

Kinhill-Otto Gold and the Directorate of Coal gave priority to North West Banko and North Suban Jeriji in Banko area, and they carried out feasibility studies on the former and pre-feasibility study on the latter.

The joint survey team between BPPT-PPTM/JICA also carried out a preliminary survey, for the purpose of finding proper coal sampling places, as stated in 6-1-3. The comparative merits of the coal deposits within the said area were investigated briefly based on the survey results, consulting with existing data and information.

(1) Movable Coal Reserves Planned to Be Mined and Stripping Ratio

Movable coal reserve planned to be mined and stripping ratio within North West Banko and North Suban Jeriji are as follows.

	Movable coal reserves planned to be mined	Stripping ratio
North West Banko	164 million tons	2.34 m ³ /ton
North Suban Jeriji	100	1.60 m ³ /ton

Movable coal reserves will increase if mining faces sink down to lower level, however it is a matter of course that the stripping ratio will rise in such a case.

(2) Coal Quality

Coal seams in the Banko area belong to a M₂ sub-division of Enim formation. Both M₂ and M₄ sub-divisions exist in Suban Jeriji area and the coal seams in North Suban Jeriji belong to M₄ sub-division.

It is said that coal seam of M₄ is worse than M₂ coal so far as quality is concerned generally, and it may be given as a conclusion that coal in North West Banko is superior to another coal, although sodium oxide contents in the ash is rather high.

Discussion on the merits and demerits of each coal from the viewpoint of moisture, ash and sulphur contents, calorific value and ash component (especially sodium oxide contents) is given below, though it may be open to the criticism since the conclusions are based on a limited number of study results.

1) Moisture Contents

Among the above mentioned three areas, the highest in moisture content is North Suban Jeriji, Central Banko is in the middle and North West Banko is the lowest.

Total moisture contents are 23 - 32% in North West Banko, 33 - 38% in Central Banko and 42 - 44% in North Suban Jeriji.

2) Ash Content

Ash contents (dried base) are 2 - 7% in North West Banko, 6 - 17% in Central Banko and 3 - 12% in North Suban Jeriji. (North West Banko is the lowest in ash contents.)

3) Total Sulphur Contents (dried base)

There is not a sharp difference in total sulphur contents among the above mentioned three areas, it is less than 0.7%, so we can expect a certain coal seam in all areas.

4) Calorific Value (net)

Calorific value measurement of coal samples under the project were also carried out by PPTM. The results are as follows:

North West Banko	3,027 - 5,684 Kcal/kg
Central Banko	3,754 - 4,307 Kcal/kg
North Suban Jeriji	3,502 - 4,289 Kcal/kg

It should be estimated that North West Banko is far superior to another and Central Banko comes to North West Banko, although not so big difference between Central Banko and North Suban Jeriji are found.

5) Ash Composition Analysis (Especially Sodium Oxide Contents in ash)

It is common knowledge that high sodium oxide content in coal does severe harm to the boiler and 7,000 PPM of sodium oxide content in the coal is considered the yardstick of permissible limit.

Although high sodium oxide content in the coal substance more than the above mentioned yardstick was not observed among the coal samples for the coal gasification test (this might be as a result of obtaining coal samples at a rather shallow depth below the surface). Shell indicated that sodium oxide content in the coal was quite within the bounds of

permissability to cause severe problems of boiler damage when the pit goes down below 40 meters from the surface in case of North West Banko.

(3) Mining Cost

There is not so great a difference in mining cost of as mined coal, so far as North West Banko and North Suban Jeriji are concerned, as shown in 6-2-3.

(4) Environmental Impact

Influence on botany and the animal ecosystem will be unavoidable when big coal surface mines (including Bukit Asam coal mine) develop with the narrow limited areas around Muara Enim one after another.

Changing the water-course of existing rivers and channels may be needed and careful consideration will be made for both the mines and inhabitants within the exploited areas.

More detailed social and environmental investigation should be carried out before coming to the decision of developing a coal mine.

(5) Overall Evaluation as Energy Resources

The Directorate of Coal planned to prepare North West Banko area for a coal supply source to Suralaya Power Generation plant.

However, the matter including Sumatra mine mouth coal field steam power plant and relative transmission line system - including HVDC power transmission system (submarine cable) - was entrusted to the steering committee headed by Prof. Dr. Habibie, the chairman of BPPT and consisted the ministers or chairmans of

BAPENAS

Ministry of Mines and Energy

Ministry of Communication and Transportation

Ministry of Development of Domestic Product

Ministry of Trade

The above mentioned committee will also draw a final conclusion on the exploitation of the south Sumatra coal field and, east and south Kalimantan coal field which entered into a production sharing contract between PTB (state owned coal corporation) and foreign or indigineous capitalists.

North West Banko is superior to other areas as a energy source from the viewpoint of reserves, coal quality, mining cost and accuracy of exploration works.

And in Banko area it makes little difference regarding mining cost between North West Banko and North Suban Jeriji, however, North West Banko coal is the best coal within the said area.

7. RESULTS OF SURVEY ON UTILIZATION TECHNOLOGY FOR LOW GRADE COAL

7-1 TECHNOLOGY FOR COAL GASIFICATION

7-1-1 Coal Gasification Mechanism

In conventional combustion the carbon in the coal is essentially converted to carbon dioxide. In contrast, gasification consists of partial combustion with a deficiency of oxygen, generally 1/5 to 1/3 of the amount theoretically required for complete combustion to carbon dioxide and water. Carbon monoxide and hydrogen, which are combustible gases, are the most predominant products of gasification. In gasification only a fraction of the carbon in the coal is oxidized completely to carbon dioxide. The heat released by partial combustion provides the bulk of the energy necessary to break chemical bonds in the coal and raise the materials to reaction temperature.

As the chemistry of coal gasification is extremely complex and uncompletely defined, only a few of the important chemical reactions are discussed here.

When coal is subjected to gasification conditions (i.e. substoichiometric oxygen), it is firstly dried by evaporation of the surface and inherent moisture. As the temperature rises, devolatilization occurs, and the weaker chemical bonds are broken, and tars, oils, phenols and hydrocarbon gases are formed. The rate of the devolatilization products depends strongly on the conditions under which they are released. In fixed-bed gasifiers, devolatilization products exit the gasifier with the gas because of low temperature and lack of oxygen where they are released. In fluidized-bed, entrained-flow and molten-bath gasifiers, uniform high temperatures cause cracking of the hydrocarbons to occur. Also, oxygen reacts with the devolatilization products to produce hydrogen, carbon monoxide and carbon dioxide. This happens to the greatest extent in entrained-flow and molten-bath reactors with the production almost entirely of carbon monoxide, hydrogen and carbon dioxide.

Fixed carbon (char), which remains after devolatilization, is gasified by reaction with oxygen, steam, carbon dioxide and hydrogen, and the gases react among themselves to produce the final gas mixture. The water gas shift reaction is favored for control of reaction temperatures and importantly affects the H₂/CO ratio but has little effect on the heating value of the product.

Fig. 7-1-1 shows important gasification reactions.

$C + O_2 = CO_2$	(exothermic--predominates at low temperature)	①
$C + 1/2O_2 = CO$	(exothermic--predominates at high temperature)	②
$C + H_2O = CO + H_2$	(endothermic--slower than above reactions)	③
$C + CO_2 = 2CO$	(endothermic--slower than above reactions)	④
$H_2O + CO = H_2 + CO_2$	(exothermic shift--rapid)	⑤
$CO + 3H_2 = CH_4 + H_2O$	(exothermic methanation)	⑥
$C + 2H_2 = CH_4$	(exothermic methanation)	⑦

Fig. 7-1-1 Principal Coal Gasification Reaction

The first five reactions are the most prominent in the gasification systems. Reactions ① and ② are combustion of carbon which is produced by the pyrolysis of coal. Reactions ③, ④ and ⑤ are called 'water-gas', 'producer-gas' and 'shift' reaction, respectively.

Water-gas reaction ③ prefers higher temperature, and, above 1,100°C, chemical equilibrium shows carbon-monoxide and hydrogen as dominant components, while lower the reaction temperature, more carbon-dioxide. Producer gas reaction ④ also becomes favorable at higher temperature of above 900°C.

The methanation reactions (the last two reactions) are favored by high pressures and low temperatures, but in most cases methane concentration is higher than equilibrium would predict because methane is also formed during devolatilization. Methane formation increases the thermal efficiency of gasification and the heating value of the product, while it is not preferable for production of synthesis gas.

Fig. 7-1-2 shows gas composition on equilibrium temperature at the pressure of 1 bar, 20 bar and 100 bar, respectively.

The rate of trace elements such as sulfur and nitrogen is also important. Sulfur in coal is converted primarily to H₂S under the reducing conditions of gasification. Approximately 5 to 15% of the sulfur is converted to COS, which adds some additional complexity to the gas clean-up step but can be handled by commercially available systems.

High temperatures and low pressures favor conversion of nitrogen in coal to N_2 , while the opposite conditions favor conversion of some of the nitrogen to NH_3 . Small amounts of HCN are also formed. Tars, oils, and phenols, if they are not destroyed, contain some of the oxygen, nitrogen, and sulfur from the coal as more complex molecules.

7-1-2 Classification of Coal Gasifier

More than ten of advanced coal gasification technologies have been developed since the first oil crisis mainly in U.S.A., W. Germany, England and Japan, and are evaluated to be ready for commercialization.

Gasification processes may be classified in a number of ways such as heat content of the produced gas, gasifying agents employed, ash removal methods and method of gas-solid contact etc.

However, the most widely used classification is based on the mode of contact between coal particles and gases. The four main types of gasification process under this mode of classification are fixed bed, fluidized bed, entrained bed and molten iron bath.

- (a) Fixed bed gasifier
- (b) Fluidized bed gasifier
- (c) Entrained flow gasifier
- (d) Molten iron bath gasifier

Fig. 7-1-3 shows the classification of principal coal gasification process and Table 7-1-1 to Table 7-1-4 show the typical performance of each gasification process.

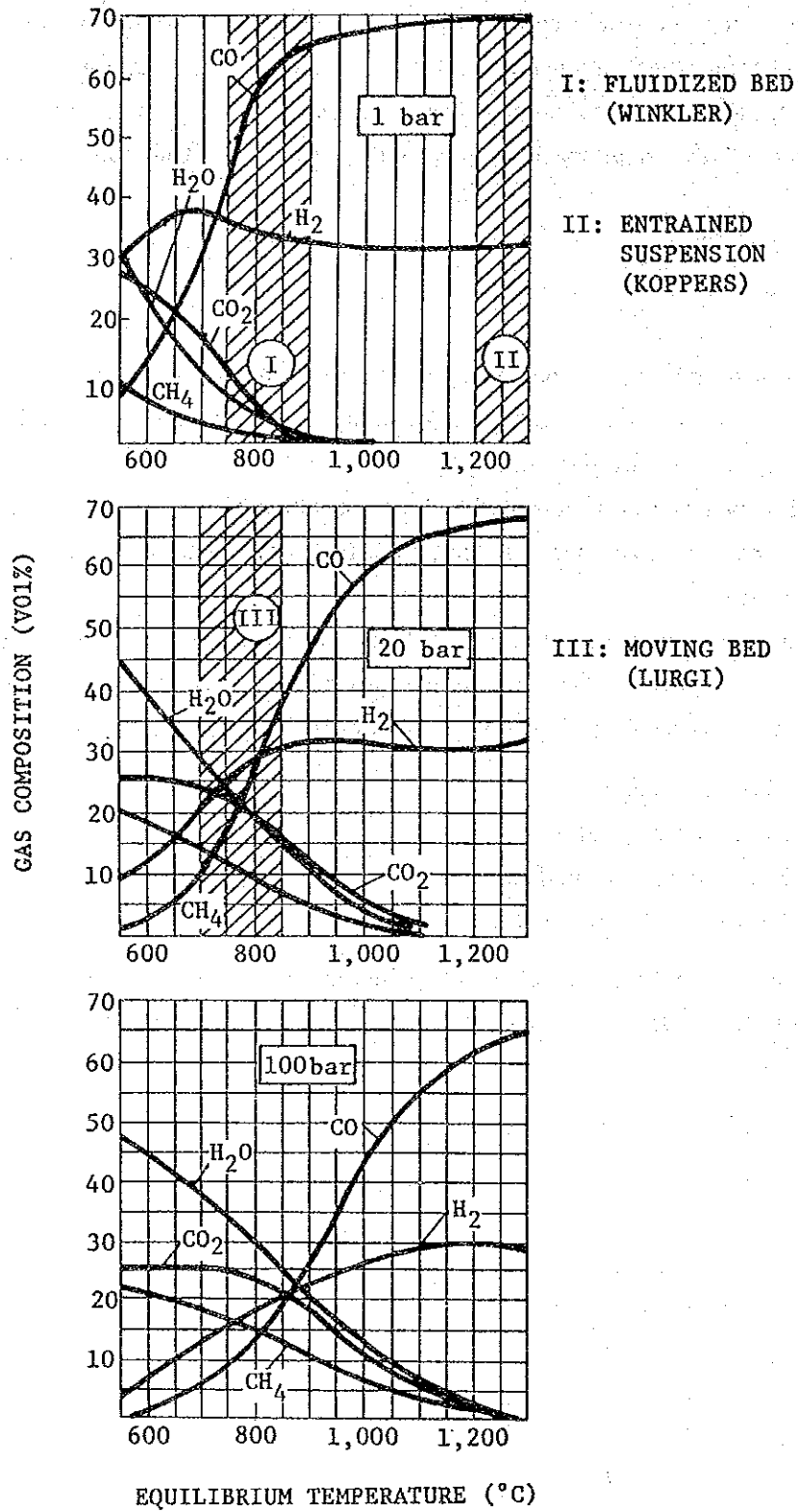


Fig. 7-1-2 Gas Composition on Equilibrium Temperature

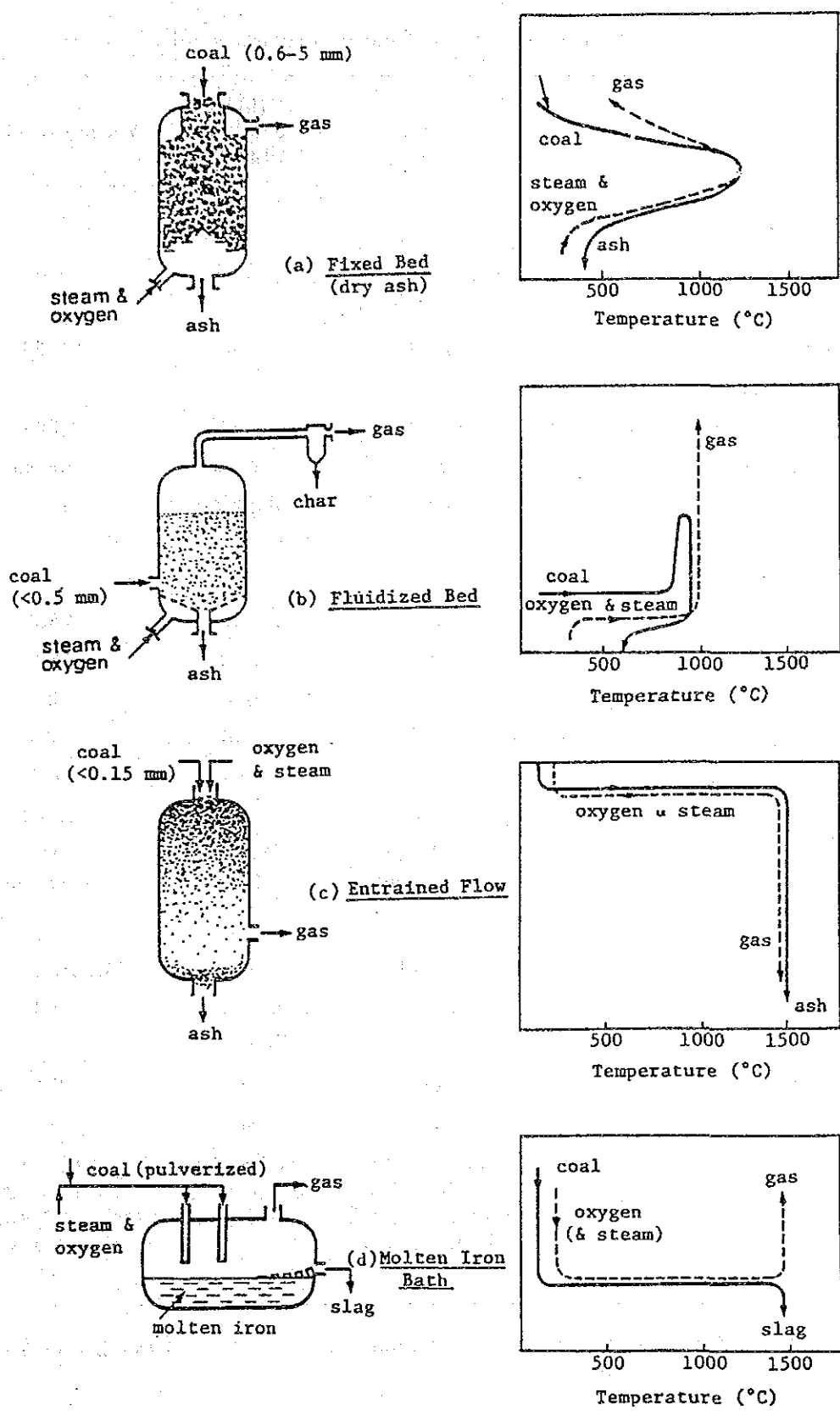


Fig. 7-1-3 Classification of Principal Coal Gasifier Types

Table 7-1-1 Performance of Gasification Processes -FIXED BED-

	Lurgi	B.G. Slagging Lurgi	Wellman-Galusha
1. Coal specification			
(a) Rank	Non-caking to mildly caking	All*1	All
(b) Size (mm)	6-40	6-40	25-50
2. Gasifier condition			
(a) Operating temperature (°C)	700-900	1,500	1,000
(b) Pressure (bar)	20-30	20-30	Atomospheric
(c) Ash removal type	Dry	Slagging	Dry
3. Gas properties			
(a) Composition (vol.%-dry)			
CO	19.0	61.0	28.6
H ₂	39.0	28.0	15.0
CO ₂	30.0	2.6	3.4
CH ₄	11.0	7.6	2.7
N ₂ & others	rest	rest	rest
(b) Heating value (kcal/Nm ³)	2,247	3,290	1,500
4. Gasifying medium	Air/Oxygen & Steam	Oxygen & Steam	Air & Steam
5. Specific consumption			
(a) Oxygen (Nm ³ /t-coal)	220-300	247	Air/Steam=6.0
(b) Steam (t/t-coal)	1.0-1.5	Less than non-slagging type	0.6
6. Carbon conversion (%)	85	99	NA
7. Thermal efficiency (%)	75	68	NA
8. Process developer	Lurgi Kohle & Mineralol-technik GmbH, W. Germany	British Gas Corporation & Lurgi	McKwell-Wellman Co., Ohio, & Wellman Galusha Co., UK

(Note) *1 : All means all types of coal which are classified as caking, mildly caking and non-caking.

Table 7-1-2 Performance of Gasification Processes -FLUIDIZED BED-

	Two Stage F.B.	U-Gas	Hy-Gas
1. Coal specification			
(a) Rank	Non-caking	All	All
(b) Size (mm)	1.5	0-6 (-200 mesh not to exceed 10%)	0.15-2.4
2. Gasifier condition			
(a) Operating temperature ($^{\circ}$ C)	900-1,000	1,050	980
(b) Pressure (bar)	20	7-20	80
(c) Ash removal type	Dry	Agglomerate	Dry
3. Gas properties			
(a) Composition (vol.%-dry)			
CO	15.1	22.0	25.0
H ₂	15.8	14.0	30.0
CO ₂	12.1	6.0	25.0
CH ₄	3.6	3.0	19.0
N ₂	52.7	rest	rest
Others	0.7	rest	rest
(b) Heating value (kcal/Nm ³)	1,280	1,370	3,270
4. Gasifying medium	Air & Steam	Air/Oxygen & Steam	Oxygen & Steam
5. Specific consumption			
(a) Oxygen (Nm ³ /t-coal)	Air 1800	NA	200-225
(b) Steam (t/t-coal)	0.71	NA	1.1
6. Carbon conversion (%)	97.8	98	98
7. Thermal efficiency (%)	75.8	NA	NA
8. Process developer	CMRC EPDC NEDO JAPAN	Institute of Gas Technology (IGT), Chicago Illinois, USA	I.G.T., Chicago, Illinois, USA

(Note) CMRC: Coal Mining Research Center

EPDC : Electric Power Development Co., Ltd.

NEDO : New Energy & Industrial Technology Development Organization

Table 7-1-3 Performance of Gasification Processes -ENTRAINED BED-

	Koppers- Totzek	Texaco	Babcock & Wilcox
1. Coal specification			
(a) Rank	All	All	All
(b) Size (mm)	-0.1	-0.1	-0.1
2. Gasifier condition			
(a) Operating temperature (°C)	1,800-1,900	1,320	1,650-1,850
(b) Pressure (bar)	1	20-80	1-20
(c) Ash removal type	Slagging	Slagging	Slagging
3. Gas properties			
(a) Composition (vol.%-dry)			
CO	52.5	46.5	65.3
H ₂	36.0	33.1	27.9
CO ₂	10.0	19.0	5.0
CH ₄	-	0.1	-
N ₂ & others	rest	rest	rest
(b) Heating value (kcal/Nm ³)	2,550	2,250	2,680
4. Gasifying medium	Oxygen & Steam	Oxygen & Steam	Oxygen & Steam
5. Specific consumption			
(a) Oxygen (Nm ³ /t-coal)	540	700-800	600-700
(b) Steam (t/t-coal)	0.1-0.5	0.7	0.2
6. Carbon conversion (%)	96	90	80
7. Thermal efficiency (%)	75-85	70-85	NA
8. Process developer	Heinrich Koppers	Texaco Development	US Bureau of Mines

Table 7-1-4 Performance of Gasification Processes -MOLTEN IRON BATH-

		MIP
1.	Coal specification	
	(a) Rank	All
	(b) Size (mm)	-0.1
2.	Gasifier condition	
	(a) Operating temperature (°C)	1,300-1,600
	(b) Pressure (bar)	3
	(c) Ash removal type	Slagging
3.	Gas properties	
	(a) Composition (vol.%-dry)	
	CO	63.7
	H ₂	34.5
	CO ₂	1.0-3.0
	CH ₄	-
	N ₂ & others	rest
	(b) Heating value (kcal/Nm ³)	2,800
4.	Gasifying medium	Oxygen & Steam
5.	Specific consumption	
	(a) Oxygen (Nm ³ /t-coal)	450-500
	(b) Steam (t/t-coal)	nominal
6.	Carbon conversion (%)	98
7.	Thermal efficiency (%)	75-85
8.	Process developer	Sumitomo Metal Ind., Ltd., Japan KHD Humboldt Wedag AG, W. Germany

7-1-3 Technology Available for Banko Coal Utilization

(1) Technology for Synthesis Gas Production

According to the results on preliminary survey on market the most prospective markets of produced gas are feedstock for synthetic fuel oil, fuel methanol and urea, which are derived from synthesis gas.

At the same time, from the results of survey on Banko coal quality, followings are pointed out as the general features of Banko coal.

- high total moisture
- low calorific value
- high volatile material
- non coking coal
- high Na_2O content in ash and a wide range of ash fusion temperature
- quite brittle and difficult to get lump coal

Taking into consideration the above-mentioned Banko coal features, oxygen blow coal gasification technology for production of synthesis gas was evaluated in miscellaneous and overall points of view.

i) Availability for Banko Coal

Banko coal has a wide variety of its quality, sodium content in ash and ash fusion temperature ($1,150^\circ\text{C}$ - more than $1,500^\circ\text{C}$). A molten iron bath gasifier has an enough flexibility for such a wide variety of coal. A fluidized bed gasifier follows next place. Other types of gasifiers have serious problems for Banko coal.

As shown in the Chapter 8, 20 kinds of Banko coal which were sampled at North West Banko, Central Banko and North Suban Jeriji were tested in the Puspipstek coal gasification test facilities.

Through these tests, it was proved that all kinds of Banko coal can be easily gasified by the molten iron bath gasification process.

ii) Gas Composition

Product gas coming from a typical gasifier contains generally hydrogen carbon monoxide, carbon dioxide, steam, methane, ethane, nitrogen and small amount of impurities. For production of derivatives, product gas will be treated to remove undesirable materials for synthesis reaction such as carbon dioxide and impurities.

However, methane, ethane and nitrogen are difficult to remove, and therefore accumulated gas in synthesis reactor must be purged from the synthesis process. As obvious from the above discussion, the most desirable gas composition of product gas is a mixture of hydrogen and carbon monoxide, and other materials are undesirable components.

As seen in Table 7-1-9, product gas from the molten iron bath gasification process shows extremely high content of CO and H₂ with less undesirable gas components.

In view of product gas composition, an oxygen blow-molten iron bath gasifier is the most superior for synthesis gas production and an oxygen blow-entrained flow gasifier follows.

An oxygen blow-fixed bed gasifier and a fluidized gasifier are not suitable for the purpose of synthesis gas production, because the product gas contains much undesirable materials.

iii) Impurity

Product gas contains a small amount of impurities such as hydrogen sulfide (H₂S), carbonyl sulfide (COS) and ammonia (NH₃) which are catalyst poison. Therefore these impurities must be completely removed by chemical treatment.

In view of impurities, a molten iron bath gasifier has better performance, because 90% of sulfur contained in coal is absorbed into slag and iron dust. Moreover, NH₃ and HCN are not formed.

It is estimated that Banko coal can be gasified also by a fluidized bed gasifier though the produced gas is not suitable to synthesis purpose.

iv) Energy Efficiency

If outlet temperature of product gas from heat recovery system is assumed to be same level, energy efficiency of gasifier depends on each carbon conversion efficiency and amount of steam content in generated gas. A molten iron bath gasifier is superior to other type of gasifier because of the highest carbon conversion efficiency and less effluent steam.

An entrained flow gasifier shows the lowest energy efficiency because of coal/water slurry feed system.

v) Gas Pressure

Required gas pressure in synthesis reaction is generally higher than 30 kg/cm²G.

3 kg/cm²G of a molten iron bath gasifier is inferior to that of other gasifiers.

vi) Operatability and Safety

An entrained flow gasifier has no surplus carbon inside of gasifier. Therefore steady operation may be easily disturbed by minor deviation of feed rate of oxygen and coal. A molten iron bath gasifier holds surplus carbon in the molten iron and effluent carbon is negligibly small amount, therefore stability and safety can be achieved.

vii) Construction Cost

It is difficult to evaluate the construction cost, because concrete cost data are not investigated at the present. However, in view of simplified process flow scheme and low pressure operation, the construction cost of a molten iron bath process is expected to be cheaper, though the maintenance cost of refractory in the gasifier may be a little expensive.

viii) Commercial Experience

A molten iron bath process has no commercial experience, though many of similar type of commercial plants are operated in the steel industry.

All taking into the consideration, overall evaluation shows that oxygen blow molten iron bath gasifier is superior for production of synthesis gas from Banko coal.

High pressure molten iron bath gasifier (higher than 3 kg/cm²G) will be better, if such a technology will be developed.

Table 7-1-5 Evaluation of Coal Gasification Technology for Synthesis Gas Production

	Fixed bed (dry ash)	Fluidized bed	Entrained flow	Molten iron bath
Availability for Banko coal	10	1	10	1
Gas composition	5	5	2	1
Impurity	4	3	2	1
Overall thermal efficiency	3	2	3	1
Gas pressure	1	1	1	3
Operatability and safety	1	1	3	1
Construction cost	3	2	2	1
Commercial experience	1	1	1	2
Total	28	16	24	11
Overall evaluation (ranking)	4	2	3	1

(Note) Lower number is better in performance.

(2) Technology for Coal Gasification Combined Cycle Power Generation

The so-called "combined-cycle power generation" consists in a combination of gas and steam turbines in order to improve the thermal efficiency and various systems of it have been proposed and tried with the development of gas turbine.

On Coal Gasification Combined-Cycle (CGCC) for power generation, investigation and technical research have been worldwide promoted.

The technology of CGCC has been developed as the CGCC is environmentally acceptable and more advanced power generation system, and therefore the CGCC is required to have reliability and economic performance for its application to power generation.

CGCC technology includes not only coal gasification technology but also hot clean gas system and high temperature gas turbine.

However, the following major technologies are still under development work, and no performance is grasped and demonstrated at the present time.

- a) Hot dry type desulfurizer
- b) Hot dry type dust removal equipment
- c) High temperature gas turbine (1,300°C or higher)

Therefore the evaluation of coal gasifier for CGCC was carried out on the basis of assumptions that above a) - c) will be well developed in the near future:

i) Availability for Banko Coal

Overall evaluation shows that air blow-pressurized type of fluidized bed gasifier is superior for CGCC power generation, providing that the technical development of hot gas clean-up system will be completed at the level of proposed objective.

ii) Gas Pressure

The gas pressure for CGCC must be higher than 10 kg/cm²G. A molten iron bath gasifier gives atmospheric pressure gas, and therefore such a atmospheric pressure gas must be cooled down and then pressurized by a compressor, resulting very low energy efficiency as total CGCC system.

Other gasifier provide 20 kg/cm²G or higher pressure gas and such a gas can be sent to a gas turbine at hot-dry conditions without cooling down, resulting very high energy efficiency as total CGCC system.

iii) Oxygen Steam Consumption

Oxygen and steam used as oxidizing agent consume much energy for production. In view of oxidizing agent, an air blow gasifier is superior to an oxygen blow type.

iv) Tar Content

Tar must be removed to avoid fouling of hot dry type desulfurizer and dust removal equipment.

To remove tar from product gas, high temperature product gas must be cooled down to 200~300°C, resulting in loss of energy. Therefore a gasifier which does not produce tar is preferable for CGCC system.

v) Impurity

Sulfur compounds (H₂S, COS) produce sulfur dioxide at the gas turbine and cause air pollution. Therefore such a sulfur compound must be removed to the reasonable level to avoid air pollution by hot dry type desulfurizer.

In case of a molten iron bath gasifier, desulfurizer is not required, because 95% of sulfur is removed in the gasifier.

vi) Calorific Value

There is no difference in evaluation of gasifier, because a gas turbine can accept low calorific gas of 1,000 kcal/Nm³.

vii) Carbon Conversion

Higher carbon conversion is effective because higher energy efficiency can be achieved.

A fluidized bed gasifier and entrained flow gasifier have a subject on carbon recycle system, because the amount of effluent carbon is higher than other gasifiers

viii) Operatability and Safety

Electricity can not be stored. Therefore steady operation and safety are especially important in evaluation. A fluidized bed gasifier and a molten iron bath gasifier in which hold much surplus carbon show more steady and safety operation for deviation of feed rate of carbon and oxidizing agent.

ix) Construction cost

An air blow fluidized bed gasifier seems to be superior to other oxygen blow gasifier because an air separation plant is not required.

x) Commercial experience

A molten iron bath gasifier is inferior to other gasifiers.

Table 7-1-6 Evaluation of Coal Gasification Technology for CGCC Power Generation

	Fixed bed (dry ash air blow)	Fluidized bed (pressurized air blow)	Entrained flow (pressurized oxygen blow)	Molten iron bath (atm. pressure oxygen blow)
Availability for Banko coal	10	1	10	1
Gas pressure	1	1	1	10
Oxygen-steam consumption	1	1	4	3
Tar content	3	1	1	1
Impurity	3	2	2	1
Gas calorific value	1	1	1	1
Carbon conversion	1	2	2	1
Operatability and safety	2	1	4	1
Construction cost (including air separation)	5	1	4	3
Commercial experience	1	1	1	2
Total	28	12	30	24
Overall evaluation (ranking)	3	1	4	2

(Note) Lower number is better in performance.

7-1-4 Detailed Evaluation of Coal Gasification Technology

According to the previous discussion, it was preliminarily concluded that the desirable technology for producing synthesis gas was a molten iron bath process.

In this section, a more detailed technical performance of the both gasification processes by molten iron bath and entrained flow has been surveyed and the final

overall evaluation of the technology in commercial scale has been studied to select the coal gasification process for producing synthesis gas, which is the most suitable for Banko coal.

(1) Development and Current Status of Molten Iron Bath Process

Coal gasification in a molten iron bath is a logical extension of basic oxygen furnace (BOF) steel making technology.

The most promising of the development efforts is the Sumitomo/KHD cooperative program.

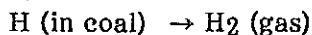
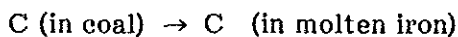
Sumitomo Metal Industries Ltd., Osaka, Japan and KHD Humboldt Wedag AG, Cologne, West Germany started the development individually, SMI with the top-blowing technology and KHD with the bottom-blowing technology.

The top-blowing technique has been developed by SMI since 1978. After achieving successful results in laboratory trials, SMI established a pilot plant with a nominal capacity of 60 t of coal per day in Kashima Steel Works being supported financially by the Japanese government.

The top-blowing technique provides for oxygen to be blown onto the iron bath at supersonic velocity through a specially designed lance together with CO₂ as a carrier gas. As in the BOF process, a dimple is created at the point where the jet hits the bath surface. This is where O₂ and coal are blown and come into contact with the molten iron.

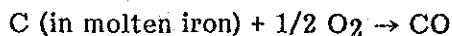
The reactions of injected oxygen and coal at the dimple are specific features of this process.

Gasification predominantly occurs within the iron bath. The coal impinging on the high temperature molten iron is cracked almost instantaneously into the carbon dissolving in the molten iron and the hydrogen liberated as H₂.

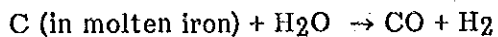
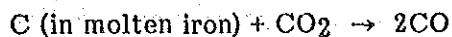


The gasification proceeds very rapidly, with the formation of CO by the reaction of oxygen and steam with the dissolved carbon.

It is estimated that the following reaction mainly takes place inside of the molten iron bath.



In case of CO₂ and/or steam injection for temperature control, the following reactions take place at the same time.



The molten iron bath process provides the following benefits:

- i) The molten iron bath completely cracks the blown coal in a short period of time and not only generates hydrogen gas but dissolves and absorbs the carbon produced by cracking.
- ii) The molten iron reacts with blown oxygen and carbon dioxide and becomes FeO, but this FeO is immediately reduced by carbon contained in the molten iron and becomes Fe while generating carbon monoxide gas.
- iii) Even if an excessive amount of coal is fed into the molten iron bath, the molten iron dissolves and absorbs an excessive amount of carbon preventing unoxidized carbon to escape from the gasifier.
- iv) Even if an excessive amount of oxygen is supplied, carbon contained in the molten iron bath reacts with excess oxygen preventing the generation of carbon dioxide gas.
- v) The molten iron dissolves and absorbs the sulfur contained in the coal and then transforms into the molten slag.

According to above mentioned activity of the molten iron, the basic principle of coal gasification mechanism of the molten iron bath gasifier is basically different from that of other gasifiers.

On the other hand, KHD has developed the bottom-blowing technique since 1975. Small scale pilot tests had been carried out in a steel converter of 6 tons iron at the metallurgical research institute (MEFOS), Lurea, Sweden. These tests were conducted for 2 years.

By using the bottom-blowing technique, coal, oxygen, flux and a cooling gas are injected continuously through tuyeres into the bottom of a liquid iron bath. A solid porous metal called "MUSHROOM" is formed above the tuyeres, which protects the tuyere tip. The exothermic oxidation of the iron at the gas/molten iron interface induces a relatively high temperature.

The liquid iron oxide formed outside of this mushroom is continuously transferred into the liquid iron bulk generating CO and H₂ through the decomposition of injected coal and the reaction with dissolved carbon in the molten iron.

The gasification reaction is strongly effected by the bath turbulence and the resulted wide dispersion of coal particle and iron oxide in the reactor.

following important advantages of molten iron bath coal gasification relative to other gasification systems were clarified.

- extremely high yield of CO and H₂ with less CO₂
- hot desulfurization by slag and iron dust
- essentially no NH₃ or HCN formation
- all types of coal and other carbonaceous materials are easily gasified.

In 1983 Sumitomo and KHD combined forces for larger scale testing and development of the process which was named Molten Iron Pure gas (MIP).

A proto-type test plant with a capacity of 240 t of coal per day was built at MEFOS in Lulea, Sweden.

The erection of the proto-type test plant was completed by August 1985.

Fig. 7-1-4 illustrates the schematic process flow of the proto-type test plant.

Table 7-1-7 shows the general design aspects of the plant.

Fig. 7-1-5 shows the reactor (gasifier) of the plant.

The reactor is designed for 240 t/d coal feed at 3 atmospheres pressure. The reactor is also designed for testing both top and bottom blowing operation.

Table 7-1-7 General Design Aspects of Proto-type Plant

Coal injection	240 t/d
Gas products	23,000 Nm ³ /h
Pressure in reactor	3 bar (absolute)
Blowing method	Top or bottom
Reactor	Drum type 4.4 mφ, 7.5 m length
Gas cooler	Boiler type 1,450°C to 400°C
Venturi scrubber	400°C to 60°C

The cylindric reactor is lined with special refractory and is equipped with several inlets for measuring and sampling purpose. The reactor has a diameter of 4.5 m, same scale of commercial size, and a length of 7.0 m, 1/2 to 1/3 scale of commercial size.

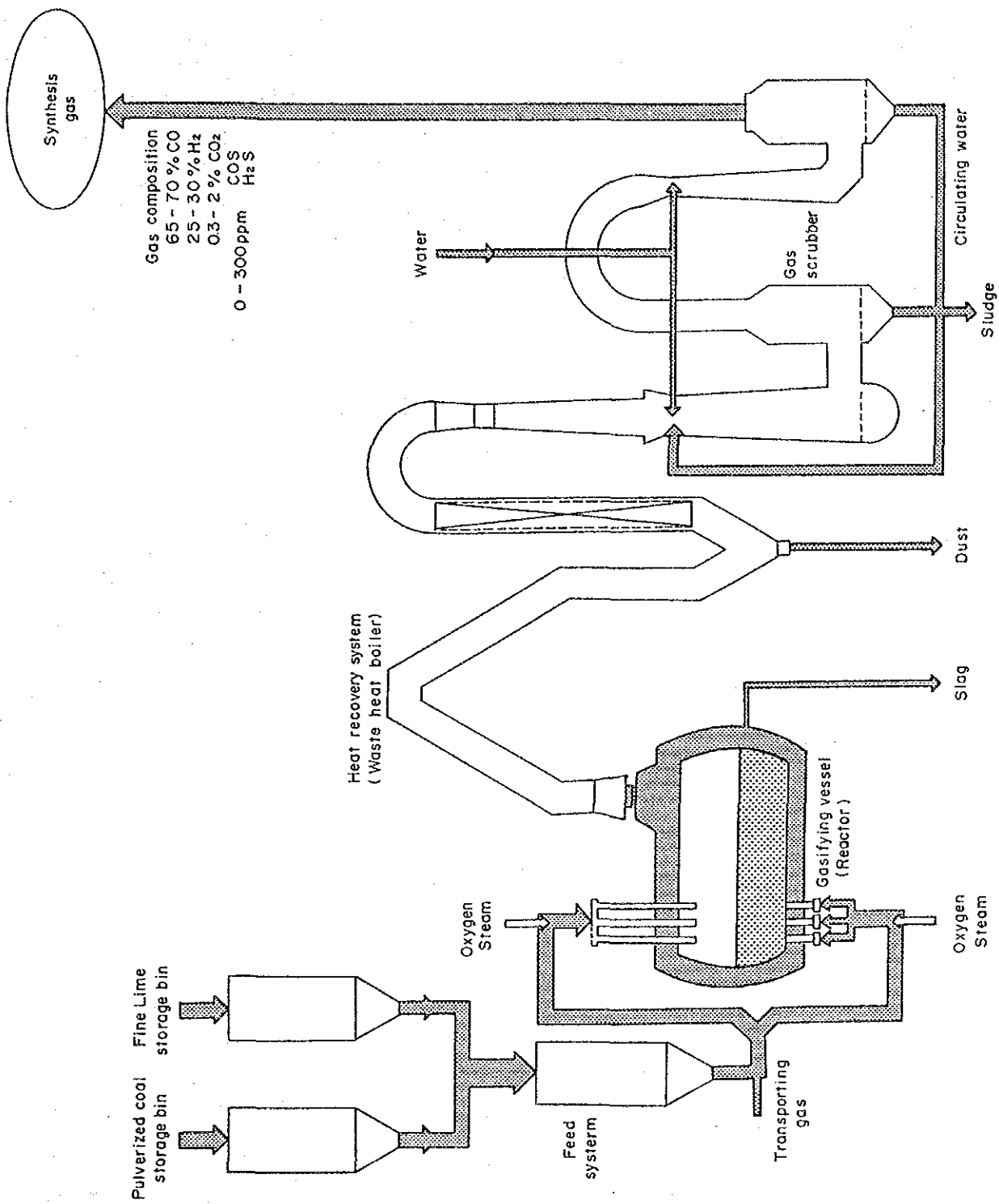


Fig. 7-1-4 Molten Iron Bath Coal Gasification Proto-type Plant (MIP Plant)

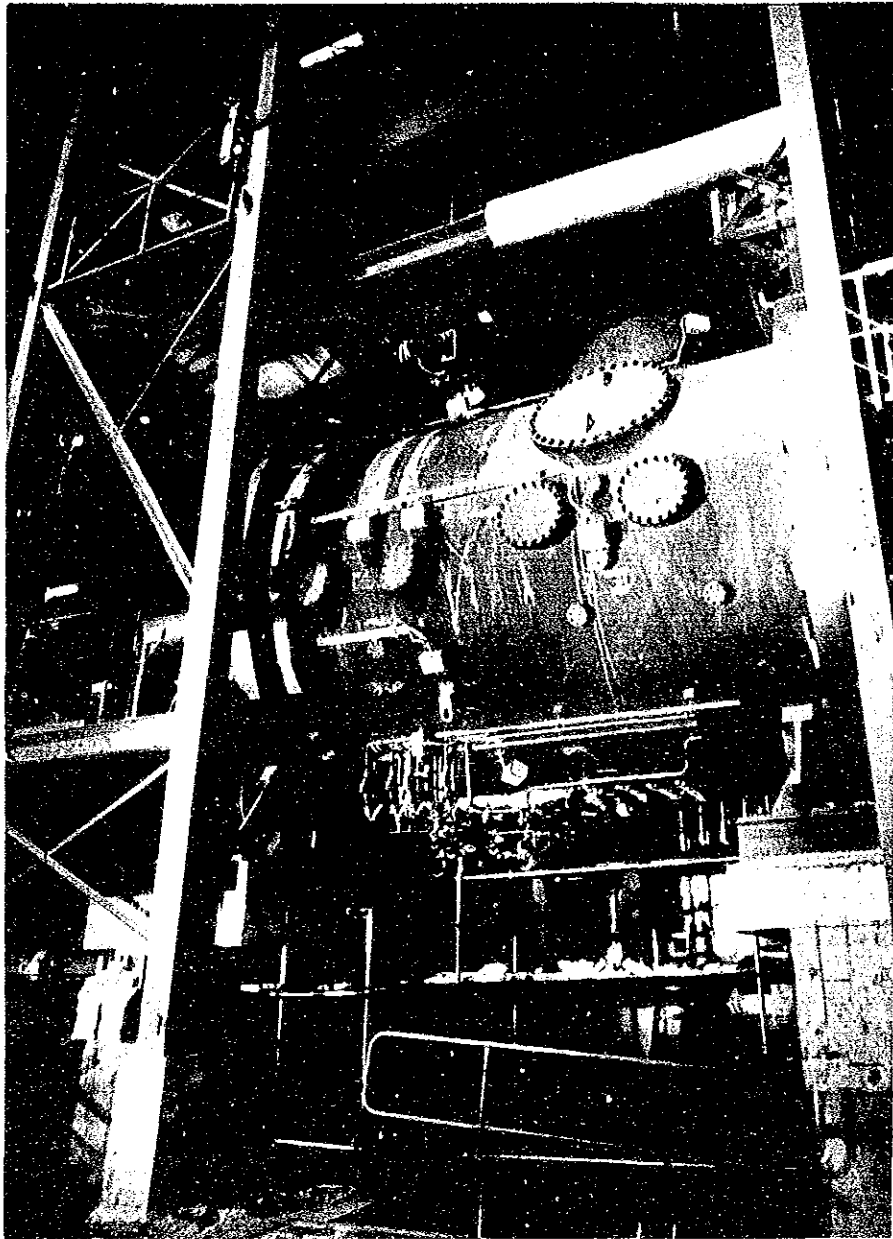


Fig. 7-1-5 Overview of the MIP Plant

Oxygen and coal are injected through top or bottom-blowing nozzles specially arranged at the reactor. Other materials required for the reaction, such as lime for adjusting the slag basicity and steam for temperature control can be supplied through the nozzle at the same time. The product gas leaving the reactor has a temperature of 1400° to 1500°C and is firstly passed over a cooler with heat recovery system and afterwards dedusted by a two-stage venturi scrubber.

The slag accumulated over the iron bath is removed as uniformly as possible using conventional slag discharging devices and then subjected to a secondary treatment.

Operation of the proto-type test plant was started in September 1985 and several bottom-blowing test campaigns have been conducted up to now.

Typical test results obtained are shown in Table 7-1-9.

Summing up the test results, it can be stated that all of the following mechanical facilities functioned well.

- coal and lime storage and mixing system
- coal injection system
- gasifier (reactor)
- produced gas recovery system
(waste heat boiler)
- gas scrubber
- measurement and control units

During the blowing periods the gasification system was stable. The deslagging under pressure was performed without interruption of the gasification operation.

The product gas contained 62~66% CO, 31~35% H₂ and 0.1~1.6% CO₂. In general, CO/CO₂ ratio in the product gas was higher in the gasification of higher grade coal than in case of lower grade coal, because excess oxygen is required, in case of lower grade coal, to keep the temperature of molten iron bath constant, resulting higher CO₂ formation.

The impurities in the gas were very low as shown in Table 7-1-9.

The gas quality is superior to those of all other coal gasification process.

The lower content of sulfur compounds in the gas and no tarly materials are one of the decisive advantages of the MIP coal gasification technology.

Because of the steady operation and mechanical reliability attained in the commercial scale proto-type plant, it can be expected that gasifier capacity of 1,500~2,000 t coal per day will be achieved in a commercial gasifier having 200~300 t of molten iron inside gasifier by enlarging the length of gasifier tested.

The both test results in the MIP proto-type plant and in PUSPIPTEK test facility (see Chapter 8) show that even lower grade coal such as Banko coal can easily be gasified by molten iron bath process in commercial scale plant.

Furthermore, a molten iron bath process has a unique feature. The iron dust from the gasifier is useful as a catalyst for coal direct liquefaction and various chemical processes.

Table 7-1-8 Composition of the Coal used in the MIP Plant

a) Ultimate Analysis

		Swedish Coal (A)	Swedish Coal (B)
Carbon	(%)	81.2	76.5
Oxygen	(%)	7.6	4.4
Hydrogen	(%)	4.7	5.7
Nitrogen	(%)	1.2	3.7
Sulphur	(%)	0.5	1.1
Ash	(%)	3.3	7.3
Moisture	(%)	1.5	1.5
Total	(%)	100.0	100.0

b) Ash Analysis

		Swedish Coal (A)	Swedish Coal (B)
Al ₂ O ₃	(%)	0.86	1.65
SiO ₂	(%)	1.11	3.77
CaO	(%)	0.29	0.21
Fe ₂ O ₃	(%)	0.58	1.44
K ₂ O	(%)	0.05	0.06
MgO	(%)	0.13	0.09
Na ₂ O	(%)	0.03	0.05
P ₂ O ₅	(%)	0.04	-
Others	(%)	0.21	-
Total	(%)	3.30	7.27

Table 7-1-9 Test Results Table

		Swedish Coal (A)	Swedish Coal (B)
Temperature of the iron bath	(°C)	1,350 - 1,400	1,380 - 1,440
% C in molten iron	(%)	3.6 - 4.1	4.1 - 4.7
Slag basicity		1.0 - 1.8	1.6 - 1.7
Coal injection	(t/h)	3.8 - 4.3	4.5 - 6.0
Coal/oxygen ratio		2.0	1.3 - 1.4
Gas pressure	(bar)	1.1 - 1.4	1.1 - 2.0
Gas composition *)			
CO	(%)	63.7 - 65.5	62.5 - 66.6
CO ₂	(%)	1.1 - 1.6	0.1 - 0.6
H ₂	(%)	32.8 - 35.2	31.2 - 34.7
H ₂ S - COS	(ppm)	10 - 40	Ca. 10

* dry & nitrogen free base

(2) Development and Current Status of Texaco Process

Initial development of the Texaco coal gasification process was conducted in the 1940s at Texaco's Montebello, California.

However, the availability of cheaper oil and gas in the late 1950s caused Texaco to direct its development efforts toward partial oxidation of oil and gas.

Because of favorable economics, over 80 commercial Texaco partial oxidation plant of oil and gas were constructed worldwide by 1982.

The oil price increases and supply disruptions after the first oil crisis have created interest in the Texaco partial oxidation process for gasification of coal.

Since the early 1970s, the research works at the Montebello laboratory have been concentrated on development of the Texaco coal gasification process.

Initial work was completed in the moderate pressure, 15 t coal per day gasifier at the site.

Since that time two additional gasifiers have been added at Montebello. Approximately 20 different coals have been tested in the last five years.

In 1977, Ruhrkohle A.G. and Ruhrchemie started up a 165 tons per day prototype plant at their Oberhausen-Holtent, West Germany. Development efforts at Oberhausen have been concentrated on the development of refractory materials, synthesis gas cooler and coal injection device.

The extensive research and development efforts undertaken at Montebello and Oberhausen over the last five years have provided a basis for scaling up the Texaco coal gasification technology to the commercial size gasifier.

Recently, Texaco coal gasification plants were adopted for the Tennessee Eastman methanol plant, Ube ammonia plant and the Cool Water gasification combined cycle power demonstration plant.

The gasifiers for the Tennessee Eastman plant, the Ube Plant and the Cool Water Project have a coal handling capacity of 900 to 1,000 t per day.

The plant in the Cool Water Project began to operate in mid-May, 1984 and has been operated successfully.

Fig. 7-1-6 is a schematic process flow of the pressurized, downflow, entrained Texaco gasifier. The feed coal is crushed and slurried in wet rod mills. The slurry water consists of recycled condensate from raw gas cooling together with make-up water. Carbon that is not converted in the gasifier can be recovered and recycled to the gasifier feed via the slurring operation.

The coal/water slurry is pumped into the gasifier burner together with oxygen. The gasification takes place rapidly at temperature in excess of $1,260^{\circ}\text{C}$ under which conditions the coal is converted primarily to H_2 , CO and CO_2 with no liquid hydrocarbons being found in the gas. The water in the coal slurry not only serves to convey the coal to the gasifier, but also moderates the gasifier temperature so that excessively high temperatures are not experienced.

The crude raw gas leaving the gasifier at $1,260\text{--}1,480^{\circ}\text{C}$ contains a small quantity of unburned carbon and a significant portion of molten ash. Depending on the end use, this gas stream would either be directly quenched in water (to cool the gas and remove solidified ash particles) or would be cooled in radiant and convection boilers for sensible heat recovery (via high-pressure saturated steam generation) prior to water scrubbing.

As mentioned above, in Texaco gasifier, coal/water slurry is fed to gasifier, so that in the case of low grade coal, higher excess oxygen is required to keep the minimum gasifier temperature, resulting in an extremely lower CO/CO_2 ratio of product gas.

Therefore, Texaco gasifier process is not suitable for gasifying low grade coals (low calorific coal).

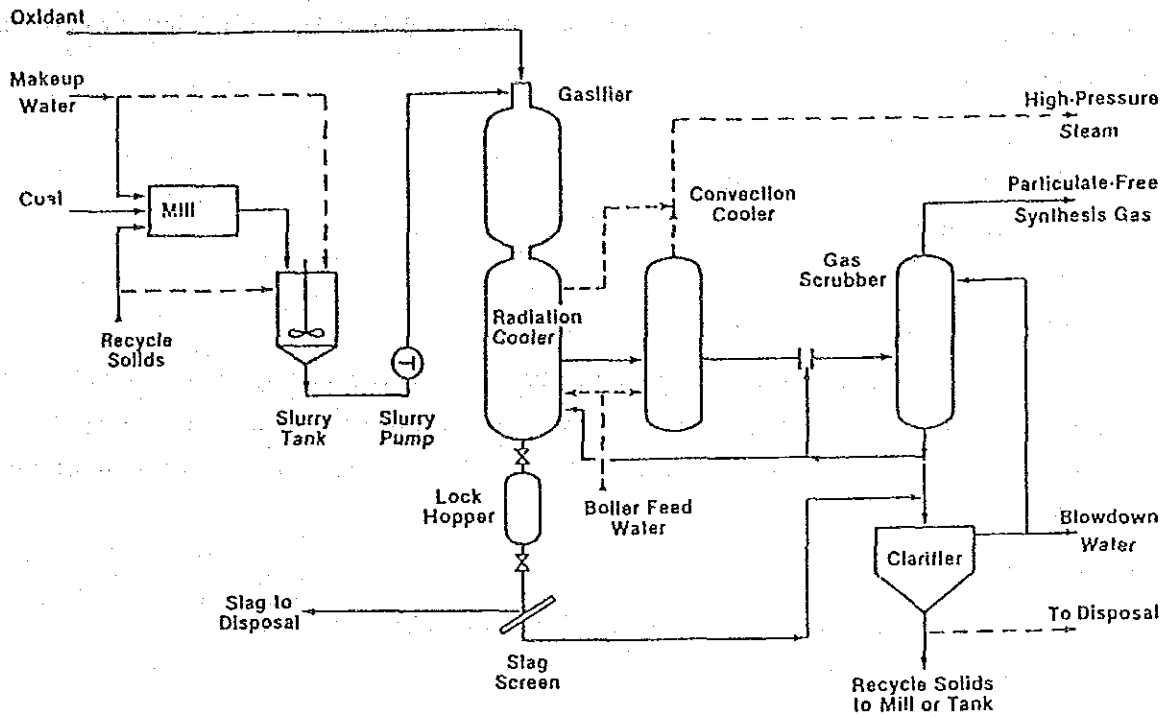


Fig. 7-1-6 Texaco Coal Gasification Process

7-2 TECHNOLOGY FOR DERIVATIVE PRODUCTION

7-2-1 Technical Possibility of Synthesis Gas Utilization

Synthesis-gas-based chemistry can roughly be classified into the following categories by chemical reaction.

- Alcohol synthesis
- Fischer-Tropsch (F/T) synthesis
- Oxo-synthesis
- Methanol-to-gasoline synthesis
- C₁ chemistry

In regard to alcohol synthesis, an excellent example of synthesis-gas-based chemistry, methanol synthesis has already been industrialized, while efforts are now being made for the development of fuel alcohol as well as higher alcohol to be used as chemical feedstocks.

Methanol is used in the following fields;

- Substitute fuel oil (Neat or Blend, MTBE and MTG feedstock)
- Chemicals feedstock
- SCP feedstock

F/T synthesis was put into practical use for gasoline synthesis with Fe-catalysts in the 1950s, but gasoline yield is low because olefin and alcohol are simultaneously produced. To increase the gasoline fraction or the diesel fraction, the development of improved processes are now under way.

Oxo-synthesis is to synthesize, from synthesis gas and olefin, aldehyde of which carbon number is larger than olefin by one. This process, which can also manufacture alcohol by hydrogenation, has already been industrialized.

Employing special zeolite as catalyst, Mobil developed a process to synthesize gasoline from methanol. The company also discovered that zeolite, used in the gasoline synthesis process, demonstrated excellent performances in aroma-synthesis and ethylene synthesis. At present, Mobil, BASF, AECI, Lurgi and Uhde are developing ethylene synthesis technologies.

Based on new catalyst technologies, such as rhodium and zeolite catalysts, involved in the aforementioned technologies, C₁ chemistry is now under development to produce such an oxygen-containing compound as ethanol, ethylene glycol and acetic acid.

Chemicals, to be directly processed from synthesis gas, as well as other utilizations of synthesis gas are illustrated in Fig. 7-2-1. Chemicals to be processed from methanol are also shown in Fig. 7-2-2. These figures are prepared regardless that processes have been already commercialized or under development.

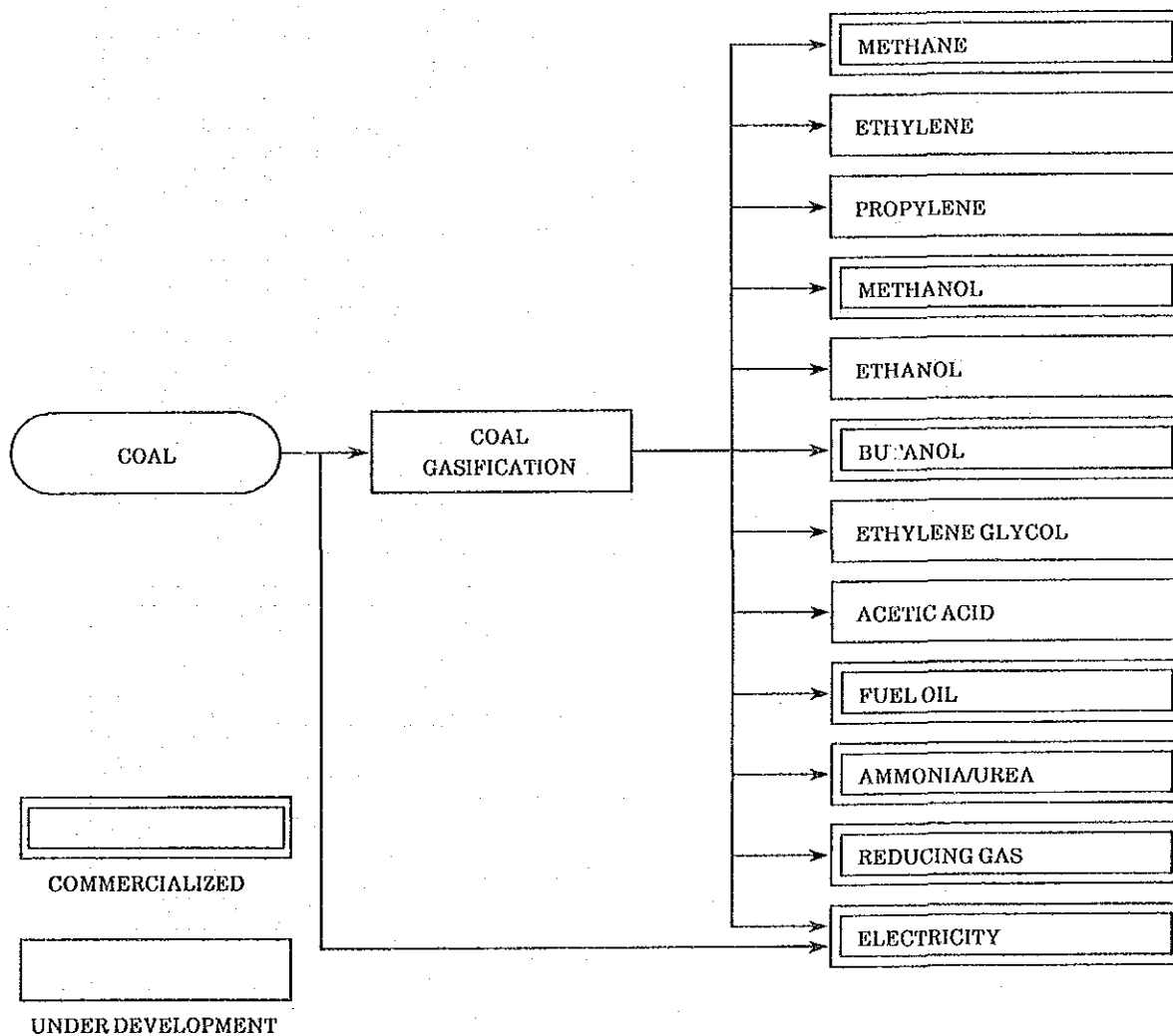


Fig. 7-2-1 Utilization of Synthesis Gas

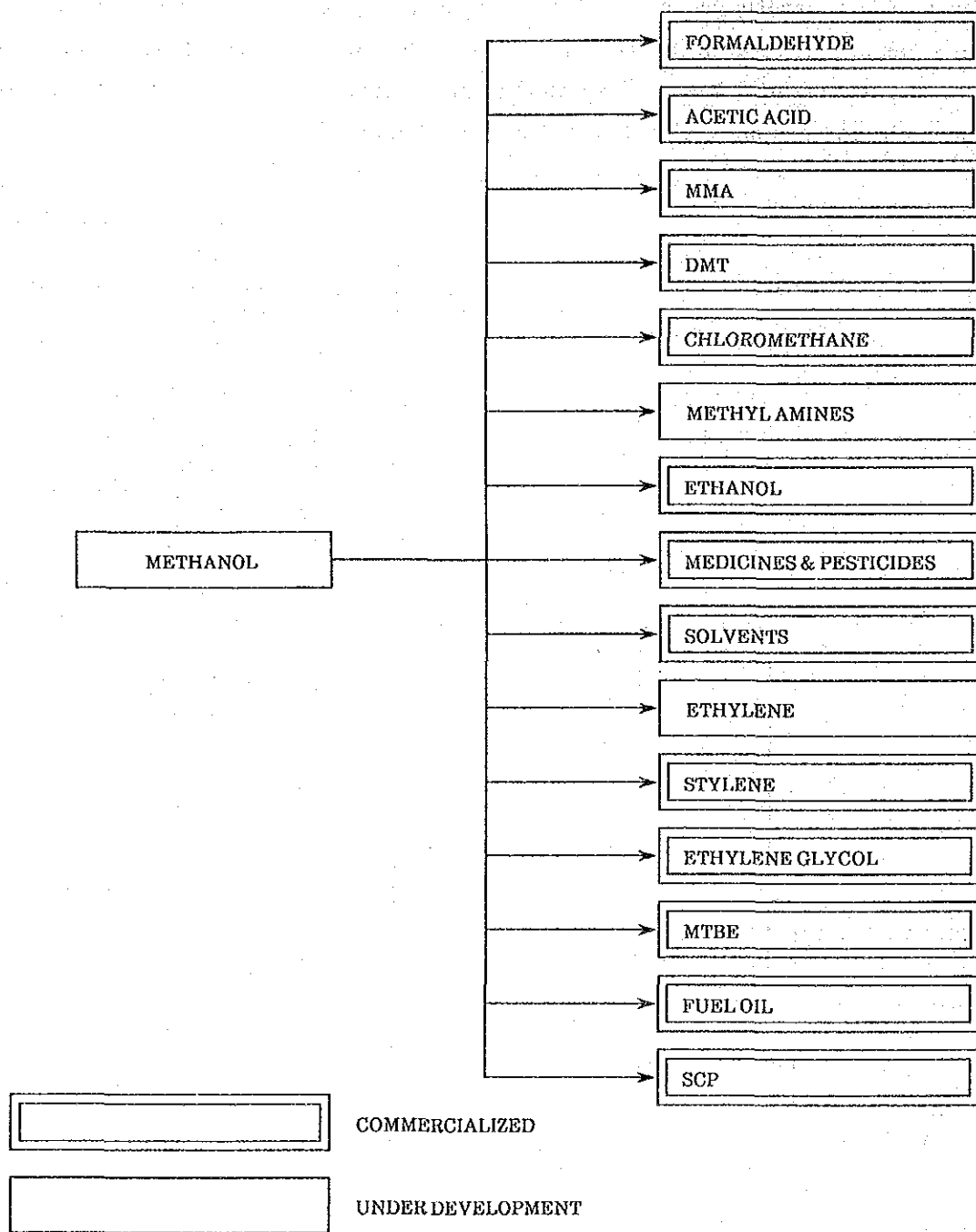


Fig. 7-2-2 Derivatives from Methanol

7-2-2 Production of Methanol

(1) Methanol Synthesis Process

1) Review on the Current Technology

Since the catalyst copper-zinc-aluminum was introduced by ICI (U.K.) in 1959, the lower pressure synthesis technology has completely replaced the higher pressure synthesis that had been applied in the world by the catalyst of zinc-chromium.

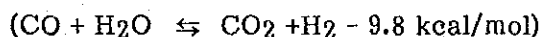
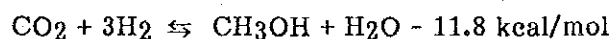
Succeeding to ICI, Mitsubishi Gas Chemicals Co. (Japan), Lurgi (West Germany), BASF and H. Topsoe have developed their own catalyst for the low pressure synthesis. All of these catalysts are different from the zinc-chromium, and they enable the synthesis in the range of 50 bar to 150 bar.

At the same time as the low pressure synthesis was commercialized, a centrifugal compressor was introduced to make larger a methanol plant capacity.

From the background of these technologies, the current prevailing capacity of a methanol plant ranges from 1,000 t/d to 2,500 t/d for the new investment of the plant construction and the synthesis pressure varies from 50 bar to 100 bar depending on the plant capacity. The higher synthesis pressure will be more economical for the larger scaled plant because of the compactness of the synthesis equipment.

2) Chemistry of Methanol Synthesis

Methanol is synthesized from CO, CO₂ and H₂ on the catalyst in gas phase through two main routes,



These reaction formulas show very simple and important factors that decide the energy efficiency and economic points, i.e.

- i) The higher pressure is preferable
- ii) The lower temperature is preferable
- iii) A lot of heat is generated

Reviewing on the reaction formulas, the stoichiometry for methanol synthesis is described in the ratio of hydrogen to carbon oxides as follows,

$$\text{Ratio} = \frac{[\text{H}_2]}{2[\text{CO}] + 3[\text{CO}_2]} = 1.0 \dots\dots\dots (\text{A})$$

or

$$\text{Ratio} = \frac{[\text{H}_2] - [\text{CO}_2]}{[\text{CO}] + [\text{CO}_2]} = 2.0 \dots\dots\dots (\text{B})$$

Either in the form of (A) or (B), the ratio should be theoretically 1.0 in (A) or 2.0 in (B).

Most of the synthesis gas from natural gas has the ratio of more than 1.0 in (A) because of the excessive amount of hydrogen in the process based upon natural gas. Generally 30% of hydrogen in excess of the stoichiometry is purged from the synthesis loop to be utilized as fuel in the reforming furnace.

On the other hand, in case of the heavy oil or the coal as feedstock for synthesis gas preparation, the produced synthesis gas has an excess of carbon oxides against hydrogen so that this excess carbon should be shifted to hydrogen through CO Shift Reaction as well as carbon dioxide which is removed in an acid gas scrubbing process. Therefore the stoichiometric ratio can be easily adjusted in case of the oil or coal gasification.

3) Methanol Converter

Once the synthesis gas is produced and purified to be sulfur-free, the synthesis process, which always form a loop, can be independently designed from the front-end synthesis gas preparation.

A reactor for methanol synthesis must meet the conditions given in Table 7-2-1. In terms of performance in particular, the reactor must present a good controllability of the catalyst bed temperature. In terms of thermostability, it must be capable of protecting the catalyst, while in terms of reaction rate, it must obtain the maximum conversion and recover the reaction heat as an energy at the highest possible level. In addition, uniform gas flow through the catalyst bed, low pressure drop and quick response to changes in operating conditions are required. Furthermore, conditions given in Table 7-2-1 for construction, material and maintenance must also be met.

Against these conditions to be met by a methanol synthesis reactor, those reactors which have so far proposed and which have presented satisfactory operational results on the level of practical application are classified into five types and shown in Table 7-2-2.

Type V is the new, double-tube type reactor proposed in this project. The characteristic features of each type are outlined below:

i) Type I

In this type of reactor, the catalyst bed is placed in multiple stages and, in each catalyst bed, the reaction proceeds adiabatically from the inlet to the outlet. The inlet temperature of each bed is controlled by quenching with the cold fresh gas, so that not only the temperature at the inlet, but also the concentration of methanol is lowered.

ii) Type II

In this type of reactor, the reaction proceeds adiabatically in each catalyst bed, like in Type I.

The heat of reaction is recovered by the waste heat boilers to a larger extent.

iii) Type III

This type aims at recovering the heat of the synthesis reaction in the form of high-pressure steam to the maximum possible extent. It is called a "tubular reactor". Compared with Types I and II, Type III gives a relatively high one-pass conversion and permits recovery of the reaction heat in the form of higher-pressure steam.

iv) Type IV

In contrast with Type III, Type IV comprises of a water tube boiler placed within the catalyst bed so as to recover the heat of reaction. Because of the complicated construction of the pressure vessel, this type of reactor involves difficulties in maintenance, such as inspection and repair.

v) Reactor is a simple, double-tube type vertical heat exchanger. The catalyst is packed in the annular space of each double tube and the boiler water circulates on the shell side. The feed gas flows first into the inner tubes from the bottom toward the top and is preheated by a part of the reaction heat in the catalyst bed. The preheated feed gas is collected in a top channel and then led into the catalyst bed from the top. The catalyst bed is cooled by the outside boiler water and by the feed gas on the inside. The gas flows in the catalyst bed and the inner tube are counter-current, and the temperature profile of the catalyst bed presents the highest temperature around at the inlet with a gradual decrease in temperature toward the outlet. This temperature profile is very favorable in terms of reaction rate and conversion. Higher conversion can be obtained with a smaller quantity of catalyst. As well-known, the methanol synthesis reaction, which is an exothermic reaction, proceeds with a higher conversion at a lower temperature and at a lower partial pressure of methanol from the point of view of the reaction equilibrium (the Le Chatelier's law). In addition, there is an ideal operational line giving the maximum reaction rate.

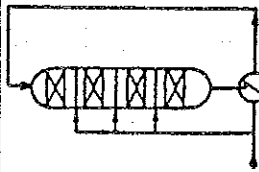
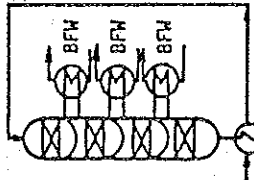
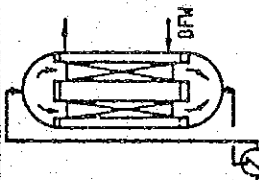
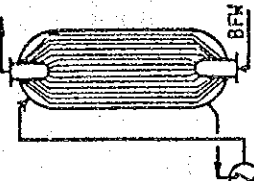
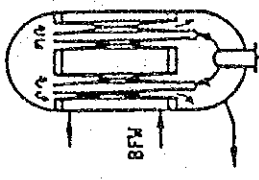
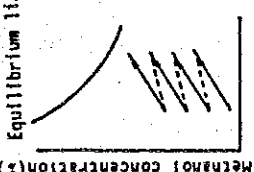
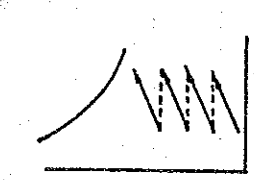
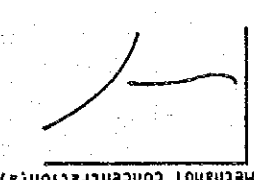
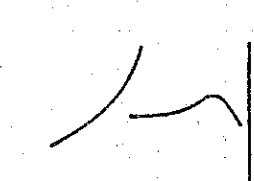
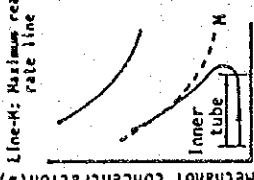
Schematic representation of these principles is given on the temperature-methanol concentration plane as shown in Table 7-2-2 and Fig. 7-2-3. In the reactor of Type V as shown in Fig. 7-2-4, the reaction can be generated while following the maximum reaction rate trajectory.

As a result, the methanol concentration at the reactor outlet can be raised remarkably.

Table 7-2-1 Conditions to be met by a Methanol Synthesis Reactor

Category	Item	Description
Performance	<ul style="list-style-type: none"> ◦ Flow ◦ Heat transfer ◦ Reaction ◦ Controllability ◦ Durability 	<ol style="list-style-type: none"> 1. Uniform distribution of gas in catalyst bed 2. Low pressure drop 3. High conversion 4. No occurrence of hot spot 5. Reaction heat recovery in the form of high-level energy, such as high-pressure steam 6. Quick response to change in operating conditions 7. Protection of catalyst against deactivation, crushing and abrasion
	<ul style="list-style-type: none"> ◦ Internal construction ◦ Tightness ◦ Thermal expansion ◦ Support 	<ol style="list-style-type: none"> 1. Simple and compact 2. No leakage between gas/coolant/outside 3. High space factor 4. Absorption of thermal expansion 5. Stable support of catalyst bed, boiler, etc.
Material	<ul style="list-style-type: none"> ◦ Strength ◦ Corrosion resistance ◦ Catalytic activity 	<ol style="list-style-type: none"> 1. Combination of materials with little differential thermal expansion 2. Resistance to carbonyl and hydrogen embrittlement 3. Prevention of impurities formation
Maintenance	<ul style="list-style-type: none"> ◦ Inspection ◦ Repair 	<ol style="list-style-type: none"> 1. Easy charging and discharging of catalyst 2. Inspection and repair possible

Table 7-2-2 Types of Methanol Synthesis Reactors

Type	I	II	III	IV	V
Reactor	Adiabatic quench type 	Interbed cooling type 	Tubular type 	Water tube cooling type 	Double tube type (Present) 
Features	<ol style="list-style-type: none"> 1) Simple structure 2) Low heat recovery 3) Higher rate of recycle gas 4) Low one-pass conversion 	<ol style="list-style-type: none"> 1) Simple structure 2) Higher heat recovery by waste heat boilers externally 3) Medium pressure steam generation 4) Higher one-pass conversion 	<ol style="list-style-type: none"> 1) High heat recovery 2) High pressure steam generation 3) Easy maintenance 	<ol style="list-style-type: none"> 1) Higher heat recovery 2) High pressure steam generation 	<ol style="list-style-type: none"> 1) Highest one-pass conversion (Closest to line-M) 2) Highest heat recovery 3) High pressure steam generation 4) Recycle gas rate less than half of conventional one 5) No special preheater
Temperature vs. Concentration	 <p>Methanol concentration (%)</p> <p>Temperature (°C)</p> <p>Equilibrium line</p>	 <p>Methanol concentration (%)</p> <p>Temperature (°C)</p>	 <p>Methanol concentration (%)</p> <p>Temperature (°C)</p>	 <p>Methanol concentration (%)</p> <p>Temperature (°C)</p>	 <p>Methanol concentration (%)</p> <p>Temperature (°C)</p> <p>Line-M: Maximum reaction rate line</p> <p>Inner tube</p>

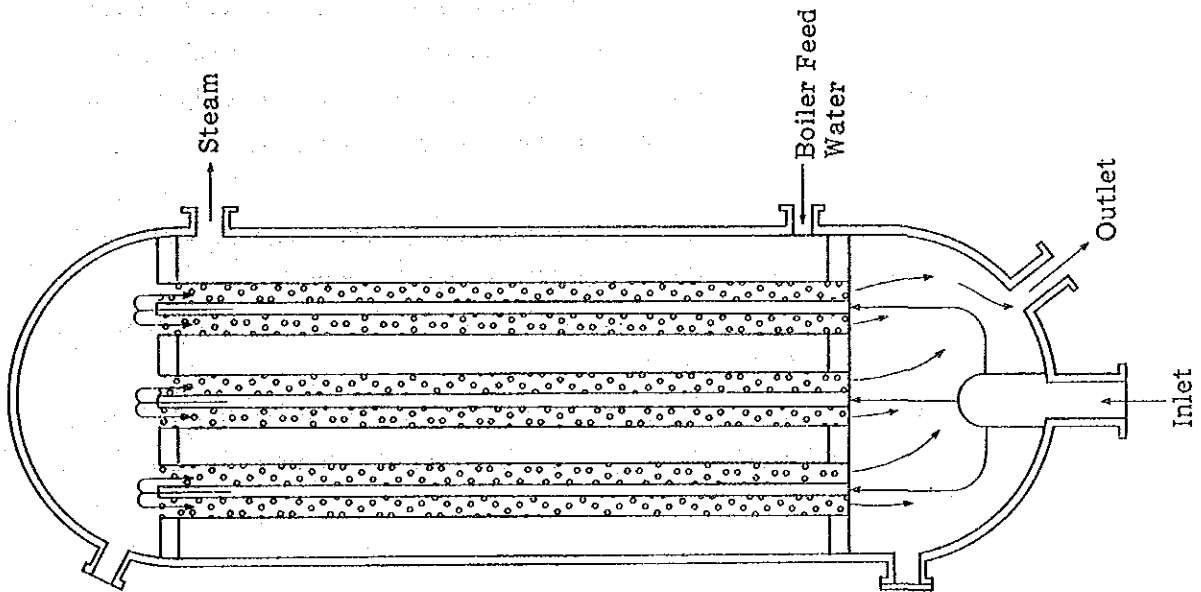


Fig. 7-2-4 Double Tube Type Reactor

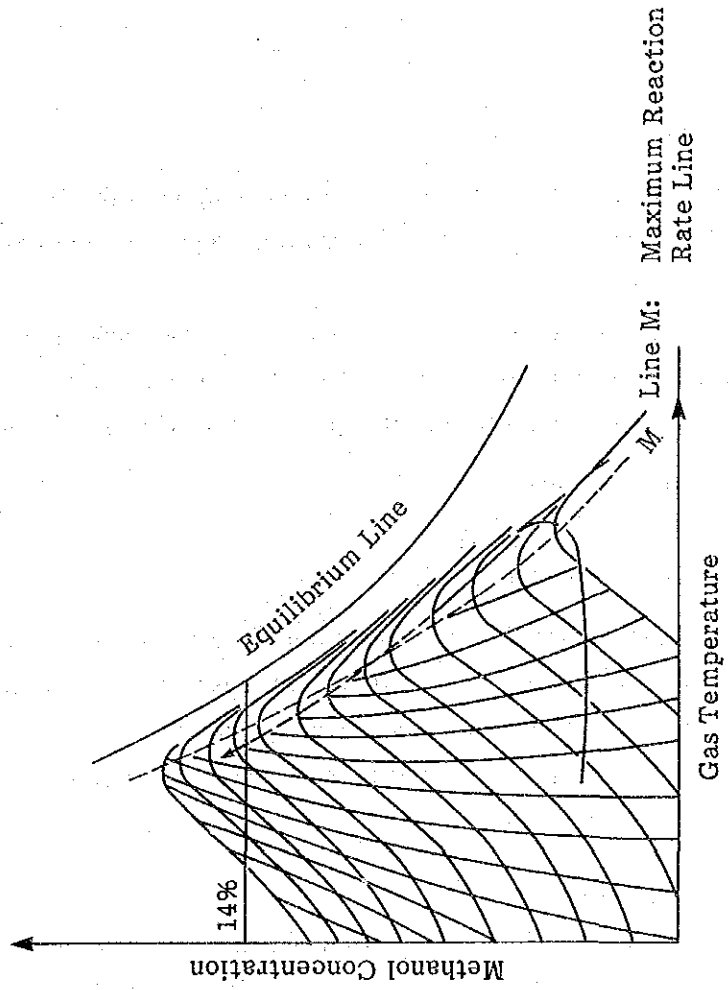


Fig. 7-2-3 Methanol Equilibrium Curve

4) Methanol Purification

Methanol produced from the synthesis loop contains water and impurities, so called "crude methanol", which shall be separated in distillation process with trayed columns.

Although the content of the impurities in the crude methanol depends on the catalyst of synthesis and the operating condition such as temperature and synthesis gas composition, the general composition is reported as follows:

- Dimethyl ether
- Higher alcohols
- Higher paraffin, etc.

and these impurities will make an azeotropic mixture with methanol and water. Therefore the distillation system is designed mainly for the separation of the impurities as well as water.

Overall process scheme and process description of methanol plant are given in Section 11-1-2.

5) Plant Capacity

As measures to introduce a fuel methanol it has been discussed how much the maximum size of the methanol plant could be constructed in a single train. It is very difficult to give a single solution to the issues because it needs always the discussion of the availability of the large-sized plant component in the world market, the transportation of large equipment and the production schedule relating to the annual turnaround or shutdown period.

The centrifugal compressor for synthesis gas compression can be designed to meet the capacity of more than 5,000 t/d in a single train.

The converter for methane synthesis can be also designed and manufactured of more than 2,500 t/d in a single train.

The refining column in the distillation can be easily made smaller in size as well as energy-efficient if it is split into two columns for the heat integration.

Through reviews on the major equipment in the methanol plant, they would not be always bottlenecks for scale-up of the plant. On the other hand the general plant component would be actually critical to make a large scaled plant in a single train because the pipes and valves, etc. are the standard components but not tailor made. The large sized high pressure valves will be expensive or it would not be available in the market.

Therefore it can be understood that the maximum size of the plant in a single train exists 2,000~3,000 t/d from the economical viewpoints although some components have to be split into two because of the transportation and the erection in such large scaled plant.

(2) Synthesis of Methanol Containing Higher Alcohols

In Europe, with the necessity of an octane booster, some major chemical and engineering companies such as Snamprogetti, I.F.P. and Lurgi have achieved their original processes to synthesize methanol containing higher alcohols (C₂ - C₅ alcohols) from synthesis gas. In the U.S., Dow Chemical developed sulfur-resistant catalyst which is applicable to synthesis gas from coal. In Japan, RAPAD (Research Association for Petroleum Alternative Development) developed Ni catalyst which produces much higher alcohols than other developing processes in the product and confirmed with pilot plant.

Fig. 7-2-5 gives a flow diagram of Snamprogetti process showing mixed alcohol production from synthesis gas.

Typical data under various operating conditions for each process are shown in Table 7-2-3.

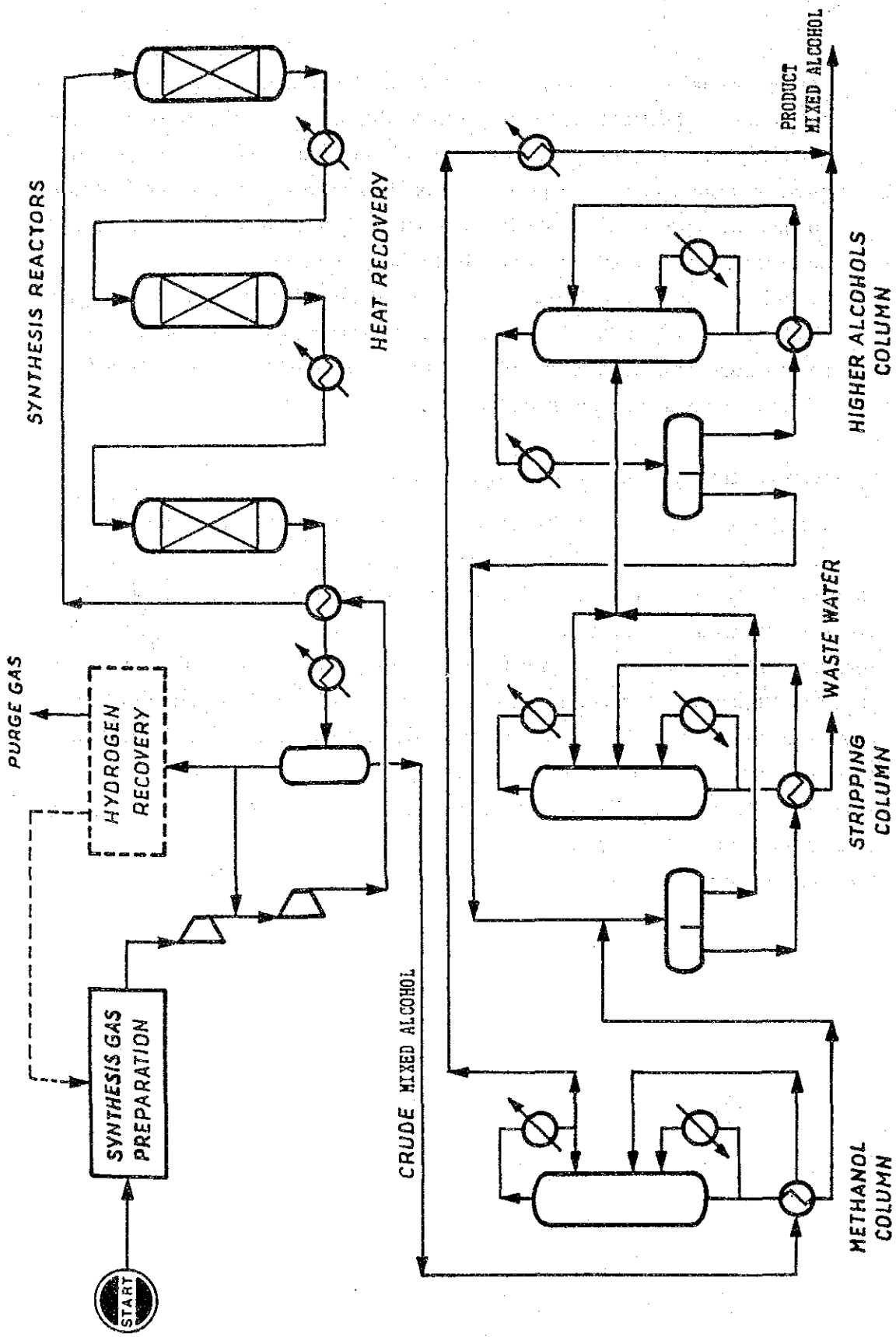


Fig. 7-2-5. Snamprogetti Process

Table 7-2-3 (a) Mixed Alcohol Synthesis (Snamprogetti Process)

Operating Condition			
Catalyst		ZnO-CrO ₃ -K ₂ O	
Temperature	(°C)	410 - 422	(330 - 430)
Pressure	(atm)	70	(90 - 180)
Space Velocity	(h ⁻¹)	11,700	
H ₂ /CO Ratio		2.4	(< 1)
Yields (wt%)			
Methanol		46.3	(68 - 72)
Ethanol		3.9	(2 - 3)
Propanol		9.4	(3 - 5)
Butanol		22.4	(10 - 15)
C ₅ ⁺ alcohol		17.7	(7 - 12)
H ₂ O		0.3	(< 0.1)

Note; () Demonstration Plant Data

Table 7-2-3 (b) Mixed Alcohol Synthesis (Dow Chemical Process)

Operating Condition					
Temperature	(°C)	302	268	296	320
Pressure	(atm)	200	100	208	173
Space Velocity	(h ⁻¹)	3,348	1,980	2,310	2,500
H ₂ /CO Ratio		1.14	←	←	←
H ₂ S,	(ppm)	0	40	110	138
Yields, (wt%)					
Methanol		50.8	36.7	24.7	16.1
Ethanol		22.3	30.4	36.8	30.3
Propanol		6.6	8.9	13.1	14.4
Butanol		1.6	1.0	3.7	4.8
C ₅ ⁺ alcohol		0.1	0.1	1.0	1.4
CH ₄		12.6	19.6	13.9	-
C ₂ ⁺ hydrocarbon		4.7	3.7	4.6	-
CO Conversion	(%)	26.3	8.0	17.0	21.2

Note; Catalyst: MoS-KOH-VIII Metal Comp.

Table 7-2-3 (c) Mixed Alcohol Synthesis (I.F.P. Process)

Operating Condition		Cu·Co (Base)	Al·Ce·Cr·Fe·La·Mn
Catalyst			
Temperature	(°C)	260 - 320	
Pressure	(atm)	60 - 100	
Space Velocity	(h ⁻¹)	3,000 - 6,000	
H ₂ /CO Ratio		2 - 2.5	
CO ₂	(%)	0 - 10	
Yields (wt%)			
Methanol		50 - 70	
Ethanol		16 - 23	
Propanol		8 - 14	
Butanol		4 - 7	
C ₅ alcohol		2 - 3	
C ₆ ⁺ alcohol		1.5 - 3	
CO Conversion	(%)	12 - 18	
Alcohol Selectivity	(%)	70 - 75	

Table 7-2-3 (d) Mixed Alcohol Synthesis (RAPAD Process)

Operating Condition		Cu·Ni·Ti	Ni·Ti	Cu·Co·Al·Na	Cu·Ni·Ba
Catalyst					
Temperature	(°C)	297	292	303	280
Pressure	(kg/cm ²)	61	60	61	61
Space Velocity	(h ⁻¹)	4,000	←	←	←
H ₂ /CO Ratio		2	←	←	←
Yields (wt%)					
Methanol		56	44	45	38
Ethanol		31	37	38	46
Propanol		4	13	10	9
C ₄ ⁺ alcohol		4	6	7	-
CO Conversion	(%)	19	19	-	19
Oxygenates Selectivity		63	44	57	69

7-2-3 Production of Gasoline

(1) Methanol-To-Gasoline (MTG) Process

1) Process Scheme

Conversion of methanol to gasoline occurs in two stages. In the first stage, feed methanol is partly dehydrated to an equilibrium mixture of dimethyl ether (DME), methanol and water. This mixture is then combined with recycled gas and passed to the gasoline conversion reactors, where the second stage reactions take place to form gasoline.

A simplified reaction sequence from methanol to gasoline is shown in Fig. 7-2-6.

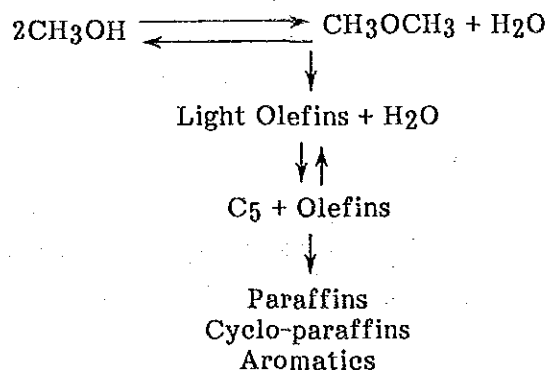


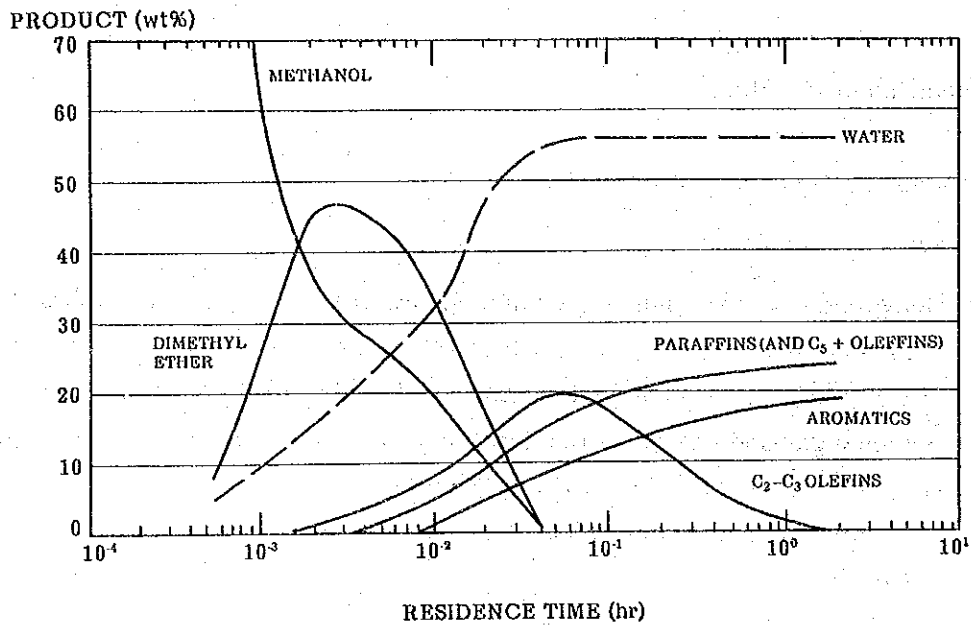
Fig. 7-2-6 Simplified Scheme of MTG Reactions

The initial dehydration of the methanol is rapid and very exothermic, and conventional dehydration catalyst is used. The olefins are then rearranged to form paraffins, cyclo-paraffins and aromatics. The key to this reaction sequence and also the key to MTG process is a specially shaped zeolite (ZSM-5 class) catalyst.

The pore structure of the catalyst effectively limits the formation of hydrocarbons with carbon chain length greater than 10 and boiling point above 200°C.

The overall reaction sequence is dependent on residence time within the reaction. This is illustrated in Fig. 7-2-7, which shows product composition as a function of residence time.

The overall reaction converts the methanol to approximately 44% hydrocarbons and 56% water. Some by-products from the reaction are small quantities of carbon monoxide, carbon dioxide and coke.



(Source) Journal of Catalyst, 56, 169-173 (1979)

Fig. 7-2-7 Product Composition and Residence Time of MTG Reaction

The first and only commercial use of MTG process is in New Zealand which produces approximately 15,000 bbl/d of synthetic gasoline from offshore Maui natural gas.

A general block flow chart of New Zealand Project is shown in Fig. 7-2-8.

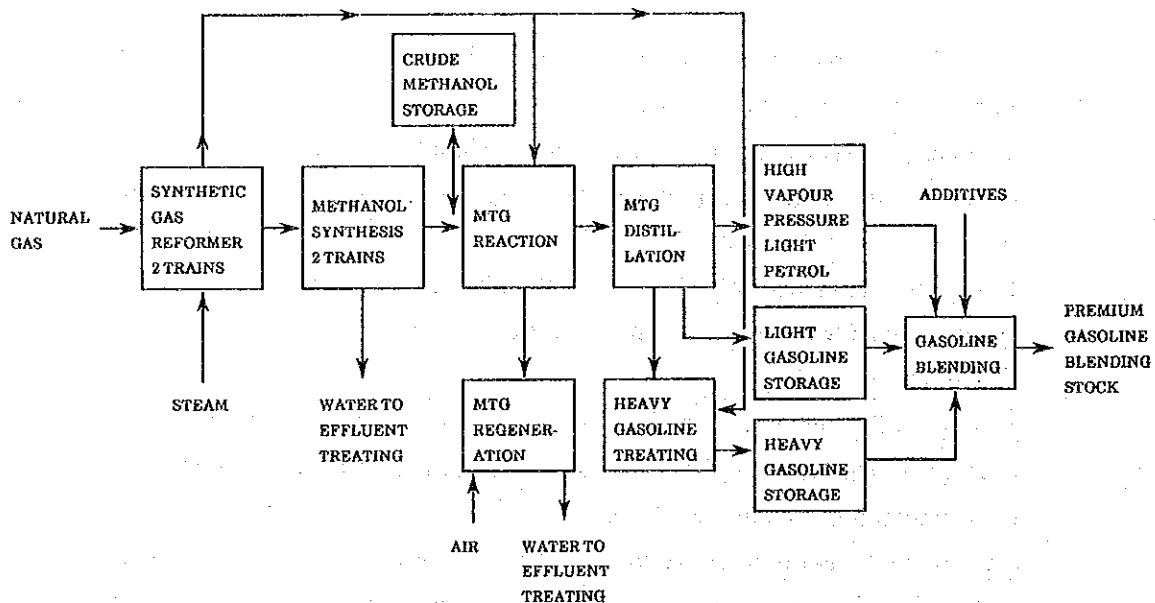


Fig. 7-2-8 Block Flow of New Zealand Synthetic Gasoline Plant

2) Product Quality

A typical analysis of MTG synthetic gasoline properties, which was reported from Mobil, is shown in Table 7-2-4.

Table 7-2-4 Typical Properties of MTG Gasoline

Components, wt %	
Butanes	2.7
Alkylate	3.2
C ₅ ⁺ synthesized gasoline	94.1
	100.0
Composition, vol %	
Paraffins	51.0
Olefins	13.0
Naphthenes	8.0
Aromatics	28.0
	100.0
Research octane No.	
Clear	93.0
Leaded, 3cc TEL/U.S. gal	100.0
Reid vapor pressure, psig	9.0
Specific gravity	0.730
Sulfur, wt %	Nil
Nitrogen, wt %	Nil
Corrosion, copper strip	1A
ASTM distillation °F	
10%	114
30%	145
50%	198
90%	330

Generally, the MTG gasoline has high quality and is comparable with conventional petroleum derived gasoline. The primary difference is the concentration of durene (1, 2, 4, 5 - tetramethyl benzene), which chemical structure is shown in Fig. 7-2-9.

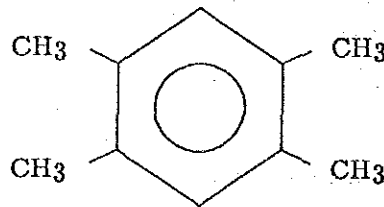


Fig. 7-2-9 Durene

This durene is an unwanted component in the gasoline because of its high melting point of 79°C, and potential substance of plugging problem in the engine carburetor system or other small tubular connections. The MTG gasoline naturally has durene contents of 3% to 7% by weight.

Road antiknock and driveability performance of MTG gasoline are equal to or better than most commercial unleaded gasoline and exhaust emission tests give results similar to those from a standard certification fuel.

(2) Synthesis Gas-To-Gasoline (STG) Process

1) Process scheme

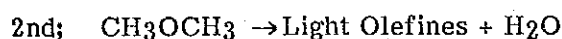
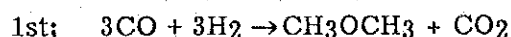
The process for manufacturing hydrocarbon liquid from synthesis gas has been put into practical use by SASOL. However, this method is incapable of selectively synthesizing a specific component such as a gasoline-range product.

Production of gasoline via methanol from synthesis gas was commercialized by the above-mentioned MTG process using ZSM-5 catalyst.

In the MTG process, two intermediate chemicals of methanol and DME are produced stepwise in the scheme of synthesis gas to gasoline.

Some attempts have been made to reduce the reaction steps, simplify the process scheme for gasoline production from synthesis gas, and the process via DME synthesis only is discussed here as STG process (two-stage STG), because gasoline synthesis directly from synthesis gas has some technical difficulties and is still the stage of primitive development.

In the two-stage STG process, synthesis gas is converted into dimethyl ether (DME) in the first stage and DME is successfully converted into gasoline in the second stage as the following reaction scheme.



The catalyst for first stage is prepared by mixing a specially designed Cu containing catalyst and a γ -alumina having dehydration activity with special techniques to generate high heat resistance and high reaction activity.

The CO conversion was achieved to be more than 80% with hybrid catalyst as is shown in Table 7-2-5.

Table 7-2-5 Comparison of Two Stage STG and One Stage STG Reaction in Bench Scale Reactor

Process		Two Stage	One Stage
H ₂ /CO (mol/mol)		1	2
Temp. (°C)	1st stage	270	300
	2nd stage	360	-
Press. (kg/cm ² G)	1st stage	40	20
	2nd stage	5	-
GHSV (h ⁻¹)		1,000	820
CO Conversion (%)		90.2	84.9
CO ₂ Selectivity (%)		24.2	10.0
HC* Selectivity (%)		75.8	90.0
Hydrocarbon Composition (wt%)			
	C ₁	0.3	25.5
	C ₂	1.1	9.7
	C ₃	5.9	5.9
	C ₄	11.8	9.9
	C ₅ ⁺ (gasoline)	79.3	49.0
	C ₁₁	1.6	0.0

* HC: Hydrocarbon

For the second stage reaction of gasoline synthesis from DME, new transition-metal silicate catalyst is utilized which has excellent activity, selectivity and durability.

Table 7-2-6 shows the results of gasoline synthesis performance of this catalyst from DME and methanol.

Table 7-2-6 Performance of New Transition Metal Silicate

Feed		CH ₃ OH		DME
Reaction Condition				
Temperature	(°C)	350	360	375
Pressure	(kg/cm ²)	1	1	1
Space Velocity	(h ⁻¹)	LHSV 1.9	LHSV 1.9	GHSV 1151
Conversion	(%)	93.7	98.5	99.7
Product Distribution	(wt%)			
C ₁ , C ₂		17.3	17.5	17.2
C ₃ , C ₄		23.5	26.3	21.5
C ₅ gasoline		69.2	66.2	68.7
DME		tr	tr	0.0
CH ₃ OH		0.0	0.0	2.5
C ₅ ⁺ /Hydrocarbons	(wt%)	69.2	66.2	70.5
Aroma/C ₅ ⁺	(wt%)	26.9	24.5	28.1
Durene/C ₅ ⁺	(wt%)	1.7	1.6	1.4

As gasoline synthesis from DME is highly exothermic, the reaction is performed in the fluidized bed for heat removal and continuous catalyst regeneration. So, this catalyst is required to have significant strength, attrition resistance and other important physical properties for its commercial use, and this is demonstrated in Table 7-2-7 that this catalyst is applicable for fluidized bed reactor.

Table 7-2-7 Physical Properties of DTG¹⁾ Catalyst²⁾

		<u>FRESH CATALYST</u>	<u>USED CATALYST</u>
A.B.D.	(g/ml)	0.50	
Surface Area	(m ² /g)	270	
Attrition Index		13	
Particles Size Distribution	(wt%)		
0 - 20 μ		0	2
0 - 40 μ		9	14
0 - 60 μ		36	57
0 - 80 μ		65	82
0 - 105 μ		90	94
0 - 149 μ		100	100
Av. Particle Size	(μ)	69	57
Coke Deposit	(wt%)	-	9.0

(Note) 1) DTG means dimethyl ether-to-gasoline.

2) DTG catalyst is filled in the 2nd reactor of two-stage STG process.

2) Pilot Plant Operation

This two-stage STG process is under development now and operation of pilot plant which capacity of one barrel of gasoline production was successfully conducted.

Fig. 7-2-10 shows the process flow diagram of the pilot plant.

It consists of synthesis gas production section by methanol cracking to prepare synthesis gas for the test purpose, dimethyl ether synthesizing section with the multiple tubes fixed bed reactor and gasoline synthesizing section with the fluidized bed reactor.

Typical yield data of this pilot plant operation and also the product quality data of gasoline from pilot plant are shown in Table 7-2-8 and Table 7-2-9.

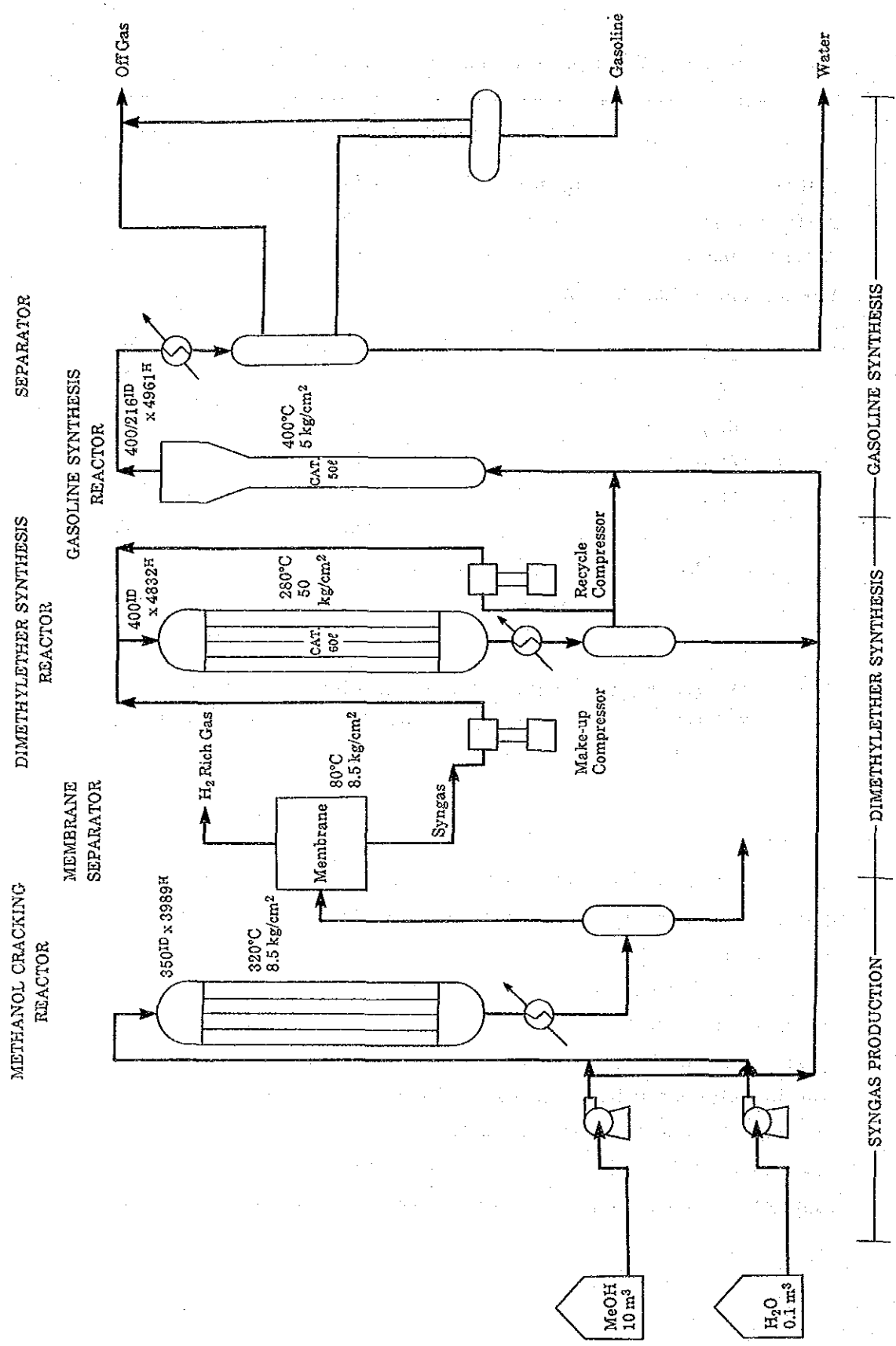


Fig. 7-2-10 1 BPD Gasoline Production Pilot Plant

Table 7-2-8 Typical Operating Condition and Yield of Pilot Plant

Run No.		STG-1	STG-2	STG-3	STG-4
Reaction Conditions					
DME Synthesis					
Temperature	(°C)	260	260	270	270
Pressure	(kg/cm ² .G)	50	50	50	40
GHSV	(h ⁻¹)	900	900	1000	920
H ₂ /CO Ratio	(-)	1	1	1	2
Recycle Ratio	(-)	1	1	0.4	0
Gasoline Synthesis					
Temperature	(°C)	400	420	420	420
Pressure	(kg/cm ² .G)	5	5	5	3
WHSV	(h ⁻¹)	0.5	0.5	0.5	0.44
CO Conversion	(%)	66.2	63.0	71.6	78.2
Gasoline Yield (C ₅ ⁺ /HC)	(%)	68.3	59.7	57.8	62.3

Table 7-2-9 Typical Product Quality of Pilot Plant

Run No.		STG-1	STG-2	STG-3	STG-4
Specific Gravity (15°/4°C)					
		0.7714	0.7609	0.7670	0.7698
Distillation Temp. (°C)					
	IBP	37.5	31.0	37.0	37.0
	30%	87.0	75.5	81.0	82.5
	50%	117.0	105.0	110.5	112.0
	70%	147.0	140.0	141.5	139.5
	90%	172.5	165.0	168.5	163.0
	EP	211.5	211.0	207.5	201.0
Hydrocarbon Type (%)					
	Paraffins	26.7	26.9	23.2	16.7
	Olefins	15.7	19.5	22.0	26.4
	Naphthenes	15.9	15.3	15.5	15.8
	Aromatics	41.7	38.3	39.3	41.1
Octane Number					
	RON	96.2	97.2	97.5	97.5
	MON	84.2	84.7	84.4	83.9

3) Evaluation of the Process

The two-stage STG process is not technically available for commercial use at present, but it has some potential for simplifying the process, upgrading the process efficiency and reducing the production cost of gasoline.

The gasoline produced in this process was found to be so high in quality and octane number that it is usable as a blending stock for premium gasoline.

Fig. 7-2-11 shows the result of preliminary feasibility study, that is conceptual design and cost estimate of commercial plant of the two-stage STG process, and it shows that this process will have a competitive cost of gasoline production against conventional petroleum gasoline in the future if cheap synthesis gas will be available.

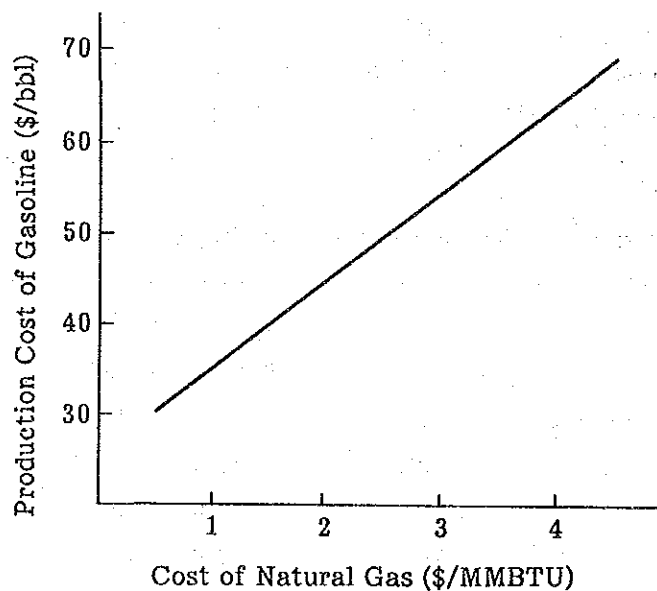


Fig. 7-2-11 Production Cost of Gasoline by Two-Stage STG Process

(Source) Report of Japan Economic Research Institute, March 1985

7-2-4 Production of Synthetic Fuel Oil (F/T Synthesis)

(1) Chemistry of F/T Synthesis

The Production of hydrocarbons from carbon monoxide and hydrogen in the presence of Fischer-Tropsch catalyst is generally known as indirect hydrogenation.



This synthesis process was discovered in 1925 and introduced with the use of Co-catalysts into such countries as Japan and Germany in the 1940s. Since then, the Lurgi-Ruhrchemie process of fixed bed type and the Kellogg process of fluidized bed type were developed, which were put to practical use in South Africa (Sasol) in 1955.

(2) Current Technology of F/T Synthesis Process

The conversion of synthesis gas to liquid hydrocarbons has been commercially demonstrated for many years at the three Sasol plants. There the synthesis gas is derived from coal.

The first Sasol plant uses fixed bed reactors for the Fischer-Tropsch reaction (ARGE type). Products contain a high percentage of heavy ends, particularly waxes. The second and third Sasol plants used fluid-bed reactors (Synthol type), and products are more in the gasoline and diesel boiling ranges. Oxygenated compounds are produced in both cases and are either recovered as chemicals, or removed to give finished transportation fuels.

Table 7-2-10 shows comparison of two types in F/T Synthesis condition and yields.

Fig. 7-2-12 shows the overall block flow diagram of the Sasol process.

Sasol Synfuel process plant covers the following process units.

a) Coal gasification

Sasol two uses Lurgi Mark IV gasifier to process a nominal 31,000 tons/day of coal.

b) Rectisol unit

The raw gas is purified using Lurgi Rectisol (refrigerated methanol) system, which removes all of H₂S and most of carbon dioxide.

c) Phenosolvan and ammonia recovery

The aqueous gas-liquor effluent from the gasifiers contains about 2,000 ppm of tar acid (phenols, cresols, etc.) and about 8,000 to 9,000 ppm of ammonia which are recovered in the Phenosolvan plant and ammonia recovery plant.

d) Synthol unit

The Synthol fluid-bed reactors produce a range of hydrocarbons concentrated in the diesel and gasoline range. The reactor is schematically represented in Fig. 7-2-13. The gas enters the reactor through a horizontal line and meets the catalyst the falls from the stand pipe via a slide valve. The catalyst at this point acts as a heat-transfer medium by raising the temperature of the preheated gas to between 300 and 315°C. A total of eight synthol units were constructed for Sasol Two.

Table 7-2-10 Product Yields of F/T Synthesis

Type		ARGE	Synthol
Developer		Lurgi-Ruhr Chemie	Kellogg/Sasol
Temp.	(°C)	230	330
Pressure	(atm)	25	22
Conversion of (CO+H ₂)	(%)	65	85
H ₂ /CO Ratio		1.7	2.8
Selectivity*, (wt%)	CH ₄	5.0	10.0
	C ₂ H ₄	0.2	4.0
	C ₂ H ₆	2.4	6.0
	C ₃ H ₆	2.0	12.0
	C ₃ H ₈	2.8	2.0
	C ₄ H ₈	3.0	8.0
	C ₄ H ₁₀	2.2	1.0
	C ₅	3.5	8.0
	C ₆ ~ C ₁₂	19.0	31.0
	C ₁₃ ~ C ₁₆	15.0	5.0
	C ₁₉ ~ C ₃₀	23.0	4.0
	C ₃₁	18.0	2.0
	NAC**	3.5	6.0
	Acids	0.4	1.0

(Note) * Selectivity is C-atoms converted

** Non acid compounds

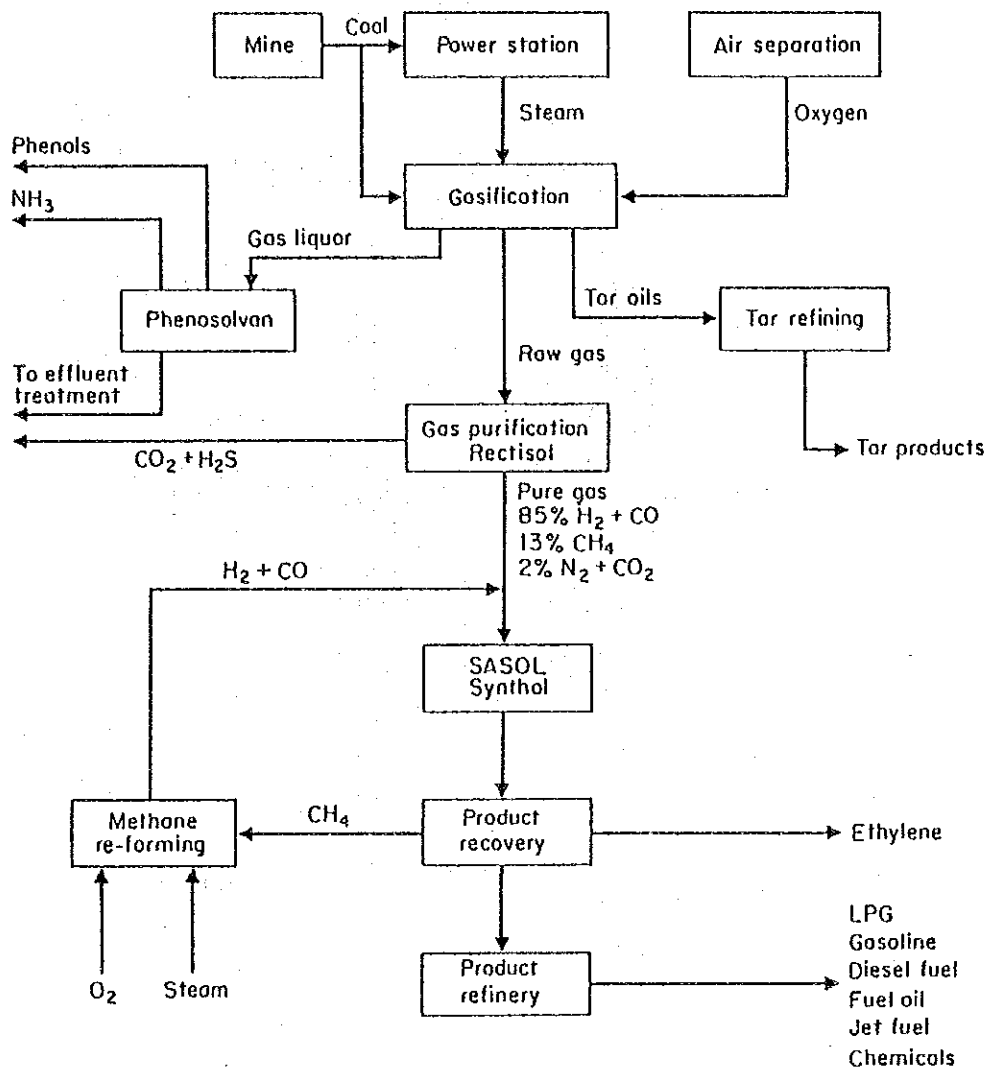


Fig. 7-2-12 Sasol Synfuel Process - Simplified Flow Sheet for Sasol Two

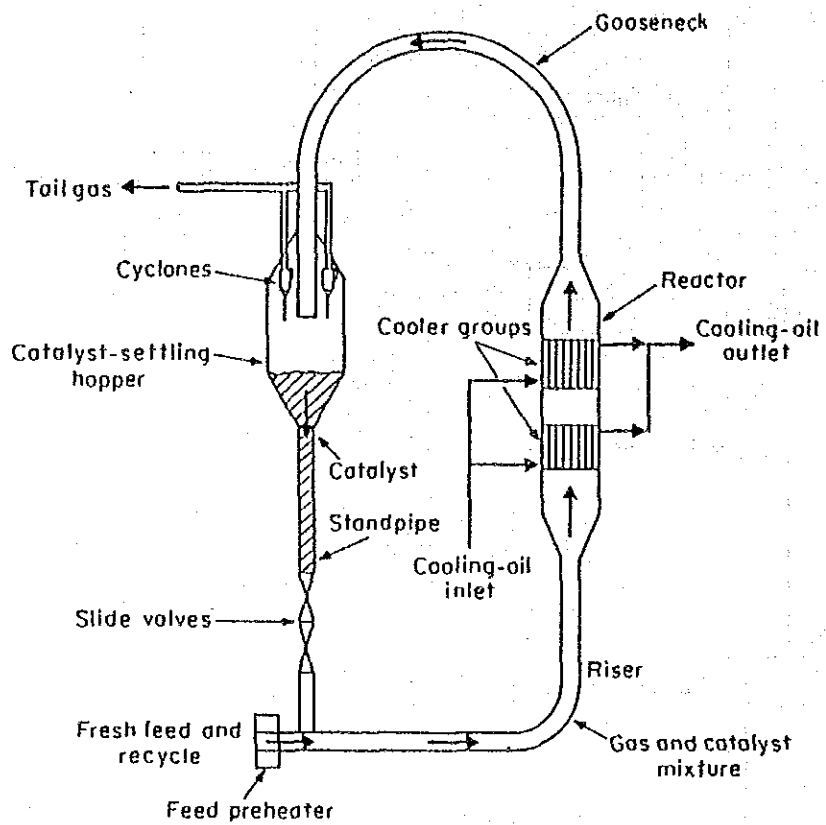


Fig. 7-2-13 Synthol Reactor

7-2-5 Production of Methyl Tertiary Butyl Ether (MTBE)

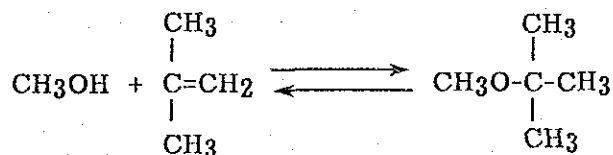
The worldwide trend toward the phasing out of lead additives from gasoline pool is creating a growing opportunity for MTBE to fill the "Octane gap".

MTBE is a high octane blending agent for motor gasoline. The Research octane number (RON) and the Motor octane number (MON) is 117 and 101, respectively.

MTBE is already blended into gasoline as octane booster in France, West Germany, Italy, Canada and U.S.A. World-wide production capacity as of 1986 amounts to more than 6 million t/y including planning plants.

(1) Chemistry of MTBE Synthesis

The synthesis of MTBE by the reaction of methanol and isobutene is an exothermic reversible reaction which is catalyzed by acidic catalysts.



Methanol Isobutene

MTBE

The selectivity for MTBE may reach 100% depending on the catalyst and the reaction temperature. The main byproducts are tertiary butyl alcohol formed from the reaction of isobutene and water, and di-isobutene formed from the dimerization of isobutene. The reaction is conducted in the liquid phase at 70~100°C over acidic cation exchange resins in packed bed. The reaction temperature is maintained below 100°C to increase the isobutene equilibrium conversion, decrease byproducts formation and prolong catalyst life which varies from one to two years.

(2) Current Technology of MTBE Synthesis Process

The current commercial practice in the production of MTBE is by reacting methanol with isobutene containing C₄ mixtures obtained from steam crackers or fluid crackers. The production of MTBE is, therefore, limited by the availability of isobutylene from the above sources.

Recent projects have demonstrated that MTBE could be produced from field butane. Normal butane (n-butane) extracted from associated or non-associated gas fields are firstly isomerized to isobutane and then dehydrogenate to isobutylene for the MTBE synthesis. The overall processing scheme for the manufacture of MTBE is given in the block diagram of Fig. 7-2-14.

The technical comparison for typical MTBE process and simplified flow diagram are shown in Table 7-2-11 and Fig. 7-2-15.

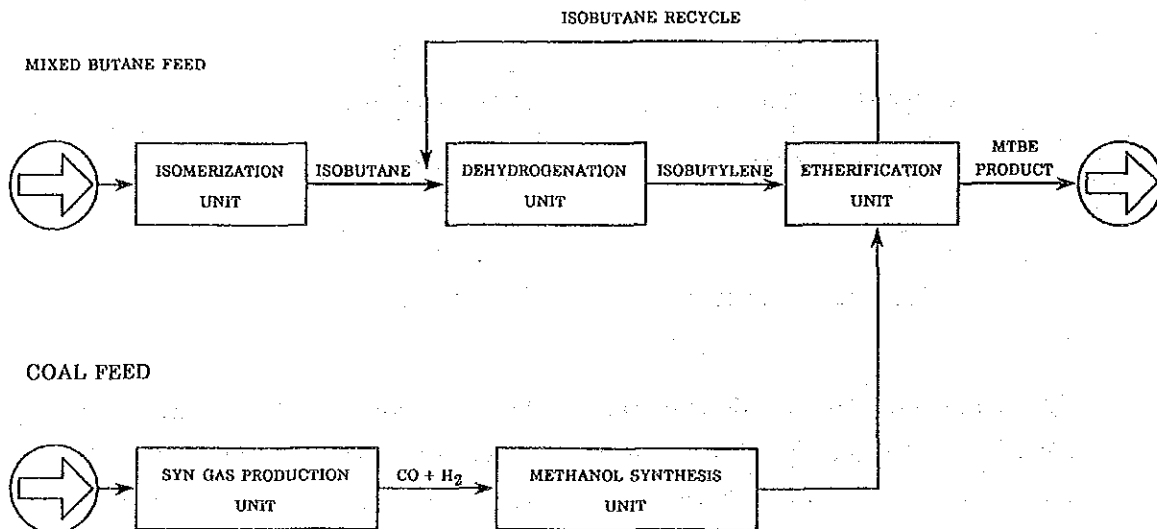


Fig. 7-2-14 MTBE Process Flow Scheme

Table 7-2-11 Comparison of MTBE Production Process

Licensor		ARCO CHEMICALS	CHEMISCHE WERKE HÜLS	SNAMPROGETTI, ANIC	ECERDÖLCHEMIE/LURGI
Reactor		Single stage fixed bed tubular reactor	Two stages, water cooled fixed bed, tubular reactor and shaft furnace type	Single stage fixed bed tubular reactor	Two stages up-stream reactor
Reaction temp. (°C)		100 ~ 155	< 100	< 100	< 100
Reaction press. (kg/cm ² G)		15.5	< 8		
Isobutylene conversion (%)		Single case 95 Two stage case 99	95 ~ 99.9	97 ~ 98 (standard) 99.9 (ultra-high-conv.)	
Catalyst		Commercially available amberlyst 15	Acidic ion exchange resin catalyst		BAYER-catalyst
Feed stock availability		FCC off gas, Spent B-B, C ₄ cut before butadiene extraction	FCC off gas, Spent B-B, C ₄ cut before butadiene extraction	FCC off gas, Spent B-B, C ₄ cut before butadiene extraction	FCC off gas, Spent B-B
Isobutylene (kg/t)		663	647	685	635
Methanol (kg/t)		361	392	361	365
Elec. (kWh/t)		9	8	10	4.8
Steam (t/t)		0.51	0.4	0.36	0.26
C.W. (m ³ /t)		18	26	30	12.8
Fuel (kcal/t)		-	-	-	-
Catalyst (US\$/t)		-	-	0.3	-
Raw Material & Utility					

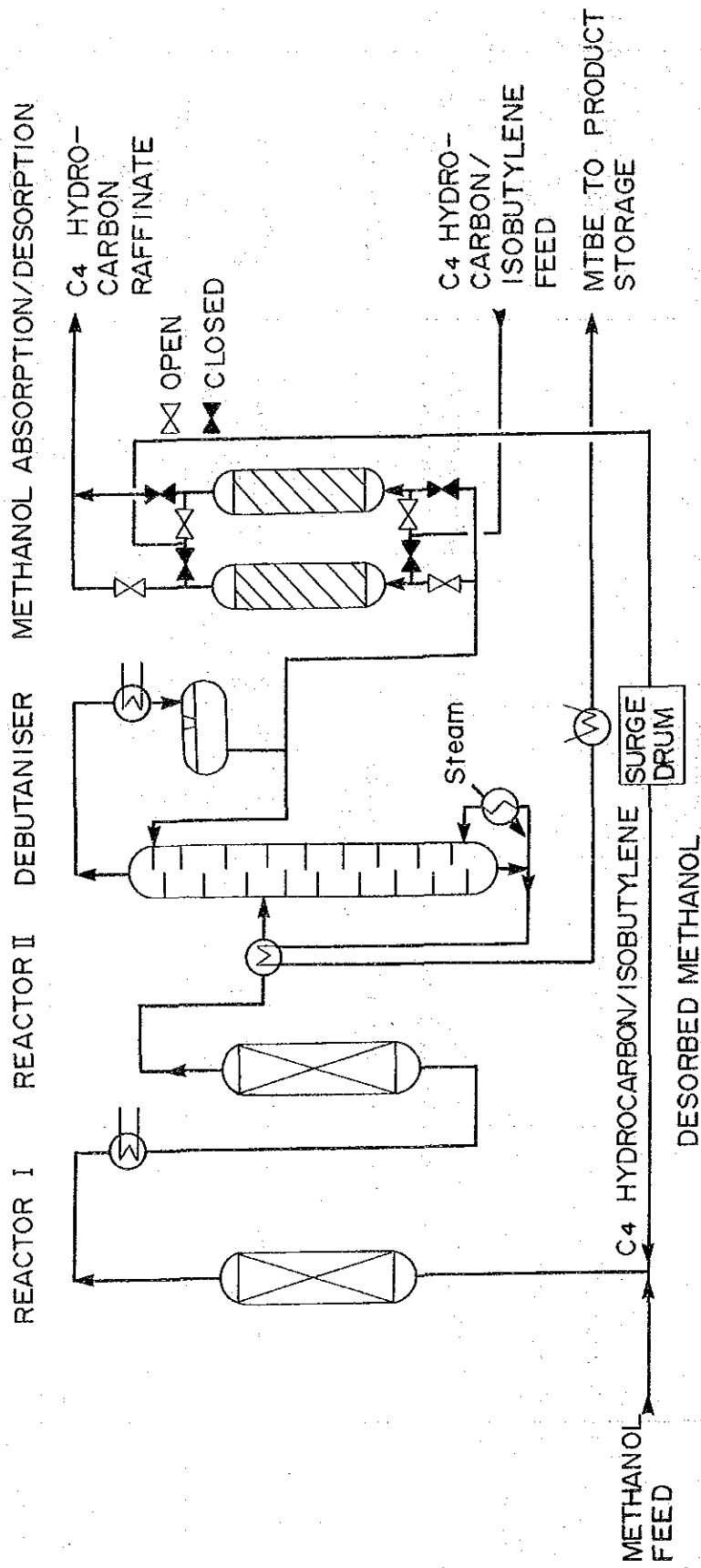


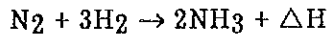
Fig. 7-2-15 MTBE Process

7-2-6 Production of Ammonia and Urea

(1) Chemistry of Synthesis

1) Ammonia

All ammonia syntheses are based on the reaction:



This reaction is highly exothermic, and consequently the design of the reactor must be such as to control the temperature at the point desired for the reaction deemed economical for the particular conditions chosen by the chemical engineers.

Since the volume of ammonia obtained is less than the combined volume of nitrogen and hydrogen, a pressure increase gives a higher percentage of ammonia at equilibrium. The conversion ratio increases several folds as the pressure increases from 100 to 1,000 atm, but the ratio of ammonia in equilibrium with the reacting gases decreases continually with a temperature rise up to 1,100°C and reaches a minimum at this temperature. The commercial processes in current use are operated at about 230 kg/cm²G and 130~140°C at reactor inlet.

2) Urea

Urea is produced from liquid ammonia and gaseous carbon dioxide at about 170~190°C and 134~145 kg/cm² abs. by the following reactions:



The first reaction is easily carried to completion, but the second usually has a conversion ratio of only 40 to 70%. Since both reactions are reversible, the equilibrium depends on the temperature, pressure, and concentration of the various components. The conversion ratio increases with rising temperature, however, urea is formed only in the liquid (solution) phase, making it necessary to maintain this phase with heat and under pressure.

(2) Outline of Ammonia and Urea Plant

Typical processes for production of Ammonia and Urea from coal-derived syngas are as follows:

1) Process Description

The ammonia/urea plant consists of the following process steps.

- Dust Removal and 1st Compression
- Co-Shift Conversion
- Acid Gas Removal
- Nitrogen Washing
- Ammonia Synthesis
- Urea Synthesis
- Evaporation and Prilling

Simplified process flow diagram is shown in Fig. 7-2-16 and 7-2-17.

i) Dust Removal and 1st Compression

The raw gas leaving the gasifier contains 50 mg/Nm³ dust.

The dust content in the raw gas is reduced to 5 mg/Nm³ and this gas is compressed to 50 kg/cm²G.

ii) CO-Shift Conversion

In order to increase hydrogen content in the raw gas, carbon monoxide is hydrolyzed into carbon dioxide and hydrogen in the converter as expressed in the following formula:



To keep the catalyst bed at a proper temperature, process steam or product gas is used to dissipate the reaction heat. Shift conversion hydrolyzes also COS to H₂S.

iii) Acid Gas Removal

The feed gas containing CO₂ and a small amount of H₂S is supplied to the acid gas absorber where CO₂ and H₂S are readily scrubbed by contacting with cold methanol resulting in 10 ppm of CO₂ in the treated gas. The treated gas from the absorber is sent to the nitrogen washing unit at a temperature of -50°C.

After CO₂ and H₂S gas dissolved in the fat solvent are recovered separately through CO₂ and H₂S strippers, the lean solvent is recycled to the absorber.

The recovered CO₂ gas (99% purity) is utilized as raw material for urea synthesis.

NH₃ SYNTHESIS SECTION

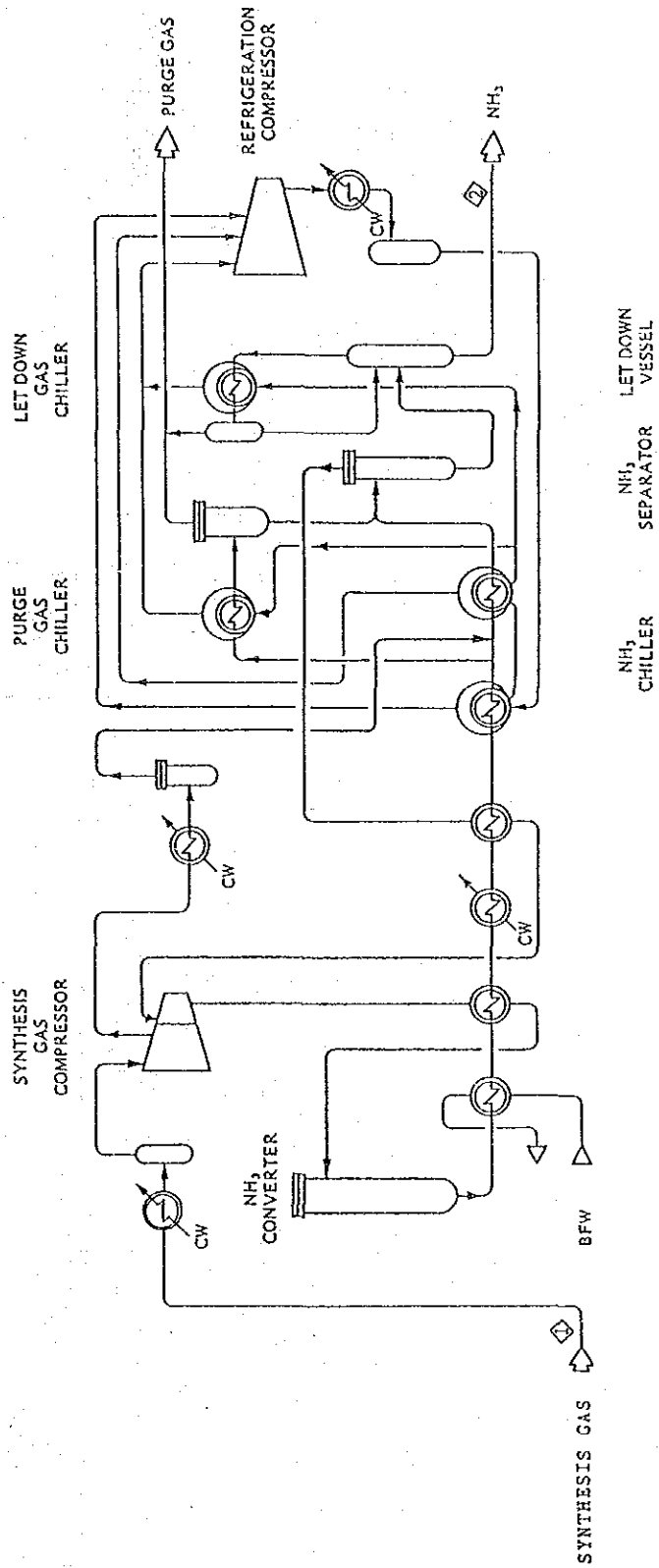


Fig. 7-2-16 Simplified Process Flow Diagram - Ammonia Production

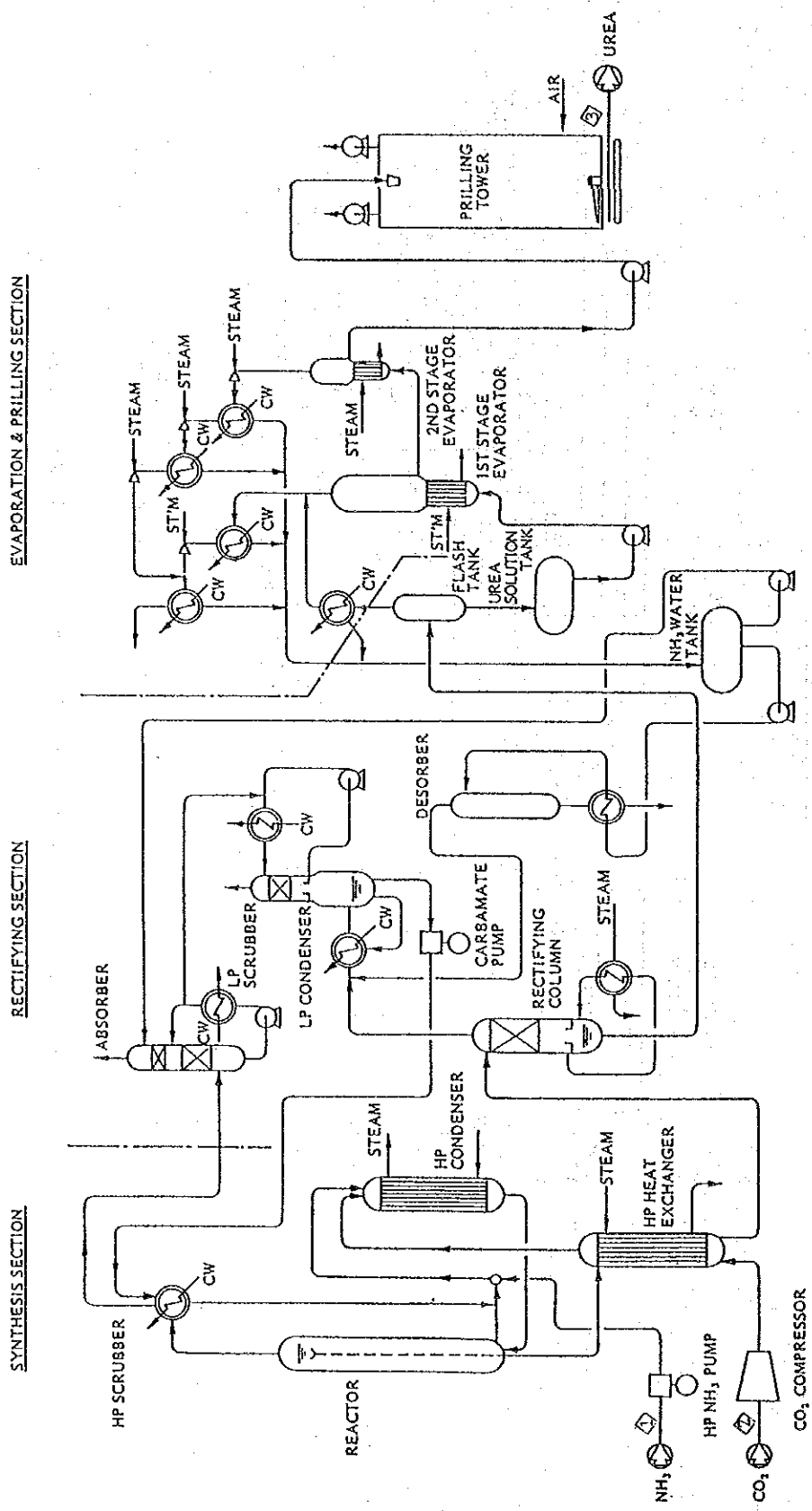


Fig. 7-2-17 Simplified Process Flow Diagram - Urea Production

iv) Nitrogen Washing

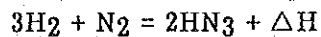
The gas from the acid gas removal unit still contains 10 ppm of CO₂ and methanol mist. Since these impurities sometimes causes plugging in the process, it is to be absorbed by molecular sieves.

The gas free from impurities is cooled and supplied to the N₂ washer where CO, methane, etc. are scrubbed by liquid nitrogen.

The treated gas leaving the top of the N₂ washer is mixed with a certain amount of nitrogen to meet the suitable H₂/N₂ ratio for NH₃ synthesis.

v) NH₃ Synthesis

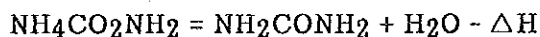
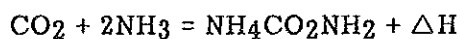
After compressed and heated to 210 kg/cm²G and 135°C, the feed gas is sent to the NH₃ converter. Ammonia is produced by the following reaction:



The effluent leaving the reactor at a temperature of 330°C is cooled through steam generator, feed gas preheater and chillers. The cold effluent is introduced to the gas-liquid separator where product ammonia is separated from the unconverted gas. The product ammonia is pumped to storage at -33°C and the unconverted gas is recycled to the converter.

vi) Urea Synthesis

Urea synthesis is expressed in the following equations:



CO₂ and liquid NH₃ produced in the upstream units are pressurized and introduced to reactor section. The reactor section consists of reactor, stripper, carbamate condenser and HP scrubber where urea synthesis takes place via carbamate formation.

The operating condition of the reactor is at about 140 kg/cm²G and 180~185°C.

Produced urea from the stripper is depressurized to 3 kg/cm²G and sent to LP recirculation section in which unconverted mixtures associated with the product urea is recovered and recycled to HP scrubber in the form of carbamate.

vii) Evaporation and prilling

The urea solution coming from the recirculation stage contains about 72% by weight of urea. This solution is concentrated to 99.8% urea in two steps under vacuum. The resultant molten stream is prilled with the aid of rotating prilling bucket.

(3) The Latest Status of Ammonia from Coal Projects

In late 1980, the TVA at Muscle Shoal, Alabama, U.S.A., began operating a 175 t/d oxygen-blown Texaco gasifier to produce ammonia syngas. TVA's objectives have been to demonstrate ammonia production from coal-derived syngas and to develop operating data for evaluating the feasibility and economics of ammonia-from-coal ventures.

In 1984 Ube Industries, Ltd., Japan commissioned four Texaco gasifiers to replace its existing steam reforming plant for production of ammonia syngas. The gasifiers are each rated at 500 t/d; the corresponding total output of ammonia is 1,000 t/d, with three operating gasifiers and one spare.

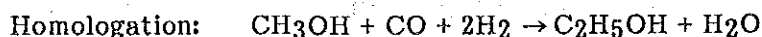
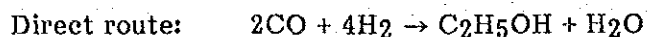
Four Lurgi coal gasifiers (Dry ash bottom type) for production of urea from coal in Lu Cheng, Xian, China remains under construction.

7-2-7 Others

The process producing methanol derivatives such as ethanol, acetic acid, ethylene glycol and single cell protein (SCP) are briefly discussed in this section. Among these processes, the acetic acid and SCP processes have been commercialized while others are under development.

(1) Ethanol Synthesis

There are two routes of ethanol synthesis, direct route and indirect one via methanol homologation.



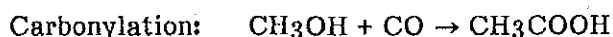
As for the direct route, Fe based catalysts of F/T type is used, while R&D on rhodium catalysts has recently been becoming popular.

As for the methanol homologation process, ethanol is synthesized from methanol and synthesis gas with ruthenium-cobalt or ruthenium-iron to which iodine or phosphorus is added.

A number of companies such as Gulf, Exxon, UCC, Celanese and Shell have patents covering the homologation of methanol to ethanol. Recent research on the direct and indirect synthesis of ethanol has been conducted by the Research Association for C₁ Chemistry (RACC), Japan.

(2) Acetic Acid Synthesis

Similar to ethanol synthesis, there are two routes of acetic acid synthesis. One is direct route and the other is indirect one via methanol carbonylation.

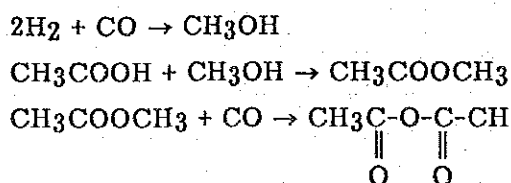


Acetic acid is also being produced by the oxidation of acetaldehyde, which in turn is produced by the oxidation of ethylene. However, the development of an improved carbonylation process is now supplanting these older processes.

In 1965, Monsanto Chemical Company discovered that rhodium combined with iodine represented a considerable more active catalyst system. It went into operation in 1970 with a capacity of 150,000 t/y.

On the other hand, direct processes currently under development in such firms as UCC, Celanese, Hoechst and Research Association for C₁ Chemistry also employ rhodium catalysts. With this type of processes, synthesis reaction takes place under pressure as high as 200~300 atm associating too many side-reactions. Therefore, it is essential to develop catalyst featuring improved selectivity and reduce pressure.

In 1983 the Tennessee Eastman Co. completed a new coal-based acetic anhydride plant in Kingsport, Tennessee. This new synthesis gas-based route is alternative one of methanol carbonylation process and is carried out in several steps.



Step 3, the carbonylation of methyl acetate to acetic anhydride, is carried out over a rhodium or nickel catalyst developed by Eastman. Eastman reacts the anhydride with cellulose to form cellulose acetate and to release acetic acid which is recycled to step 2. Therefore the route is a net consumer of methanol and carbon monoxide, but not of acetic acid.

The synthesis of acetic anhydride in Eastman is of particular interest because it may be the first chemical intermediate to be made in the U.S. since 1956 using synthesis gas obtained by the gasification of coal.

The synthesis gas for the plant is produced by coal gasification using two 900 t/d Texaco gasifiers.

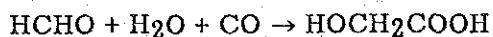
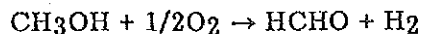
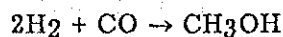
Methanol is produced by a Lurgi-licensed process at the rate of 500 t/d of methanol.

(3) Ethylene Glycol Synthesis

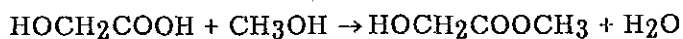
Ethylene glycol is currently produced by the hydration of ethylene oxide, which is produced by the selective oxidation of ethylene. In other hand, considerable research is in progress to develop an efficient process for production of ethylene glycol directly from synthesis gas.

1) Indirect Synthesis

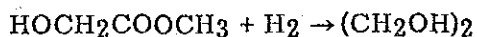
The process had been in commercial operation from 1940 through 1967 by Du Pont at the rate of about 70,000 t/y. The reaction sequence is summarized below:



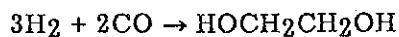
Glycolic acid



Methyl glycolate



Net Reaction

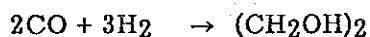


Catalysts are cobalt compounds such as cobalt acetate and fluoride, and operating conditions are 150~400°C and 500~700 atm.

2) Direct Synthesis

Union Carbide has developed technology to produce ethylene glycol directly from CO + H₂ synthesis gas using rhodium complex catalyst.

The principal chemical reactions involved are the following:



Ethylene glycol



Propylene glycol



Glycerine



Typical reaction conditions from patent example; 220°C, 550 atm, H₂/CO=1.

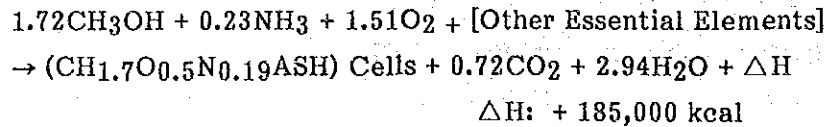
Japan's Research Association for C₁ Chemistry has also developed catalysts featuring excellent selectivity and activity for direct conversion of ethylene glycol from synthesis gas.

As other indirect synthesis route, Ube Industries and Union Carbide has

jointly developed a process for production of ethylene glycol via oxalate esters.

(4) Single Cell Protein (SCP) Synthesis

The single cell protein (SCP) is made from the bacterium methylophilus methylotrophus - a gram negative aerobic rod shaped methanol obligate.



The cells are grown in a fermenter which is fed with methanol, oxygen (supplied as air), nitrogen (supplied as ammonia), and inorganic nutrients such as phosphorus, calcium, iron, magnesium and potassium.

The content of nutrients in SCP which are of key nutritional and economic importance are as follows:

Moisture	8.0 (%)
Protein	72.0
Fat	8.5
Ash	10.0
Lysine	4.1
Methionine + Cystine	1.9
Threonine	3.3
Tryptophan	1.0
Calcium	1.3
Phosphorus	2.5
Sodium	0.2

SCP contains a wide range of B vitamins and is rich in biotin, riboflavin, folic acid and pantothenic acid.

The process steps of SCP synthesis are as follows:

a) Fermentation

The fermenter is a tower which has a central riser and twin downcomers. Compressed air, fed into the base of the riser, produces bubbles, reduces liquid density, and causes the liquid to rise.

At the top, carbon dioxide is released from the solution.

In the fermenter, the water temperature is lowered and nutrients are added to support culture growth. Initial growth is rapid, the cell mass doubling every two hours. After about 30 hours from the start-up, the cell concentration reaches 3% and harvesting is commenced. Culture is withdrawn continuously from the fermenter and pumped to the harvesting section. The liquor recycled from harvesting is balanced with added nutrients to maintain the 3% cell concentration in the fermenter.

b) Harvesting

The culture is withdrawn continuously from the fermenter and, by addition of phosphoric acid, sulfuric acid and steam, the stream is acidified and heated. The combined acid/heat treatment causes the cells to produce an easily centrifuges mixture of flocs and liquor.

The centrifuges produces two streams - 20% concentrate cream which is fed to the driers and the concentrate liquor which is reesterilized and recycled to the fermenter.

c) Drying

The concentrate cream is neutralized by the addition of sodium or calcium hydroxide. The SCP plant uses usually a flash drier to produce a granular product.

7-3 TECHNOLOGY FOR ELECTRICITY GENERATION

7-3-1 Possibility of Banko Coal Utilization by Pulverized Coal Firing Boiler

A pulverized coal firing boiler introduces the pulverized coal and air for combustion, mixes these reactants, ignites the combustible mixture and distributes the flame envelope and the products of combustion at high temperature to the heat absorbing surfaces of the steam generator, and is the most typical type of a boiler.

However, the application of the pulverized coal-firing boiler to Banko coal should be avoided for the following reason.

(1) Combustion Characteristics of Banko Coal

The Banko coal is likely to exhibit similar combustion characteristics to typical brown coals currently used in pulverized coal firing boilers. However, Shell report has pointed out that "the following indicative analysis of the Banko coal, particularly the high sodium levels found in the lower seams, suggests that it should be regarded as a problem coal which could result in severe fouling and slagging in utility boilers".

Table 7-3-1 Ash Analysis of Banko Coals (by Shell)

SiO ₂	20.0	-	61.0	(wt%)
Al ₂ O ₃	19.0	-	41.0	
Fe ₂ O ₃	0.8	-	17.0	
TiO ₂	0.8	-	17.0	
CaO	0.6	-	1.3	
MgO	0.2	-	6.6	
Na ₂ O	0.2	-	20.0	
K ₂ O	0.2	-	0.6	
Mn ₃ O ₄	0.04	-	0.79	
P ₂ O ₅	0.04	-	0.79	
SO ₃	0.58	-	13.0	

(2) Present Situation of Pulverized Coal Combustion Technology for Coal Containing High Sodium-in-ash

In U.S.A, the firing of low grade coals in pulverized fuel units got off to a slow start and it was not until 1960s before the first units were put into operation.

These were designed with sodium-in-ash contents of up to 5% in mind and major operational problems were experienced when higher percentage sodium-in-ash was actually encountered. The fuels to be used for the series of new generation boilers include coals of up to 10% sodium in ash. To cater to these difficult coals much more conservative boiler designs are being used with low-rated furnaces and specific provisions for flexibility in furnace operation. From the viewpoint of such experiences, the question of slagging and fouling with such coals of high sodium-in-ash as Banko coal can be summarized in the following way:

- i) In the light of world experience it can be said that proven technology and considerable operational experience are available for the use of fuels with up to 5% sodium-in-ash.
- ii) Technology has been developed but experience is still being gained with fuels containing 10% sodium-in-ash.
- iii) Fuels containing more than 10% sodium-in-ash are now being considered for new power projects but it will be the late 1980s before they become commercial propositions.

7-3-2 Possibility of Banko Coal Utilization by Coal Gasification Combined-Cycle System

(1) Present Situation of Combined-Cycle Power Generation

There are various combined-cycle power plants, as shown in Fig. 7-3-1, now in operation, using natural gas or oil as fuel as shown in Table 7-3-2, resulting in 24,000 MW of the total output, which is equally distributed in U.S.A. and Europe by respective 10,000 MW. In U.S.A., the greater part (85%) of it is covered by the exhaust gas heat recovery cycle system, whereas in Europe the predominant part (94%) by the exhaust gas fired cycle system.

In Japan, four large scale power plants, using LNG as fuel, covered by the exhaust gas heat recovery cycle are in operation.

However, Coal Gasification Combined-Cycle (CGCC) for power generation is not yet commercialized because of low economics.

(2) Development of Coal Gasification Combined-Cycle Power Plant

The Coal Gasification Combined-Cycle which has the advantage of high energy efficiency and environmental effect has been worldwidely developed to raise the security of the power source.

In U.S.A., Cool Water Project of CGCC was promoted and plant operation started in 1985.

The net thermal efficiency of Cool Water Project is estimated to be approximately 31%, comparatively lower than 37% of conventional coal-firing steam cycle system, because the project applies coal water slurry system, wet gas-cleanup system and oxygen as oxidant. However the project is notably watched through the world because it is the first demonstration plant of CGCC system.

In Japan, CGCC development and technical research is promoted with 40 t/d fluidized-bed gasification test plant by Sunshine Project and 200 t/d entrained-bed gasification test plant by NEDO (New Energy and Industrial Technology Development Organization).

The development of Advanced Gas Turbine of 1,300°C class and dry clean-up system has been promoted in Japan as well as in U.S.A., one of which is by Sunshine Project of Japan.

The topic of technical development of the CGCC as shown in Fig. 7-3-2 is on technology of advanced gas turbine as well as gasification and dry gas-cleanup system.

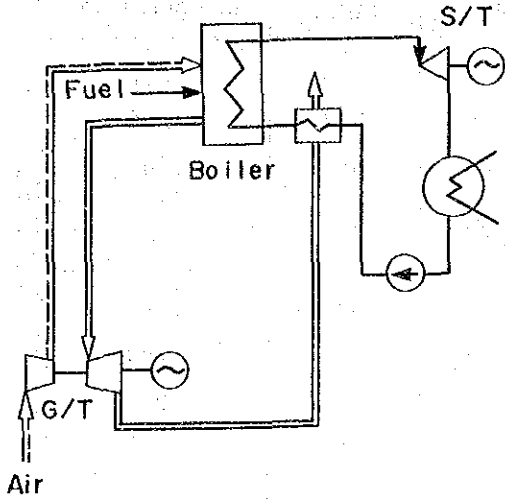
For gas turbine inlet temperature, thermal efficiency of the CGCC is promised to be improved as the temperature is rising, as shown in Fig. 7-3-3, indicating the possibility of realization of high efficiency power plant.

As a conclusion, it is understood that the prospects of CGCC system for Banko coal depends on technical development of the above mentioned systems in the future.

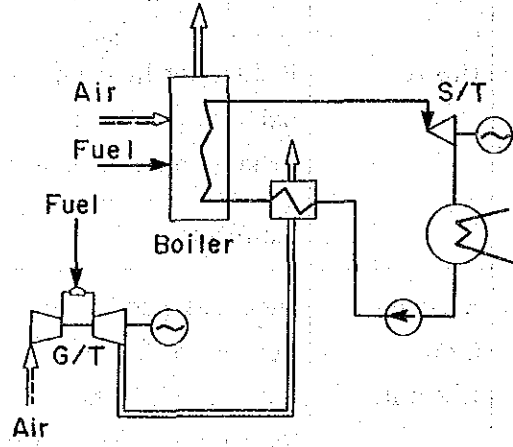
Table 7-3-2 World-Wide Combined-Cycle Power Plant Installations

District	Plant type	No. of units	Total output (MW)	Commencement of operation
U.S.A	Feedwater heating	1	70.0	1949
	Exhaust gas fired	10	1392.5	1958
	Exhaust heat recovery	35	7990.6	1968
	Subtotal	47	9453.1	-
Europe incl. U.S.S.R.	Supercharged boiler	5	941.0	1963
	Feedwater heating	1	312.0	1964
	Exhaust gas fired	26	8862.0	1964
	Exhaust heat recovery	4	265.5	1960
	Subtotal	36	10380.5	-
Asia incl. Japan	Exhaust gas fired	2	258.0	1968
	Exhaust heat recovery	8	4455.0	1979
	Subtotal	10	4713.0	-
Total		93	24546.6	-

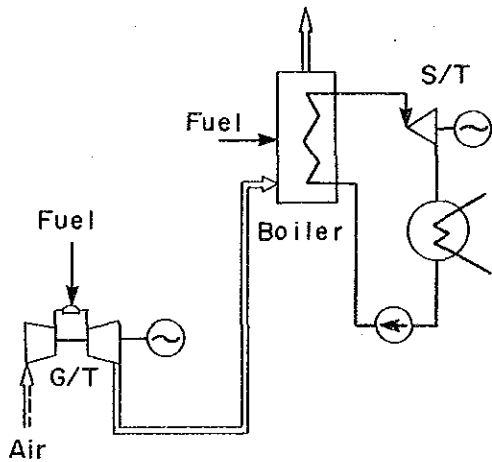
SUPERCHARGED BOILER CYCLE



SIMPLE FEED WATER HEATING CYCLE



EXHAUST GAS FIRING CYCLE



EXHAUST GAS HEAT RECOVERY CYCLE

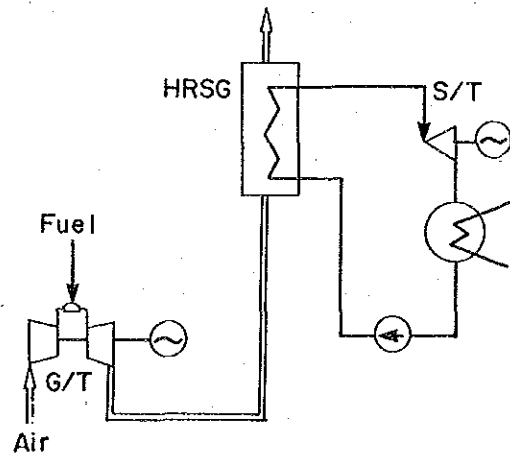


Fig. 7-3-1 Type of Combined-Cycle Plant

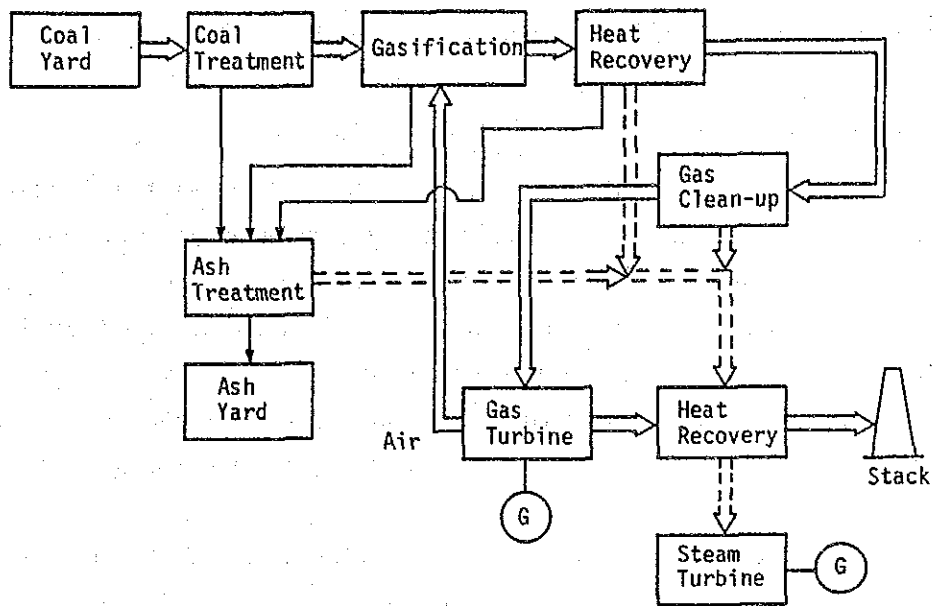


Fig. 7-3-2 Scheme of Coal Gasification Combined-Cycle Power Plant (Integrated)

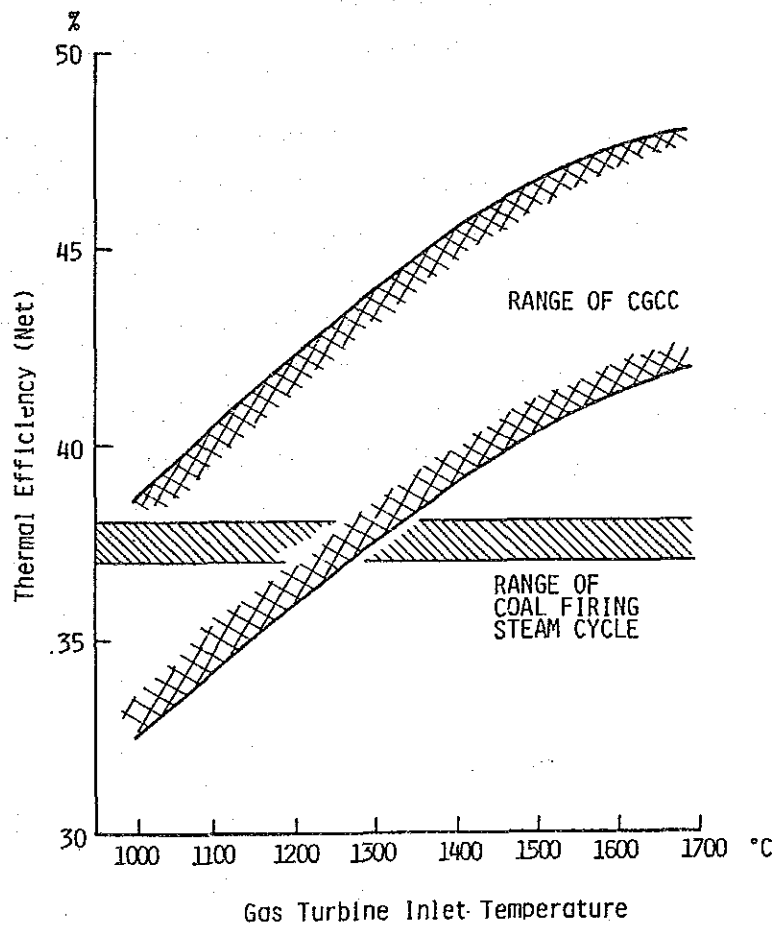


Fig. 7-3-3 Thermal Efficiency of Coal Gasification Combined-Cycle

7-3-3 Possibility of Banko Coal Utilization by Fluidized Bed Boiler

(1) Present Situation of Fluidized Bed Combustion System

Though it is expected that modified technology of conventional coal firing system, available for the use of more than 10% sodium-in-ash, will be developed, fluidized-bed combustion system for electric power generation is more prospective because the technology has a versatility for various fuels including difficult-burn coal and high sodium-in-ash coal.

Fluidized-bed combustion can burn coal efficiently at a temperature low enough, in the range of 700~900°C, to avoid many of the problems caused by sodium-in-ash.

A low bed temperatures held eliminates the potential for slag formation on the water-cooled walls of the furnace. Another benefit is the formation of lower levels of nitrogen oxides compared to other combustion methods.

The outstanding advantage of fluidized-bed combustion (FBC), then is its ability to burn high-sulfur coal in an environmentally acceptable manner without the use of flue-gas scrubbers.

The atmospheric fluidized bed (AFB) technology for steam and electric generation got a big boost recent years when three electric utilities in U.S.A. decided to install demonstration plants, ranging in size from 110 to 160 MW, one as circulating fluidized bed type (CFB), one as spreader coal feed bubbling fluidized bed type (retrofit from conventional boiler to fluidized bed) and one as pneumatic coal feed bubbling fluidized bed type.

As for the industrial field, fluidized bed combustion boilers are already going into commercial stage as shown in Fig. 7-3-4 and Fig. 7-3-5.

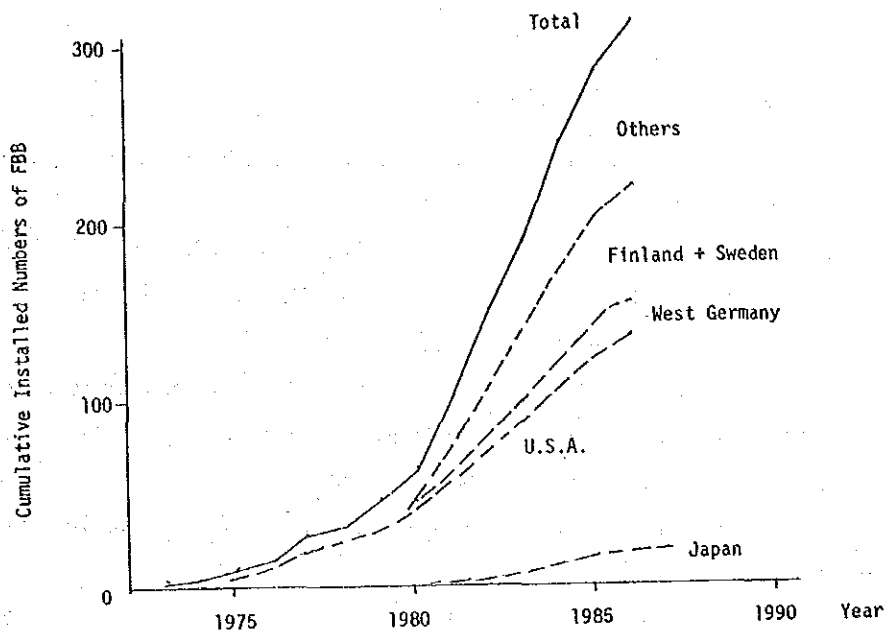


Fig. 7-3-4 Installed Numbers of FBB in the World

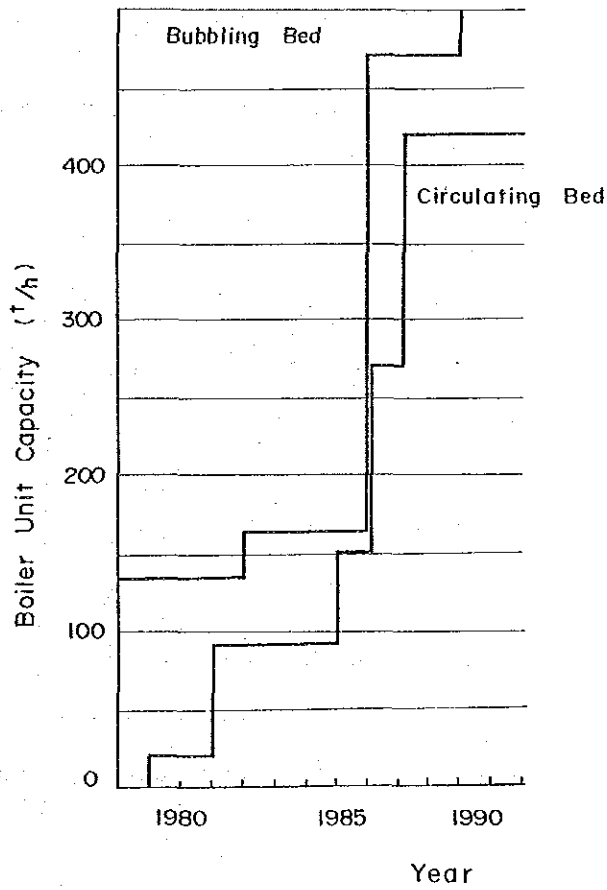


Fig. 7-3-5 Max. Unit Capacity Records of FBB in the World

(2) Classification of Fluidized Bed Boiler

AFB technology is generally classified into two types, bubbling bed type and circulating bed type.

The bubbling bed boiler is also called as the classic fluidized bed and the circulating fluidized bed boiler is called as the 2nd generation fluidized bed according to the development time lag.

The latter is superior to the former concerning the combustibility, NO_x emission and consumption rate of sorbent, although the initial cost of the latter is said to be higher than the former in the range of small capacity.

Fig. 7-3-6 is an example of a schematic diagram of the bubbling bed fluidized bed boilers.

There are two alternatives, with or without an external heat exchanger (fluid bed heat exchanger), in case of circulating fluidized bed boilers.

Fig. 7-3-7 shows an advanced type of the circulating fluidized bed boiler aiming at high combustibility and low NO_x and SO₂ emission simultaneously, whereas the recirculating convective cyclone section is changed from the high temperature type to the middle temperature type resulting in the decrease of cyclone trouble.

The fluidized bed boiler would be one of the best choices for the Banko coal which contains high sodium in ash.

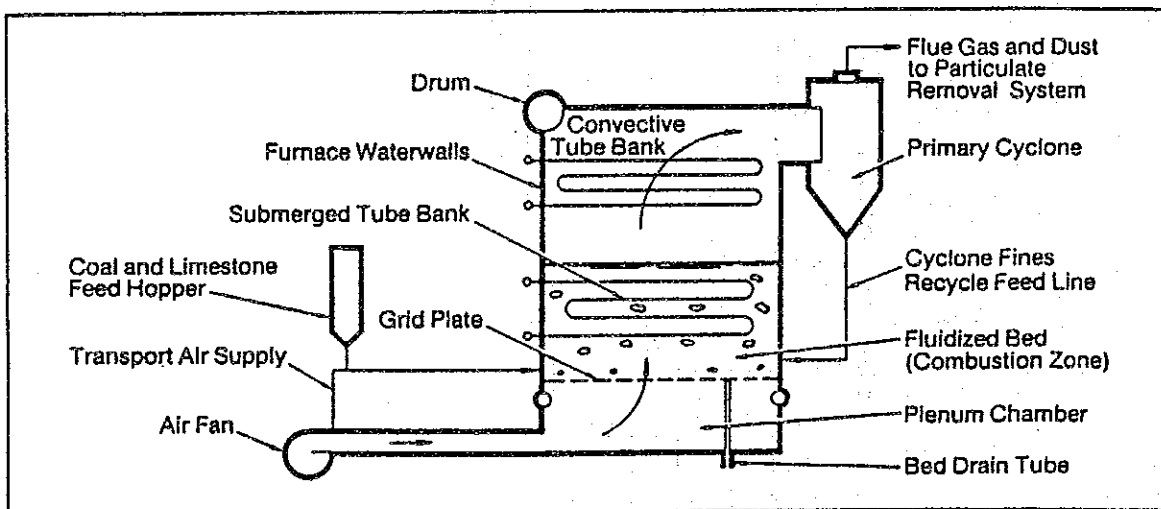


Fig. 7-3-6 Scheme of Bubbling Fluidized Bed Boiler

7-4 TECHNOLOGY FOR METHANOL ENGINES

7-4-1 Advantages of Fuel Methanol

Methanol favorably satisfies the basic condition for an alternative fuel because of its possible vast supply obtained mainly from coal and natural gas. And therefore it has been the subject of intensive study to clarify its suitability to engines since the oil crisis in 1973. These studies range from basic research work done by computer simulation to the demonstration of the actual methanol vehicle fleet in all continents including America, Europe, Asia, Oceania and Africa.

The accumulated results from these practices have already revealed the advantages of methanol as a fuel conclusively in two essential aspects, performance and environmental effects.

Among the two types of reciprocating engines (Otto cycle and Diesel cycle) and the gas turbine, diesel engines suffer the most difficult technical handicap in burning methanol but they also enjoy the maximum benefit out of this type of combustion, mainly smoke free exhaust gas. Because of these conditions, quite a bit of research has been carried out on the methanol utilization in diesel engines.

From a performance aspect, which is the crucial condition to determine the adaptability of a fuel to engines, methanol can produce about 10% more power than gasoline in Otto engines and quite comparable results in diesel engines.

Fig. 7-4-1 shows an example of drastic power boost obtained in the low speed range in a diesel based methanol engine used in the vehicle test.

There is significant advantage of methanol fuel in view of user acceptability, since the higher low end torque brings comfortable drivability, particularly in commercial vehicles such as trucks and buses. The output at high speed, namely the rated speed, the same advantage is not distinguished though it is quite comparable with diesel oil.

Other requirements in engine performance such as the noise, acceleration, startability and so on, are also mostly equivalent with the performance of petroleum fuel engines. Therefore it is concluded that methanol fuel is quite suitable for essential performance in engines.

From an environmental aspect, methanol is more than just an acceptable fuel. It can be a positive countermeasure for the exhaust gas emission from petroleum fuel engines.

The largest advantage of methanol, the reduction in nitric oxides and smoke, come from its nature, but in addition, hydrocarbon and carbon monoxide are reduced by providing a oxidation catalyst which is produced by its smoke free characteristics.

The only drawback of methanol from an environmental point of view is the high aldehyde emission, particularly formaldehyde. It is reduced to a comparable degree with petroleum fuel engines by providing the catalytic converter.

The possibility of reducing these exhaust gas emissions is well expressed in Fig. 7-4-2, where nitric oxides is about the half of that of petroleum fuel engines and hydrocarbon and carbon monoxide are also advantageous.

With these advantageous aspects, excellent performance as fuel for engines and the superior effect on environment, methanol can be a highly promising alternative fuel.

7-4-2 Characteristics of Fuel Methanol

(1) Characteristics of Methanol as a Fuel for Engines

Among many different properties of methanol from other fuels as in Table 7-4-1, six properties are perhaps the most important ones in order to utilize methanol in engines, particularly in diesel engines. These are cetane number, calorific value, viscosity and boiling point, and in addition, corrosivity and aldehyde emission when burned.

The extremely low cetane number of methanol, or in other words high octane number, makes it impossible to ignite methanol in a compression ignition manner (as in diesel engines). In contrast it behaves as a favorable fuel in Otto engines with its high octane number. Therefore as far as the diesel engine is concerned, the nature of methanol prevents it from being used in conventional diesel engines, and to clear up this obstacle, the technology is not yet completely ready at the present time.

The low calorific value of methanol, only half that of diesel oil or gasoline, is not disadvantageous in obtaining comparable horsepower output as with other fuels, and rather it gives more output than gasoline due to the lower stoichiometric air fuel ratio. But it is an inevitable handicap in using methanol in automobiles, because in such application the increased fuel tank size and weight are unfavorable in vehicle design and efficiency. Also the necessity of doubling the fuel injection in diesel engines sometimes causes difficulty in designing fuel injection pumps.

The low viscosity of methanol also adds problems to the fuel injection system in diesel engines. Those components such as the fuel injection pump and the injection nozzle have the inner parts whose lubrication relies entirely on the fuel viscosity, and this necessitates certain works in developing methanol engines.

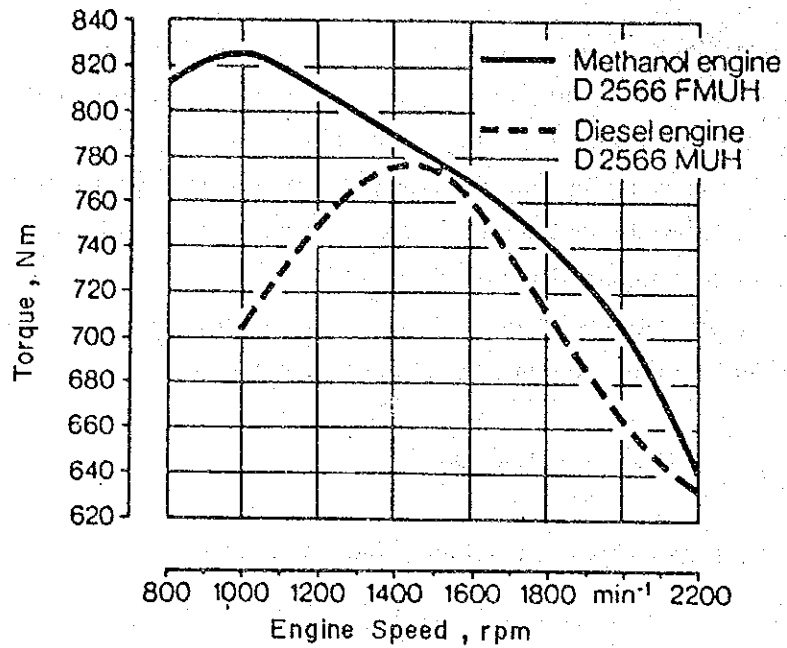


Fig. 7-4-1 Possible Low Speed Torque Boost with Methanol Diesel Engines
 (Source) VI International Symposium on Alcohol Fuels, 1984

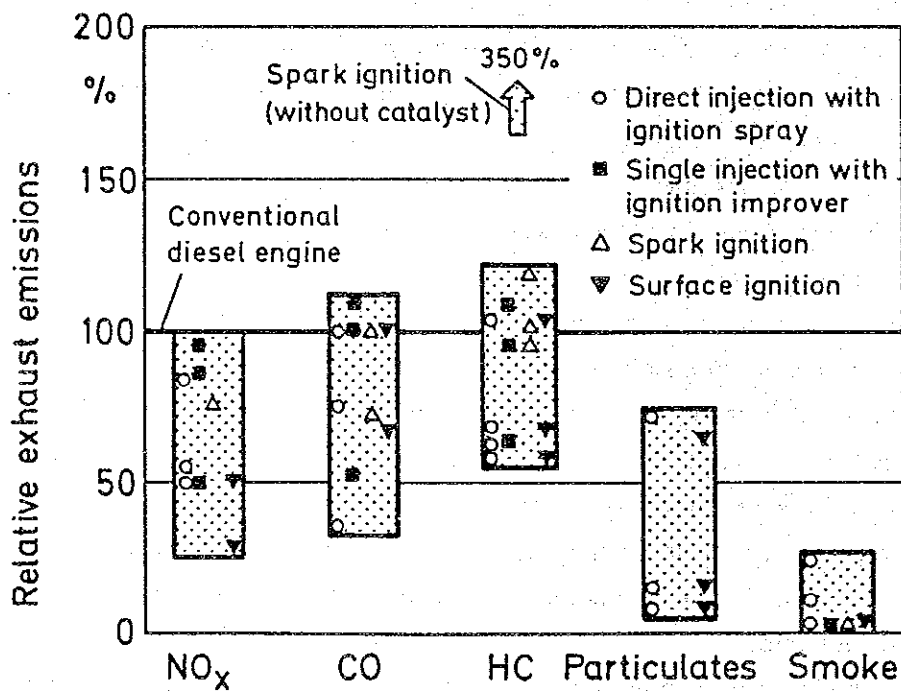


Fig. 7-4-2 Relative Exhaust Emissions for Alcohol-Diesel and Diesel Derived Engines

(Source) VI International Symposium on Alcohol Fuels, 1984

The low boiling point is not a critical factor in developing methanol engines but it tends to vaporize fuel easily so that fuel is not fed into the engine, and therefore a supplemental feed pump is needed to pressurize the fuel line to encounter the vapor lock problem.

The high corrosivity of methanol to materials including metals, rubbers and plastics is common to all kind of engines. Care has to be taken not only in fuel lines but also in the combustion chamber where the intermediate products by chemical reaction are sometimes corrosive to metals.

Table 7-4-1 Properties of Alcohol and Hydrocarbon based Fuels

	Gasoline	Methanol	Ethanol	MTBE	10% methanol blending	10% ethanol blending	7% MTBE blending	Diesel oil
Chemical formula	C ₄ ~ C ₁₀ mixture	CH ₃ OH	C ₂ H ₅ OH	C ₃ H ₁₂ O				C ₁₂ ~ C ₁₈ mixture
Molecular weight	100 ~ 105	32.0	46.1	88.1				
Composition	Carbon Hydrogen Oxygen C/H ratio	85 ~ 88 12 ~ 15 ~ 0 5.6 ~ 7.4	37.5 12.6 49.9 3.0	52.1 13.1 34.7 4.0	68.1 13.7 18.2 5.0			
Specific gravity (15/4°C)	0.70 ~ 0.78	0.793	0.789	0.747				0.830
Reid vapor pressure (37.8°C, lb/in ²)	7 ~ 15	4.6	2.5	7.8				
Boiling point (°C)	27 ~ 227	64.4	78.5	55.2				90% point < 350
Dissolving quantity to water	240 ppm	∞	∞	6.9%				
Dissolving quantity of moisture	88 ppm	∞	∞	1.4%				
Kinetic viscosity (37.8°C, cSt)	0.37	0.47	0.85	~ 0.31				(3.2)
Lower calorific value (Kcal/kg)	≈ 10,500	4,770	6,380	8,380	9,890	10,060	10,040	10,300
(Kcal/l)	≈ 7,720	3,770	5,040	6,270	7,330	7,450	7,620	8,541
Carburetion latent heat (Kcal/kg)	≈ 83	280	220	77	104	98	83	abt. 60
(Kcal/l)	≈ 60	220	175	57	76	76	62	
Theoretical air/fuel ratio (kg/kg)	14.3 ~ 14.8	6.4	9.0	11.7	13.7	14.0	14.4	14.8
Air/fuel mixture lower calorific value (Kcal/kg)	660 ~ 690	645	638	660				652
Air/fuel mixture carburetion latent heat (Kcal/kg)	≈ 5.4	87.8	22.0	6.1				abt. 3.8
Octane number	Research method Motor method	107 ~ 109 89	107 ~ 109 90	117 102	≈ 95.5 ≈ 86	≈ 95 84.5 ~ 86	≈ 93 84.5 ~ 85	- -
Cetane value	≈ 12	3	8	-				45 ~ 50
Ignition point	≈ -45	11.1	12.8	-27.8				> 50
Automatic firing temperature	≈ 425	467	424	460				316
Combustion limit (in air: Vol.%)	1.4 ~ 7.6	6.7 ~ 36.0	4.3 ~ 19.0	1.6 ~ 8.4				1.0 ~ 8.0
Laminar-flow combustion speed (cm/sec)	33~47	44						33~47

Note: Gasoline mixed in regular gasoline; Specific gravity: 0.736; RON: 90 to 92; MON: 82 to 84; Lower calorific value: 7,729 kcal/l

(Source) Report from the Institute of Energy Economics, Japan IEE-SR181

The last unfavorable feature of methanol is the aldehyde emission from the exhaust gas, specifically formaldehyde. It is reported that it is produced from the unburned methanol in the exhaust system and is a very stimulative gas to human senses with little concentration. Therefore it is a major research subject to reduce the aldehyde in developing methanol engines although there is no regulation at this moment all over the world.

Because of methanol's unfavorable nature, it is necessary to do intensive work to utilize methanol in engines even though technical difficulty depends on the type of engines. These differences in technological difficulty for the three typical engines currently in use, Otto, diesel and gasturbine engines, are briefly summarized as follows:

Otto engine; Corrosivity is the only major handicap. There is essentially no structural modification necessary and it is quite simple to utilize methanol. Engine startability and the cylinder wear are typical problems but these will be solved within the current technologies for engines.

Diesel engine; All of the six properties before mentioned are handicaps. Among them the cetane number is the major concern, and there are quite a few methods proposed in dealing with this nature of methanol. This and low viscosity are responsible for the insufficiency in durability and thermal efficiency in present methanol diesel engines. But the rest of the engine performance criteria are quite comparable with the performance of the petroleum fuel engines.

Gas turbine; Basically there is no handicap in using methanol in this engine except care must be taken for the corrosivity in the fuel line.

(2) Effect of Methanol on Health and Environment

In order to utilize methanol as fuel for engines, it is also important to consider the effect of methanol on human health and environment in handling the fuel. This has to be considered from several view points such as toxicity to human being and other living creatures, biomass in the land and underwater living creatures, and fire and explosion hazards.

Table 7-4-2 indicates the toxic limit of methanol when swallowed. The non-toxic limit per body weight is much lower for human beings compared with animals. Table 7-4-3 is the comparison of the inhaling limit of several fuel vapors in human beings and odor threshold. It indicates that the inhaling limit of methanol is as safe as common gasoline but more caution has to be taken since methanol is less detectable by odor.

Table 7-4-2 Acute Toxicity of Methanol, LD₅₀ Values (g/kg body weight) for Peroral Administration

Mouse	10
Rat	10
Rabbit	7 - 9
Dog	8 - 9
Monkey	3
Man	0.8 - 1.4

(Source) I.E.A. Executive Committee, 1985

Table 7-4-3 Threshold Limit Values and Detectable Concentrations for Various Motor Fuels and Fuel Components

Fuel	TLV (ppm)	Odor Threshold (ppm)
Benzene	5*	1 - 5
Diesel oil (mist)	3 mg/m ³	low
Ethanol	1000	10 - 350
Gasoline	200**	low
Isobutanol	50	0.7 - 2
Isopropanol	200	3
Methanol	200	50 - 2000
Tert. butanol	50	0.7
Toluene	80	0.25 - 2
Xylene	80	0.1 - 2

* Causes Cancer

** Depends on hydrocarbon composition; figure without benzene

(Source) I.E.A. Executive Committee, 1985

The effect of methanol on the biomass when it is spilt over the soil is shown in Fig. 7-4-3. This graph indicates the recovery rate of the biomass in the soil one year after the soil is contaminated by several fuels. Methanol has no worse effect than gasoline in this view but caution must be taken with methanol blended with gasoline (denoted as M-15, with 15% methanol). Methanol is even less hazardous when spilt in water. It is water soluble thus the concentration will become very low in a pond or in the sea.

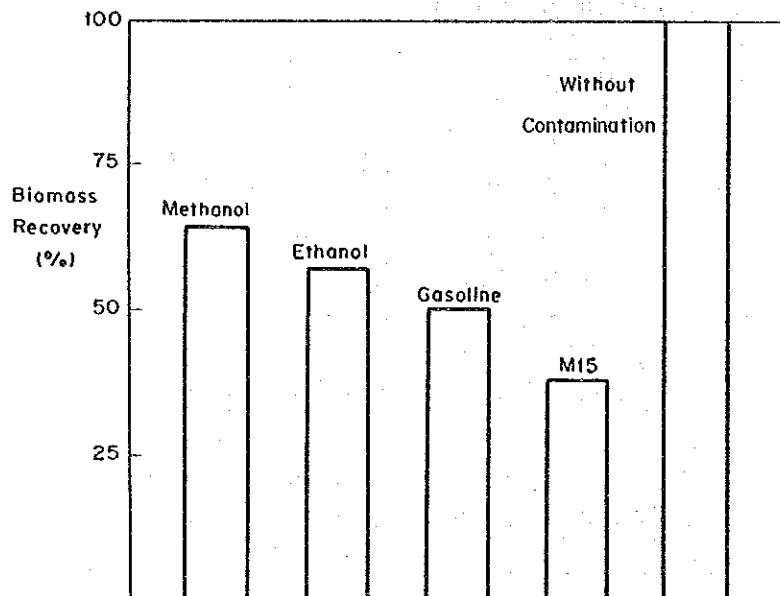


Fig. 7-4-3 Biomass (% of normal) One Year after Soil Contamination of Various Fuels

(Source) I.E.A. Executive Committee, 1955

Explosion hazard is compared in Table 7-4-1. Possibly the most hazardous nature of methanol is its wide flammability limits compared to other fuels. It implies that a explosive flame will be generated if a torch is brought to the inlet of a fuel tank filled with methanol, while with gasoline there is a less explosive flame. However, in ordinary handling situations, it will be easily avoided by a flame arrester. Another point in dispute is the nature of methanol's flame. It has an invisible blue flame when burned thus it is hard to detect the onset of a fire. The positive nature of methanol when burned is that the lower heat radiation of the methanol flame reduces the risk of a burn.

The relative hazards of methanol fuel from those different points of view are summarized in Table 7-4-4 where methanol is given the lowest points in recognition of the least hazardous fuel. At least it implies that it is safe if methanol is handled with the same care as gasoline in fueling.

Table 7-4-4 Relative Hazard of Motor Fuels, Based on Physical and Chemical Properties

Risk	Relative Hazard (1=low, 7=high)			
	Gasoline	Diesel	Methanol	LPG
Leakage	3	1	2	5
Evaporation	3	1	2	4
Release to the environment	5	6	3	4
Autoignition	6	5	4	3
Spark ignition	2	1	-	3
Flammability	2	1	5	3
Deflagration	5	6	1	2
Heat radiation from fire	6	7	1	5
Health effects	7	5	6	4
Total	39	33	24	33

(Source) I.E.A. Executive Committee, 1985

7-4-3 Technology for Methanol Engines

Many methods are proposed in order to utilize methanol in engines, which will be classified in several ways depending on the view point, both theoretically and practically. Here, for easy understanding to non specialists without spoiling technical correctness, are those classified in the three conventional engines; Otto, diesel and gas turbine. There are methods which can not be classified within these three groupings and these are described in one of the above mentioned categories for convenience.

(1) Utilization of Methanol in Otto Engine

As described previously, methanol has high octane number and is a fairly good fuel to use in Otto engines. Basically there are no structural modifications necessary to use it. Only several adjustments and material concern are needed as engineering detail. Therefore the effort has been made not only to make it usable in Otto engines but also to make the most of its advantageous nature.

1) Conventional Otto Engine

In this engine form methanol has an advantage in increasing the power output. Since the fuel is burned near the stoichiometric air fuel ratio (theoretical ratio), in these types of engines, the output depends on the energy (calorific value) input into the engine cylinder. Taking the difference of the stoichiometric air fuel ratio between gasoline and methanol and the calorific value as in Table 7-4-1 (in weight basis) into consideration, fuel input in energy by using methanol can be about 6% more than by using gasoline. Also the high octane rating of methanol makes it possible to give higher knock limit than gasoline, thus the compression ratio can be raised about 20%. This can bring higher thermal efficiency, which in turn enables the engine to generate more power output. Combining those two factors, the total power increase will be close to 10% compared to gasoline. This situation is well demonstrated in Fig. 7-4-4. It is observed that the maximum power output increase is 9% along with the improvement in thermal efficiency. The compression ratio is raised to 11.5 by 20%. The efficiency is also improved by other properties of the fuel, such as the leaner air fuel mixture which is made possible by the wider flammability limit shown in Table 7-4-1.

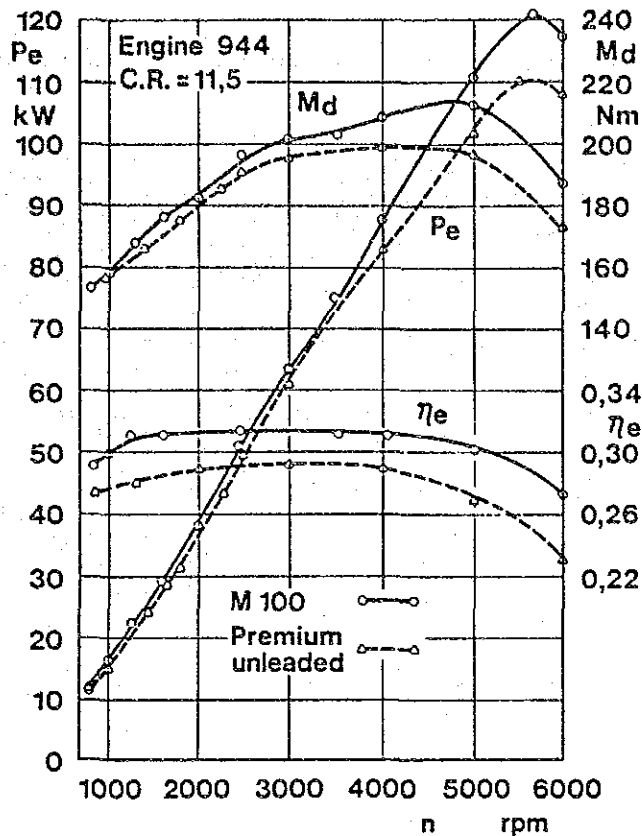


Fig. 7-4-4 Performance of Otto Methanol Engine

(Source) VII International Symposium on Alcohol Fuels, 1986

The leaner combustion is also advantageous in the exhaust emission. In addition to the great benefit of NO_x reduction due to large latent heat of methanol. This advantage in exhaust gas emission is well shown in Table 7-4-5 where it is observed that lean combustion plays an important role. One drawback in the exhaust gas emission is the high aldehyde concentration due to the fuel nature. Thus the technology has to be satisfactory for the aldehyde emission as well.

One disadvantage of performance in using methanol in these Otto engines is the difficulty in starting the engine in cold weather. This is due to the large latent heat which is advantageous to NO_x reduction as mentioned above. It is overcome without much difficulty by such methods as using small amount of gasoline for the engine starting and warming up periods, which can be shut off and methanol will flow in automatically as the coolant temperature rises. Also a blend of methanol and gasoline such as M85 (85% methanol) will be helpful to improve the starting characteristics of the fuel, however with a slight sacrifice of the benefit obtained by neat methanol as described.

Table 7-4-5 Emission Characteristics of Lean Burn Methanol Otto Engine

A/F ratio calibration	Exhaust emission (gm/mi)			Fuel economy (mpg)	
	T.HC	CO	NOx	M85	Gasoline equiv.
Stoich.	0.36	3.06	0.26	16.9	30.8
Stoich. (Dummy cat)	1.89	8.50	3.20	—	—
Partial lean	0.31	1.88	0.51	17.8	32.4
Partial lean (Dummy cat)	3.11	4.88	1.45	—	—

'86 Standard			
Federal	0.41	3.4	1.0
Calif	0.41 (0.39)	7.0	0.7

* Energy density ratio on a volume basis equals 1.82

(Source) VII International Symposium on Alcohol Fuels, 1986

2) Flexible Fuel Vehicle (FFV)

As mentioned above, technologically it is very soon to bring methanol fuel into practical use in Otto engines. However, methanol is not advantageous in commercial use because of the fuel station situation during the introductory period of fuel methanol, thus it is more practical at present time to develop vehicles which can be driven by both methanol and gasoline. The Flexible Fuel Vehicle which can be operated by any mixing ratio of methanol and gasoline has been developed for that reason. The concept is made possible because of methanol suitability to Otto engines which does not require major modification from gasoline engines except adjustment of air fuel mixing ratio at the carburetors. The flexible fuel system currently in development is a device which can detect the right mixture ratio of methanol and gasoline in the fuel by a sensor and adjust automatically the air fuel ratio accordingly. Therefore the attention is focussed on the development of a sensor which can detect the methanol gasoline mixture correctly. The sensor which was originally invented by TNO, a Netherland company, and has been improved by Ford Motor Co. successively, optically detects the mixture ratio by the color of the fuel.

3) Gasified Methanol

In an effort to use methanol efficiently, the gasified methanol engines have been developed by several organizations. The concept for this method is to vaporize the liquid methanol by the heat of the engine cooling water, and the vaporized methanol gas mixture with air is burned in the engine cylinder in the same manner as ordinarily Otto engines. The system is illustrated in Fig. 7-4-5. This method gives uniform fuel gas distribution in the combustion chamber, which enables combustion with lean fuel mixture to bring higher efficiency and lower NOx emission.

Quite high efficiency is observed in Fig. 7-4-6. The vaporization by the engine coolant is facilitated by the low boiling point of methanol (as in Table 7-4-1) compared to gasoline. The major drawback of the system is the startability of the engine. One must wait for a certain time before the engine is started since the supplemental heater has to be used to vaporize methanol at the starting. Another disadvantage of this method is that the whole system is relatively complicated and very large. For that reason it is *generally more suitable for the stationary engines rather than for automobile applications*. The exception may be the application in the city bus, in which the complicated system is fit within the large bus body and the engine is not very often shut down and re-starting is not usually be required during daily operation.

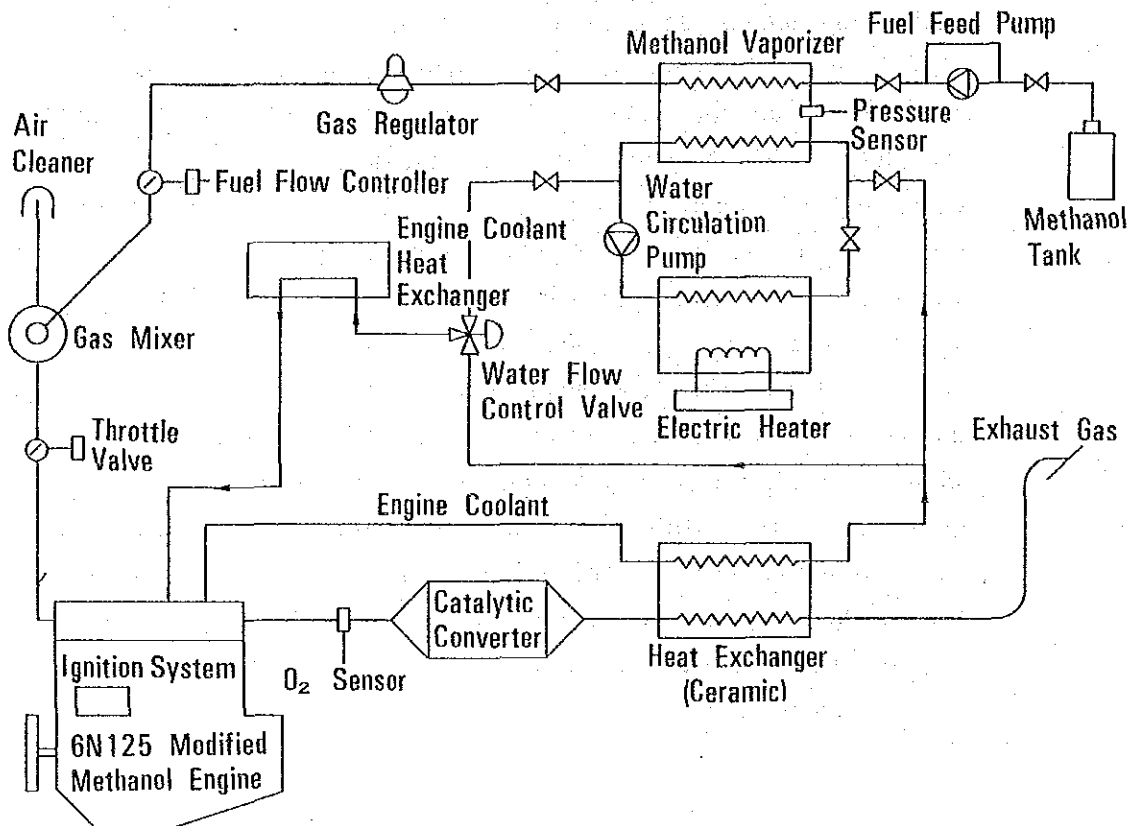


Fig. 7-4-5 Schematic of Gasified Methanol System

(Source) VIII International Symposium on Alcohol Fuels, 1988

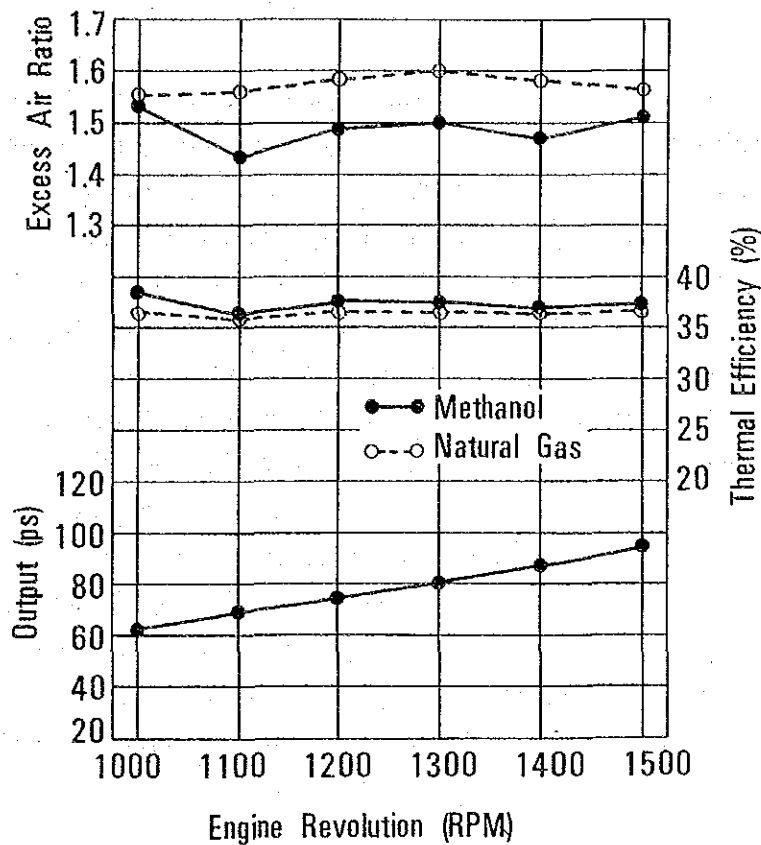
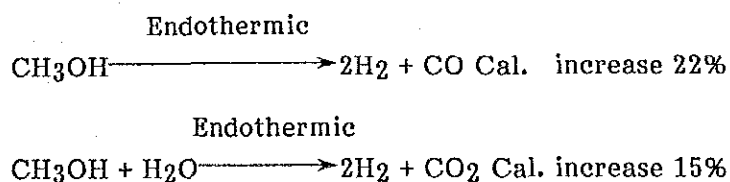


Fig. 7-4-6 Thermal Efficiency of Gasified Methanol Engine
 (Source) VIII International Symposium on Alcohol Fuels, 1988

4) Reformed Methanol

To utilize methanol in reformed gas is a further effort to efficiently make the most of methanol. This method is not necessarily categorized in Otto engine application, but in the engine cylinder it is burned in a similar fashion as in the gasified methanol or ordinary gas engine, and therefore it is reasonable to explain it within this category.

This method is similar to the gasified methanol engine in that the liquid methanol is vaporized through the heat exchanger but the difference is that methanol is not just vaporized but reformed to other species by the endothermic chemical reaction, which contains more calorific value than original methanol. The key chemical reaction of the concept is as follows.



It is expected that the total improvement in the thermal efficiency by burning the products (CO and H₂) are about 10% compared with liquid methanol, and perhaps this is the most efficient way of utilizing methanol in engines. However, practically there are several obstacles which are likely to prevent its realization. In the first place, the reformed methanol system is much more complicated as in Fig. 7-4-7 than the gasified methanol system. It is quite questionable that it will be commercially accepted with such complexity and the estimated high cost of the system, since it only improves efficiency by 10%. Secondly, the gas occupies more cylindrical volume for the same fuel weight input and this prevents the engine from obtaining the comparable output as with other fuels. Thirdly, there are number of technological obstacles to be solved, such as the stable and efficient reforming of methanol, and the problem of back-fire associated with burning hydrogen gas. Taking all these consideration it is appropriate to remark that it is still quite a far away for the reformed methanol technology to be practically considered.

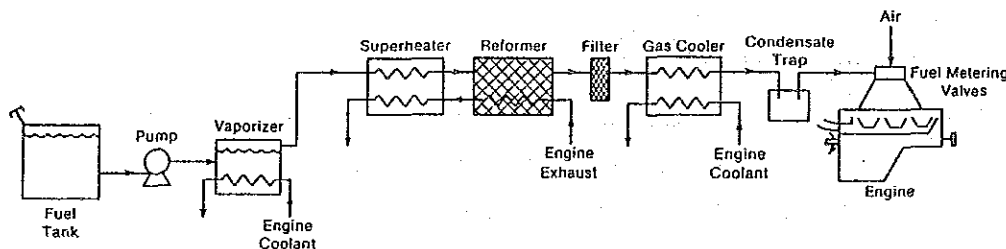


Fig. 7-4-7 Reformed Methanol Fuel System

(Source) VI International Symposium on Alcohol Fuels, 1984