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PEAT AS A RAW MATERIAL FOR AMMONIA

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ABSTRACT

Kemira Oy has built a demonstration ammonia plant based on peat. The cost of the project amounted to FIM 230 million. The production was started in autumn 1988. The existing oil-based ammonia plant was modified to use also peat gas in production.

Peat gasification has been in productional use with a partial capacity for thousands of hours together with oil gasification. The problems encountered have been due to the heterogeneous quality of peat. Difficulties have also been caused by the high naphthalene content of gas and by blockages in the cyclone recycle pipe of the gasification. Technical solutions for these problems are available, which proves that synthesis gas and ammonia production from peat on a commercial scale is technically possible.

The project is considered to be of great significance, because peat is the only indigenous raw material for synthesis gas available in Finland. The economic conditions at Oulu have been reasonable due to the local factors, such as established peat production, partial use of the existing ammonia plant and the existing factory area and personnel.

Kemira can start a peat-based production with a capacity of 80,000 t/a even at short notice, if necessary. Kemira owns peat areas even for bigger production capacities. The properties of peat are quite similar to those of brown coal or biomass, so the experience in processing of peat may be applied also to these raw materials.

1. INTRODUCTION

In Finland, ammonia is produced only at the Oulu Works of Kemira Oy. The production was started in 1952, with coal as raw material. Later the process was changed to employ heavy fuel oil. In the 1950-1970's the production was expanded approximately at the same rate as domestic consumption and the maximum production amounted to almost 300,000 t/a. In 1969, a plant based on naphtha reforming was commissioned, though ten years later, despite being in good condition and operationally reliable, the plant ceased operation due to the unfavourable price development of its raw material. After that a plant based on the use of heavy oil has been operating, its annual production amounting to 80,000 tonnes.

Kemira's interest in the gasification of peat for the raw material for ammonia dates from the second energy crisis in 1979. In the years 1980-1981 the applicability of peat in processes developed for coal was investigated on the basis of commercial offers.

The objective was to begin a large-scale production in the mid-1980's. The sharp rise in energy and ammonia prices, however, tailed off, and the situation no longer forced to take rapid action.

However, measures decided in connection with the project were continued by acquiring peatlands and preparing them for production, as well as investments in the branch; acquiring a shareholding in a company involved in peat production was a principal example of this. The work on ensuring the reliability of the gasification technique through test runs in foreign pilot plants was initiated.

The decision on engineering of the project was made in autumn 1985 and on building in January 1986. Ammonia was produced for the first time from peat in August 1988.

At the company level the supply of nitrogen raw material has been ensured in various ways. Productions in Holland, Belgium and England constitute the principal sources. Kemira has also a long term contract for ammonia import from the Soviet Union. The peat ammonia project is a part in the overall picture.

2. PEAT AS A FEEDSTOCK

The properties of Finnish peat are rather close to those of lignite or brown coal. Brown coal is gasified commercially to produce synthesis gas in several countries. In countries like the USA and West Germany high sums have been invested in the development of the technology for the gasification of brown coal. The application of the technique developed for brown coal is a natural approach to the gasification of peat.

The use of peat in Finland has been both significant and economically competitive quite a long time. The price has been fairly competitive with that of coal in areas where there are large peat reserves. In the Oulu area there is abundantly peat and production on a commercial basis is well established. A 200 MW power plant of the City of Oulu is peat-fired and has been in operation for fifteen years. The entire city of Oulu with its 100,000 inhabitants is heated by energy derived from peat. In the same manner the Kemira Oulu Works produce the necessary steam using peat.

Peat production in Finland employs two different techniques, the products being milled peat and sod peat. The milled peat (raw peat) has a low bulk density and poor flowing properties, and its moisture content is about 50 %. Sod peat is produced by pressing the peat through nozzles to sods with about 85 % moisture content and by drying the sods to about 40 % moisture content on the production field.

3. PEAT AND BIOMASS

Peat is formed as a result of decomposition of the plants growing on bogs and can be regarded as biomass. This phenomenon, called humification, is very slow. In peat bogs being in natural state the peat layer is growing 0.2-1.0 mm/a. The peatland is exploitable, when the depth of the peat deposit reaches about 2 meters, the area is large enough and the location suitable.

It has been estimated that in Finland there are 500,000 hectars of such peatland available but the maximum economical transport distance is within a range of 100 kilometres.

When preparing peatland for harvesting, the first action is draining. This stops the peat growth; therefore peat cannot be regarded as a renewable resource. The fully mined peatland is anyhow a good area for forest or biomass production. In nothern countries, where free areas are huge, but temperatures low, the biomass production is probably the best way to utilize solar energy.

The possibilities to use these areas for biomass production by means of fast growing willow (Salix) have been studied by Kemira and the University of Oulu. The main goals of the research work are to develop suitable Salix clones for these areas and to evaluate the effects of peat soils, liming, fertilization etc. on the growth of willows. The results so far suggest that the biomass production of fast growing willows may be increased, but it is not yet clear, if the combination of sufficient winter resistance and high productivity is possible.

The gasification techniques of peat and biomass chips are quite similar. In the future, when the peat deposits have been fully utilized, it will be possible to produce biomass for energy and synthesis gas production in the same areas.

The comparison between different carbonaceous materials is given in Table 1.

4. GASIFICATION PRINCIPLES

Basics of gasifying carbonaceous material are its devolatilization to char as well as the reaction of carbon with different gasification agents. The conversion to gaseous products depends on thermodynamical equilibrium and the kinetics of these chemical reactions. Different gasification processes have been developed for different feedstocks.

There are three main types of gasification processes:

- moving bed (Lurgi)
- fluidized bed (Winkler)
- entrained phase (Koppers-Totzek).

The principles of different gasification processes have been given in the literature on the subject.

Table 1. Characteristic Data of Various Carbonaceous Materials

Carbon-carrier	Calorific value LHV kJ/kg (maf)**	Volatile matter maf %	Reaction velocity* k_m cm^3/gs
Wood	17 650 - 18 200	81.8 - 86.7	3.4 - 16
Peat	22 270 - 22 320	61.3 - 73.1	4.13
Soft brown coal	25 040 - 27 040	48.5 - 55.1	3.6 - 8.0
Hard brown coal	27 850	45.6	3.8
Bituminous coal high volatile	28 350 - 31 480	31.8 - 34.6	0.46 - 0.68
Bituminous coal medium volatile	31 200	29.4	0.28

* of char gasified by CO_2 at 900°C and 30 % conversion
** moisture and ash free

All processes are in commercial use. The applicability depends above all on the properties of the raw material. For highly reactive feedstocks like peat, biomass and lignite the fluidized-bed technology is advantageous, because gas with reasonably good quality (low tar and hydrocarbon content) can be produced at a temperature which is lower than the melting point of ash.

At least the following reactions are included in all gasification processes:

Heterogeneous reactions gas/solid

Heterogeneous watergas reaction	$C + H_2O \rightarrow CO + H_2$	+119 kJ/mole
Boudouard reaction	$C + CO_2 \rightarrow 2CO$	+162 kJ/mole
Hydrogenating gasification	$C + 2H_2 \rightarrow CH_4$	- 87 kJ/mole
Partial oxidation	$C + 1/2\ O_2 \rightarrow CO$	-123 kJ/mole
Oxidation	$C + O_2 \rightarrow CO_2$	-406 kJ/mole

Homogeneous reactions gas/gas

Homogeneous watergas reaction	$CO + H_2O \rightarrow H_2 + CO_2$	- 42 kJ/mole
Methanation	$CO + 3H_2 \rightarrow CH_4 + H_2O$	-206 kJ/mole

Also different pyrolyse reactions take place.

When producing synthesis gas carbon monoxide and hydrogen are the desired components, the content of which in the produced raw gas must be optimal in view of the influences of production and investment costs.

The thermal energy required by endothermic reactions is produced by oxidation reactions. Therefore it is advantageous for the quality of the produced gas, if the raw material is dried. In our case peat is dried to a moisture content of 15 % before being fed into gasification.

The pressure rise changes the equilibrium towards the higher methane content. So the rise in the gasification pressure, when producing synthesis gas decreases the compression costs, but on the other hand results in poorer gas quality.

5. CHOICE OF THE GASIFICATION PROCESS

Before starting the full scale project, pilot experiments were carried out at plants overseas in order to minimize technical risks. Test runs using the following three processes were carried out with peat delivered from Finland in 1984-1985:

- HTW (high-temperature-Winkler) process in Germany
- U-GAS process in the USA
- MINO process in Sweden.

The choice of the process went in favour of the German HTW process. The HTW licence is owned by Rheinbraun AG, while the engineering is carried out by UHDE GmbH. One strong argument in favour of this choice was the full-scale gasification plant of Rheinbraun AG, designed for use of brown coal.

6. PROCESS CONCEPT

It is significant that the handling and gasification of peat are only a small part (20-30 %) of the overall investment in the ammonia plant. The downstream processes place extremely great demands on the operational reliability of the gasification plants as well as on the quality of the gas. In the investments made the downstream section of the fuel oil-based plant's process was utilized. The removal processes of carbon dioxide, hydrogen sulphide and methane had to be modified as the gasification of peat involves a gas analysis of different form than that of the oil-based process. Moreover, the possibility of using oil gasification is maintained. At Oulu also formic acid and hydrogen peroxide are produced from synthesis gas. Carbon monoxide, the feedstock of formic acid process, is taken as side stream from gas after the Amisol wash. Hydrogen for the hydrogen peroxide plant is taken from the cold box. The process concept is shown in Figure 1.

The sulphur content of peat is low, about 0.15 %. That is why the sulphur recovery is not needed. The gas containing hydrogen sulphide is passed from the Amisol wash into the fluidized bed boiler, where it oxidizes and a part of sulphur is mixed up with ash and a part discharges with flue gases.

When gasifying oil the sour gas is fed into the wet catalytic sulphuric acid process, for which the sour gas obtained from peat gasification is too dilute.

Peat sods are crushed to a particle size of less than 4 mm to make the peat properties suitable for fluidized bed. Before the gasification process peat has to be dried to a moisture content of about 15 %. Damp peat would lead to synthesis gas of poor quality (high carbon dioxide content). The better transportation and feeding characteristics of drier peat also increase operational reliability.

The oxygen required for the gasification is produced at the Oulu plants in an air separation process, from which the nitrogen required later in the ammonia production is also obtained.

In the gasification the crushed and dried sod peat is pressurized to 10 bar in lock-hoppers and then fed into the reactor by screws. Oxygen and steam are blown under the peat so that the peat bed is fluidized. In the fluidized bed and in the upper section of the reactor the previously mentioned reactions take place at 750-950 °C temperatures (Figure 2).

The residual dust which has not undergone any reaction is separated in cyclones, circulated partly into the reactor and released from pressure through the lock-hopper system, as is the ash. To burn the residual carbon, the ash and dust are then fed to a boiler. The final cleaning from the solid material takes place in scrubbers. Steam and district heat are produced from the heat generated in the process.

Figure 3 shows Kemira's peat gasification plant at Oulu.

7. TEST RUNS

The first heating of the gasifier was performed in May 1988. The first successful start-up followed on June 3, 1988. The gas produced was fed to the flare.

During this first period of the operation it became apparent that the flowing properties of peat deteriorate, if it is heated up to a temperature range of 160-170°C. Due to this the pressure and temperature used for drying had to be decreased. The peat must always be superheated in regard to water vapour, because wet peat does neither flow well. The temperature range 130-150°C has been possible.

During the next start-up period after holidays gas was produced from peat for ammonia production for the first time on August 20, 1988. At this time the high naphthalene content of gas was discovered. Difficulties with naphthalene are due to its crystallization, which blocks up the piping and heat exchangers. Also the lignite gasification in Berrenrath had problems with naphthalene during the start-up period. The problems were settled there by changing the process and flowing conditions.

During the pilot plant runs of the HTW process with peat in 1984-1985 no high naphthalene contents were discovered.

During the operation periods subsequent to the first start-up problems to be considered besides those caused by naphthalene crystallization were:

- variations in peat quality
- capacity of peat crusher
- particle size distribution
- troubles with feeding equipment of peat drying, which disturbed smooth operation
- blockages in the 1-cyclone of the gasifier.

All these factors probably contribute to the high naphthalene content as well.

During the operating periods up to now the recycle pipe of the hot cyclone has always been blocked up at the latest within a few days of operation. This does not prevent the production, but affects the naphthalene content and carbon conversion rate.

Why the construction concerned operates with lignite under any circumstances but not with peat, is still unclear. A probable cause is the low softening temperature of peat ash. The fine ash particles become sticky and begin to deposite in places, where the flowing conditions are favourable for it.

Table 2 presents a summary of the knowledge obtained during the test run periods up to now.

Table 2. Summary of the operating periods of the peat gasification.

Operating period	Date	Duration	Cause of shut-down	Remarks
1	03.06.88- 06.06.88	3 days	Trip by high differential pressure in the waste heat boiler.	First peat to gasification, gas to flare. Great difficulties with peat feeding (lock-(lock-hoppers).
2	17.06.88- 21.06.88	5 days	Trip caused by process control unit.	Difficulties in feeding: caking in lock-hoppers.
3	17.08.88- 29.08.88	12 days	Failure of peat crusher.	Gas to production for the first time. Problems with naphthalene.

Operating period	Date	Duration	Cause of shut-down	Remarks
4	07.09.88-09.09.88	2 days	Unintended emergency stop.	No stable run. Flange leaks in waste heat boiler.
5	16.09.88-23.09.88	7 days	Power failure outside the plant.	Part of gas to production. Problems with naphthalene.
6	28.09.88-20.10.88	22 days	Failure in process control system.	Production only from peat gas for 5 days, oil gasification out of use. Pressure max. 9 bar, feed max. 20 t/h.
7	04.11.88-03.12.88	30 days	Planned shut-down.	Feed max. 24 t/h. Testing of benzene injection into gas, nevertheless problems with naphthalene. Peat particle size too small. Recycle pipe blocked.
8	02.01.89-27.01.89	25 days	Naphthalene blockages.	Slag formation in gasifier. Found during inspection.
9	28.02.89-27.03.89	27 days	Planned shut-down.	Different tests with 50 % load. Same problems as before.
10	05.06.89-07.06.89	3 days	Ash removal blocked.	Lower gasification temperatures as before. Aim to keep recycle pipe open.
11	15.06.89-16.06.89	2 days	Waste heat boiler blocked.	
12	09.08.89-11.08.89	2 days	"	
13	17.08.89-19.08.89	3 days	Blockages in peat feeding and waste heat boiler.	
14	25.08.89-01.09.89	7 days	Planned shut-down.	Testing of naphthalene removal.

Operating period	Date	Duration	Cause of shut-down	Remarks
15	02.10.89-06.11.89	36 days	Leakage in gas pipe after waste heat boiler.	Best productional run. Naphthalene removal in use. 24 days' production only from peat.
16	14.12.89-24.01.90	41 days	Planned shut-down.	Longest uninterrupted run parallel with oil gasification.

Most of the operation time the peat gasification has been tested along with the oil gasification at the rate of 50 % of the nominal capacity.

There has been some testing at the maximum capacity, too. The best rate achieved has been 90 % of the nominal capacity.

The total production of ammonia amounts to over 10,000 tonnes. In addition to this gas has been led to the power plant to be used as fuel gas. The longest operation time without a break has been 41 days. The maximization of the total operation time and the peat gasification capacity has not taken the top priority. It has been regarded more important to secure the continuous production of formic acid, hydrogen peroxide and ammonia and to minimize the costs.

The decision to construct a naphtalene removal unit was taken in the beginning of 1989 when it became apparent that naphthalene problem could not be solved otherwise. In the latest test runs the unit was in operation. Nahthalene is removed from the gas with benzene formed during the gasification. Benzene is separated by the Amisol wash downstream the gasification and recycled to the naphthalene removal.

In autumn 1989 also a parallel peat crusher was acquired and installed.

In some test runs dolomite has been added to peat. Dolomite binds the sulphur contained in peat into ash andm may raise the melting point of ash and prevent catalytically the naphthalene formation.

Also peat has been mixed with sawdust of 40 % by weight. This has not caused any problems during short periods. However, the periods have been too short for reliable balances and final conclusions.

8. CONCLUSIONS

Design value for synthesis gas ($CO+H_2$) is 1,100 NM^3/t dry peat.

The values achieved in continuous run have been approximately 1,000 Nm^3/t. The main reasons for deviations are as follows:

- high proportion of fines in peat feed, which causes high rates of eluriation from the fluidized bed
- the blockage of the dust recycle pipe from the first cyclone to the reactor
- the operation of the gasifier at reduced capacity, not in optimum conditions.

Although the longest operation periods have been over a month, also the operational reliability and regularity would need further development in order to achieve the normal level of ammonia plant. However, we have come to the conclusion that it is technically possible to produce synthesis gas and ammonia from peat on a commercial scale.

Figure 4 shows the price development of ammonia and oil in the 1980's. If the prices rise to the same level as in the beginning of the 1980's ammonia production using peat as raw material will be economical at Oulu. The prices of alternative raw materials and products should be still higher before new big scale plants based on coal, peat and biomass would be economical to establish. However, it is important to develop technical preparedness early enough, now when the prices are developing peacefully.

As a result of this demonstration plant Kemira has a basic know-how available. In the present price situation it is not economical to use peat gasification in continuous production. The next start-up of peat gasification will take place in autumn 1990 for a restricted running period in order to have minor testing and to retain operational skills already obtained.

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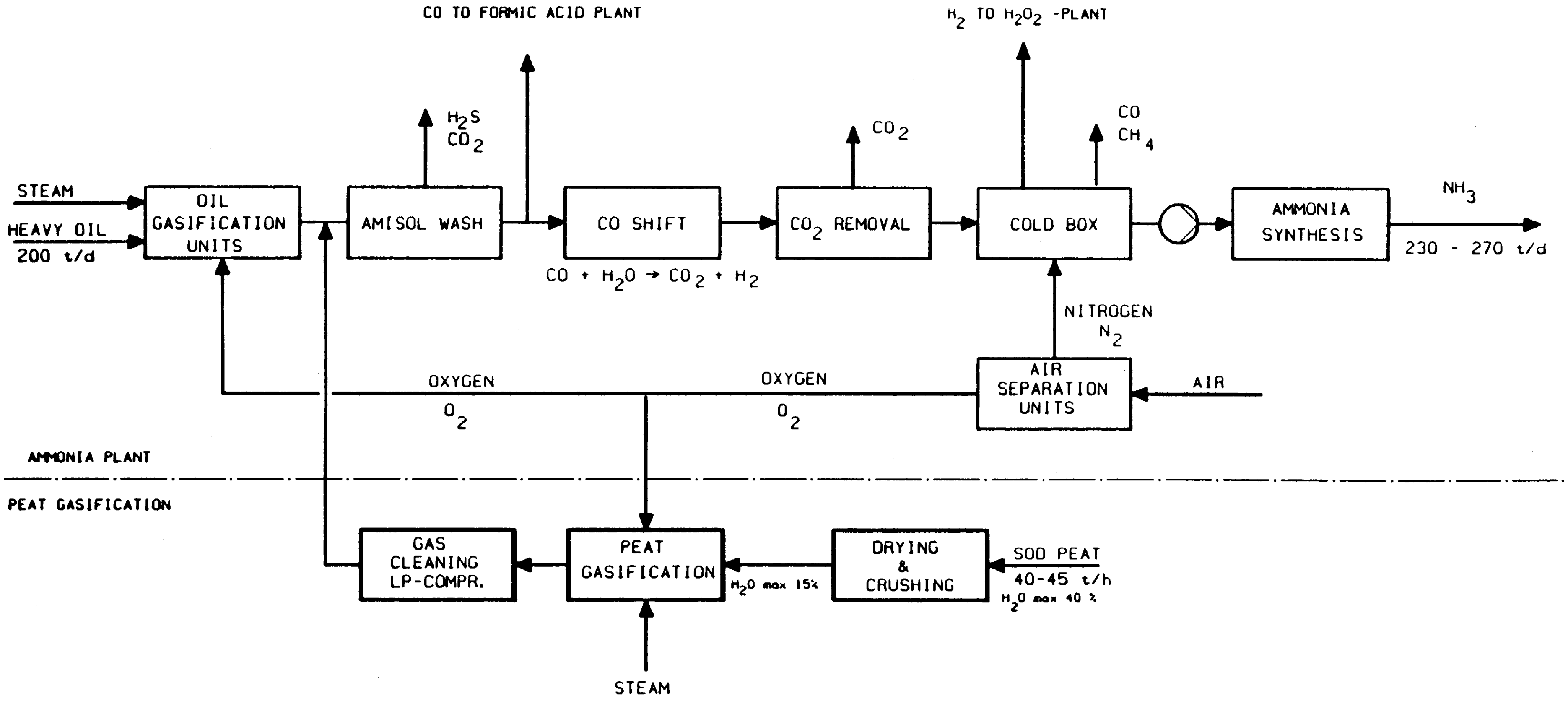

Figure 1. Integration of peat gasification to the existing ammonia plant of Kemira Oy at Oulu.

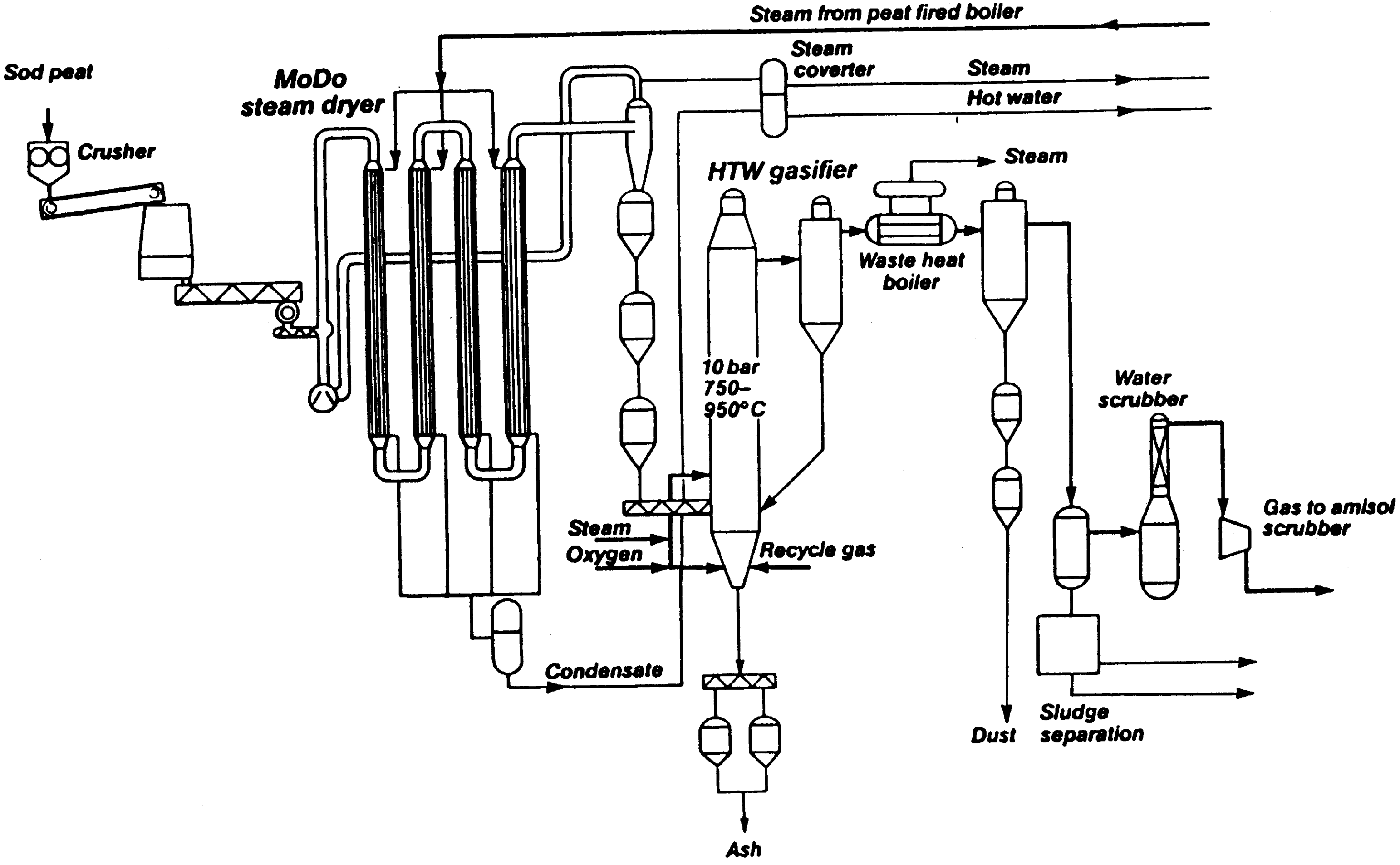

Figure 2. Flow diagram of peat drying and gasification.

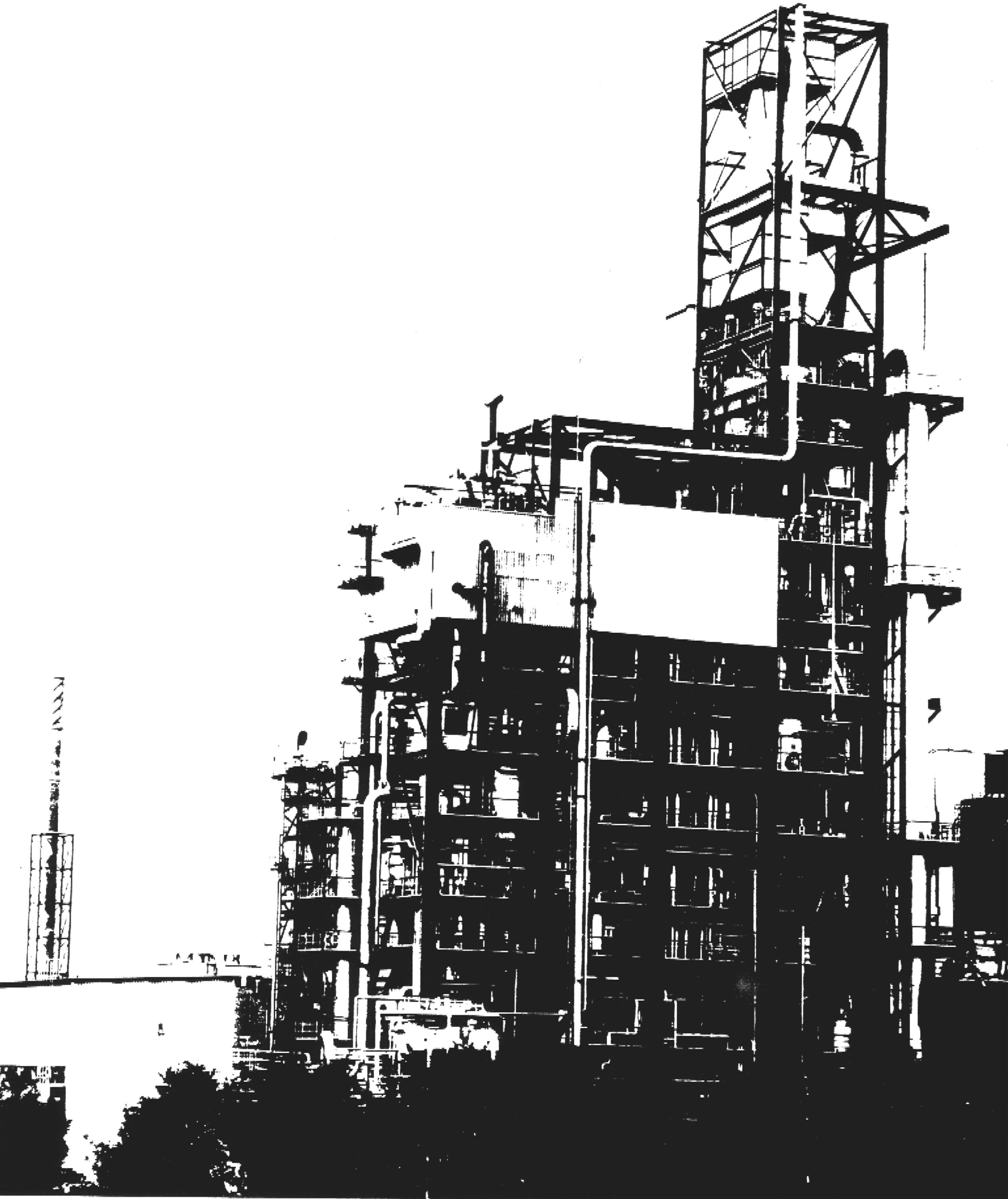

Figure 3. Kemira's peat gasification plant at Oulu. The highest point is about 65 meters above the earth level.

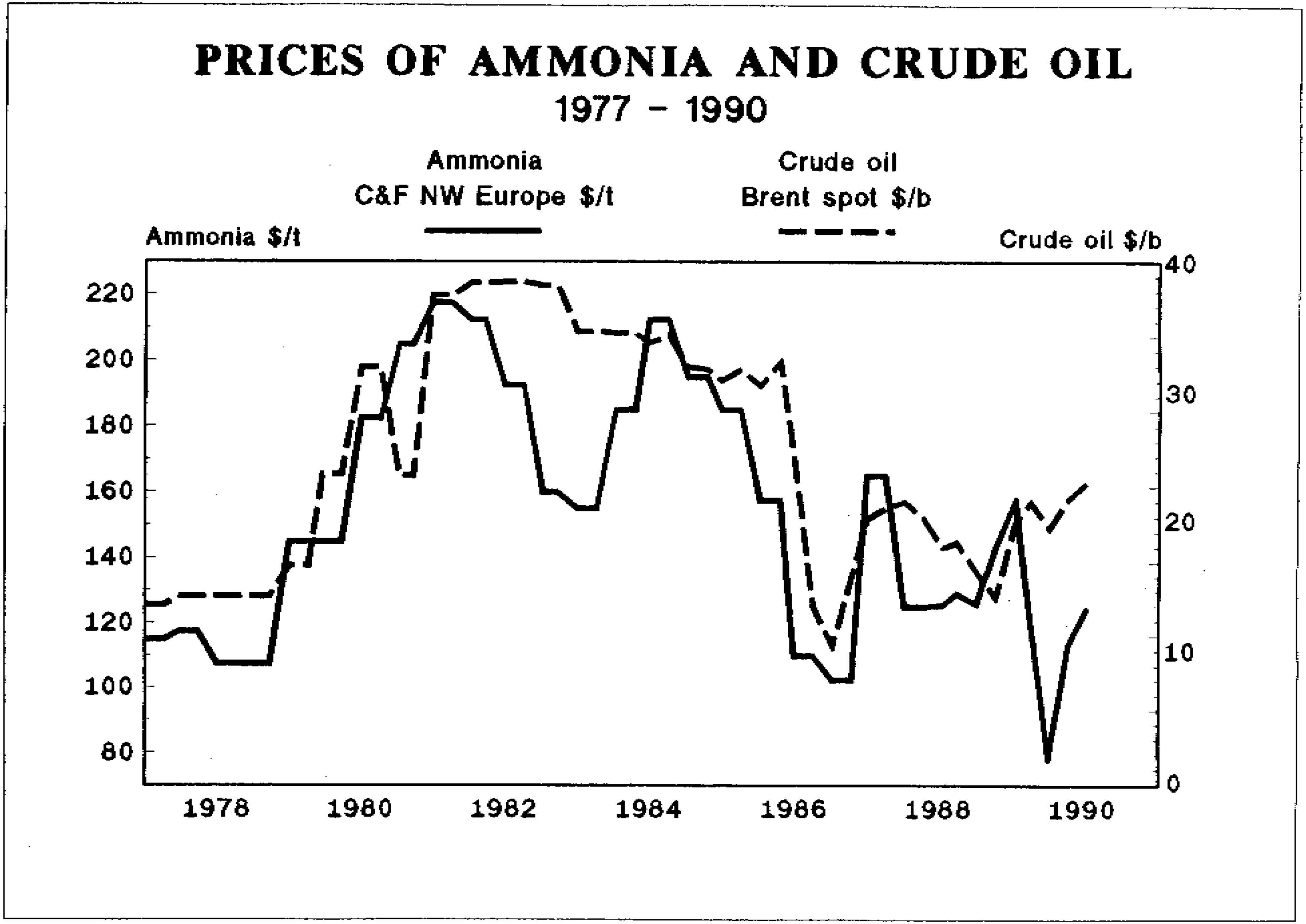

Figure 4. Prices of ammonia and crude oil in 1977-1990