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CO-PRODUCTION OF METHANOL IN AMMONIA PLANTS

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RESUME

Dans les unités d'ammoniac, il se forme du CO_2 comme sous-produit lorsque l'on fabrique le gaz de synthèse. Ce CO_2 est séparé du gaz de synthèse et exporté, quelquefois vers l'atmosphère, parfois totalement ou en partie vers une unité adjacente d'urée. Lorsque CO_2 est en excès, alors une méthanolation ou une co-production de méthanol peut être une option intéressante car elle confère une souplesse accrue de production ainsi que d'autres avantages.

L'unité de co-production consiste en un réacteur de synthèse de méthanol suivi par un nouveau méthaneur. L'unité est située entre les deux enveloppes du compresseur de gaz de synthèse, soit en aval du dernier stage d'entrée du gaz d'appoint. Ce dernier implique des modifications de la deuxième enveloppe du compresseur, mais il est souvent intéressant parce qu'il augmente la production et réduit le passage des oxydes de carbone vers le méthaneur.

A la partie antérieure de l'unité d'ammoniac, la faible variation de température et le méthaneur existant sont complètement by-passés. L'élimination de CO_2 et la forte variation possible de température sont en partie évitées pour laisser des quantités suffisantes d'oxydes de carbone dans le gaz 'de synthèse pour la production désirée du méthanol.

Le gaz de synthèse est comprimé et envoyé au réacteur de synthèse de méthanol. Ce réacteur est du type à eau bouillante, exigée par la réaction fortement exothermique du méthanol. Le catalyseur est placé dans un certain nombre de tubes. Le côté enveloppe du réacteur est rempli d'eau bouillante. Le réacteur fonctionne avec un seul passage ; le recyclage n'est pas nécessaire à cause de la pression élevée. Le gaz de sortie du réacteur est refroidi dans un échangeur alimentation/effluent et un refroidisseur d'eau avant d'entrer dans un laveur à l'eau/séparateur de méthanol.

Le gaz de synthèse sortant du séparateur de méthanol est préchauffé dans un second échangeur d'alimentation/effluent et dans un réchauffeur d'entretien avant entrée dans un nouveau méthaneur. A la sortie de celui-ci, le gaz est refroidi et le condensat séparé avant recyclage du gaz de synthèse vers l'unité d'ammoniac, immédiatement avant le point d'extraction.

Le nouveau méthaneur est un réacteur adiabatique fonctionnant exactement comme l'ancien, seulement à une pression légèrement élevée.

Cependant, la production de méthanol consomme une partie de l'hydrogène auparavant utilisé pour l'ammoniac et, comme il faut maintenir le rapport entre l'hydrogène et l'azote à l'entrée de la boucle d'ammoniac, la teneur en azote doit être réglée en réduisant le débit d'air vers le reformer secondaire et en augmentant la charge du reformer primaire, si possible, ou une unité de récupération de gaz de purge doit être installée.

De plus, la concentration en méthane du gaz d'appoint pour la boucle d'ammoniac augmente un peu du fait de la baisse de température de sortie du reformer secondaire lorsque le débit d'air est réduit et comme la synthèse de méthanol ne sépare pas le CO_2 quantitativement. Le temps d'arrêt du compresseur d'air de procédé et le niveau accru de produits inertes sont quelques-uns des facteurs qui peuvent limiter la production de méthanol.

Les avantages de la co-production sont :

- *Le méthanol est produit à un faible coût par unité comparé aux unités complètement construites*
- *La souplesse du procédé permet au propriétaire de fabriquer le produit offrant la plus grande marge bénéficiaire*
- *Le méthanol peut servir de matière première à une nouvelle diversification de produits (formaldéhyde-urée, formaldéhyde, acide acétique, etc.).*

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INTRODUCTION

During recent years a significant interest for the concept of co-production of methanol in ammonia plants has developed.

Two plants have so far been built, both based on technology from Haldor Topsøe A/S, and the interest in the concept seems to continue.

The rationale for these units are that they, compared to a grassroots methanol plant, are fast to install, low in investment, compact and easy to operate.

The industrial experience and the potential performance, in particular for larger units, will be described in this paper.

## INCENTIVES FOR CONVERSION FROM AMMONIA TO METHANOL

The ammonia/urea industry is a mature industry in many parts of the world. In industrialized countries the demand is constant or receding, and in developing countries, the growth in demand is modest. As a consequence, many plants are operating below maximum capacity as illustrated in Table 1.

TABLE 1

Ammonia Capacity Utilization by Regions % of Nominal Capacity			
	1989/1990	1992/1993*)	1995/1996*)
Africa	64	67	72
America	93	95	94
Asia	84	84	85
Europe	83	79	79
"USSR"	83	79	79
Oceania	91	91	91
Source: World Bank Nitrogen Survey, 1992	*) Forecast		

Figure 1: Relative Demand Growth by Methanol and Derivates

Source: World Bank Nitrogen Survey 1993/Methanol Suppliers 1992-93
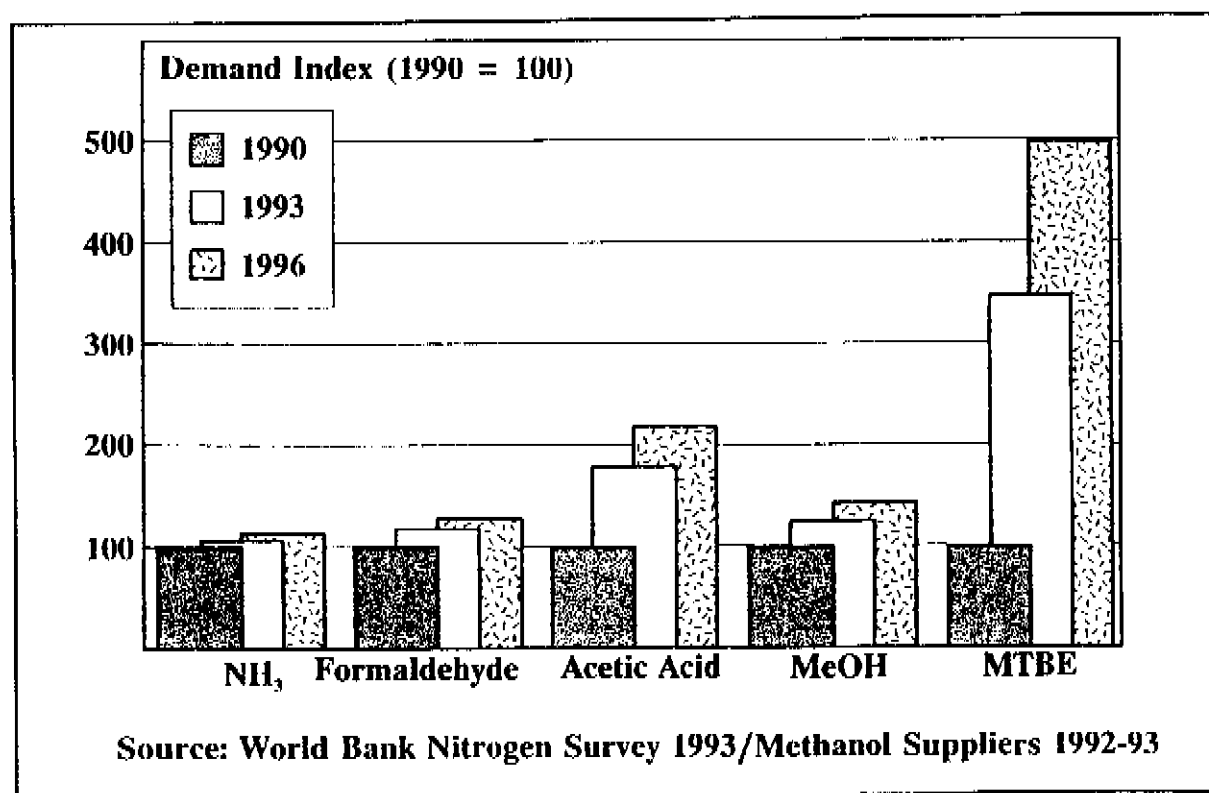
Operating below maximum capacity is not desirable. The fixed cost and depreciation are unaffected, and plant efficiency is reduced when operating below design capacity. Therefore, making a profit becomes much more difficult. In this situation it should be considered to convert the "un-utilized" ammonia production capacity to methanol co-production.

Methanol has a better demand development in general, but especially some of the derivates are of interest:

Having in mind the conditions illustrated in **Table 1 and Figure 1**, the following advantages may be listed:

* *Utilization of Unused Capacity*
  If the ammonia plant is operating below maximum capacity, a co-production unit utilizing the capacity margin will obviously increase profitability.
  For instance, the co-production unit could absorb the seasonal cycles in fertilizer demand.

* *Breaking into Less Mature Markets with Better Demand Growth*
  Methanol and its derivates are used in industry and as clean burning fuel additives. Industry and the clean fuel market are growing faster than the fertilizer market.

* *Risk Reduction by Product Diversification*
  The co-production technology allows easy control of the balance between methanol and ammonia. Thus it will be possible to choose the product giving the highest profit margin, and to some extent reduce the impact of price cycles.

* *Low Investment Cost per Tonne of Methanol Co-produced*
  The methanol co-production technology utilizes the existing reformer, compressors and utilities. The investment cost per tonne of methanol is therefore competitive even compared to world scale capacity grassroots methanol plants.

* *Low Operating Cost*
  The operating and maintenance personnel from the ammonia plant will in most cases be able to handle the methanol plant as well. This keeps wages down.

  In some cases where un-utilized capacity in the ammonia plant is used for methanol co-production, operating efficiency will improve as well. In any case, the co-production unit will experience the operating efficiency of a large plant which is significantly better than that of a stand-alone methanol plant of the same capacity.

* *Shorter Construction Time*
  The unit is much simpler than a grassroots facility, and long lead items such as compressors are avoided. Therefore, the time from contract to commissioning is reduced.

* *Longer Catalyst Life in the Shift Section of the Ammonia Plant*
  In order to provide carbon oxide for the methanol synthesis, the plant section from downstream - the waste heat boiler to the make-up gas compressor in the ammonia plant will be partly by-passed. The by-pass over the shifts will allow operation with lower catalyst activity in the shifts. However, the flexibility to return to 100% ammonia would then be impaired.

THE METHANOL CO-PRODUCTION PROCESS

The subject of co-production of methanol and ammonia has been discussed for some years, but mostly in new plants or from purge gases.

Topsøe's objective was to develop a low cost, add-on unit for an existing ammonia plant. The low cost requirement efficiently eliminated the purge gas option, because of the need for a very expensive compressor compressing CO_2 from close to ambient pressure to at least 50 bar. From the start is was obvious that a low cost solution could not include a new compressor.

This is relevant because pressure is of paramount importance for the methanol synthesis reaction. This is illustrated in **Figure 2**, where a typical synthesis gas is equilibrated at different pressures.

Besides, the methanol reaction is favoured by high CO/CO_2 ratio as illustrated in **Figure 3**.

The fact that high pressure and high CO/CO_2 ratio is beneficial to the process has led Topsøe to conclude that the best location for the methanol co-production unit is between the two casings of the make-up gas compressor in the ammonia plant. The lay-out of the modified unit is illustrated in **Figure 4**.

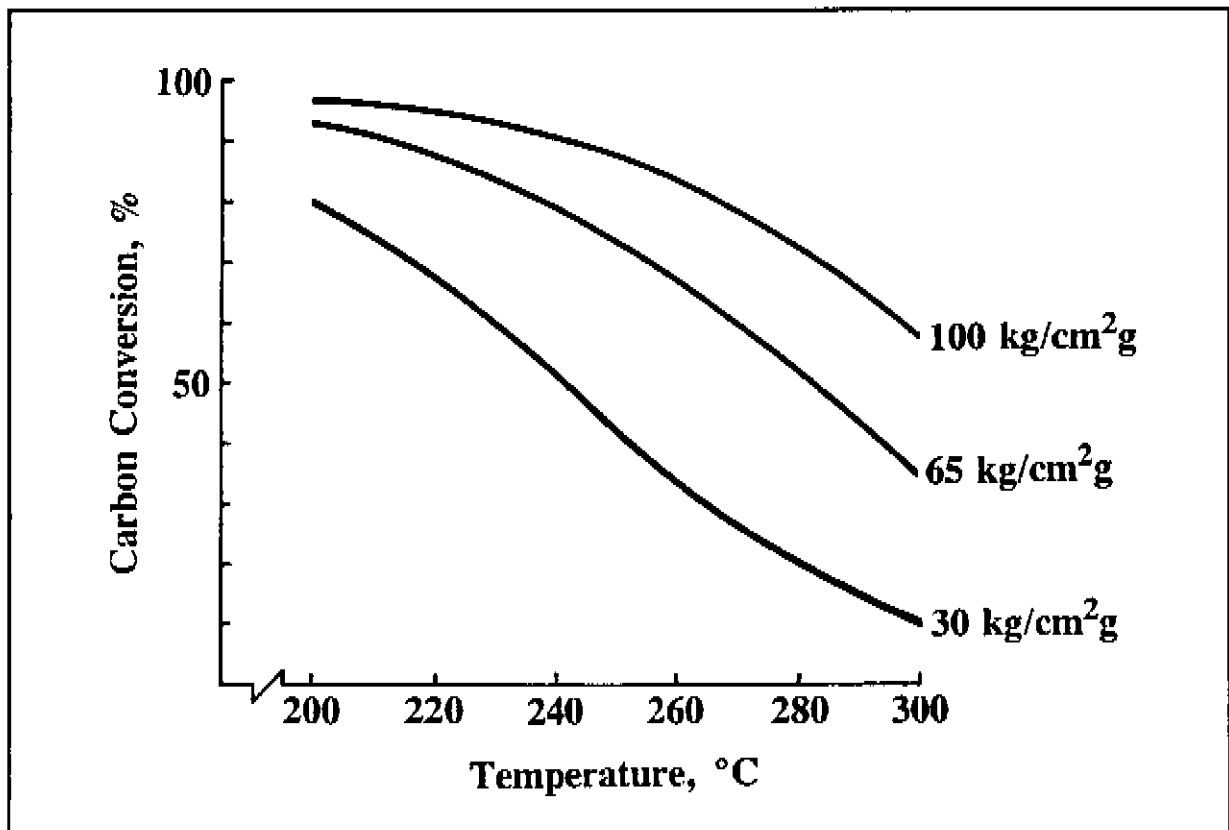## Figure 2: Pressure Dependence of Methanol Equilibrium Conversion

Figure 3: Methanol Equilibrium Conversion of Typical Gas at 65 bar
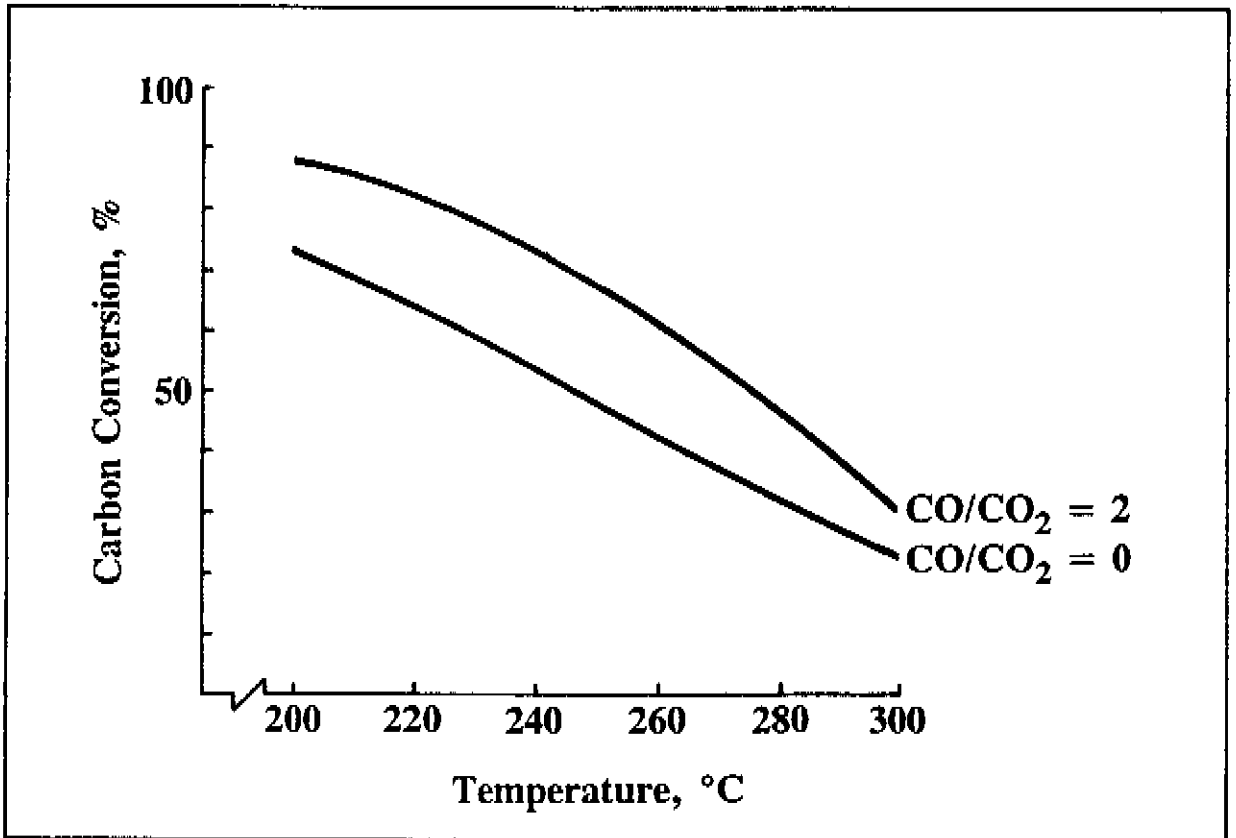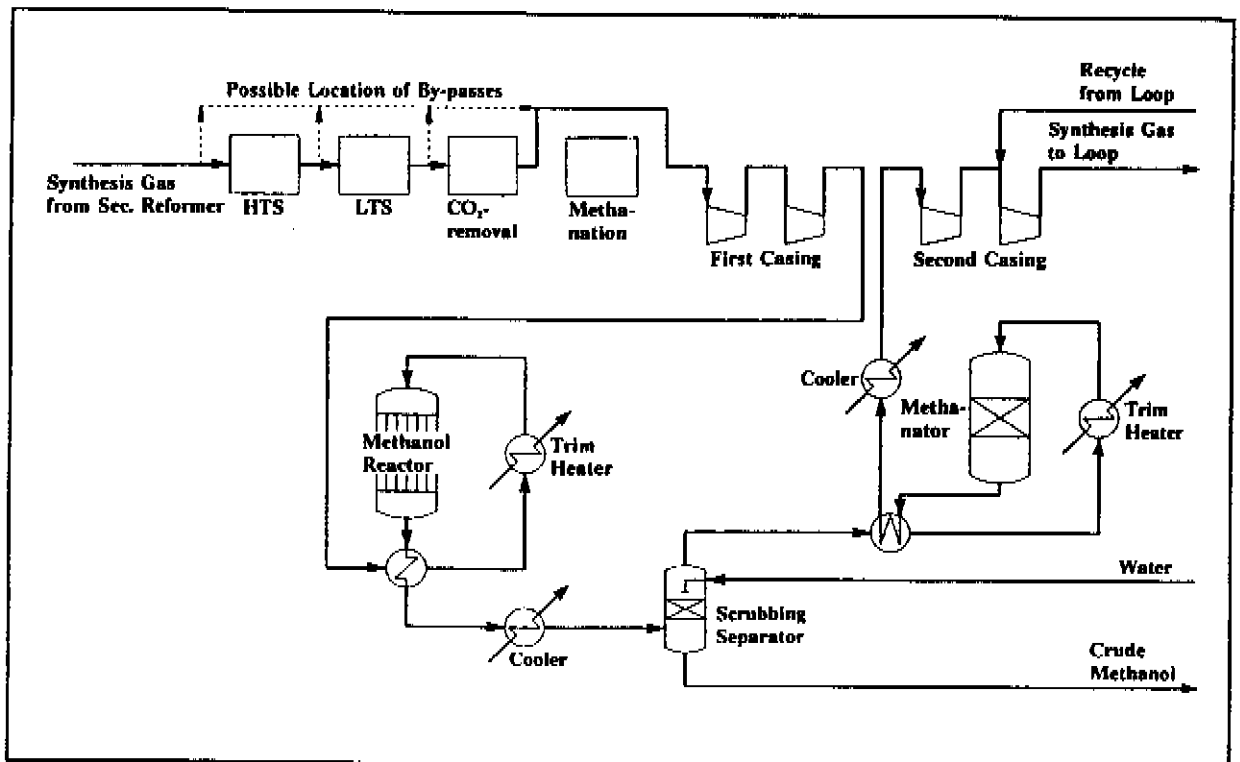

Figure 4: Co-production at High Interstage Pressure

PROCESS DESCRIPTION

The co-production units consists of a methanol synthesis reactor followed by a new high pressure methanator. In the front-end of the ammonia plant the low temperature shift, the CO_2-removal, the existing methanator, and possibly the high temperature shift are by-passed, wholly or partly to leave sufficient amounts of CO and CO_2 in the synthesis gas for the desired methanol production. As indicated in Figure 3, a high CO/CO_2 ratio is desired. A certain minimum of CO_2 is required, however, due to catalyst kinetics.

The synthesis gas is compressed in the first synthesis gas compressor casing and led to the methanol synthesis reactor. The reactor is a boiling water type reactor, necessitated by the strongly exothermic methanol reaction. The catalyst is located in a number of tubes. The reactor is cooled by boiling water on the shell side. The reactor is operated in a once-through fashion; recirculation is not required because of the high pressure.

At the gas outlet the reactor is cooled in a feed/effluent exchanger and a water cooler before it enters a combined water scrubber/methanol separator. Optionally, methanol may be removed by a chiller. This will eliminate the need for a high pressure water pump for the scrubber. The effect on the methanol slip is marginal.

At the synthesis gas exit the methanol separator is preheated in a second feed/effluent exchanger and in a trim heater before entering the new methanator. Exiting the methanator the gas is cooled, and condensate is separated before the synthesis gas is returned to the ammonia plant to the second casing of the synthesis gas compressor.

The new methanator is an adiabatic reactor like the old one (same inlet temperature, same catalyst type), but operating at significantly higher pressure.

The methanol production can easily be decreased by reducing the by-pass over the shift and CO_2-removal sections, thus depriving the methanol synthesis of its CO and CO_2 feedstock. In principle, the turndown ratio is 100%, but rather than running the unit at very low loads, say below 25%, the new unit should be run intermittently, if very low loads are required.

PRESSURE DEPENDENCE

In theory it would be even better to install the unit after the last stage of the make-up gas compressor, where the pressure is higher, but this location is not feasible in reality, partly because the gas is inaccessable at this point in many plants, partly because a leak from the methanol unit to the ammonia loop or reverse is unacceptable.

Typical contemporary world-scale ammonia plants are designed with a nameplate capacities of 1000 to 1500 ton/day ammonia, and they operate with a ammonia loop pressure of about 140 to 220 bar. This in turn leads to a pressure between the casings of about 65 and 100 bar. The interstage pressure of 100 bar is very suitable for the methanol co-production unit leading to a single-pass carbon conversion in excess of 90%. The single pass carbon conversion at 65 bar is significantly less as illustrated in **Figure 6** and in order to avoid excess slip of CO and CO_2 in 1000 MTPD ammonia plants, it is necessary to install a second methanol reactor as illustrated in **Figure 5**.

Figure 5: Co-production at Low Interstage Pressure
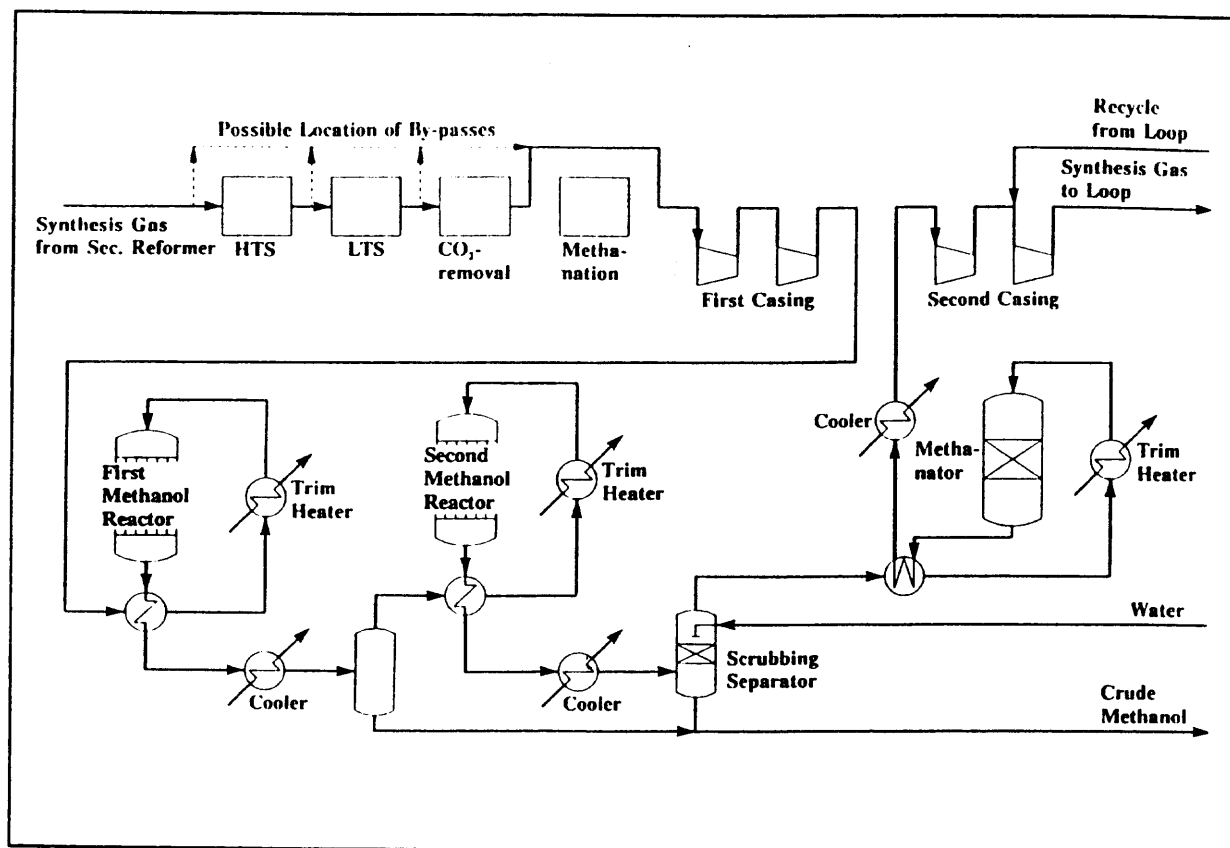
The second methanol reactor is an inexpensive adiabatic reactor, applicable because the majority of the reaction heat is absorbed in the first methanol reactor. The reaction profiles for the two alternative interstage pressures are compared in **Figure 6**.

METHANOL PURIFICATION

The crude methanol product will contain water and certain by-products at levels which will not be acceptable for most uses. Therefore, a purification unit is required or the crude must be sold to a neighbouring methanol plant with excess distillation capacity.

The lay-out and energy consumption of the distillation unit will depend on the required specification for the purified product, but in most cases a two-column lay-out would apply for production rates up to 400 MTPD.

The heat input required for two-column distillation for product quality US Federal Grade AA, the most often encountered commercial specification, is approx. 1.2 Gcal/MT methanol, equivalent to approx. 2300 kg/MT methanol of low pressure steam (3.5 kg/cm^2g). However, if the methanol is dedicated for some specific purpose such as fuel, formaldehyde or acetic acid, the distillation may be slightly relaxed, and energy consumption and investment will be reduced.

The typical lay-out of a two-column distillation unit is shown in **Figure 7**. In the first column, the stabilizer column, the various low boiling compounds, in particular dimethyl-ether, are separated from the methanol/water mixture. In the second column, the concentration column, water and methanol are separated, and high boiling compounds, in particular higher alcohols, are concentrated and removed. Vapour from the top of the stabilizer column is cooled in an overhead condenser, and the vapour/liquid mixture is collected in an overhead accumulator. Volatile gases leaving the top of the accumulator are sent to the fuel or flare header.

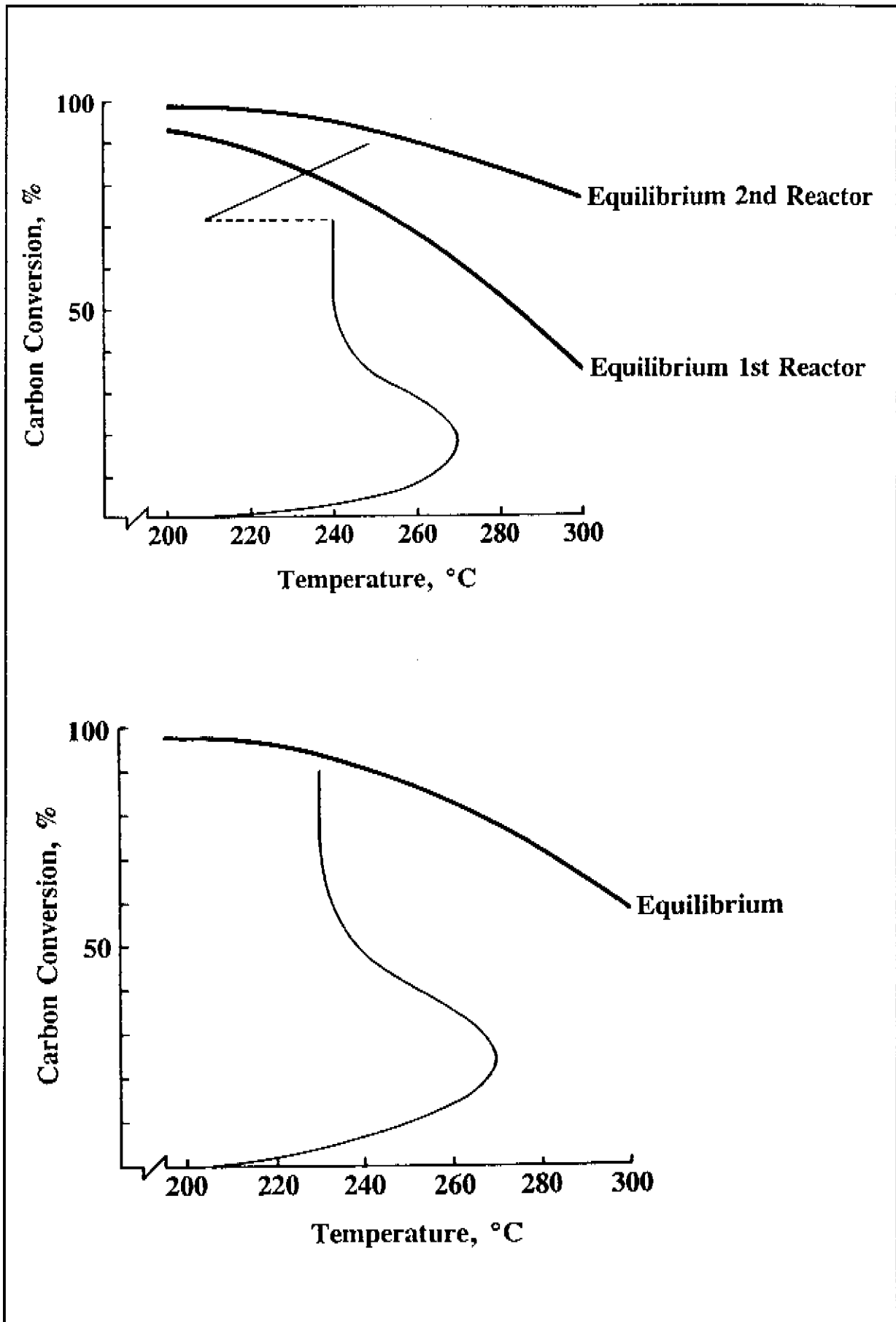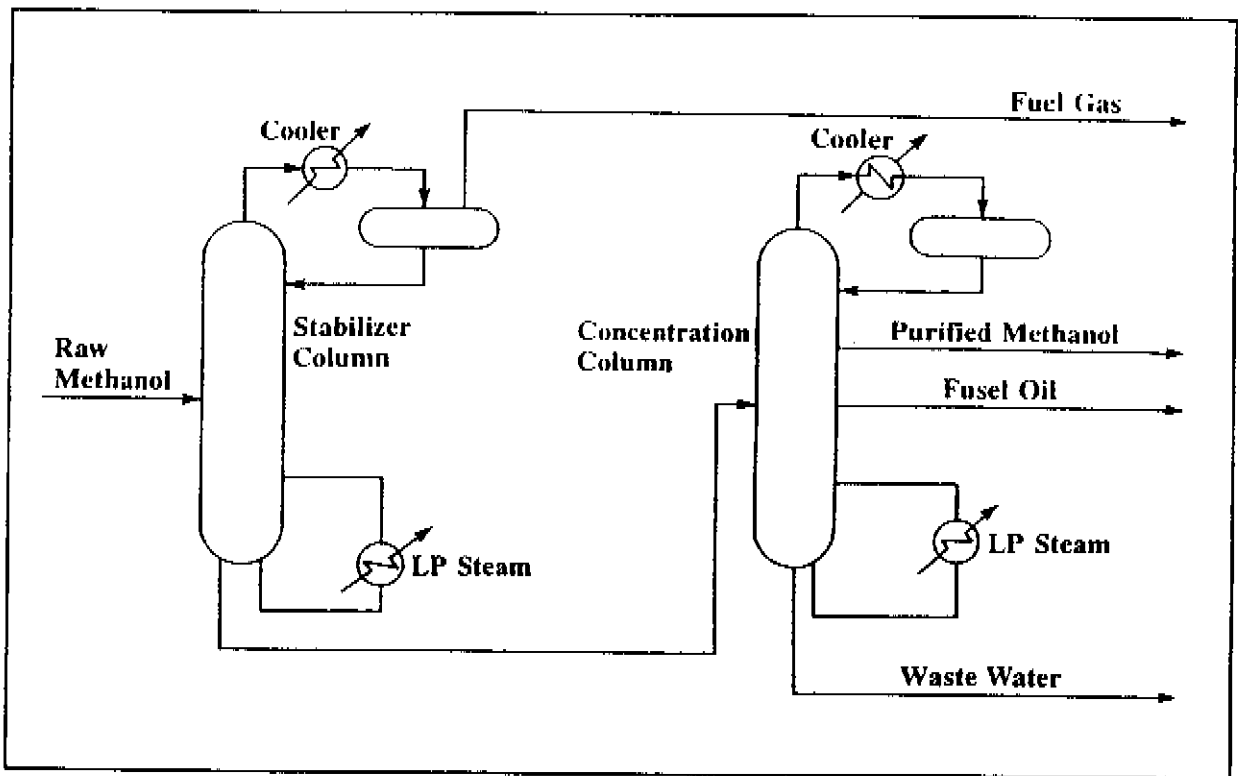Figure 6: Typical Carbon Conversion Profiles at Low and High Interstage Pressure

Figure 7: Methanol Distillation

From the bottom of the stabilizer column raw methanol is pumped to the concentration column. In this column, water is separated at the bottom. Part of the water can be recycled to the top of the stabilizer column to improve the separation of the various low boiling compounds. Higher alcohol impurities are withdrawn in a small purge stream in the lower part of the column. Methanol product is removed several trays below the top and cooled in the methanol product cooler before it is transferred to the methanol shift tank for analysis of the quality. After successful analysis the methanol product is transferred to the methanol storage tank. Vapour from the top of the concentration column is condensed in an overhead condenser and returned to the column through an overhead accumulator.

INDUSTRIAL EXPERIENCE

In 1991 a contract became effective for installation of a methanol co-production unit operating at high pressure in an ammonia plant in the Middle East. The plant is from 1967 and is characterized by lack of a low temperature shift conversion. Instead CO was removed in a copper wash, which was very energy intensive, and polluting the nearby river.

The methanol co-production unit was installed to substitute this copper wash and the final CO_2 wash. The design parameters are given in **Table 2**.

TABLE 2

Design Parameters for the Middle East Installation	
Original Plant	
Design NH_3 capacity, MTPD	360
Start-up year	1967
Licensor	BASF
Modified Plant with Co-production Unit	
Nameplate methanol capacity, MTPD	72
Operating range, MTPD methanol	25-100
Product quality	US Federal Grade A
Ammonia capacity @ 72 MTPD MeOH, MTPD	286
CO, inlet/outlet, mole%	4.79/0.05
CO_2, inlet/outlet, mole%	0.52/0.02
Carbon efficiency, %	99

Topsøe supplied process engineering and equipment, while the civil engineering, construction and erection were carried out by the plant owner under supervision of Topsøe. The unit was started up in the spring of 1993, about 2 years after effective contract.

The tie-in to the existing plant took place during a normal 1 month turnaround. Operators for the unit were selected from the existing staff and trained part time during 1 month prior to start-up.

The plant is very compact, the plot area for the co-production unit is 10 by 10 m, and the distillation is 10 by 14 m. The photos in **Figures 8, 9 and 10** show the plant just after commissioning.

In April/May 1994 a similar facility was started up for Terra International Inc. in Woodward, Oklahoma, USA. This methanol co-production unit allows Terra International Inc. to produce up to 400 STPD methanol in a 1400 STPD ammonia plant. The ammonia capacity is 1000 STPD at full methanol production.
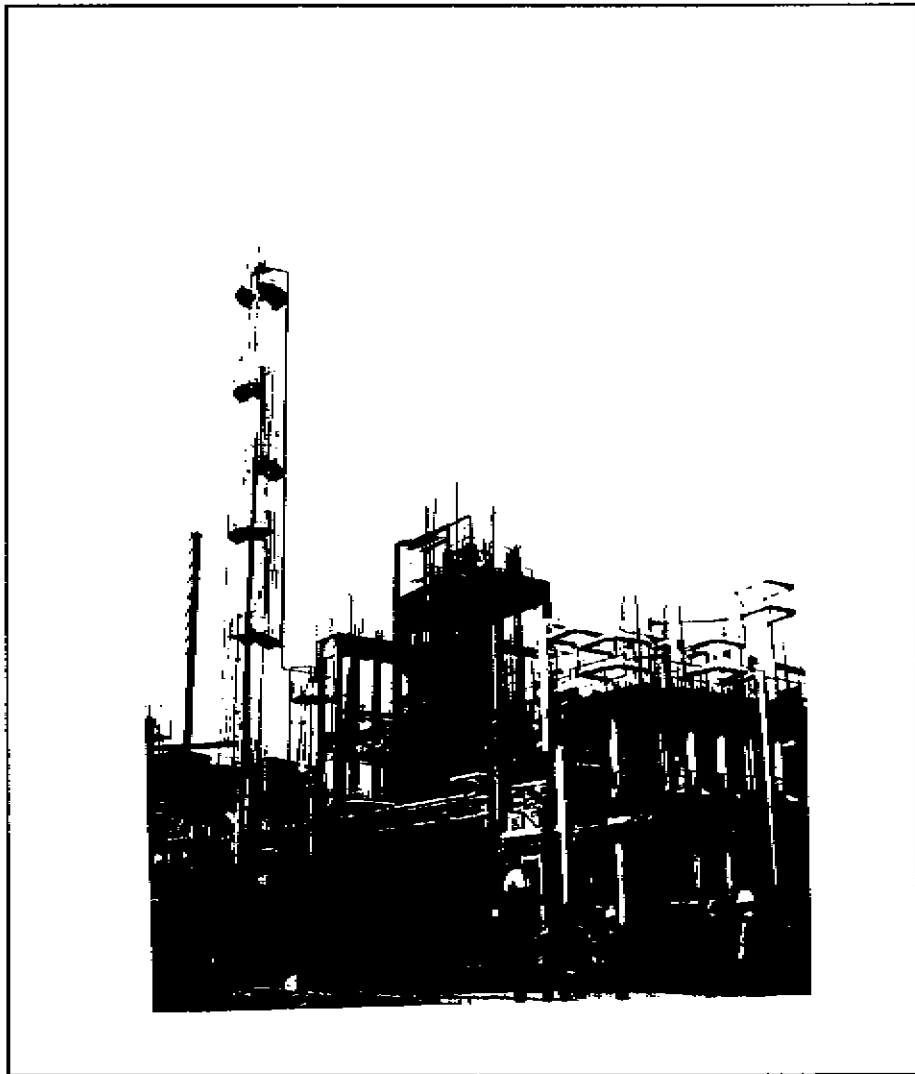
Figure 8: The Modified Plant
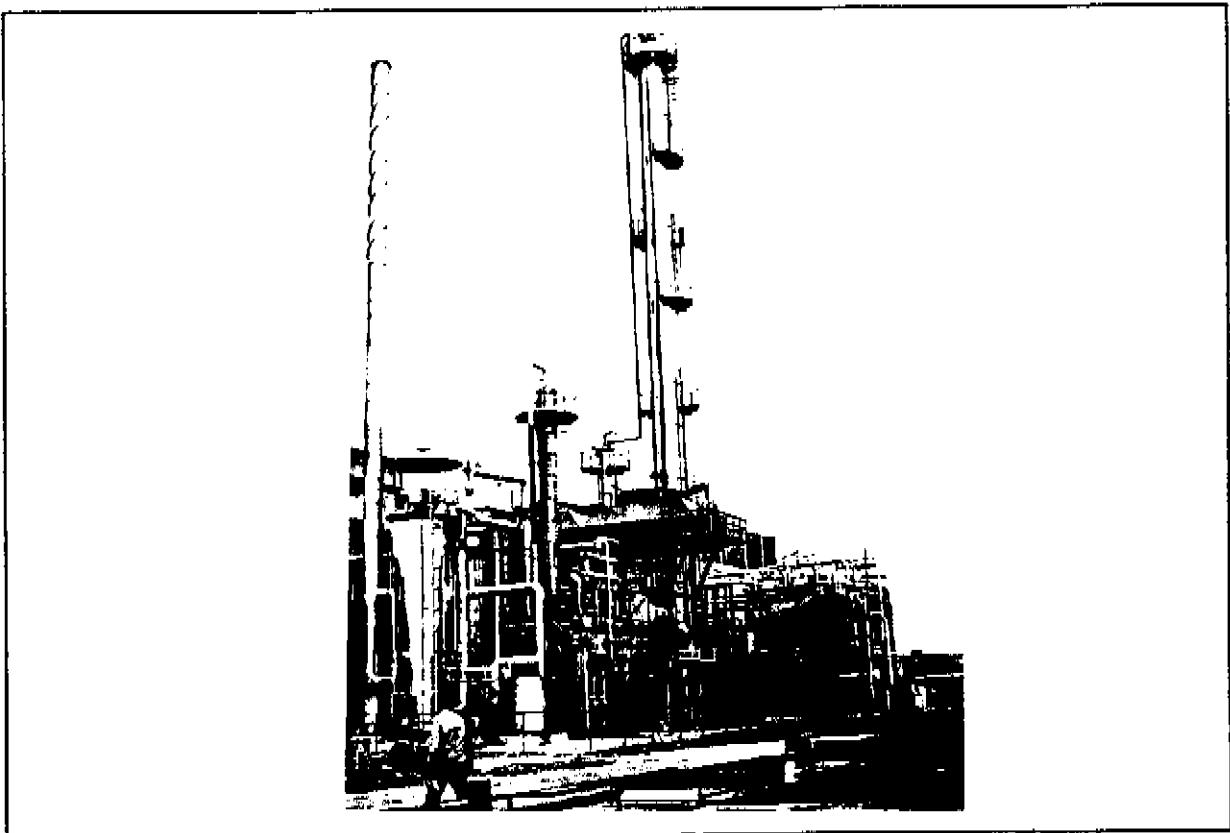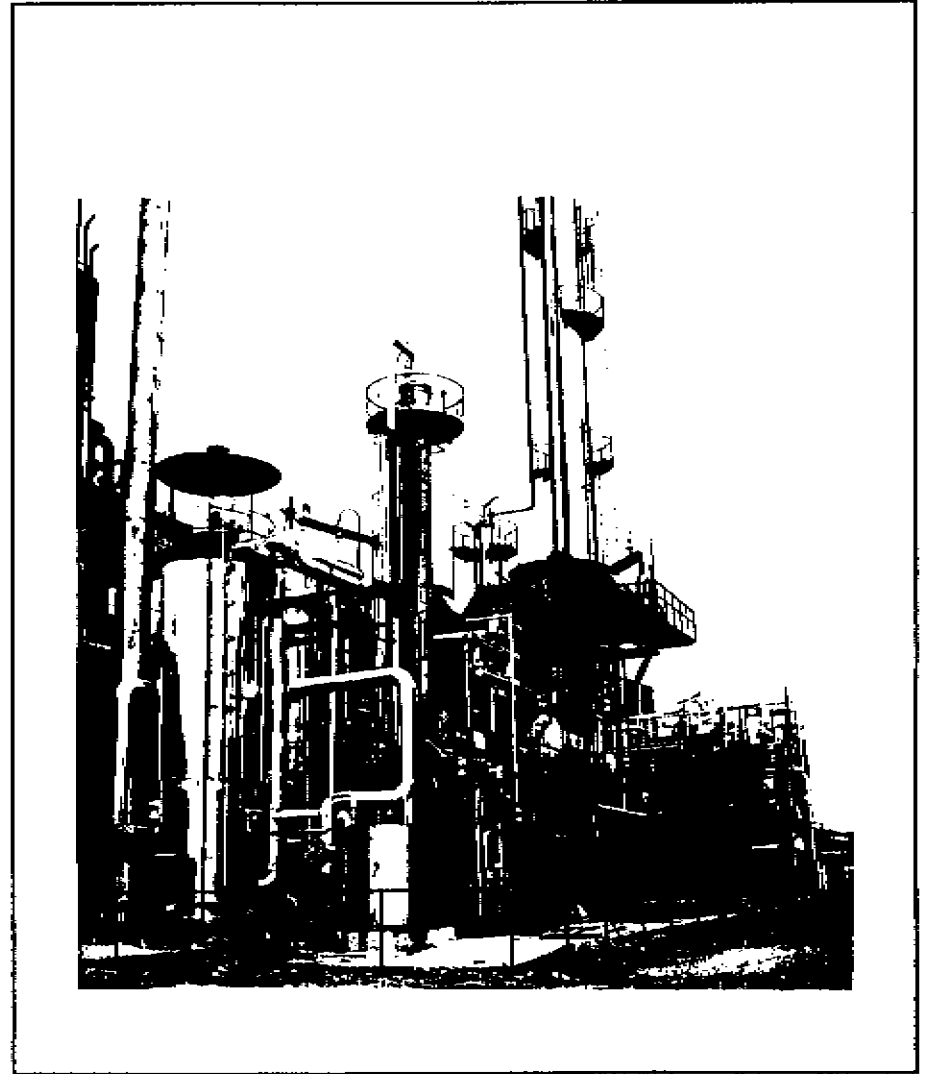
Figure 9: The Co-production Unit

Figure 10: Close-up of Distillation Section

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## TYPICAL PERFORMANCE OF THE HIGH PRESSURE CO-PRODUCTION TECHNOLOGY

In order to give some general ideas of what may be accomplished in a contemporary plant, the potential benefits have been evaluated for a 1350 MTPD ammonia plant with a three-stage synthesis gas compressor and an interstage pressure between second and third stage of 100 bar.

From the reaction scheme it should be realized that hydrogen is consumed by production of methanol:

$$2H_2 + CO \quad \_ \quad CH_3OH$$
$$3H_2 + CO_2 \quad \_ \quad CH_3OH + H_2O$$
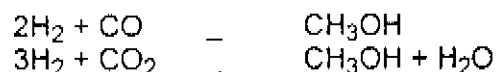
The hydrogen consumed for methanol is not available for ammonia, and consequently the potential ammonia production will drop as methanol production is increased. This is illustrated in Figure 11.

Figure 11: Potential Ammonia Loss as Function of Methanol Production
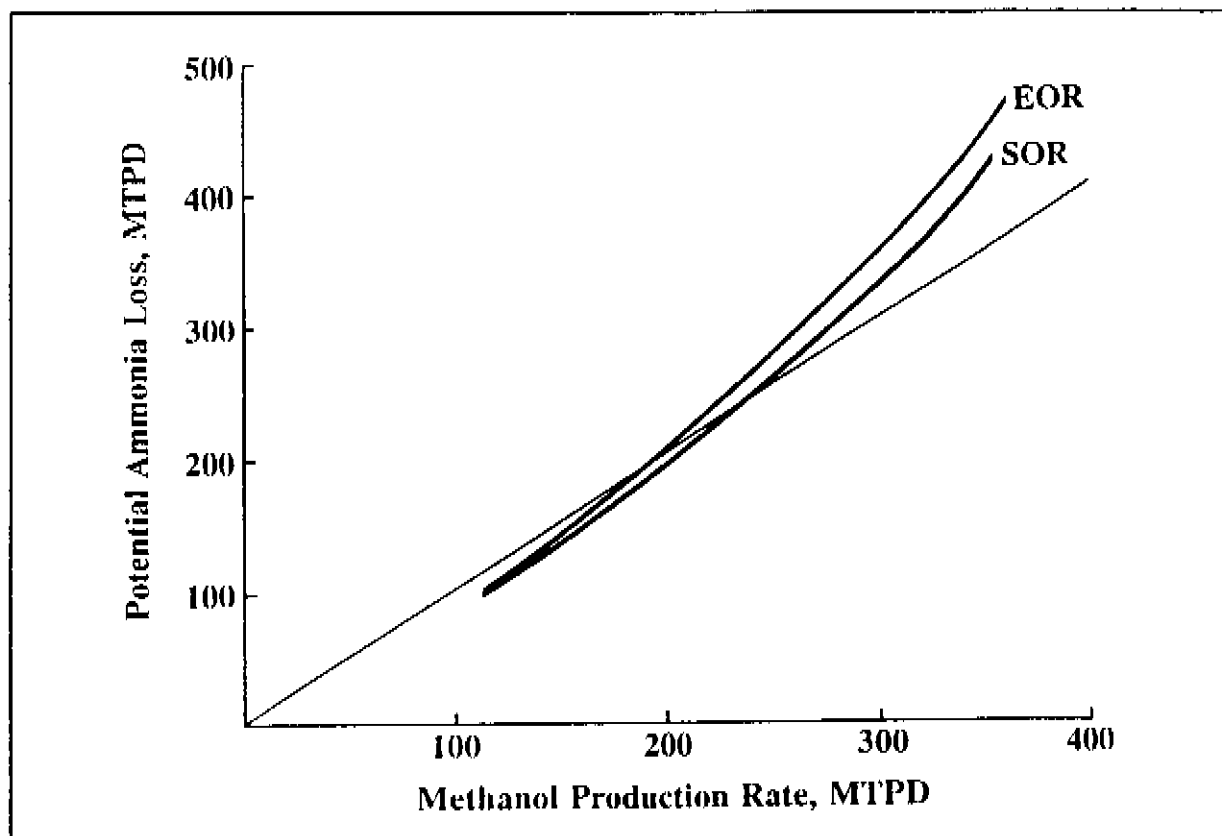
The straight line in the figure shows an ammonia loss rate of 1. The curves show that the loss rate increases slowly with the methanol production. It is also shown that ammonia loss increases slightly as the methanol synthesis catalyst ages.

It should be noted that the ammonia loss, as accounted for above, is deductable from the nameplate production capacity, not necessarily the actual production. If the plant is operating below full capacity, the ammonia loss is of course of no interest whatsoever.

The consumption of hydrogen by the methanol reaction has another effect, namely the reduction of the hydrogen to nitrogen ratio inlet the ammonia synthesis. Although a H_2/N_2 ratio slightly below 3 is favourable for ammonia synthesis catalyst activity, the existing equipment will not be able to handle too large a drop in this ratio. If nothing is done to compensate for the hydrogen depletion, the H_2/N_2 ratio will drop quite rapidly as shown in Figure 12.

The excess of nitrogen is best reduced by increasing the load on the primary reformer, or by reducing air flow to the secondary reformer. The latter will reduce the exit temperature and the methane slip, but these effects have lesser impact on the production rate than the H_2/N_2 ratio.

Based on the assumption that primary reforming cannot be increased, the exit conditions outlet the secondary reformer wll be as illustrated in **Figure 13**.

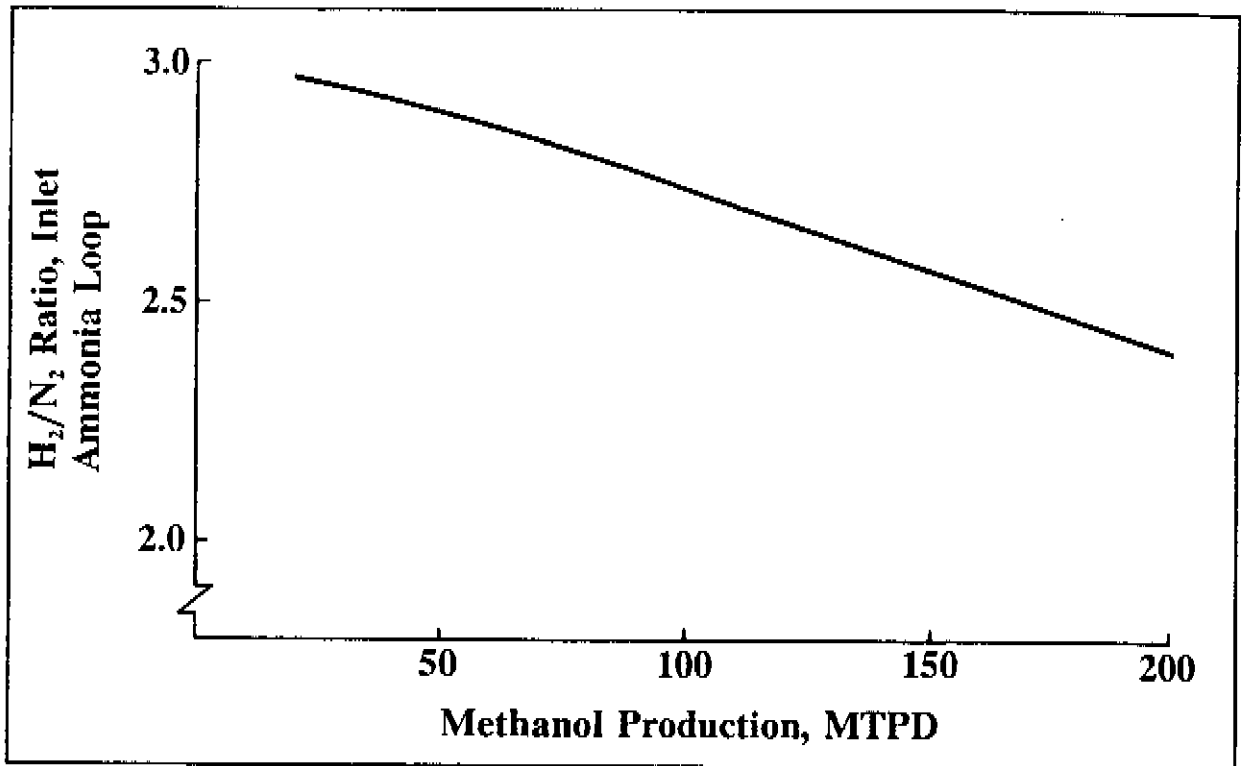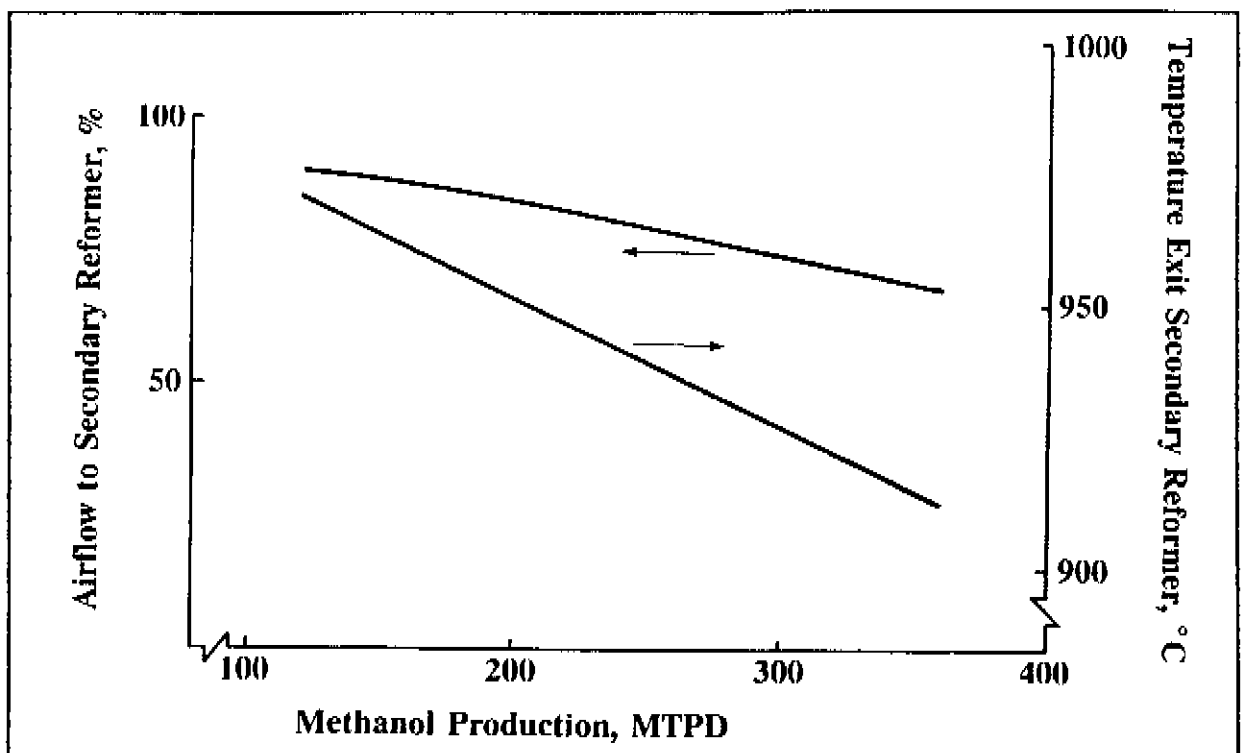Figure 12: H_2/N_2 Ratio as Function of Uncompensated Methanol Production

Figure 13: Secondary Reformer Exit Conditions Required to Compensate H_2/N_2 Ratio

An example of the obtainable performance figures are illustrated in Table 3.

TABLE 3

Typical Performance Figures			
Case	Base	Methanol Co-production	
		SOR	EOR
Ammonia production, MTPD	1350	1095	1085
Methanol production, MTPD	-	240	240
Ammonia loss, MTPD	-	255	265
CO_2 production, MTPD	1675	1295	1285
Natural gas feed and fuel, index	100	101	101
HP steam production, index	100	96	95
Process cooling water, index	100	90	91
Chilling duty, index	100	99[1]	101[1]
Main compressor power [2], index	100	88	88

[1] Assuming chilling in co-production unit
[2] Main compressors taken as process air compressors, synthesis gas compressor and recirculator

As indicated in the table, the HP steam production is slightly reduced, but at the same time the power requirement of the HP steam consuming equipment is reduced, and a fair amount of saturated MP steam is produced in the methanol co-production unit. The pressure of this saturated MP steam will most likely be lower than in the existing MP grid, and a new purpose for this steam must be found. If no options are available within the plant, the steam may be depressurized and used in the reboilers in the methanol distillation. The natural gas flow is practically constant.

Besides, the key figures show that cooling water and chilling requirements are within existing limits, at least when distillation of the methanol is not considered. For the distillation of the methanol, up to 1.2 Gcal/MT of methanol worth of condensing LP steam and the equivalent amount of cooling water should be allocated, depending on the required quality of the product methanol. Part of this steam may be supplied from the methanol boiling water reactor.

The typical economic parameters are listed in Table 4.

TABLE 4

Economic Parameters	
Maximum methanol capacity, % of original NH_3 nameplate	25-30
Energy consumption per ton of methanol, % of energy consumption for ammonia[1]	95
Installed cost/MT of methanol, % of world-scale (2500 MTPD) grassroots plant[2]	80
[1] Excluding methanol distillation.	
[2] Including methanol distillation.	

The figures in Table 3 and 4 are typical. The co-production process is customized for each ammonia plant to accommodate the restrictions of existing equipment and utilities. In order to assess all implications to the existing plant, both process and utilities, it is necessary to build a rigorous computer model simulating heat and mass balances at the new conditions.

SPECIAL FEATURES

Finally, it should be noticed that certain plant features favours the co-production technology, viz:

* *Availability of cheap oxygen or hydrogen*
  to maintain the H_2/N_2 ratio without affecting the reformer section by using enriched air in the secondary reformer or injecting the hydrogen downstream the shift section

* *Bottlenecks in process air compressor, waste heat boiler, shifts, CO_2-removal, methanator or refrigeration system*
  these systems or equipment items will be by-passed or run at reduced loads compared to 100% ammonia production, and investments required to remove such bottlenecks might, as a more positive alternative, be invested in a co-production unit

* *Gasification front-end*
  better control of H_2/N_2 ratio originating from the air separation unit

* *High pressure CO_2-removal*
  combines high pressure with high concentrations of CO + CO_2 without stringent requirements on carbon conversion.

* *Consumption/demand for methanol on-site or in neighbouring facilities*

If any of the above features are present, a co-production unit will be even more desirable.

SUMMARY

Co-production technology for partial conversion of ammonia capacity to methanol capacity holds several advantages such as product diversification and better market perspectives. It will allow utilization of unused capacity, if relevant, and it offers flexibility to manufacture the product with the best profit margins. Most importantly, however, it will allow the ammonia plant owner to enter the methanol market faster and at lower cost than for grassroots methanol plants, even methanol plants with world-scale capacities.

Topsøe believes that the best way to tap this potential is to install a methanol co-production unit at high pressure between the casings of the synthesis gas compressor. The process has been demonstrated in an ammonia plant in Middle East since the spring of 1993; another unit was put on-stream in the U.S. during April/May 1994, and the process has thus been demonstrated commercially.