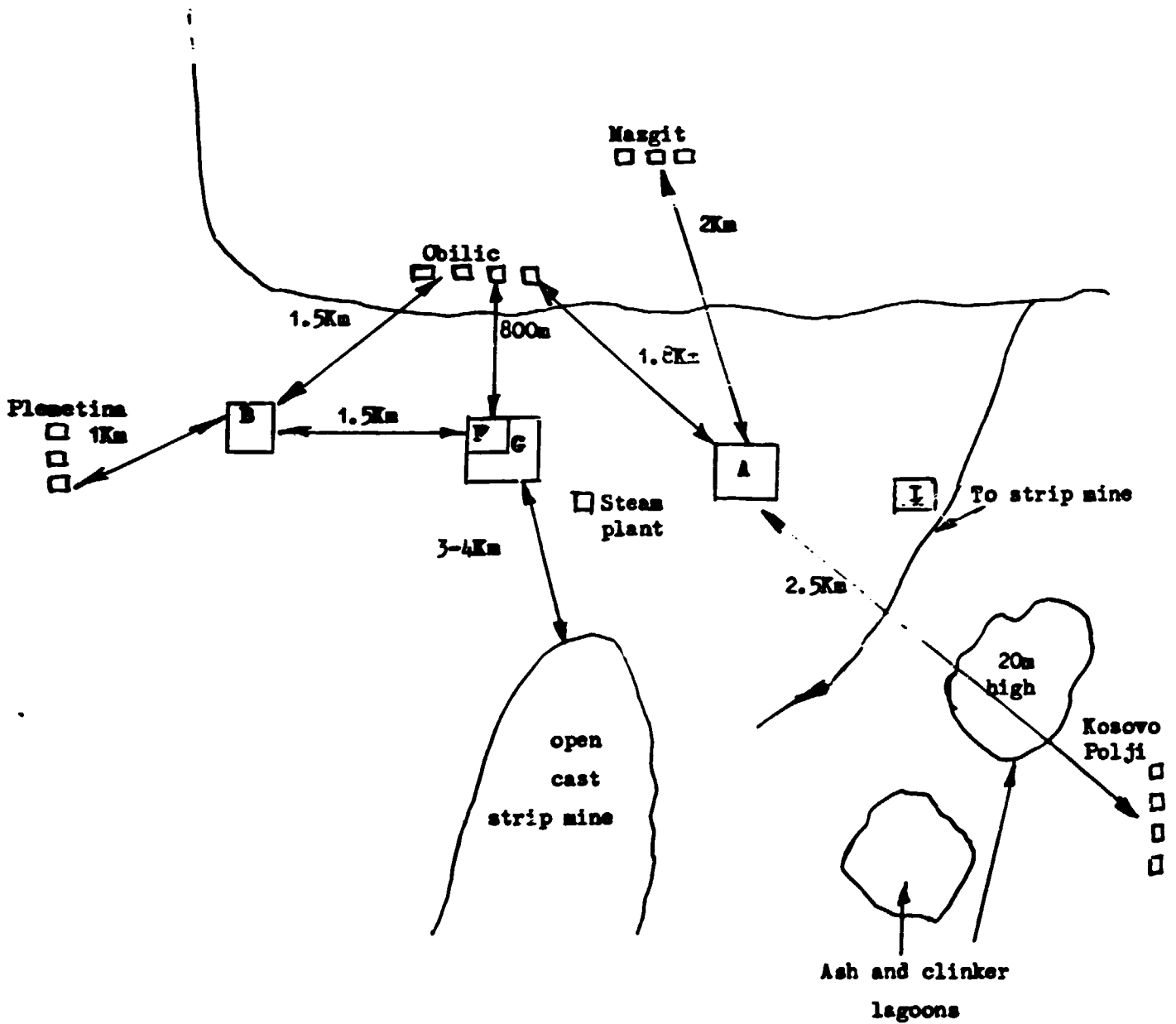


Fig. 2

Approximate locations  
of areas of interest

Scale 1 : 600,000

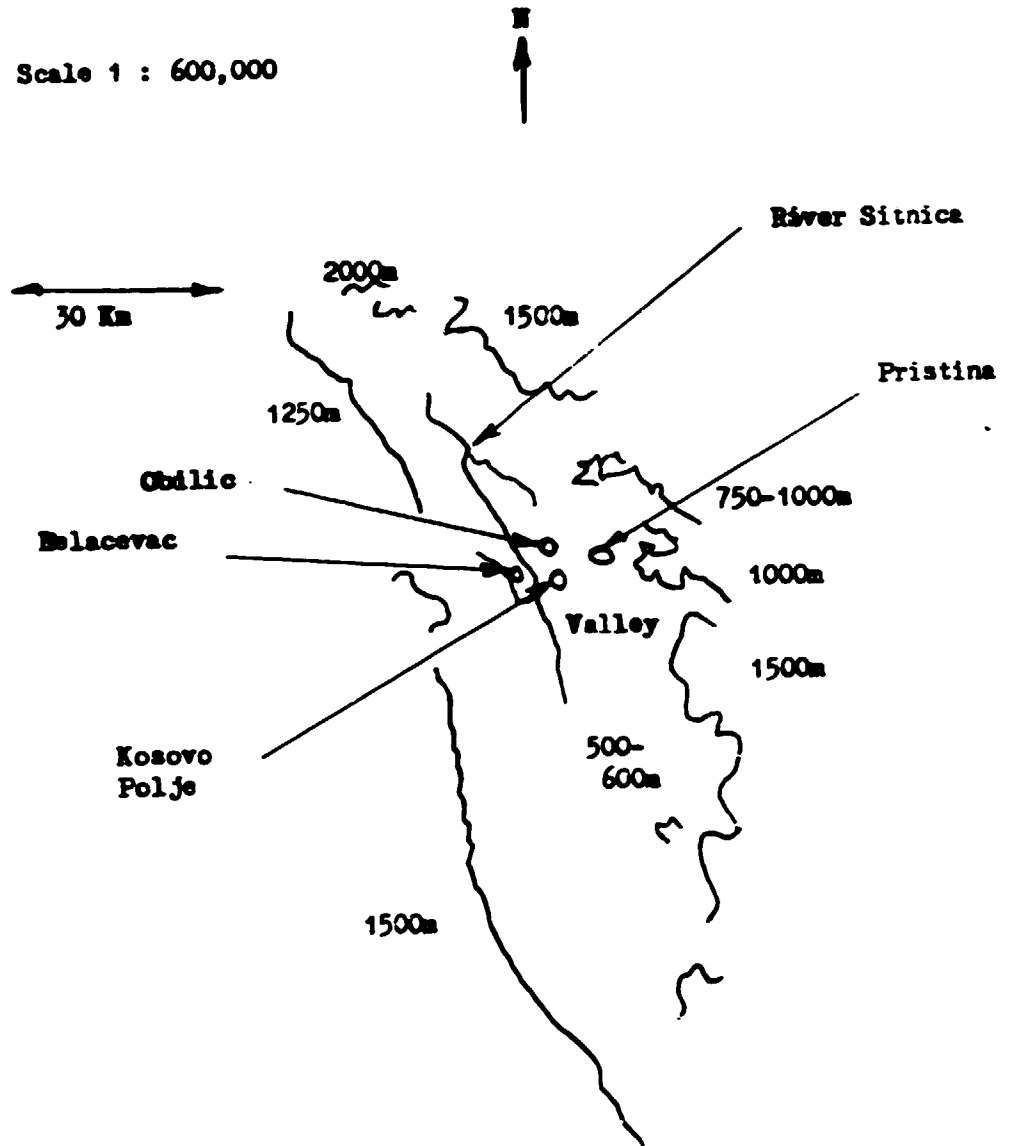
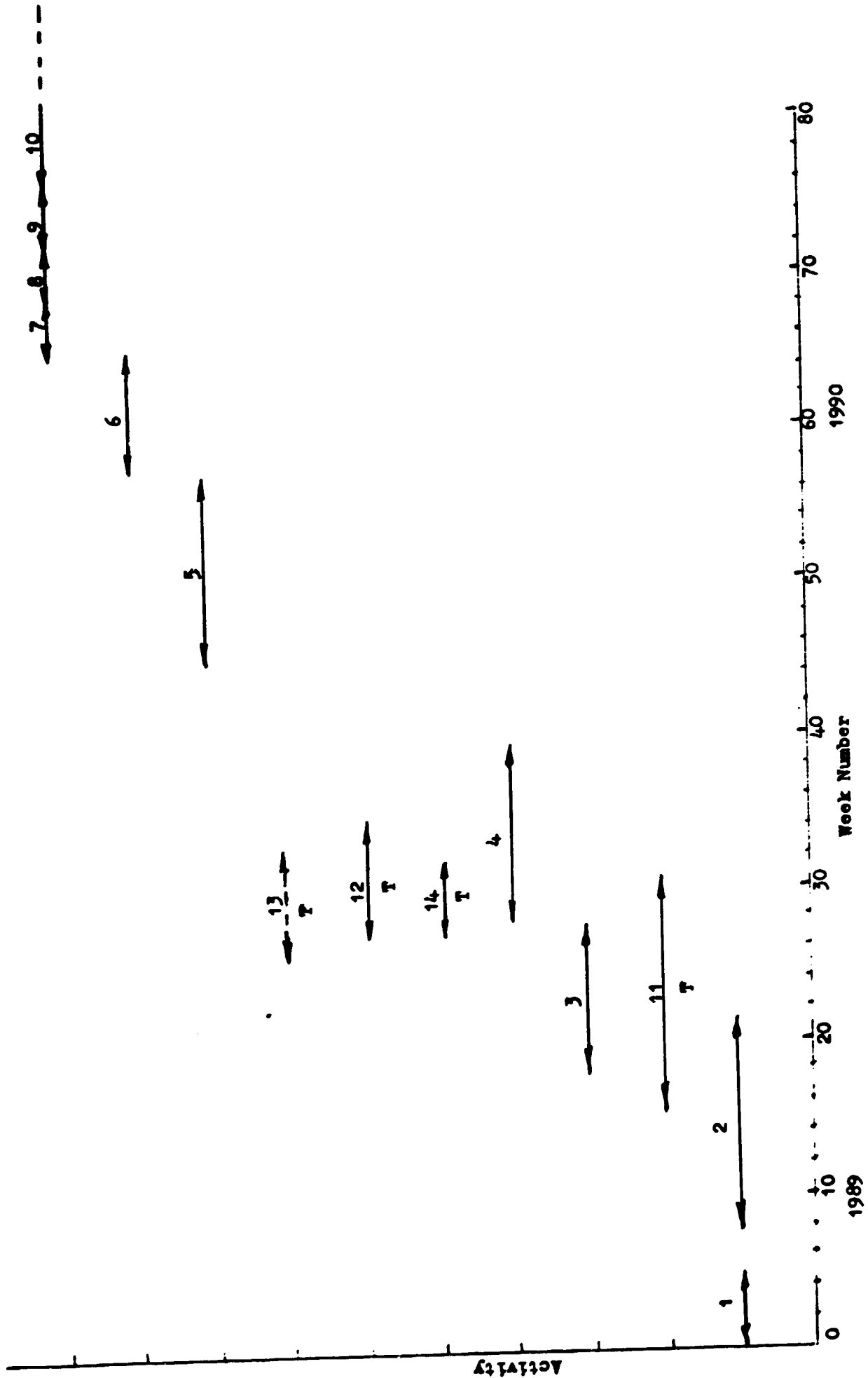
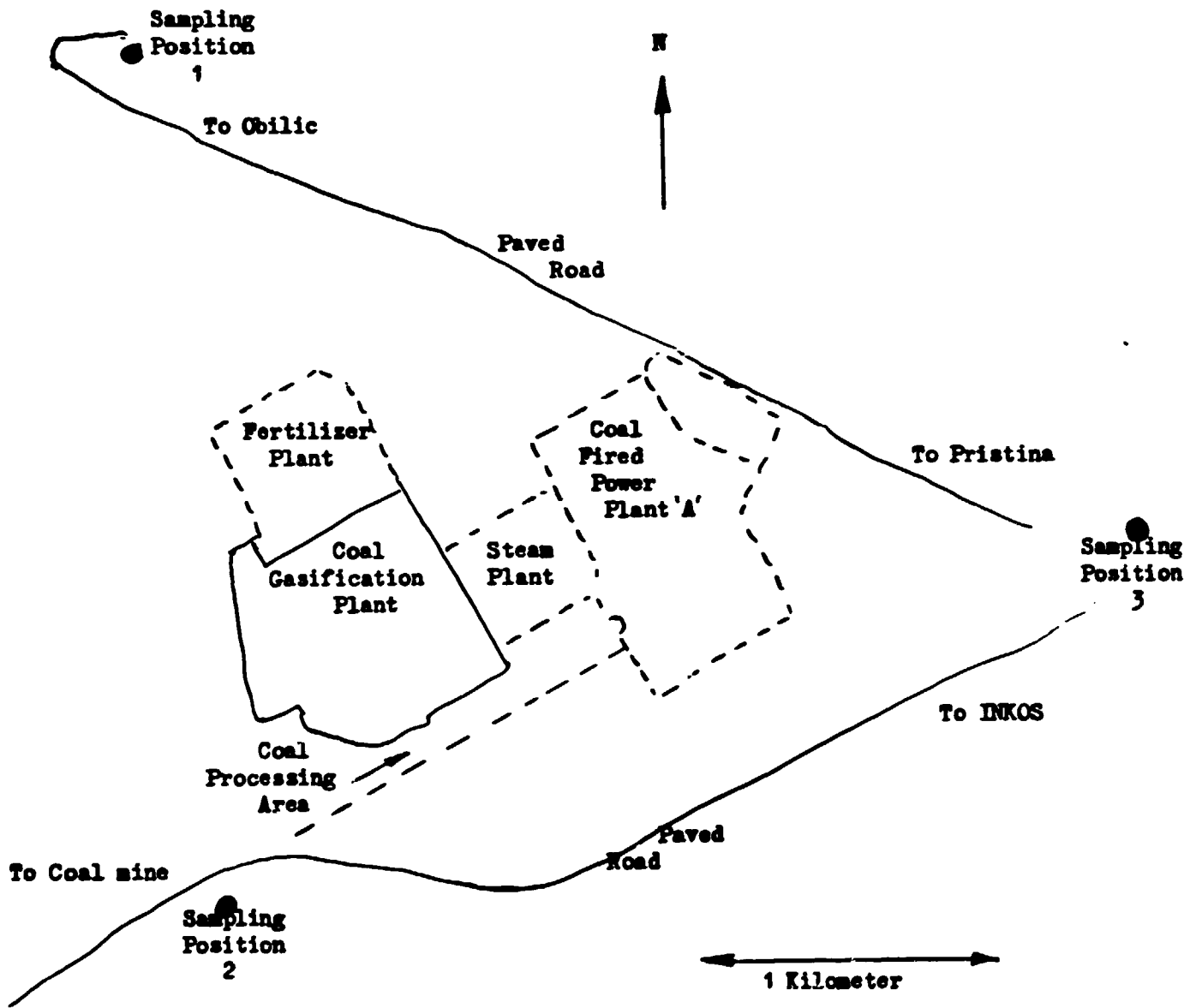


Fig. 3      Topography of Local Area

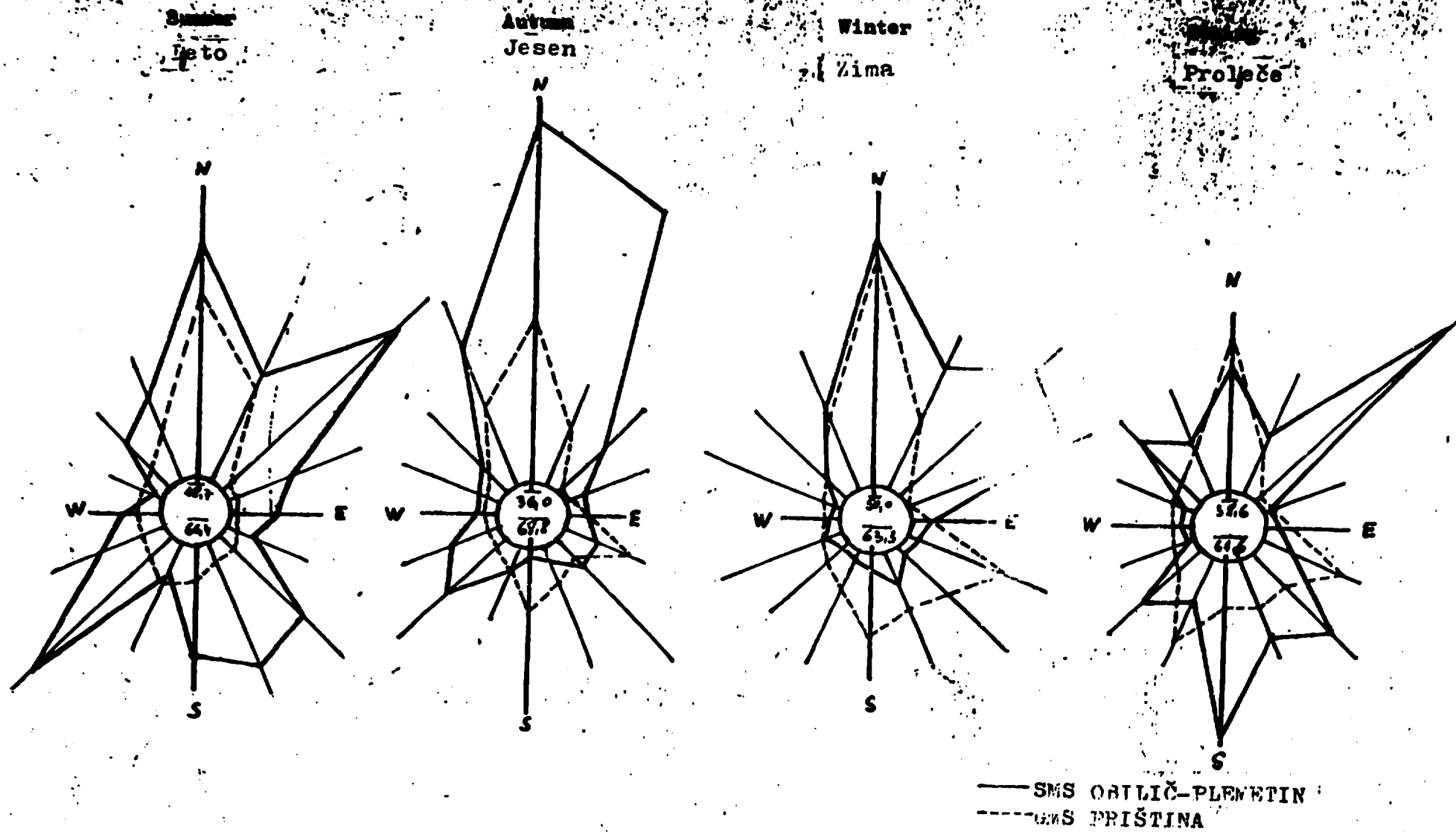


**Fig. 4** Bar Chart for Activity (Gasification)



**Fig. 5** Location of Gasification Plant and Sampling Positions





**Fig. 6** Wind Rose

Sl. 8. Ruže vjetrova SMS Obilić-Plemetina i GMS Priština za 1978 god.  
 po godišnjim dobima

**APPENDIX A**

**UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION**

**JOB DESCRIPTION**

**DP/YUG/87/019/11-51**

**Post title:** Expert in the use of gas chromatography for the detection of toxic organic pollutants arising from the gasification of lignite.

**Duration:** 0.3 m/m

**Date required:** September 1988

**Duty Station:** Pristina, Yugoslavia

**Purpose of project:**

1. Strengthening the Institute for Research and Development (INKOS) by providing modern equipment, expertise and staff training enabling them to perform investigations in the field of organic toxic pollutants and, later on, applying the research results to concerned industries.
2. Assisting "INKOS" in:
  - a) Categorizing toxic organic pollutants generated during coal gasification;
  - b) Preparing guidelines (in form of a manual) for operational and management methods as well as know-how for maximizing industrial and plant safety;
  - c) Providing scientific information on risk assessment of the impact on health, living conditions and work environment;
  - d) Contributing to the development of threshold limit values for toxic organic pollutants (direct support);
  - e) Contributing to the design (from the standpoint of environmental protection) of new coal gasification and similar plans being planned for Yugoslavia.

**Duties:**

The expert will execute the following tasks in cooperation with the Institute for Research and Development, (INKOS), in the Socialist Autonomous Province of KOSOVO:

1. Assist INKOS staff prepare neutral technical specifications for analytical instrumentation to be used in the detection and quantification of organic pollutants. This may include a gas chromatograph ancilliary detection and sampling equipment.
2. Suggest potential host institutions and content of training for the proposed fellowships and study tours concerning the use of gas chromatography in the detection and quantification of organic pollutants.
3. Advise on the sampling programme to be undertaken by INKOS to enable them monitor effectively the extent of pollution, by toxic organic compounds, of the immediate environment around the Kosova gasifier plant.
4. Prepare a report in English for the concerned National Authorities, UNDP and UNIDO, setting out the mission findings and recommendations.

**Language:** English

**Background information:**

Electrical power generation at the Kosova complex is based on the mining and utilization of lignite. The following units are in operation:

- Open pit mines "Belaqevc" and D. Sello"
- Thermal power stations "Kosova-A" and "Kosova B".
- Lignite gasification plant (Lurgi process).
- Fertilizer plant
- Coal drying plant
- Cogeneration plant

These plants constitute a permanent danger to health and environment. The lignite gasification plant is located 5 km. from Pristina, Kosova, Yugoslavia.

The gasifier plant capacity is  $480 \times 10^6 \text{ Nm}^3$  clean gas per year (8000 hours of operation). Fuel heating value about 16,7 MJ/Nm<sup>3</sup>. The plant is operated under a pressure of 25 bar. The generators are of the "Lurgi" type (diameter 3,6 m) and it produces gas which is partly used as fuel and partly for fractionation i.e. for the recovery of hydrogen which is further used for amonia synthesis. The fraction of gas after is enriched with ethane which is mixed with the remainder of the clear gas. The gasification plant consists of :

1. A gasifier plant with condensation plant (six generators, capacity 18,000 Nm<sup>3</sup>/h Raw gas per generator);
2. A Rectisol plant for purification of raw gas;
3. A phenol plant with biological purification of waste waters;
4. A plant for air separation.

Justification for this project is found in the need to monitor emissions of potentially harmful organic compounds to the environment. Quantification of these emissions is the necessary first step to undertaking remedial action involving improvements to operating procedures and the installation of pollution control equipment. Following identification of organic pollutants, (qualitative and quantitative), pollution-reduction measures can be recommended including operating guidelines and establishing threshold limits for toxic compounds. It is also necessary to establish an on-going monitoring (sampling and analysis) process to provide for continuous protection of the environment in the vicinity of the coal gasifier plant. The monitoring procedures for toxic organic pollutants will serve as a model for pollution control at other similar chemical process installations.

The emission of a large number of pollutants to the environment is caused by lignite gasification. The following groups of compounds will be investigated:

- aliphatic hydrocarbons
- aromatic hydrocarbons
- N - aromatic compounds
- S - aromatic compounds
- polycyclic aromatic hydro carbons
- N - heterocyclic hydrocarbons

The given investigation model will include a detection (measuring and determination) of organic toxic pollutants at all three phases:

- gaseous
- liquid
- solid

The project will generate the following outputs:

1. Full operational capability of "INKOS" to undertake the following environmental monitoring and protection measures applied to emissions of organic toxic pollutants:
  - a) Sampling of gas/liquid/solid media at plant site and in the immediate vicinity of the Kosova Lurgi coal gasification plant.
  - b) Determination of selected organic toxic pollutants in samples.
  - c) Categorizing these pollutants according to the risk they present to environment and health.
  - d) Make recommendations on measures which could be taken to minimize emissions of organic pollutants (modifications to process and process operation, introduction of environmental protection plant) and to minimize risks to health and environment.
2. Established a permanent monitoring system at the Kosova coal gasifier for the continuous recording and reporting of environmental emissions to improve industrial safety and environmental quality.

**Background Information:**

3. The following technical results:
- a) Toxicity of raw materials, products and by-products (waste streams) associated with coal gasification based on their content of selected organic compounds.
  - b) List of these materials in order of their toxicity.
  - c) Basic data for the evaluation of health risk to gasifier plant operation personnel and members of the general public residing near the plant. This data will be used to suggest remedial measures for elimination of the most dangerous pollutants and to define threshold limit values (TLV) of toxic organic compounds.  
  
Guidelines will be established on measures to be taken to minimize production of pollutants, modifications to process and process operation etc.
  - d) Provision of some of the data required for an investigation of the cumulative influence of organic pollutants over wider areas and longer periods of time and their direct and indirect effects on the population's health.
4. Evaluation of existing methods for monitoring atmospheric pollution caused by coal gasification and development of new sampling and analytical techniques for detection of toxic organic pollutants.

## APPENDIX B

### LURGI-BASED COAL GASIFICATION PLANT - KOSOVO

#### B1. General Plant Information

The Kosovo Basin Gasification Plant has an output capacity of  $480 \times 10^6$  Nm<sup>3</sup> of clean gas and consists of the following sections:

- (a) Generator Section: 6 generators with a capacity of 18,000 Nm<sup>3</sup> of raw gas each with arrangements for coal supply and slag disposal.
- (b) Condensation.
- (c) "Rectisol" Section for gas cleaning with a gas delivery station.
- (d) Air decomposition section (oxygen plant).
- (e) Tar and medium oil separation section.
- (f) "Phenosolvan" section for phenol separation.
- (g) Section for biological wastewaters cleaning.

Lignite, size class -60 + 6 mm, dried in accordance with the "Fleissner" procedure is used for gasification.

The Plant includes the possibility for further fractionation of 77 per cent of stated output ( $480 \times 10^6$  Nm<sup>3</sup>/year) in order to separate the hydrogen required for ammonium synthesis. Upon hydrogen separation, the gas is a fraction enriched with methane subsequently being mixed with the rest of clean gas. The resulting mixture ( $256 \times 10^6$  Nm<sup>3</sup>/year) represents a pipeline gas with a net heating value of 4000 kcal/Nm<sup>3</sup> supplied into the distribution network.

B2. The crude gas is produced in the gasifiers under a pressure of 25 bars and temperature of 300°C. It is firstly washed in the gas scrubbers and then indirectly cooled in the heat exchangers and condensation unit up to 30°C. This

enables separation of liquid by-products such as tar, heavy tar, gas liquor and light oil. Liquid by-products are separated in the tar separation unit and then discharged in storage tanks.

Heavy tar is deposited in the nearby dump and the gas liquor is treated in the phenosolvan unit.

The crude gas with a temperature of 30°C goes to the rectisol plant where naphtha, H<sub>2</sub>S, COS and CO<sub>2</sub> are separated by direct washing. The purified heating gas has with a maximal content of 3 ppm H<sub>2</sub>S + COS and up to 2 vol % of CO<sub>2</sub> is distributed to the industry (consumers).

An additional washing of the purified gas is needed for the ammonium synthesis whereby CO<sub>2</sub> concentration is reduced to 10 ppm.

The gas liquor is treated in the phenosolvan unit. Its final products are: phenol and ammonia solution.

The waste water from the gasification plant contains 40-70 mg/l volatile and 400-600 mg/l total phenols. Such a concentration is biologically reduced to 1.5-3 mg/l volatile and 90 mg/l total phenols.

There are 7 tanks for tar, medium oil (naphtha, crude phenol and ammonia solution) and a pump station for their delivery.

The oxygen plant supplies oxygen and protective nitrogen to the gasifiers; stripping nitrogen to the rectisol unit and nitrogen (99.99%) to the unit for ammonium synthesis.

The outlet pressure of the produced gas is 21 bars. It is sufficient for its transport to the consumers.

About 40% of the totally produced gas is used for ammonium, i.e. fertilizer production and 60% as heating gas.

## B2. Process Flow Diagrams, Sampling Points and Summary of Emissions

The process flow diagrams and sampling points are given in Figs B1-B7. Data of concentrations and emissions obtained during a CSEPA investigation are summarised in Tables B1-B4 for specified sampling points.

TABLE B1. - Emissions of Major Pollutants from the Gasification of  
10 t/h of Dried Lignite

- (a) Various vents in sections: Generators, Phenosolvan, Tar Separation and Storage  
Sampling points 2.2, 3.2, 13.1, 13.3, 13.5, 13.7, 14.5, 14.9, 15.3

Pollutants	Flow (Nm <sup>3</sup> /h)	Concentration (g/Nm <sup>3</sup> )	Amount (g)
Sulphur (H <sub>2</sub> S), COS, CH <sub>3</sub> SH, CH <sub>3</sub> , CH <sub>2</sub> SH) as "S"	3615	1.06	3832
Ammonium (NH <sub>3</sub> )	"	0.11	398
Phenols	"	1.28	4627
Cyanhydrogen (HCN)	"	0.0099	35.8
Hydrocarbons (C <sub>n</sub> H <sub>m</sub> )	"	0.4	1446
Hydrogen (H)	"	0.3773	1364
Carbon monoxide (CO)	"	1.239	4478
Carbon dioxide (CO <sub>2</sub> )	"	86.59	313032
Methane (CH <sub>4</sub> )	"	0.0627	227
Particulates	"	41.08	148498



**TABLE B1. - Emissions of Major Pollutants from the Gasification of  
10 t/h of Dried Lignite (Contd)**

(b) CO<sub>2</sub> vent in section - Rectisol  
Sampling point 7.2

Pollutants	Flow (Nm <sup>3</sup> /h)	Concentration (g/Nm <sup>3</sup> )	Amount (g)
Sulphur (H <sub>2</sub> S), COS, CH <sub>3</sub> SH, CH <sub>3</sub> , CH <sub>2</sub> SH) as "S"	1702	0.258	43.9
Ammonium (NH <sub>3</sub> )	"	0.01	17.0
Phenols	"	0.068	115.7
Cyanhydrogen (HCN)	"	0.0153	26.0
Hydrocarbons (C <sub>n</sub> H <sub>m</sub> )	"	6.557	11169
Hydrogen (H)	"	0.7193	1224
Carbon monoxide (CO)	"	0.0	0.0
Carbon dioxide (CO <sub>2</sub> )	"	1860	3165700
Methane (CH <sub>4</sub> )	"	5.713	9726

8

(c) Large Flare for Waste Gases from the Plant  
Sampling points 20.1 (including 3.6, 13.6, 7.1)

Pollutants	Flow (Nm <sup>3</sup> /h)	Concentration (g/Nm <sup>3</sup> )	Amount (g)	Amount after burning (g)
Sulphur (H <sub>2</sub> S), COS, CH <sub>3</sub> SH, CH <sub>3</sub> , CH <sub>2</sub> SH) as "S"	3348	26.88	89994	
Ammonium (NH <sub>3</sub> )	"	0.52	1741	
Phenols	"	0.04	134	
Cyanhydrogen (HCN)	"	0.1	335	
Hydrocarbons (C <sub>n</sub> H <sub>m</sub> )	"	13.4	44863	
Hydrogen (H)	"	2.534	8485	
Carbon monoxide (CO)	"	45.2	151247	
Methane (CH <sub>4</sub> )	"	3.344	11196	
Carbon dioxide (CO <sub>2</sub> )	"	1635,6	5475896	6154000
Nitrogen oxides (NO <sub>2</sub> )				5164
Sulphur dioxide (SO <sub>2</sub> )				179988

**TABLE B1. - Emissions of Major Pollutants from the Gasification of  
10 t/h of Dried Lignite (Contd)**

**(d) Slag Sampling point 12.2**

<b>Pollutants</b>	<b>Flow (t/h)</b>	<b>Concentration (g/t)</b>	<b>Amount (g)</b>
<b>Sulphur as "S"</b>	<b>1.625</b>	<b>1.33</b>	<b>2.161</b>
<b>Hydrocarbons as "C"</b>	<b>1.625</b>	<b>4.60</b>	<b>7.475</b>

**(e) Wastewater - Sampling point 12.3**

<b>Pollutants</b>	<b>Flow (t/h)</b>	<b>Concentration (g/t)</b>	<b>Amount (g)</b>
<b>Sulphur "S" (Sulphites, Sulphates, thiosulphates, rhodanides, hydrogen sulphid)</b>	<b>1.0</b>	<b>155</b>	<b>155</b>
<b>Ammonium</b>	<b>1.0</b>	<b>1.9</b>	<b>1.9</b>
<b>Phenols</b>	<b>1.0</b>	<b>1.227</b>	<b>1.227</b>
<b>Hydrocarbons as "C"</b>	<b>1.625</b>	<b>4.60</b>	<b>7.475</b>

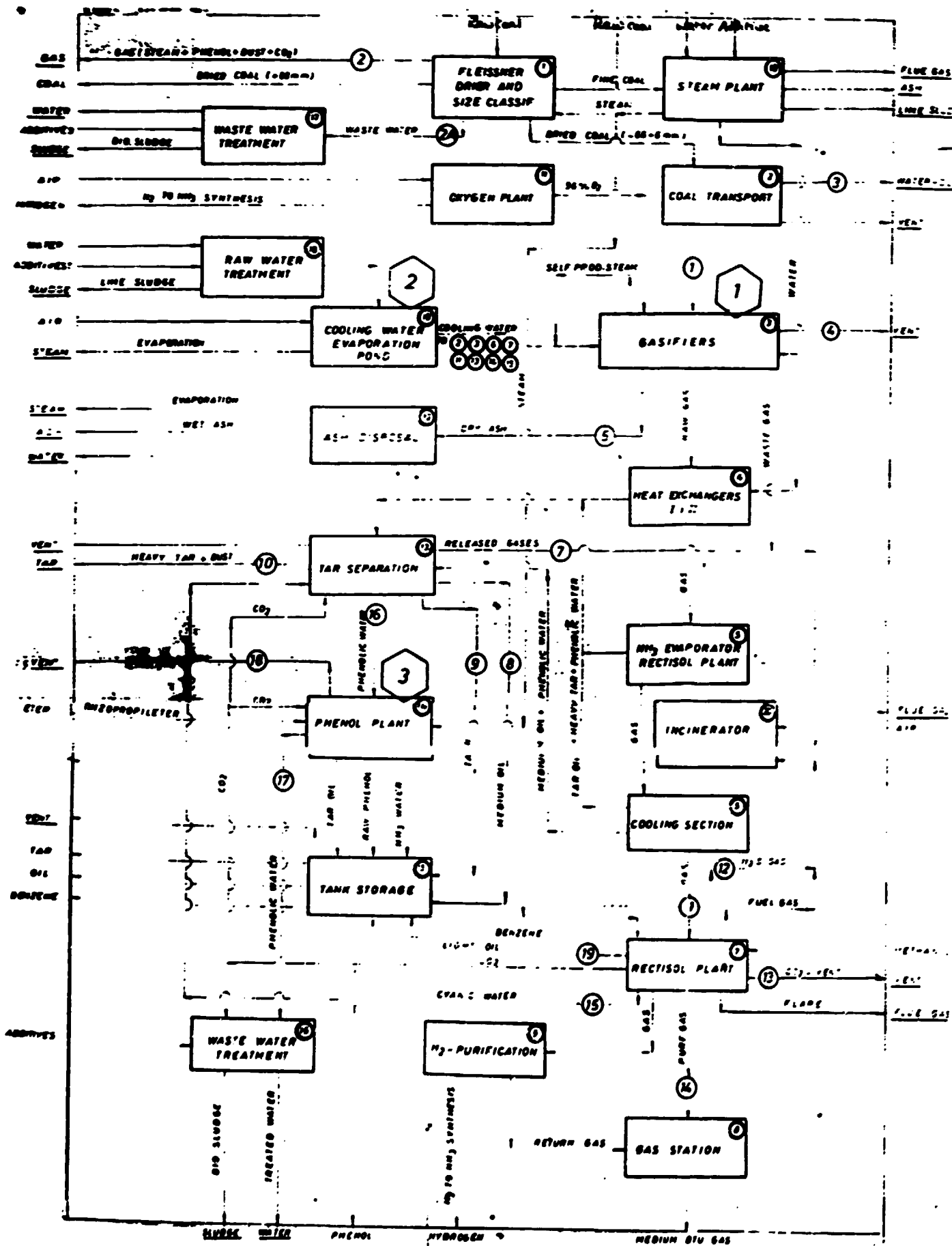
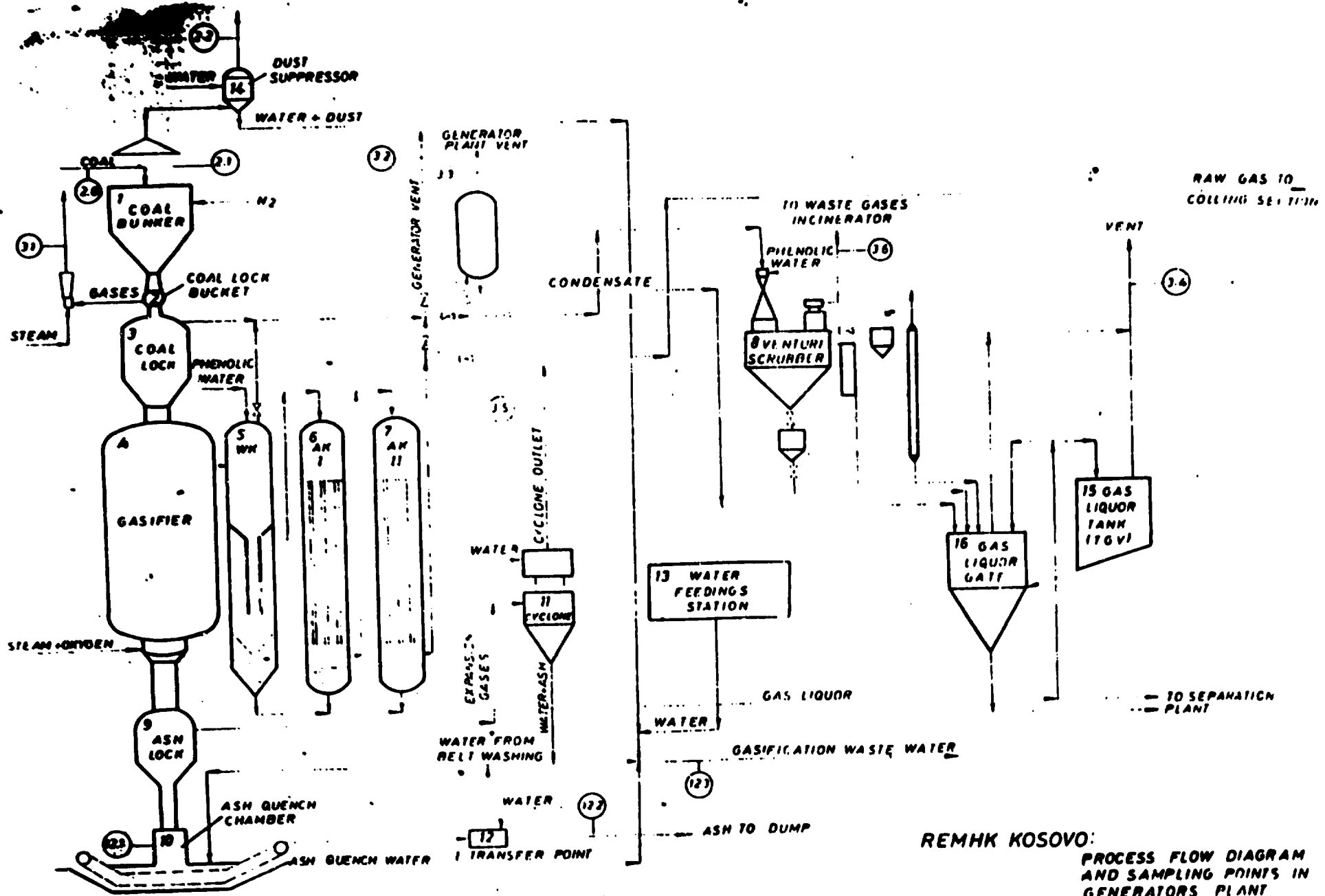
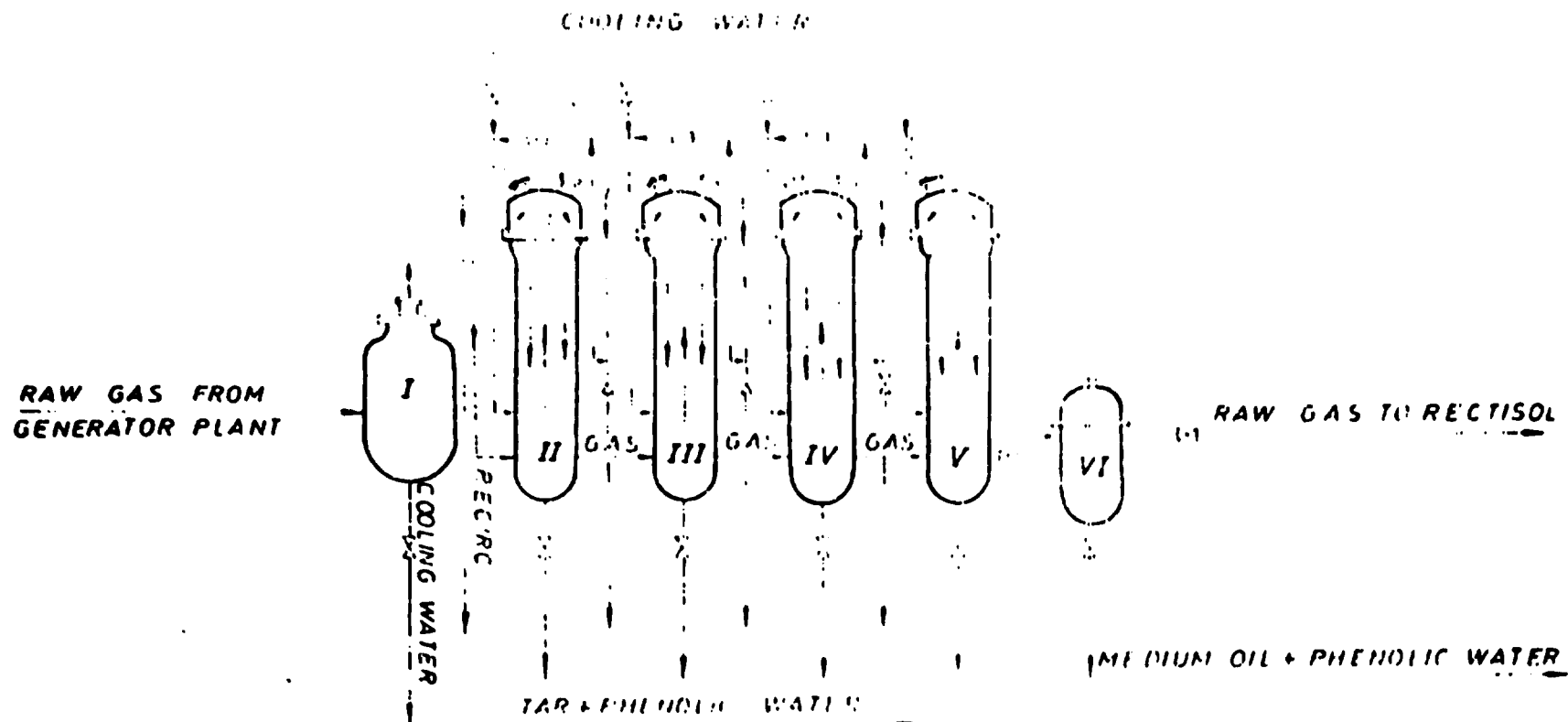


FIG. 01 PROCESS FLOW DIAGRAM FOR GASIFICATION PROCESS IN REMHK KOSOVO  
 LEGEND: (C) SAMPLING POINT (H) AMBIENT AIR



REMHK KOSOVO:  
 PROCESS FLOW DIAGRAM  
 AND SAMPLING POINTS IN  
 GENERATORS PLANT

FIG. B 2



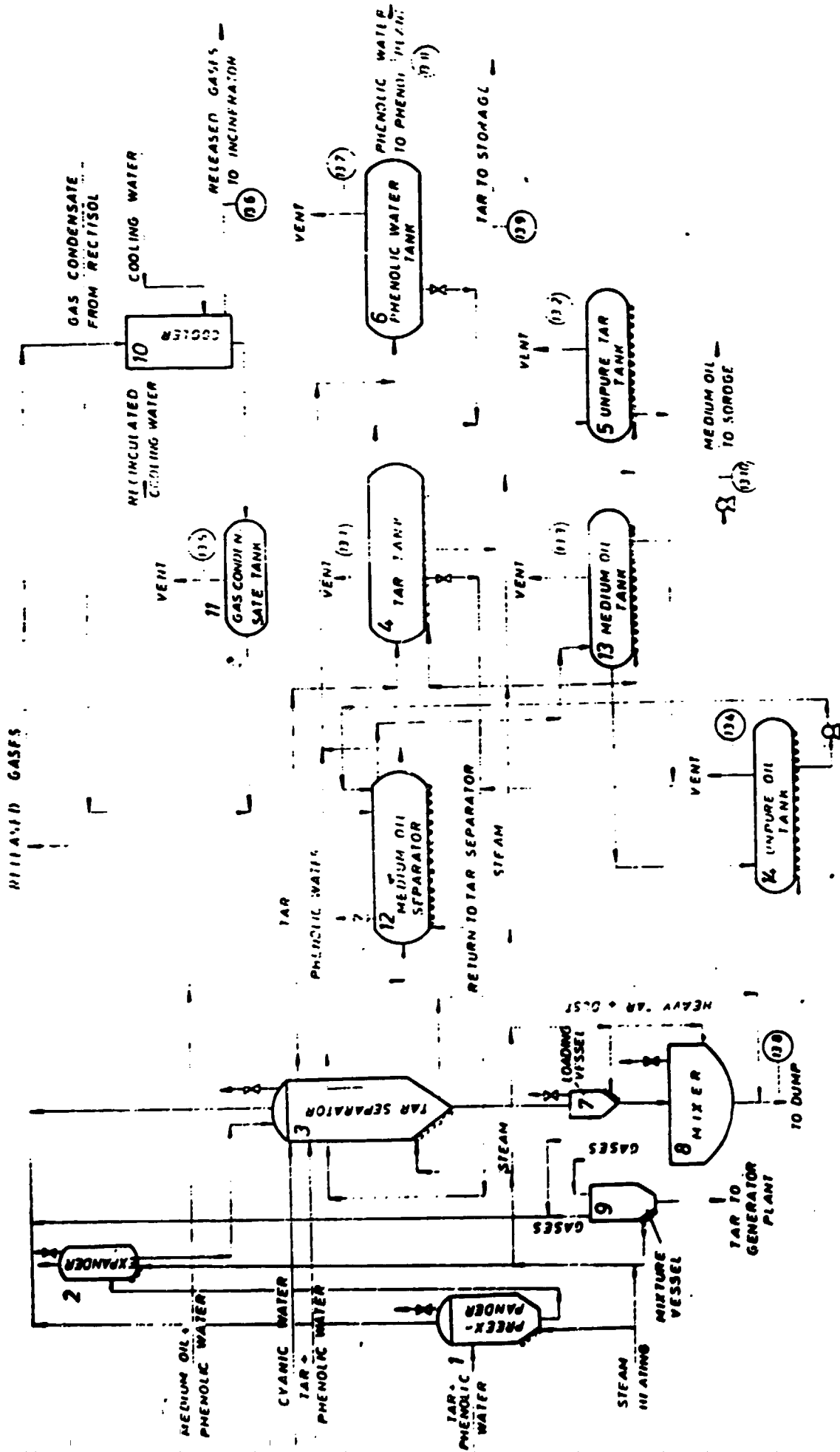
LEGEND:

- I TAR SEPARATOR
- I, III, IV, V COOLERS
- VI DROP COLLECTOR

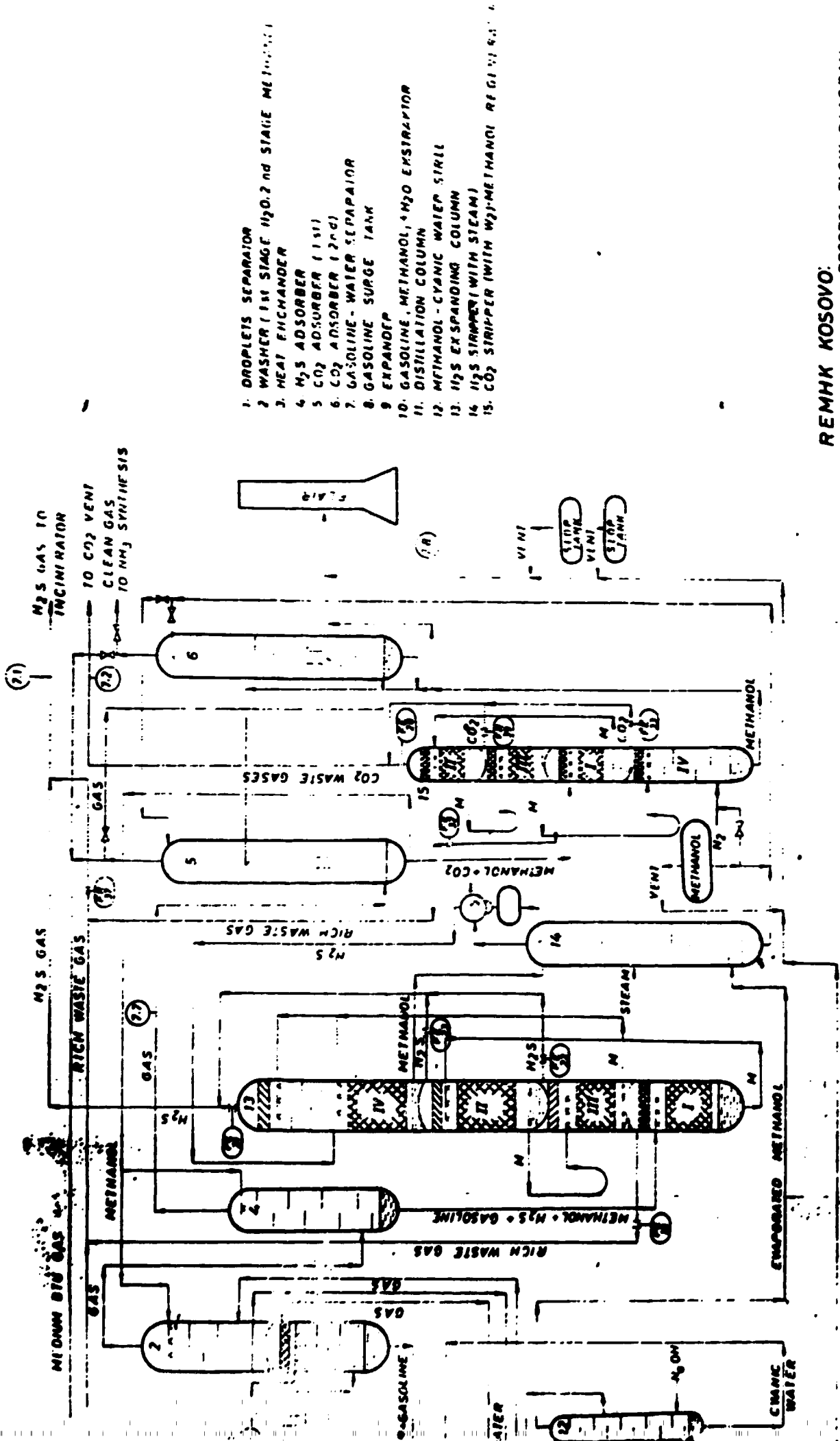
REF: MK KOSOVO.

COOLING SECTION  
PROCESS FLOW DIAGRAM

FIG B3



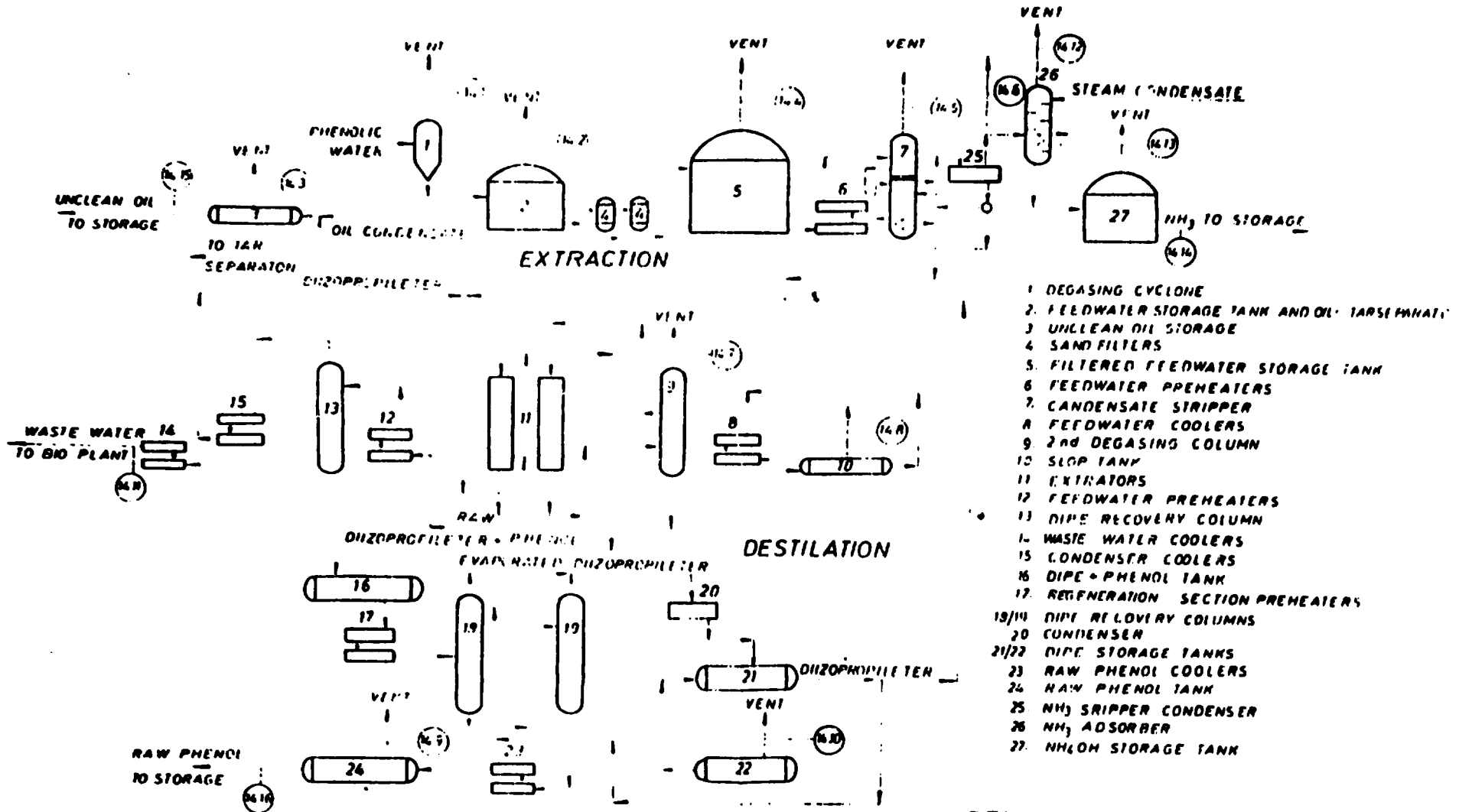
REM'IK KOSOVO:  
 PROCESS FLOW DIAGRAM  
 AND SAMPLING POINTS IN  
 TAR SEPARATION PLANT  
 FIG. 54



1. DROPLETS SEPARATOR
2. WASHER (1st STAGE H<sub>2</sub>O, 2nd STAGE METHANOL)
3. HEAT EXCHANGER
4. H<sub>2</sub>S ADSORBER
5. CO<sub>2</sub> ADSORBER (1st)
6. CO<sub>2</sub> ADSORBER (2nd)
7. GASOLINE - WATER SEPARATOR
8. GASOLINE SURGE TANK
9. EXPANDER
10. GASOLINE, METHANOL, H<sub>2</sub>O EXTRACTOR
11. DISTILLATION COLUMN
12. METHANOL - CYANIC WATER STRIP
13. H<sub>2</sub>S EXPANDING COLUMN
14. H<sub>2</sub>S STRIPPER (WITH STEAM)
15. CO<sub>2</sub> STRIPPER (WITH W<sub>2</sub> METHANOL REGENERATOR)

REMHK KOSOVO:  
 PROCESS FLOW DIAGRAM  
 AND SAMPLING POINTS IN  
 RECTISOL PLANT

# PRECLEANING



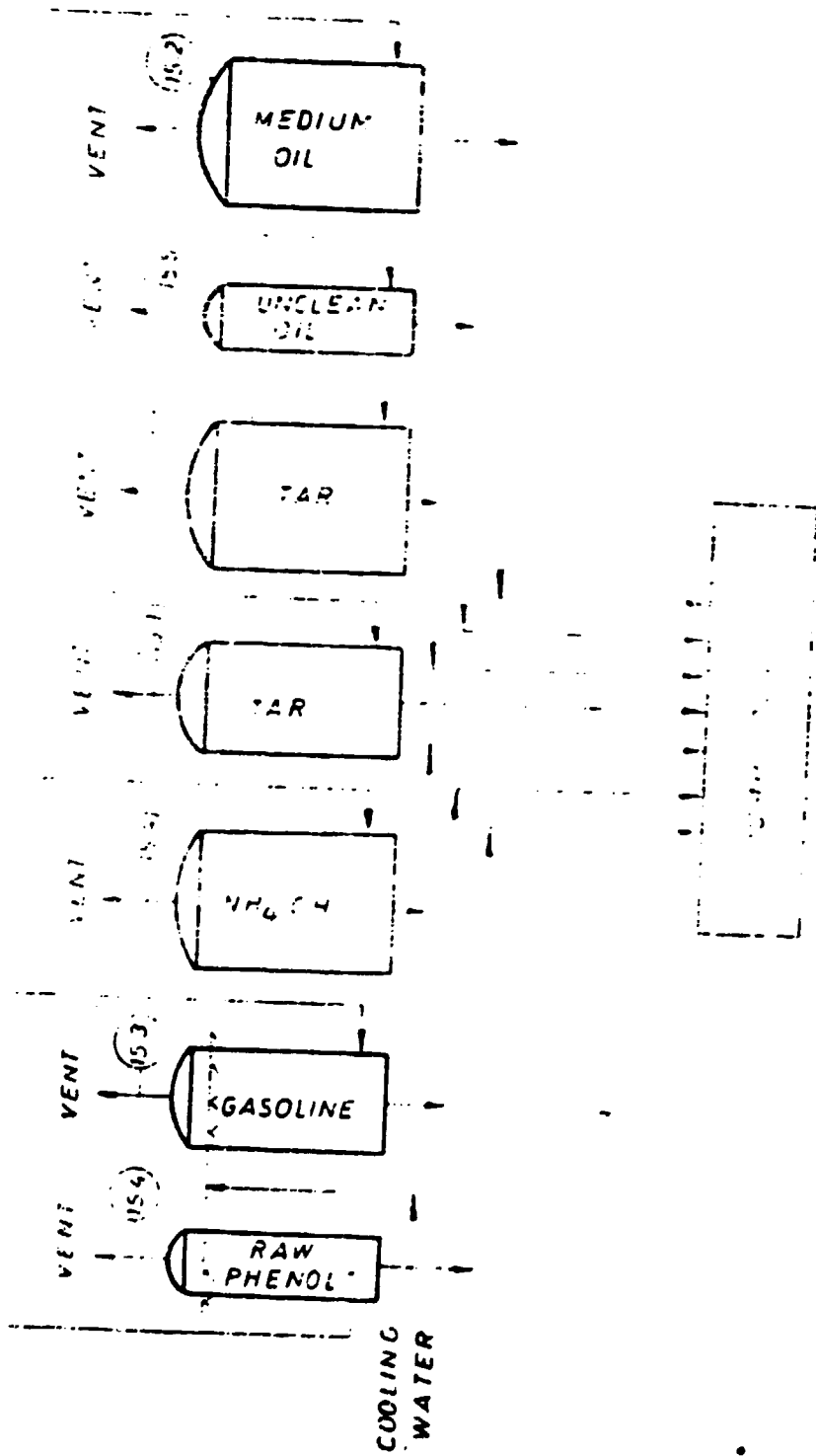
- 1 DEGASING CYCLONE
- 2 FEEDWATER STORAGE TANK AND OIL TAPSEPHANT
- 3 UNCLEAN OIL STORAGE
- 4 SAND FILTERS
- 5 FILTERED FEEDWATER STORAGE TANK
- 6 FEEDWATER PREHEATERS
- 7 CONDENSATE STRIPPER
- 8 FEEDWATER COOLERS
- 9 2nd DEGASING COLUMN
- 10 SLOP TANK
- 11 EXTRACTORS
- 12 FEEDWATER PREHEATERS
- 13 DIPE RECOVERY COLUMN
- 14 WASTE WATER COOLERS
- 15 CONDENSER COOLERS
- 16 DIPE + PHENOL TANK
- 17 REGENERATION SECTION PREHEATERS
- 18/19 DIPE RECOVERY COLUMNS
- 20 CONDENSER
- 21/22 DIPE STORAGE TANKS
- 23 RAW PHENOL COOLERS
- 24 RAW PHENOL TANK
- 25 NH<sub>3</sub> STRIPPER CONDENSER
- 26 NH<sub>3</sub> ADSORBER
- 27 NH<sub>4</sub>OH STORAGE TANK

REMHK KOSOVO:

PROCESS FLOW DIAGRAM  
AND SAMPLING POINTS IN  
PHENOSOLVAN PLANT

FIG 86





ROSHAR KOSOV

PROCESS FLOW DIAGRAM  
AND SAMPLING POINTS  
IN STORAGE

FIG 67