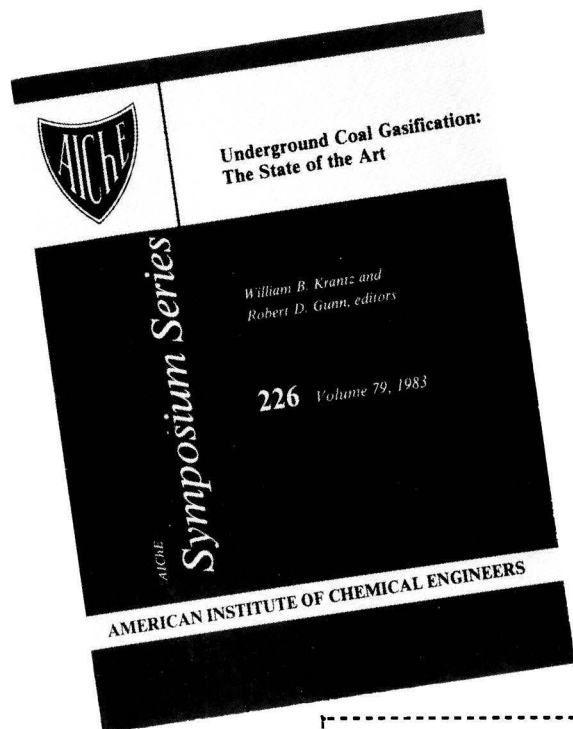# ENERGY PROGRESS

Underground Coal Gasification: The State of the Art

CONTENTS

Underground Coal Gasification:
The State of the Art

*William B. Krantz and
Robert D. Gunn, editors*

AIChE Symposium Series

226 *Volume 79, 1983*

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ENERGY PROGRESS

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Cover: Oil Refinery in Jeddah, Saudi Arabia ©1987 Shostal Associates

Energy Shorts

New Technology To Impact World-Wide Oil Production and Use

The development and patenting of a new technology for more efficient utilization of crude oil and other heavy hydrocarbons that will help reverse the nation's increasing dependence on imported oil was announced recently by Petroferm, Inc.

"Preatomized Fuel™ (PAF™) technology will utilize low value refinery by-products and reserves of heavy crude oil," said William R. Galloway, Jr., chairman and president of Petroferm Inc., Fernandina Beach, FL, developer of "PAF."

"This process will convert the world's heavy hydrocarbons and difficult refinery by-products to combustible fuels and promises fuel and operational cost savings to utilities and industrial plants, the nation's largest individual users of fuel oil," he said.

Describing the process as "basically defying the old adage that oil and water don't mix," Galloway said that "PAF is an emulsion — or mixture — of water and extremely thick residuum or heavy crude. "PAF" can be stored and handled like commonly used No. 2 fuel oil but will compete directly with No. 6 fuel oil. It burns much more cleanly and efficiently than No. 6 oil.

" 'PAF' is based on our extensive research with biochemical emulsifiers," said Galloway. The head of the privately-owned firm said the technology employs sophisticated chemical systems developed and tested by the company which not only allow the viscous oil to be emulsified but which effectively maintain the low viscosity oil-in-water state.

Although now relying on imported oil for nearly 40% of its oil requirements, the United States ranks third in heavy crude reserves after Venezuela and Canada. The world's known reserves of heavy crude are about four times more plentiful than conventional oil, and some experts predict that heavy crude will be required for one-third of the world's oil supply by the year 2000.
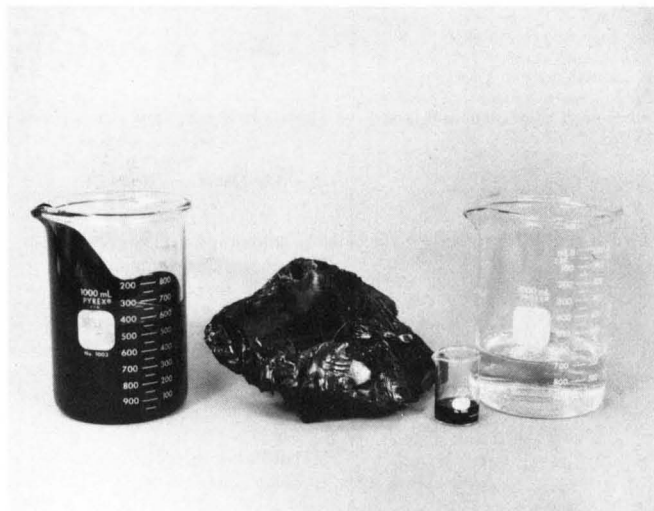
Before and after: contrast between heavy hydrocarbon (top) and fluid "PAF" (bottom beaker, being poured).

To convert viscous hydrocarbons to usable fuel: A newly patented technology developed by Petroferm Inc. mixes the tar-like heavy hydrocarbon (top center) with a specialty chemicals mixture (smaller beaker top right center) and water (top right beaker), to make Preatomized Fuel™ (PAF™) (bottom beaker), which burns more efficiently and cleaner than No. 6 oil. This is in contrast to current methods which require the use of valuable No. 2 oil mixed with hydrocarbons to make No. 6 oil.
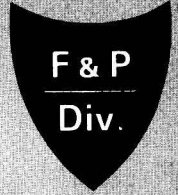
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Election Results

We congratulate all the new officers and wish them well in their new jobs in the coming year. Our thanks are extended to the unsuccessful candidates and to the outgoing officers, particularly Calvin B. Cobb, our Past Chairman.

Future Meetings And Programming

Your help in presenting papers, organizing sessions, or developing new programming areas is needed. If you have a desire to participate in the Fuels and Petrochemicals Division programming activities or wish further information, please contact:

Bill Rodgers, Chairman,
F&PD Programming
(615) 574-6819

The programming committee will meet in Minneapolis on Sunday morning, August 16th, at 9:00 A.M. (room to be announced). Please join us with your ideas and input.
The Fuels and Petrochemicals Division plans the following sessions for the upcoming meetings:

Minneapolis	August, 1987	12 Sessions
New York	November, 1987	14 Sessions
New Orleans	March, 1988	30 Sessions

There will be joint programming with the Heat Transfer and Energy Conversion Group and the Health and Safety Division. Be sure to keep posted on the details in the upcoming issues of *Chemical Engineering Progress*.

We are very pleased to welcome a large number of new members to the Petrochemical Programming Subcommittee. They are Alan Ellis of Chevron, Stanley Herzog of H-R International, Gary Luce of Wright Killen & Co., Ray Rennard of Chevron, and Andrei Rhoe of Lummus Crest.

AIChE Announces Major Changes in Meeting Presentation Scheduling

Changes Effective with 1987 Summer National Meeting in Minneapolis

AIChE Council, at its meeting of November 1, 1986 in Miami Beach, approved the recommendations of the Executive Board of the Program Committee (EBPC) and the Publication Committee, to change the scheduling requirements for proposals to present papers at AIChE meetings, submission of manuscripts, and related topics. Following is a description of the approved changes which are being incorporated in the scheduling of AIChE's 1987 Summer National Meeting in Minneapolis.

Speakers will have up to five additional months prior to a meeting to submit **Proposals To Present** to Session Chairmen. Proposals to Present must be received by Session Chairmen no later than six months prior to a meeting. A proposal may be submitted any time before that, once Session Chairmen have been identified (usually one to two years before a meeting) and announced in *CEP*. All Proposals to Present received at least six months prior to a meeting will be considered by Session Chairmen. Session Chairmen are asked not to make final selections until six months prior to the meeting.

Sixty word abstracts of accepted presentations will be eliminated from the Meeting Program Book. Instead, when a proposal is accepted for presentation (five months prior to the meeting), Session Chairmen will mail each speaker a revised Presentation Acceptance Form with room for each speaker to prepare a **one-page extended abstract** of his or her presentation. Speakers must return the completed, clearly typed Presentation Acceptance form, with abstract, to Session Chairmen at least ten weeks prior to the meeting. These abstracts will be collated by session, reproduced, and distributed free to meeting attendees upon registration at the meeting.

The **Meeting Program Book** will contain all the information it now contains except for the 60-word abstracts. It will be mailed to all members of the Institute on the same schedule as it is now - 10 weeks prior to the meeting.

Speakers will no longer be required to submit **manuscripts** to the AIChE Manuscript Center three months prior to the meeting date to meet the deadline for microfiche preparation. Speakers will be required to submit full manuscripts (four copies) to Session Chairmen one month before the meeting.

Microfiche of presentations will be prepared immediately after each meeting. This will allow preparation of better organized and more complete fiche. Microfiche will continue to be sold at each meeting and orders for a current meeting's microfiche can be placed at the Publication Sales Desk at the meeting, or through AIChE's other regular sales channels.

A photocopying service will be set up at each meeting to allow meeting attendees to purchase hard copies of full manuscripts. Meeting attendees will be able to order copies of manuscripts 24 hours or more in advance of a session or group of sessions. It is the responsibility of each Session Chairman to make sure that reproducible copies of all papers in the session are submitted to National Headquarters so that this service can be set up effectively. The length of the total manuscript (including copies of slides) should be kept under 40 typewritten pages.

AIChE will no longer ask authors to sign a **Transfer of Copyright** agreement at the time a paper is submitted for presentation. Only those authors whose papers are accepted for publication by AIChE will be asked to sign the Copyright Transfer. Authors will be notified when a paper is accepted for publication or is to be released.

To protect the author's copyright interests, each manuscript submitted to Session Chairmen, whether the author wishes it to be considered for publication or not, must have the following on the title (cover) page:

"Title
Author(s)
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Prepared for presentation at [Meeting Name/Date, Session Name/ Session #]
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UNPUBLISHED"
(Employees of the U.S. Government who prepared the work as part of their employment should omit the copyright statement.)

Effective with the Minneapolis Summer Meeting, speakers will be permitted to use **overhead projectors** during their presentations. Guidelines for preparation of overhead transparencies and the use of overhead projectors and other audio-visual equipment will be available shortly from AIChE's Meetings Department.

The table below shows the beginning and end dates of the activities described above. Anyone who wishes more information on the schedule changes, forms, or submission requirements and dates, should call or write to

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345 East 47th Street
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New AIChE Schedule for Meeting Presentations

MONTHS PRIOR TO MEETING DATE

EBPC Appoints Meeting Program Chairman (MPC)
First Announcement of Meeting in *CEP*
Session Chairmen Selected by MPC
Announcement of Sessions in *CEP*
Speakers Request Proposal to Present Forms from AIChE Meetings Dept. or Session Chairman or MPC
Proposal to Present Forms Submitted to Session Chairman by Speakers
Session Chairmen Review Proposals and Select Speakers
Session Chairmen Submit Final Session Information to MPC
Session Chairmen Send Presentation Acceptance Forms to Speakers and Request Extended Abstracts from Speakers
MPC Submits Final Program Copy to New York (excluding Abstracts)
Meeting Program Book Mailed
Speakers Submit Typed Abstracts to Session Chairmen
Chairmen Submit Abstracts to New York
Speakers Submit Manuscripts to Chairmen
Chairmen Submit Manuscripts to New York

Conditioning Coal Gas With Aqueous Solutions of Potassium Carbonate: Operating Data

Ronald W. Rousseau, James K. Ferrell, and James S. Staton

Department of Chemical Engineering
North Carolina State University
Raleigh, North Carolina 27695

Gases generated by the gasification of coal in a fluidized bed reactor were conditioned with aqueous solutions of potassium carbonate. The solutions and operating conditions were selected so as to represent commercially available systems, for example the Benfield process. The data obtained from these experiments illustrate the effects of a variety of process variables on the separation of CO_2, H_2S and COS from a feed gas containing differing concentrations of acid gases. The key process variables were absorber temperature and pressure, ratio of the flow rates of solvent and gas, effectiveness of stripping, and K_2CO_3 concentration in the solvent.

INTRODUCTION

A number of processes have been developed for the gasification of coal and several of these are in commercial use; however, most gas cleaning processes were developed for the natural gas and petroleum refining industries and may not be well suited to treat gases produced from coal [5]. All of the gasification processes produce desired gaseous compounds such as CO, H_2 and CH_4, and all of them produce some undesirable compounds. The gas usually contains large quantities of CO_2 may also contain sulfur and nitrogen compounds, aliphatic and aromatic hydrocarbons and trace compounds containing metals such as mercury and lead. Removal of most of the CO_2 from the gas is necessary to produce a high-Btu gas, or for the gas to be useful in chemical synthesis operations, and many of the other constituents, especially H_2S and other sulfur gases, must be removed for environmental or processing requirements related to the use of the gas. Table 1 shows a typical gas analysis from the fluidized bed gasifier at North Carolina State University.

Most existing gas cleaning processes were developed to treat gas streams having relatively low acid gas content, few trace contaminants, and a high ratio of H_2S to CO_2 [2]. These processes, which are often called acid gas removal systems (AGRS) because of the acidic nature of CO_2 and H_2S, are used extensively in the natural gas and petroleum industries to "sweeten" gas streams. The primary objectives of the work described here were to evaluate the performance of a class of chemical solvents that use aqueous solutions of potassium carbonate in treating coal gas and to examine the role of AGRS operating conditions in determining the removal of undesired constituents from the coal gas.

Gas cleaning processes which use aqueous potassium carbonate solutions may be divided into two groups: those in which absorption takes place at ambient temperatures and those in which absorption takes place at elevated temperatures approximating those at which the solvent is regenerated [7]. The latter type, referred to as hot potassium carbonate processes, were originally developed by Benson and coworkers at the U.S. Bureau of Mines as part of a program to produce liquid fuels from coal [3]. The general concept of the Benson process formed the basis for this study.

The overall stoichiometry of the reaction of CO_2 in an aqueous carbonate solution is

$$CO_2 + H_2O + CO_3^= \leftrightarrow 2HCO_3^- \qquad (1)$$
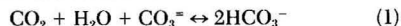
which is the dominate reaction of CO_2 at pH values greater than 8, and industrial hot potassium carbonate processes typically operate in the pH range 9 to 11 [1]. This reaction takes place by the following mechanism:

$$CO_3^= + H_2O \leftrightarrow HCO_3^- + OH^- \qquad (2)$$

$$CO_2 + OH^- \leftrightarrow HCO_3^- \qquad (3)$$

The primary reaction of H_2S in carbonate solutions is the proton transfer reaction with the hydroxide ion to form the hydrosulfide ion and water

$$H_2S + OH^- \leftrightarrow HS^- + H_2O \qquad (4)$$
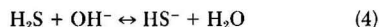
The reactions of Equations 3 and 4 may be combined to form a shift reaction [1]

$$H_2S + HCO_3^- \leftrightarrow HS^- + CO_2 + H_2O \qquad (5)$$
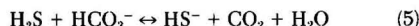
which illustrates that the equilibria of CO_2 and H_2S are not independent.

Correspondence should be addressed to R. W. Rousseau. James S. Staton is currently at Ethyl Corporation, Research and Development Department, P.O. Box 341, Baton Rouge, LA 70821

Compound	Mole % Dry Basis or ppm
H_2	34.2813
CO	10.7741
CH_4	5.1599
CO_2	28.6266
N_2	20.3062
H_2S	1857 ppm
COS	32 ppm
Thiophene	20 ppm
CH_3SH	23 ppm
C_2H_5SH	0
CS_2	0
Ethylene	1761 ppm
Ethane	2783 ppm
Propylene	694 ppm
Propane	277 ppm
Butylene	316 ppm
Butane	080 ppm
Benzene	492 ppm
Toluene	143 ppm
Ethylbenzene	11 ppm
p-Xylene	6 ppm
m-Xylene	16 ppm
o-Xylene	8 ppm

Another important contaminant, COS, also is absorbed by potassium carbonate solutions and undergoes hydrolysis to form CO_2 and H_2S:

$$COS + H_2O \leftrightarrow CO_2 + H_2S \qquad (6)$$
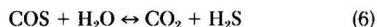
The conversion is enhanced by absorption at elevated temperatures [8].

Since all proton transfer reactions are extremely rapid, the reaction of H_2S may be considered instantaneous in comparison with diffusion [9]. The absorption of CO_2 is, however, much slower than that of H_2S and it is thought to be limited by the kinetics of the reaction of Equation 3. This difference in rates of absorption allows selective separation of H_2S in some situations, and it has led to the use of additives in other situations that increase the rate of CO_2 absorption by increasing the rate of the reaction in Equation 3. These additives, called rate promoters, are used in all commercially available hot potassium carbonate processes and usually distinguish such processes from one another.

EXPERIMENTAL SYSTEM

General procedures for start-up and operation of the pilot plant facility used in the present study are given in earlier publications [4, 6]. The system (shown schematically in Figure 1) usually required approximately six hours to achieve steady-state operation, which was defined as a period of operation during which measured process variables, such as flow rates, temperatures, pressures and gas compositions, were constant. The feed to the acid gas removal system was referred to as the sour gas, while the product gas from the absorber, the flash gas and the stripper gas were referred to as the sweet gas, the flash gas and the acid gas, respectively.

Gas and liquid samples were taken periodically throughout a run. Gas samples were taken in one-liter stainless steel or glass bombs; those used for analysis of trace components were taken in bombs internally coated with Teflon. A complete discussion of sampling and analysis was given earlier [10]. Periodic samples of the sweet gas from a typical run (ACIL-26) are shown in Figure 2. Once a steady-state condition had been reached, operation was continued for two to three hours while operating

variables were recorded and samples of key streams were taken. During this steady-state period, measured values of all process variables were averaged over five minute intervals and stored by a data acquisition system.

The closure of mass balances on the major components in the gas was used to evaluate the accuracy of measured flow rates and compositions for each run. Values used in testing closure were obtained by averaging the measured variables over a period of time (typically one hour) preceding and the time at which steady-state samples were taken. If the overall mass balance closure was not within 5%, data associated with the sample period were not used in evaluating the operation. It should be noted that a few of the components included in the mass balance were present in such small amounts that slight errors could lead to closures in component balances that did not meet the stated criterion. In such cases, judgment was used to decide if the data on these components were to be used.

Figure 1. Acid Gas Removal System.

Figure 2. Approach of sweet gas compositions to steady state in Run ACIL-26.

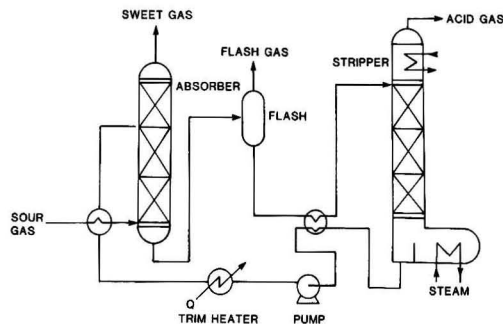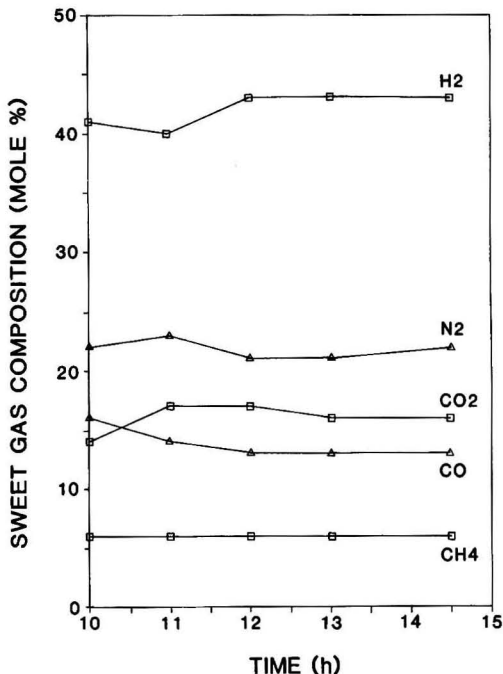| Species	Sample Train	PCS Exit	Sour Gas	Sweet Gas	Flash Gas	Acid Gas
H_2	34.2813	34.7186	34.4422	46.8976	14.0271	0.0000
CO	10.7741	10.7518	10.8414	15.7307	2.9015	0.0000
CH_4	5.1599	5.1487	5.1280	7.3119	1.5708	0.0000
CO_2	28.6266	28.8228	28.6884	2.6099	52.4464	97.6699
N_2	20.3062	19.6964	20.0576	26.5563	28.5243	1.7285
H_2S	0.1857	0.1853	0.1835	0.0022	0.2242	0.5955
COS	0.0032	0.0032	0.0034	0.0011	0.0015	0.0000
Thiophene	0.0020	0.0020	0.0020	0.0023	0.0036	0.0000
CH_3SH	0.0023	0.0023	0.0021	0.0020	0.0055	0.0009
C_2H_5SH	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CS_2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Ethylene	0.1761	0.1766	0.1740	0.2363	0.1017	0.0000
Ethane	0.2783	0.2818	0.2762	0.3753	0.0620	0.0000
Propylene	0.0694	0.0705	0.0692	0.0930	0.0296	0.0000
Propane	0.0277	0.0281	0.0277	0.0371	0.0042	0.0000
Butylene	0.0316	0.0324	0.0302	0.0405	0.0110	0.0000
Butane	0.0080	0.0085	0.0079	0.0111	0.0034	0.0000
Benzene	0.0492	0.0509	0.0486	0.0648	0.0778	0.0052
Toluene	0.0143	0.0152	0.0139	0.0204	0.0011	0.0000
Ethylbenzene	0.0011	0.0013	0.0009	0.0017	0.0011	0.0000
p-Xylene	0.0006	0.0007	0.0007	0.0010	0.0006	0.0000
m-Xylene	0.0016	0.0018	0.0013	0.0028	0.0016	0.0000
o-Xylene	0.0008	0.0010	0.0008	0.0017	0.0010	0.0000
Totals	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000

TABLE 2. (CONTINUED) MASS BALANCE FOR AGRS-POTASSIUM CARBONATE SOLVENT (RUN ACIL-33)

Species	Total Flow In (mol/h)	Total Flow Out (mol/h)	Recovery (%)
H_2	261.864	265.654	101.4
CO	82.427	89.056	108.0
CH_4	38.988	41.401	106.2
CO_2	218.118	216.973	99.5
N_2	152.498	154.570	101.4
H_2S	1.395	1.243	89.1
COS	0.026	0.006	24.4
Thiophene	0.015	0.013	86.7
CH_3SH	0.016	0.014	84.3
C_2H_5SH	0.000	0.000	—
CS_2	0.000	0.000	—
Ethylene	1.323	1.340	101.2
Ethane	2.100	2.125	101.2
Propylene	0.526	0.527	100.1
Propane	0.210	0.210	99.8
Butylene	0.229	0.229	100.0
Butane	0.060	0.063	104.7
Benzene	0.369	0.379	102.7
Toluene	0.106	0.115	109.0
Ethylbenzene	0.007	0.010	141.8
p-Xylene	0.005	0.006	107.2
m-Xylene	0.010	0.016	161.7
o-Xylene	0.006	0.010	159.5
Totals	760.300	773.960	101.8

Table 2 shows a typical data set of stream compositions and the calculated mass balance closure for one of the runs used in this study. Complete mass balance results and all gas analysis data for the runs of this study are given by Staton [11].

EXPERIMENTAL OBSERVATIONS

Table 3 gives a listing of the AGRS operating conditions for the runs of this study, and Table 4 shows a summary of the CO_2, H_2S and COS analyses in the sour gas (the AGRS feed gas) and sweet gas streams for each run. As can be seen, the composition of the sour gas varied significantly, making interpretation of results somewhat difficult. Table 5 shows the percentage removals of CO_2, H_2S and COS for these runs. The following discussion summarizes the major findings of the runs listed in Tables 4 and 5. A run-by-run analysis is given by Staton (1985).

The importance of the stripper operation was verified experimentally by observing the composition of the sweet gas produced under various stripper operating conditions. For example, consider the data in Figure 3, which were obtained by operating the stripper with sufficient steam input to the reboiler only to cause heating of the solution to its boiling point with little actual boilup of steam. The K_2CO_3 concentration in the solvent used in the run was 10 wt%. Clearly, poor stripping resulted in steadily increasing H_2S concentrations in the sweet gas, and this observation is supported by the low H_2S closure (approximately 32%) in the mass balances for this run. Interestingly, the COS and CO_2 contents of the sweet gas were essentially constant over the operating period shown in Figure 3.

Repetitive runs made after several intervening runs demonstrated that the solvent experienced no permanent loss in capacity. For example. Runs ACIL-24 and ACIL-28 were made at essentially identical conditions with roughly the same removals of CO_2 and H_2S resulting. Successive runs were also made to test the reproducibility of the experimental data. For example, Run ACIL-36 and ACIL-38 were successive duplicates. As shown in Table 5, the removals of CO_2 and H_2S agree well and indicate good reproducibility.

The effect of diethanolamine (DEA), which is often used as a rate promoter for the absorption of CO_2, was examined by comparing data on successive runs, one (ACIL-35) in which the solvent was a 30% K_2CO_3 solution free of DEA and a second (ACIN-1) in which the AGRS solvent was a solution of 30% K_2CO_3 and 5 wt% DEA. Previous experimental results using one and two sections of packing in the absorber had indicated that the absorber was operating in what is referred to as a pinched condition; i.e., equilibrium between CO_2 in the gas and in the liquid existed at at least one location in the absorber.

TABLE 3. ACID GAS REMOVAL SYSTEM OPERATING CONDITIONS

Run Number	ACIL-23	ACIL-24	ACIL-25	ACIL-26	ACIL-27
Solvent Composition (wt%)					
Water	100	90	90	90	90
K_2CO_3	0	10	10	10	10
Diethanolamine	0	0	0	0	0
Solvent Circulation					
Rate (L/min)	3.3	3.3	3.3	3.3	3.3
Absorber					
Pressure (kPa)	3095	3082	1703	2400	1474
Packing Height (m)	4.33	4.33	4.33	4.33	2.16
Sour Gas Flow (mol/h)	746	762	830	800	666
Liquid Inlet Temp (°C)	33	34	35	35	34
Gas Inlet Temp (°C)	40	41	42	40	41
Flash Tank					
Pressure (kPa)	515	496	496	1000	613
Liquid Inlet Temp (°C)	32	35	36	35	34
Stripper					
Pressure (kPa)	131	131	131	131	134
Packing Height (m)	4.33	4.33	4.33	4.33	4.33
Liquid Inlet Temp (°C)	33	37	37	37	35
Steam Flow (kg/h)	13.6	13.1	12.5	13.0	14.5
Steam Temp (°C)	174	173	174	174	175

Run Number	ACIL-28	ACIL-29	ACIL-30	ACIL-31	ACIL-32
Solvent Composition (wt%)					
Water	90	80	80	80	80
K_2CO_3	10	20	20	20	20
Diethanolamine	0	0	0	0	0
Solvent Circulation					
Rate (L/min)	3.3	3.3	3.3	3.3	3.3
Absorber					
Pressure (kPa)	3083	1790	1785	1782	3156
Packing Height (m)	4.33	2.16	4.33	2.16	2.16
Sour Gas Flow (mol/h)	746	798	780	748	799
Liquid Inlet Temp (°C)	27	102	100	117	102
Gas Inlet Temp (°C)	37	19	20	17	14
Flash Tank					
Pressure (kPa)	498	533	577	570	572
Liquid Inlet Temp (°C)	30	94.	91	103	94
Stripper					
Pressure (kPa)	131	134	134	238	134
Packing Height (m)	4.33	4.33	4.33	4.33	4.33
Liquid Inlet Temp (°C)	31	96	93	105	96
Steam Flow (kg/h)	17.7	17.6	17.3	21.8	16.0
Steam Temp (°C)	173	172	172	172	171

Run Number	ACIL-33	ACIL-35	ACIL-36	ACIL-38	ACIN-1
Solvent Composition (wt%)					
Water	80	70	70	70	65
K_2CO_3	20	30	30	30	30
Diethanolamine	0	0	0	0	5
Solvent Circulation					
Rate (L/min)	3.3	3.3	2.91	2.91	3.3
Absorber					
Pressure (kPa)	1785	1780	3158	3152	1776
Packing Height (m)	2.16	2.16	2.16	2.16	2.16
Sour Gas Flow (mol/h)	760	743	659	686	759
Liquid Inlet Temp (°C)	116	104	100	100	104
Gas Inlet Temp (°C)	19	20	22	25	24
Flash Tank					
Pressure (kPa)	578	505	509	571	570
Liquid Inlet Temp (°C)	106	97	94	92	97
Stripper					
Pressure (kPa)	134	134	135	134	135
Packing Height (m)	4.33	4.33	4.33	4.33	4.33
Liquid Inlet Temp (°C)	102	94	89	88	93
Steam Flow (kg/h)	19.6	23.1	14.3	16.0	16.4
Steam Temp (°C)	172	173	173	171	172

TABLE 3. (CONTINUED) ACID GAS REMOVAL SYSTEM OPERATING CONDITIONS

Run Number	ACIN-2	ACIN-3	ACIN-5	ACIN-6	ACIN-7
Solvent Composition (wt%)					
Water	65	65	65	80	80
K_2CO_3	30	30	30	20	30
Diethanolamine	5	5	5	0	0
Solvent Circulation					
Rate (L/min)	3.3	5.5	3.3	3.3	3.3
Absorber					
Pressure (kPa)	1774	1773	1772	1763	1763
Packing Height (m)	2.16	2.16	2.16	2.16	2.16
Sour Gas Flow (mol/h)	725	699	739	730	736
Liquid Inlet Temp (°C)	105	110	93	101	105
Gas Inlet Temp (°C)	24	30	30	32	30
Flash Tank					
Pressure (kPa)	567	567	565	553	556
Liquid Inlet Temp (°C)	96	102	88	94	97
Stripper					
Pressure (kPa)	148	154	134	134	134
Packing Height (m)	6.49	4.33	4.33	4.33	4.33
Liquid Inlet Temp (°C)	92	101	86	89	93
Steam Flow (kg/h)	17.4	24.2	*	30.2	32.2
Steam Temp (°C)	172	173		172	172

* Str N_2 flow = 270 mol/h
Str N_2 temperature = 26°C

TABLE 3. (CONTINUED) ACID GAS REMOVAL SYSTEM OPERATING CONDITIONS

Run Number	ACIN-8	ACIN-9
Solvent Composition (wt%)		
Water	80	75
K_2CO_3	20	20
Diethanolamine	0	5
Solvent Circulation		
Rate (L/min)	2.91	2.91
Absorber		
Pressure (kPa)	1761	1754
Packing Height (m)	2.16	2.16
Sour Gas Flow (mol/h)	681	674
Liquid Inlet Temp (°C)	103	101
Gas Inlet Temp (°C)	30	29
Flash Tank		
Pressure (kPa)	555	549
Liquid Inlet Temp (°C)	94	95
Stripper		
Pressure (kPa)	134	133
Packing Height (m)	4.33	4.33
Liquid Inlet Temp (°C)	91	91
Steam Flow (kg/h)	28.9	15.9
Steam Temp (°C)	172	173

Consequently, any increase in the rate of absorption of CO_2 due to the amine could not be observed. As shown in Table 5, there appears to be a slight increase in the removals of CO_2 and COS that may be associated with an increased CO_2 solubility due to the addition of DEA.

In run ACIN-5 stripping was accomplished with an inert gas stream (N_2) rather than with reboiled water vapor. The reboiler was operated with a small flow rate of steam to maintain the system at an elevated temperature, but at a steam flow rate smaller than that required to generate a detectable vapor stream in the packing. As can be seen in Table 5, CO_2 removal was 70.2%, H_2S removal was 97.9% and COS removal 35.5%. Although the removal of H_2S was much higher than that for CO_2 and COS, examination of the H_2S content of the sweet gas stream (Table 4) shows that H_2S removal was far from what is generally considered acceptable.

Figure 4 shows the percentage of the inlet CO_2 that was removed as a function of K_2CO_3 concentration for runs at two absorber pressures. As shown, the absorber pressure appeared to have a large effect on CO_2 removal at low concentrations of K_2CO_3. At both pressures tested, CO_2 removal was not increased significantly as the K_2CO_3 concentration was increased from 20% to 30%. H_2S removal was independent of K_2CO_3 concentration at the high absorber pressure and increased only slightly with K_2CO_3 concentration at the lower absorber pressure (Figure 5). The percentage removal of COS, shown in Figure 6, increased with absorber pressure but decreased as the concentration of K_2CO_3 was increased from 20% to 30%, at both pressures tested.

A valid measure of selectivity is the ratio of moles of H_2S absorbed per mole of CO_2 absorbed; experimental values of this ratio are shown in Figure 7 as a function of

TABLE 4. SUMMARY OF SOUR AND SWEET GAS COMPOSITIONS

Run No.	Sour Gas			Sweet Gas		
	CO_2	H_2S	COS	CO_2	H_2S	COS
ACIL-23	27.5	0.188	0.0030	24.3	0.098	0.0029
ACIL-24	28.4	0.196	0.0057	13.9	ND	0.0049
ACIL-25	29.5	0.242	0.0029	20.3	0.0056	0.0027
ACIL-26	28.5	—	—	17.0	—	—
ACIL-27	25.5	0.250	0.0056	18.2	0.0078	0.0050
ACIL-28	25.4	0.401	0.0064	10.3	ND	0.0047
ACIL-29	23.4	0.276	0.0099	2.49	0.0036	0.0021
ACIL-30	27.9	0.271	0.0053	9.36	0.0039	0.0013
ACIL-31	24.8	0.178	0.0086	0.76	0.0016	0.0010
ACIL-32	20.7	0.176	0.0116	0.40	ND	0.0014
ACIL-33	28.4	0.203	0.0034	2.57	0.0022	0.0011
ACIL-35	29.8	0.161	0.0029	2.12	0.0019	0.0011
ACIL-36	29.4	0.165	0.0132	1.39	0.0006	0.0034
ACIL-38	29.6	0.226	0.0051	0.73	0.0016	—
ACIN-1	24.3	0.280	0.0111	0.52	0.0018	0.0012
ACIN-2	24.6	0.312	0.0156	0.53	0.0007	0.0022
ACIN-3	23.0	0.223	0.0153	0.63	0.0014	0.0015
ACIN-5	24.3	0.264	0.0117	9.02	0.0070	0.0096
ACIN-6	23.8	0.199	0.0118	2.81	0.0008	0.0039
ACIN-7	23.6	0.191	0.0104	0.50	ND	0.0018
ACIN-8	25.1	0.263	0.0117	1.19	0.0007	0.0028
ACIN-9	23.6	0.279	0.0132	0.25	0.0010	0.0007

ND = none detected <5 ppm for H_2S

TABLE 5. REMOVAL OF CO_2, H_2S AND COS

Run	% Removed		
	CO_2	H_2S	COS
ACIL-23	12.2	48.6	4.5
ACIL-24	56.7	100	22.7
ACIL-25	38.1	97.9	20.0
ACIL-26	—	—	—
ACIL-27	40.0	97.3	24.3
ACIL-28	67.8	100	39.6
ACIL-29	91.4	98.7	81.5
ACIL-30	73.6	98.8	64.7
ACIL-31	97.8	99.0	92.2
ACIL-32	98.4	100	90.3
ACIL-33	93.3	99.1	76.9
ACIL-35	94.8	99.2	72.7
ACIL-36	96.5	99.7	80.5
ACIL-38	98.2	99.5	—
ACIN-1	98.4	99.5	91.7
ACIN-2	98.4	99.8	89.4
ACIN-3	97.8	99.5	92.5
ACIN-5	70.2	97.9	35.6
ACIN-6	90.8	99.7	74.4
ACIN-7	98.4	100	87.0
ACIN-8	96.4	99.8	81.3
ACIN-9	99.2	99.7	95.8

Figure 3. Effect of H_2S accumulation on sweet gas composition in Run ACIL-27.

sulting in a decrease in the physical solubility of gases in the solvent. These results support the need for an accurate process model to allow a better understanding of AGRS operation.
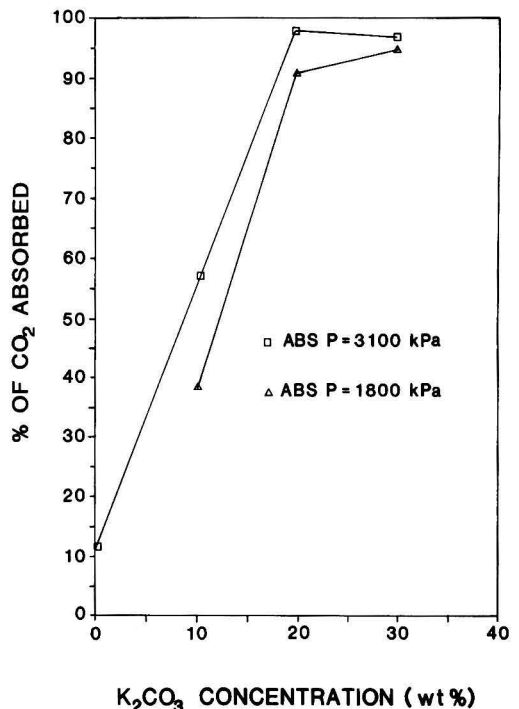
Figure 4. Measured effect of absorber pressure on removal of CO_2.

K_2CO_3 concentration at both absorber pressures tested. Increased selectivity, as shown by a decrease in the ratio of absorbed materials, was observed with increasing K_2CO_3 concentration and increasing pressure; however, there appeared to be no change with absorber pressure using the 30% solution of K_2CO_3. While the data indicate a high potential for selectivity, operating conditions were not selected to study this effect.

The results presented here illustrate the complex nature of absorption and regeneration with chemical solvents. For example, changing solvent composition or stripper pressure changes the boiling point of the solvent and hence the system operating temperature. Such changes in process variables may result in an increase in the rate and driving force of a chemical reaction while re-
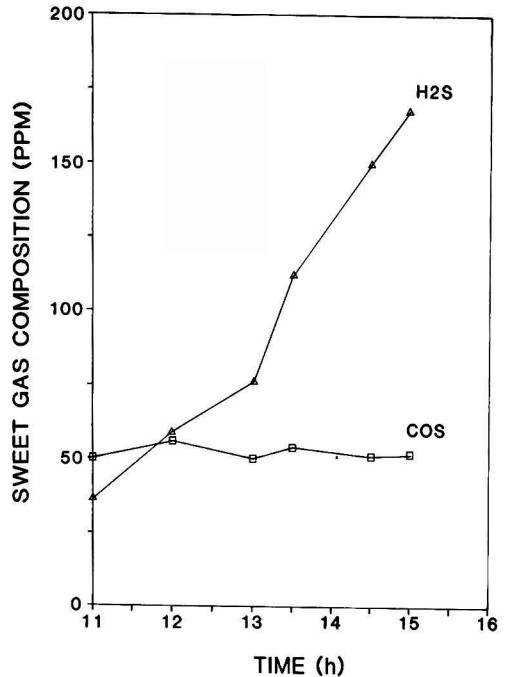
Figure 5. Measured effect of absorber pressure on removal of H_2S.
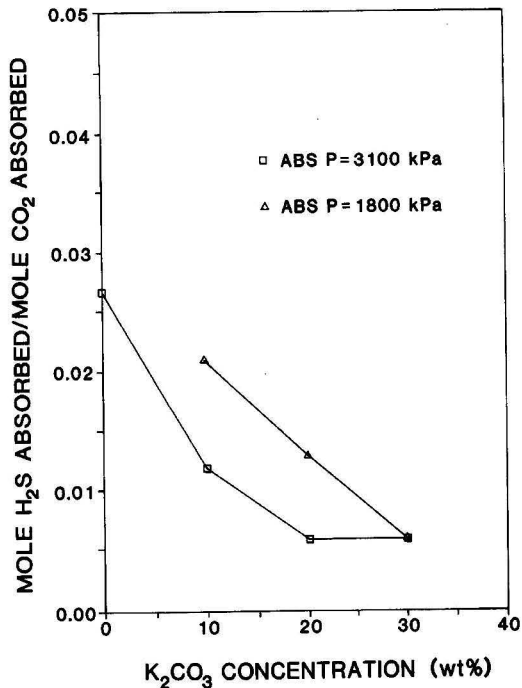
Figure 7. Measured selectivity of AGRS.

Figure 6. Measured effect of absorber pressure on removal of COS.

CONCLUSIONS

In the present work an experimental program was conceived and executed to evaluate the performance of aqueous solutions of hot potassium carbonate in conditioning gases produced from coal. Several operational variables were purposefully manipulated to examine their effect on the removal of carbon dioxide, hydrogen sulfide and carbonyl sulfide from the gas exiting the absorber. As a result of the experimental efforts several conclusions regarding the use of potassium carbonate can be drawn:

1. No loss of solvent activity as a result of irreversible reactions with coal gas species was observed.
2. CO_2 removal ranged from 38.1% to 98.4% at the conditions examined, and was, in general, highly sensitive to AGRS operating conditions and solvent composition. The effect of H_2S and other coal gas species on the removal of CO_2 appeared to be small.
3. The absorption of CO_2 was found to be insensitive to solvent composition when the absorption of CO_2 was controlled by equilibrium between the gas and liquid phases at the top of the absorber column.
4. The absorption of CO_2 was found to be highly dependent on solvent regeneration.
5. The regeneration of CO_2, accomplished by flashing was negligible at the conditions examined.
6. H_2S removal ranged from 97.3% to 100% at the conditions examined and was found to be insensitive to solvent composition. The absorption of H_2S was found to be controlled primarily by equilibrium between the gas and liquid phases at the top of the absorption column.
7. COS removal ranged from 20.0% to 95.8% at the conditions examined and appeared to be a function primarily of absorber temperature.
8. Selective removal of H_2S and COS may be obtained with AGRS operating conditions that include low K_2CO_3 concentrations, low absorber pressures and high absorber temperatures.

9. The absorption of coal gas species that do not participate in a reaction in the solvent was found to be insensitive to solvent composition at the conditions examined. The absorption of these species was found to be controlled by equilibrium between the gas and liquid phases at the bottom of the absorber column.

10. Diethanolamine, an additive commonly used to increase the mass transfer rate of CO_2, appeared to have no significant effect on the fates of other coal ga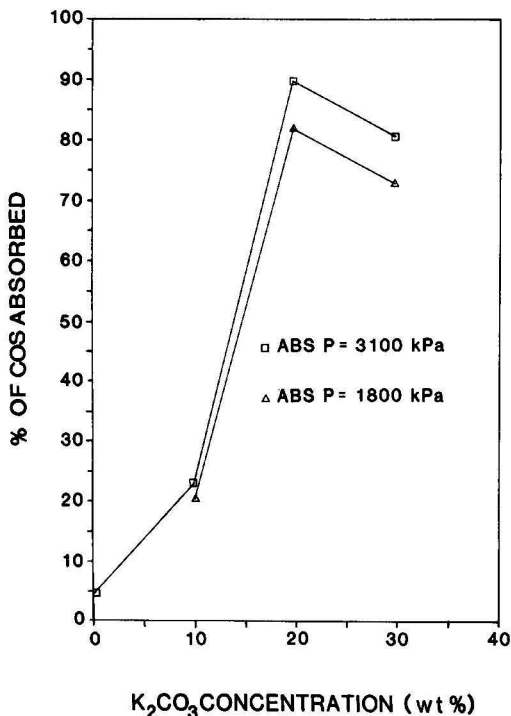s species. This additive appeared to increase the absorption of CO_2 slightly when such absorption was controlled by equilibrium between the gas and liquid phases in the absorption column.

ACKNOWLEDGMENT

LITERATURE CITED

1. Astarita, G., D. W. Savage and A. Bisio, *Gas Treating with Chemical Solvents*, John Wiley and Sons, New York, 1983.
2. Auyang, L., Y. C. Liu, M. Petrik and L. Siwajek, "Trace Contaminants Challenge Synfuels Acid Gas Removal," *Acid and Sour Gas Treating Processes*, S. A. Newman, Ed., Gulf Publishing Co., Houston, 1985.
3. Benson, H. E., J. H. Field and R. M. Jimeson, "CO_2 Absorption Employing Hot Potassium Carbonate Solutions," *Chem. Eng. Prog.*, **50**, 356 (1954).
4. Ferrell, J. K., R. M. Felder, R. W. Rousseau, J. C. McCue, R. M. Kelly and W. E. Willis, "Coal Gasification/Gas Cleaning Test Facility; Volume 1 Description and Operation." EPA Report No. 600-7480-0460, Research Triangle Park, N.C., 1980.
5. Ghassemi, D., D. Strehler, K. Crawford and S. Quinlivan, "Applicability of Petroleum Refinery Control Technology to Coal Conversion," EPA Report No. 600/7-78-190, Research Triangle Park, N.C., 1978.
6. Kelly, R. M., "Use of Methanol as a Solvent in an Acid Gas Removal System Coupled with a Coal Gasifier I. Operation II. Simulation," Ph.D. Thesis, North Carolina State University, Raleigh, 1981.
7. Kohl, A. L. and F. C. Riesenfeld, *Gas Purification*, 4th ed., Gulf Publishing Company, Houston, 1985.
8. Rib, D. M., S. G. Kimura and D. P. Smith, "Coal-Gas Cleanup Facility," *Env. Prog.*, **2**, 86 (1983).
9. Savage, D. W., G. Astarita and S. Joshi, "Chemical Absorption and Desorption of Carbon Dioxide from Hot Carbonate Solutions," *Chem. Eng. Sci.*, **35**, 1513 (1980).
10. Staton, J. S., S. W. Rousseau and J. K. Ferrell, "Solvent Regeneration in Conditioning Gases form Coal," in *Acid and Sour Gas Treating Processes*, S. E. Newman, Ed., Gulf Publishing Co., Houston, 1985.
11. Staton, J. S. "Performance and Modeling of a Hot Potassium Carbonate Acid Gas Removal System in Treating Coal Gas," Ph.D. Thesis, North Carolina State University, Raleigh, NC, 1985.

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Selection of Technology for Synthesis Gas Based Products in Saudi Arabia

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Different technologies to profitably adapt the Kingdom's industrial potential to the realities of the marketplace.

INTRODUCTION

With vast proven natural gas reserves, Saudi Arabia had harnessed this vital natural resource as a keystone to the industrialization and diversification of its economy. Through Saudi Basic Industries Corporation (SABIC), this natural gas is being converted into chemicals that form the raw materials for an extensive range of industrial and consumer products. The development of these products, however, has depended upon SABIC selecting the most effective technologies available to profitably adapt the Kingdom's industrial potential to the realities of the marketplace, thus creating new sources of revenue for Saudi Arabia.

PRODUCTS BASED UPON SYNGAS

It is generally recognized that natural gas is the standard of the industry for producing synthesis gas (syngas) and offers the lowest capital and operating costs. It also offers the greatest flexibility in adjusting the H_2/CO ratio. It is also one of the non-renewable energy resources which is the least polluting. Natural gas is an important resource apart from its energy content. It provides essential chemical raw materials for fertilizers, plastics, drugs, solvents, detergents, synthetic rubber and synthetic fibers. It is used in gas turbines that drive electric generators. It requires no complicated burners, leaves no ash and can be piped from distributor to user as needed, thereby eliminating problems of storage and delivery. Gas heating systems operate at high efficiency, delivering 80% of theoretical heating value of the gas, the highest thermal efficiency of any common fuel. Syngas is made by a number of processes. Steam reforming can be used on natural gas or naphtha, whereas partial oxidation using either the Texaco or Shell processes can be applied to heavier petroleum fractions [1].

The rapid development of new commercial processes based on syngas may lead to a switch to other carbon containing materials to make a range of traditional product using novel catalysts. When the same number of moles of syngas are used, a very different number of pounds of product can theoretically be made. The reason why fewer pounds of product are obtained from ethylene, for example, is the need to produce useless water, whereas more pounds of useful product result if some or all of the oxygen is retained in them [2].

Huge volumes of natural gas reserves are available throughout Saudi Arabia. This fact, coupled with the knowledge of the comparative advantages which characterize the use of this resource, offers a valid explanation why natural gas has replaced coal and naphtha as a basic source of energy and as a feedstock for the manufacture of syngas.

There is little argument of the fact that the development of efficient utilization of natural gas as a raw material is basically linked to the successful development of process catalysts. In view of the anticipated need for more sophisticated catalysts, it is expected the research and development process, apart from being costly, will require exhaustive effort. But it will surely result in the creation of new products that will prove vital for a number of industrial applications. An example of the use of syngas is SABIC's application of methane as both a feedstock and a fuel in its methanol and fertilizer industries.

TYPICAL AMMONIA TECHNOLOGY

The production of liquid ammonia is accomplished by the catalytic steam hydrocarbon reforming process to produce raw syngas under pressure followed by CO-shift, purification of raw syngas and ammonia synthesis. In the process, methane is decomposed by steam according to the basic equation:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$
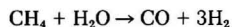
The primary reformer converts about 70% of methane feed into raw syngas in the presence of steam using a nickel catalyst. In the secondary reformer, air is introduced to supply the nitrogen and to provide heat for the remaining reforming reaction. Secondary reformer effluent is cooled in waste heat boilers and delivered to the CO-shift converter containing two charges of catalysts, which are:

1. Conventional high temperature catalyst which is iron based (HTS).
2. Low temperature shift catalyst which is copper/zinc based (LTS).

Utilizing two types of shift catalysts to shift carbon monoxide to carbon dioxide retains the advantages of each type so that the rate of reaction is high in (HTS), and the more favorable equilibrium is attained with the (LTS).

$$CO + H_2O \rightarrow CO_2 + H_2$$
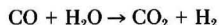
The shift reactor effluent is cooled and routed to the gas purification section. CO_2 is removed from the syngas by

absorption in one of a number of systems, e.g. hot carbonate, MEA (monoethanolamine), Selexol, etc. The carbon dioxide effluent from the stripper in the purification section is directed to the urea facilities. After CO_2 removal, residual CO and CO_2, which are poisons to the ammonia synthesis catalyst, are removed by methanation. The following reaction takes place:

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$
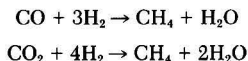
The resulting pure syngas is compressed and mixed with a recycle stream which is introduced to the last stage of the compressor. The gas mixture is then passed to the syngas converter, where this reaction takes place in the presence of iron dioxide catalyst:

$$3H_2 + N_2 \rightarrow 2NH_3$$
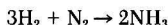
The converter effluent gases are cooled. Anhydrous liquid ammonia is then condensed and separated from the recycled gas. Uncondensed inerts are purged from the synthesis loop.

The essential steps in the process are shown in Figure 1 and can be briefly described as follows:

1. Natural gas is desulfurized to remove trace elements of sulfur.
2. Natural gas is steam reformed over a catalyst (primary reforming) producing a syngas composed of hydrogen, carbon monoxide, carbon dioxide and water.
3. The gas leaving the primary reformer is reacted with air over a catalyst (secondary reformer). The air provides the source of nitrogen.
4. Carbon monoxide in the gas from the secondary reformer is converted to carbon dioxide in shift converters by reaction with steam over a catalyst; additional hydrogen is formed.
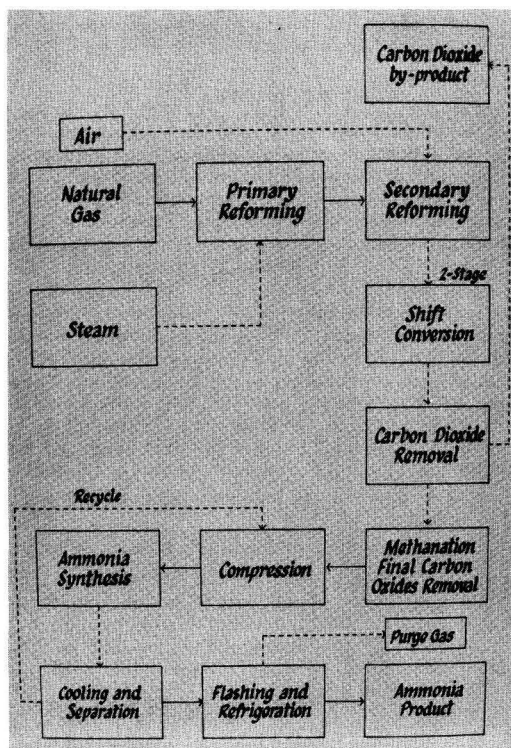
Figure 1. Ammonia—typical steps.

5. Carbon dioxide is removed by absorption, water is condensed from the gas stream and residual carbon oxides are removed (methanation).
6. The syngas, which is now composed of a 3:1 molar ratio of $H_2 : N_2$, is then compressed to required synthesis pressure.
7. Ammonia synthesis occurs in a high pressure reactor (converter) over an iron catalyst using a recirculating loop.

ENERGY CONSUMPTION

Universal increases in energy costs have provided the economic driving force for substantial energy-reduction measures in ammonia plant designs. The significant reductions in energy for current designs have resulted in a consumption in the region of 27.5 MM Btu, or even lower MM Btu's of natural gas as a feedstock and fuel per-metric-ton of ammonia, compared to as high as 44 MM Btu's per-metric-ton in plants designed during the 1970-1973 period.

TYPICAL METHANOL TECHNOLOGY

The methanol synthesis step is currently conducted at low pressure (50-100 atm) and low temperature (220-270°C) with a copper catalyst. This catalyst is vulnerable to contamination by sulfur and other trace impurities. For example, the sulfur content must be limited to well below 1 ppm by weight.

Methanol is produced by the catalytic reaction of syngas over the catalyst in a recirculating synthesis loop:

$$CO + 2H_2 \xrightarrow{\text{Catalyst}} CH_3OH$$
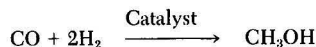
Some carbon dioxide is normally present in the syngas and is converted to methanol:

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$
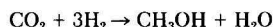
Synthesis pressures as low as 50 atm and converter operating temperature in the region of 240°C have been employed in current technology. The older plants required pressures of around 300 atm and temperatures of about 400°C. High pressure plants are being converted to low pressure operation in order to reduce energy consumption.

Methanol synthesis requires an $H_2 : CO$ molar ratio of 2:1 (although in practice the synthesis is carried out with some excess hydrogen present for kinetic and other reasons). The steam reforming of natural gas, i.e.:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$
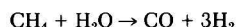
yields a syngas with an $H_2 : CO$ molar ratio of 3:1.

Plants based on natural gas feedstock must therefore either:

1. Purge excess hydrogen from the loop.
2. Add CO_2 from an external source to adjust the $H_2 : CO$ ratio.

The process of Mitsubishi Gas Chemical Company [3] uses composite oxides of copper, zinc, aluminum and boron which can be prepared by adding an alumina solution to the mixture of water soluble copper, zinc, and boron compounds and then firing the total mixture. Methanol production is more or less standard following the basic reactions (Figure 2) indicated previously. The major differences among the various licensed processes are in the catalyst used to carry out the methanol synthesis reaction and in the design of the converter vessel in which the reaction is carried out. The reaction pressure when the above catalyst is used is in the range of 20 to 300 kg/cm2 and temperature is in the range of 150° to 300°C. The pro-
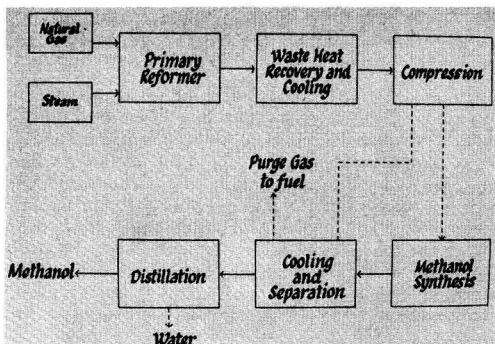
Figure 2. Methanol—typical steps.

cess of ICI comprises reacting carbon monoxide or carbon dioxide, or both, and hydrogen at temperatures in the range of 160° to 300°C in the presence of a catalyst containing the oxides of copper, zinc and aluminum in the ratios: 30:40:10; 40:40:20; 60:30:10 and 75:20:5 [4].

INDIRECT AND DIRECT UTILIZATION OF METHANE

The most important products which have multiple applications (Figure 3) are:

1.) Ethylene Glycol. 2.) Acetic Acid. 3.) Ethanol. 4.) Cl-C6 Alcohols. 5.) Olefins and Gasoline.
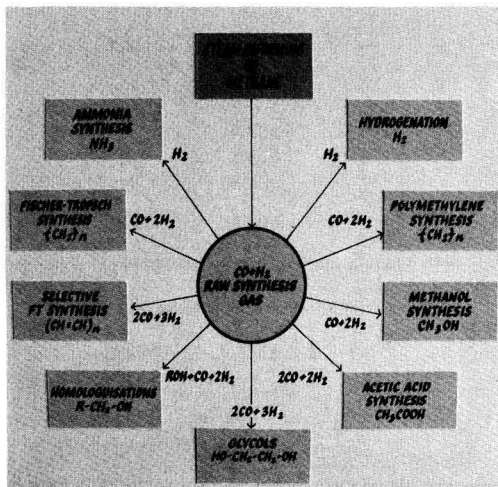
Figure 3. Indirect utilization of methane.

Production of EG in Kg/Kg of Product	
Syngas (H2/CO Ratio = 2.0)	1.19
Oxygen	0.31
Methanol	0.04
Ammonia	0.005

Figure 4. Direct utilization of methane.

In order to advance the scientific research in this field, the various types of companies in the industrial countries must cooperate with all countries that have abundant reserves of natural gas, such as the Kingdom of Saudi Arabia. Such a cooperation in the research and development area, with consequent commercialization of emerging processes, is motivated not only by the supply of raw materials, but by a number of other common interests, among which principally is the provision of basic services and infrastructures, prerequisites to all industries (Figure 4).

Ethylene Glycol (EG)

Industrial research emphasis has been placed on a variety of gas-based processes for ethylene glycol production:

1.) Direct production from syngas. 2.) Carbonylation of formaldehyde. 3.) Hydroformylation to glycolaldehyde. 4.) Reductive hydroformylation of formaldehyde to EG. 5.) Oxidative coupling. 6.) Condensation of H CO. 7.) Redox.

Figure 5 illustrates the various commercial and proposed routes to EG. However, only the direct production from syngas via the UCC-UBE joint program over homogeneous rhodium cluster catalysts are discussed. Other companies are active in the area of rhodium catalyst, including Mitsui Petrochemicals. Some work on the direct use of syngas with ruthenium catalysts has been published by Texaco and Gulf (now Chevron) [5]. In 1980, ICI described a process in which ruthenium catalyst is supplemented with rhodium to obtain high activity and 70% selectivity by weight to EG and its acetate derivatives.

The GO Process of UBE/UCC is based on syngas as raw material to produce ethylene glycol. It could be competitive in locations where ethylene is expensive. It reached the pilot plant scale, but further scale-up work was stopped in early 1984 because of unfavorable syngas versus ethylene prices. Therefore, the GO Process is attractive where syngas is economically available and other alternative sources of feedstocks are relatively costly. The GO Process consists of three main sequential reactions.

Figure 5. Generalized syngas-based routes to EG.
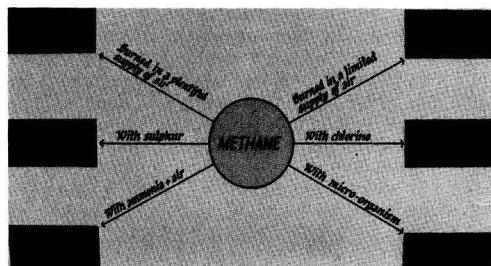
Figure 6. Typical values for raw material requirements of EG.

1. Preparation of methyl nitrate.
2. Carbonylation/coupling methyl nitrate to dimethyl oxalate.
3. Hydrogenation of dimethyl oxalate to ethylene glycol.

A fourth reaction, the generation of nitric oxide, is necessary only to provide nitric oxide for start-up and make-up, since this material is recycled in the process.

The overall reaction converts 2:1 syngas and oxygen to ethylene glycol at the expense of one mole of water (Figure 6).

$$2CO + 4H_2 + \tfrac{1}{2} O_2 \rightarrow HOCH_2CH_2OH + H_2O$$
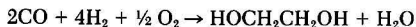
The advantage of this process is that the pressure can be reduced to improve the selectivity. The commercial success of this process will depend upon raising the selectivity and reducing the pressure and residence time (7).

Acetic Acid Synthesis (Direct Process)

There are three processes for synthesizing acetic acid:

1. Carbonylation of methanol (BASF Process, Monsanto Process).
2. Isomerization of methyl formate.
3. Direct process from syngas.

The carbonylation of methanol is becoming the main route of acetic acid synthesis. However, if a high efficiency catalyst is developed for acetic acid synthesis for the direct process from synthesis gas, there is a possibility that such a process will become superior to the carbonylation of methanol in terms of equipment, plant expenses and energy cost.

Ethanol Synthesis

Three ethanol synthesis routes are being studied:

1. Vapor phase direct synthesis.
2. Liquid phase direct synthesis.
3. Liquid phase indirect synthesis (homologation reaction).

Where methanol is reacted with syngas:

$$CH_3OH + 2H_2 + CO \rightarrow CH_3CH_2OH + H_2O$$
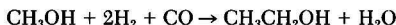
The vapor phase direct synthesis is the most advantageous, if the efficiency of catalyst is disregarded, because the separation of product is relatively easy:

$$4H_2 + 2CO \rightarrow CH_3CH_2OH + H_2O$$

Technical problems related to catalysts in these methods have to be solved since the life of catalysts greatly influence the cost, bearing in mind that the expensive rhodium (RH-) type catalysts are used in very large amounts. Future improvement is expected.

Davy McKee of the U.K. developed a process to produce ethanol from natural gas which combines several commercially proven processes. The first step is the production of methanol from natural gas by steam reforming and conventional low-pressure synthesis. Methanol is then carbonylated to crude acetic acid. The next step is to esterify acetic acid with recycled ethanol to produce ethyl acetate, or to use methanol to make methyl acetate. The ester is then hydrogenated to ethanol and this is the key process which uses the unique low-pressure hydrogenation technology [8]. Davy's concept is to optimize the use of natural gas in a well integrated and self-contained system. This process could be used to produce fuel-grade alcohol for gasoline blending [9].

C₁C₆ Alcohols from Syngas [10]

Alcohol synthesis is a favorable way to upgrade syngas because of positive thermodynamics, low-yield of by-products and attractive economics. The Institut Francais

du Petrole (IFP) developed a process to produce a C_1-C_6 alcohol mixture, suitable to be used directly as a motor fuel blending component at a level of about 8 vol %.

IFP process: This consists of using highly active C_2+ alcohol synthesis catalysts, operating under low pressure methanol synthesis conditions and yielding high flexibility in the heavy alcohol content of the alcohol mixture produced. The IFP catalyst is based on a homogeneous mixed-oxide system containing copper and cobalt as key components. The flexibility of performance allows varying alcohol phase composition, from 20 to about 50 wt% C_2 + alcohols. The reaction also produces few by-products such as hydrocarbons, methyl and ethyl esters and ketones.

Dow process for higher mixed alcohols: Dow Chemical has taken the wraps off a new process designed to use natural gas to produce a mixture of methanol and low molecular-weight alcohols, ranging from ethanol through pentanols, in varying ratios. Although the mostly primary alcohols can be readily separated by conventional means, such as distillation, the mixture itself may have more commercial potential than any of its components. The first step in Dow's process is a fairly conventional partial oxidation of methane to syngas in a ratio of hydrogen to carbon monoxide of 1.0:1.2. After scrubbing to remove the carbon dioxide that is formed along with CO, the syngas is passed over a catalyst, molybdenum sulfide, to produce the alcohols [11] as shown in Figure 7. The at-
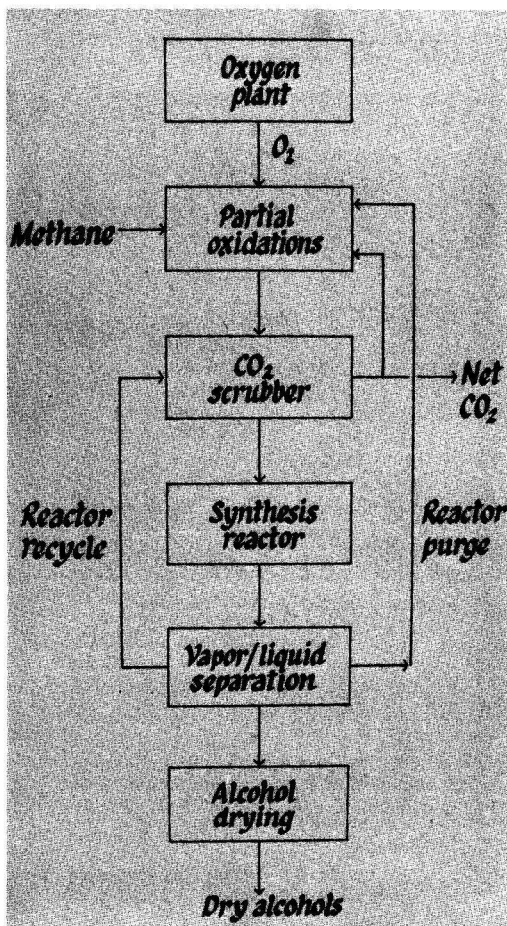
Figure 7. Dow process for higher mixed alcohols.

tractiveness of the mixture over its constituents stems from its potential value as an octane-boosting blending component for gasoline. The problem with alcohols in general and methanol in particular is that they tend to increase the vapor pressure of gasoline. Moreover, methanol itself in the presence of water in gasoline, causes phase separation. So a cosolvent such as higher alcohol must be used to prevent phase separation in use. If alcohols are used, some of the butanes in gasoline must be "backed out" to keep the vapor pressure within acceptable limits.

MAS process [12]: "Methanolo ed Alcoli Superiori" (MAS) is a mixture of 70 wt% methanol and 30 wt% higher alcohols. MAS Process has been developed jointly by Snamprogette and Haldor Topsoe. A 12,000 Mt/y MAS plant was started-up in 1982 in Pisticci (Southern Italy). The MAS produced in this plant is used to carry out tests in blends with gasoline, both with bench-mounted car engines and on a car fleet, and sold within the Italian market under the trade name "Supere." It is reported that MAS has low tendency to phase separation, higher octane blending and reduces exhaust emissions.

C2 oxygenates from syngas [13]: For glycol formation, Texaco Chemical preferred bi-metallic catalysts such as ruthenium-rhodium dispersion catalysts in quaternary phosphium salt melts, and for oxygenates such as acetaldehydes, acetic acid, C_1 to C_3 alcohols and their acetate esters, the ruthenium-cobalt combinations in the presence of quaternary ammonium salts (Figure 8). All of the formulations are iodide-free. Each of the oxygenates is the result of either carbonylation or carbonylation followed by hydrogenation. The chemistry of the system is well established in the homogeneous catalysis literature, but it is very complex because of competing and parallel reactions. There also may be complications from the high reactivity of some of the intermediates formed in the reaction systems.

New Zealand Project: Gasoline from Syngas

A plant for producing gasoline directly from methanol by the Mobil Process was completed in July 1985 and was put into operation in the summer of 1986. This plant is operated by New Zealand Synthetic Fuel Corporation (a joint venture owned 75% by the New Zealand Government and 25% by Mobil Oil Corporation), and is designed to produce high-octane, low-sulphur gasoline, at an annual rate of 570,000 tons (14,450 b/sd). About 50% of New Zealand's traffic fuel will be supplied by the plant. A total estimated investment of $1,475 million was needed [14]. The prime contractor was Bechtel Petroleum Inc. The methanol section is based on the ICI low pressure process and was undertaken by Davy McKee. The plant is to produce 93 octane gasoline and it is believed that the price can be slightly lower than that of imported gasoline. The Mobil Process uses ZSM-5 catalyst in a fixed bed. It is said that if a second plant is constructed, it will employ a fluidized bed.

Mobil MTG Process

Mobil has been developing and commercializing zeolite (crystalline aluminosilicate) cracking catalysts since the 1950's. One type of shape— selective zeolite—was found with a unique channel structure distinctly different from the familiar wide-pore faujasite and the narrow-pore zeolites (it is selectively penetrated by molecules of intermediate size). Mobil found that it could convert methanol and other oxygen compounds into a mixture of hydrocarbons with the composition, octane number, boiling range and other specifications of high quality gasoline [15]. The ZSM-5 catalyst composed primarily of silicon, aluminum and oxygen is made up of thousands of unique pores. When methanol enters through these pores, the molecules are reformed to emerge as high-octane gasoline and water (Figure 9).

The structure of the ZSM-5 class catalyst is as follows: The lines represent oxygen atoms in a siliceous framework. It contains a novel configuration of linked tetrahedra consisting of eight five-membered rings. These units join through edges to form chains and sheets leading to the three dimensional structure. It contains two intersection channels (elliptical 10-membered ring straight channels and sinusoidal fortuitous channels). The sizes of these channels are just wide enough to produce hydrocarbons boiling in the gasoline range. That is, the reaction product terminates at carbon number 10.

This is the reason why the gasoline selectivity is so high in the MTG process. MTG has been demonstrated in a fixed-bed four b/d unit with two adiabatic catalyst beds. In the first reactor the methanol is dehydrated to an equilibrium mixture of methanol, dimethyl ether and water. The products from this reactor are diluted with recycle gas and converted to hydrocarbons in the second reactor. MTG also has been demonstrated in a four b/d fluid-bed pilot unit. Later Mobil, UHDE and URBK decided to investigate jointly the scale-up of the fluid-bed MTG process in a 100 BPD demonstration plant in West Germany. The project is supported financially by the governments of the United States and West Germany. The plant is located at the URBK facility near Bonn; the plant start-up was trouble-free and occurred in December 1982 [16].

The initial step of the MTG reaction is the reversible dehydration of methanol to dimethyl ether. These two oxygenates dehydrate further to give light olefins, which in turn react to heavier olefins. This process is called "Mobil Methanol to Olefin (MTO)." Finally, the olefins rearrange to paraffins, cycloparaffins and aromatics. This process is called "Mobil Olefin to Gasoline and Distillate
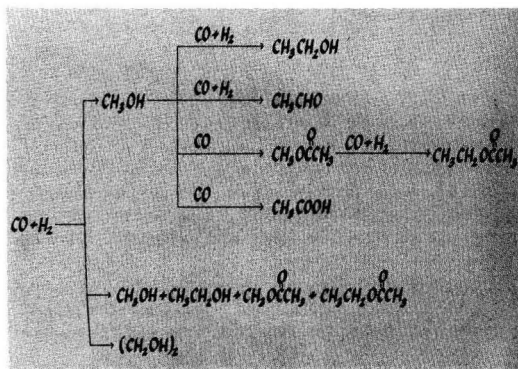
Figure 8. Bi-metallic catalysts lead to C_2 oxygenates from syngas.
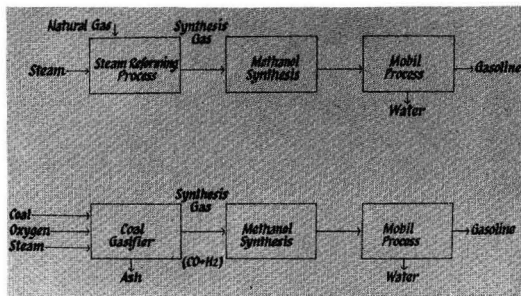
Figure 9. Mobil MTG process.

(MOGD). Almost no hydrocarbons are found higher than C_{10} due to the shape-selective nature of zeolite. For every 100 tons of methanol converted, 44 tons of hydrocarbons and 56 tons of water are formed [17]. This process provides an additional source of chemical feedstocks and transportation fuels from syngas via methanol. In the conversion of methanol to hydrocarbons over ZSM-5 catalyst, more than 100 different categories of olefins, paraffins and aromatics have been identified by using radioactive (14C) tracer compounds.

The reaction is thought to follow the sequence:

$$\text{Methanol} \underset{H_2P}{\overset{-H_2O}{\rightleftharpoons}} \text{Dimethylether} \overset{-H_2O}{\longrightarrow}$$

$$C_2 \text{---} C_5 \text{ Olefins} \longrightarrow \text{Paraffins and Aromatics}$$
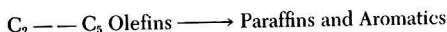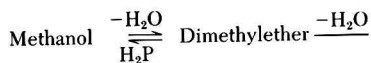
It was found that the alkylation of light olefins with methanol or dimethyl ether is a major pathway for the formation of larger olefins with one more carbon atom (18). Paraffins are mainly produced by hydrogen transfer reactions to their corresponding olefins (Figure 10). It is reported that ethylene could be produced from methanol by the following reaction.

$$2CH_3OH \longrightarrow C_2H_4 + 2H_2O$$
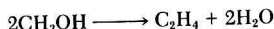
through the use of a molecular shape selective zeolite (19). Publications by various universities and patents by industrial laboratories show that interest in the process is growing rapidly.

Shell Middle Distillate Synthesis (SMDS) (20)

Shell has announced that it has found a set of catalysts which can improve the value and quality of liquid products produced in a Fisher-Tropsch type synthesis using

1- Chemistry of MTG

$$nCH3OH \longrightarrow (CH2)n + nH2O$$

100 tons   44 tons + 56 tons

2- Typical yields wt. % of methanol charges

Methanol + Ether	0.2
Hydrocarbons	43.2
Water	56.0
CO, CO2	0.1
Coke, Other	0.2

3- Reaction Path

$$2CH3OH \rightleftharpoons CH3OCH3 + H2O$$

First Process

Light Olefins + H2O

⇕

C5 + Olefins

Second Process

Paraffins, Cycloparaffins, Aromatics

Figure 10. Summary of MTG process.

carbon monoxide and hydrogen (which is easily made from natural gas). The products are sulfur-free and predominately in the gas oil and kerosene ranges. Shell has proven the process in a pilot plant in Holland and is now prepared to invest in a commercial-size plant in Malaysia, or some other suitable country as the next stage of developing the process.

Fischer-Tropsch Synthesis

This process is concerned with conversion of syngas to hydrocarbons and oxygenated chemicals. There still may be hope for this kind of technology (especially if one contemplates using more active catalyst). It produces a large array of both hydrocarbons and oxygenates. Such a broad spectrum poses problems not only in product recovery, but also in balancing market demand with product slate. There are three synthetic fuel plants operating in South Africa based upon coal gasification.

1. SASOL One: Started-up in 1955, produces motor fuels via Lurgi Coal Gasification, followed by the Fisher-Tropsch process.
2. SASOL Two: Started-up in 1981-1982.
3. SASOL Three: This uses a promoted iron catalyst in the Fischer-Tropsch process and operates at medium pressure with a fluidized bed.

The product distribution is broad and includes light hydrocarbons as well as waxes [21]. Current catalysts are relatively costly. Most of the better Fischer-Tropsch catalysts are noble metals that are very expensive. Any new wave of interest in C_1 catalysis should have as one aim the replacement of these catalysts with less expensive ones that have good stability with at least as great a selectivity as present catalysts.

Ethylene from Synthesis Gas by Direct Fischer-Tropsch Synthesis [22]

The process is characterized by the reaction of carbon monoxide with hydrogen to give hydrocarbons with water and/or carbon dioxide as by-products using newly developed catalysts. The usual range of reaction conditions is five to 30 atm and 150°C to 350°C in fluidized bed reactor. Constituents of catalysts are iron, nickel and cobalt. H_2/CO ratios range from 0.5 to 2.0. The reaction to ethylene may be written as:

$$4H_2 + 2CO \text{ - - - - - - } C_2H_4 + 2H_2O$$

Several patents have been granted, but all the work has been done on a bench scale. There are major questions pertaining to catalyst life, conversion and whether it will be possible to scale up the process.

SABIC has applied the technologies and processes noted above, together with its own empirical determinations, in order to make the most effective use of these technical resources.

SABIC PROCESS EVALUATION CRITERIA

While SABIC recognizes the significance of the use of a certain technology and its impact on the corporation's profitability, as well as on the country's scientific advancement, *yet it believes that the purchase of such a technology in the form of different types of licenses covering designs or patents cannot in itself be regarded as a transfer of such a technology, unless it is accompanied by the following actions:*

1. Performance of economic and technical planning, taking into account universal and domestic factors, as well as a thorough survey of the market requirement.
2. Execution of capital intensive projects, such as the basic and secondary industries including the appro-

priate infrastructure.
3. Provision of training.
4. Integration, maintenance and smooth operation of public utilities.
5. Continued improvement and development of the various processes.

The foregoing clearly illustrate the serious and significant role undertaken by SABIC in order to select and transfer to the Kingdom the most advanced and reliable technology.

SUMMARY OF BASIC ASSESSMENT INFORMATION REQUIRED BY SABIC

In this section some of the standards and criteria are highlighted which will be used by the SABIC evaluation team to form a balanced judgement and produce a firm recommendation for review and approval by senior management.

History of process development: This is not critical, but aids SABIC's team in assessing the capability and acumen of the licensor and his awareness about the market needs. It may also give some indication of future improvements.

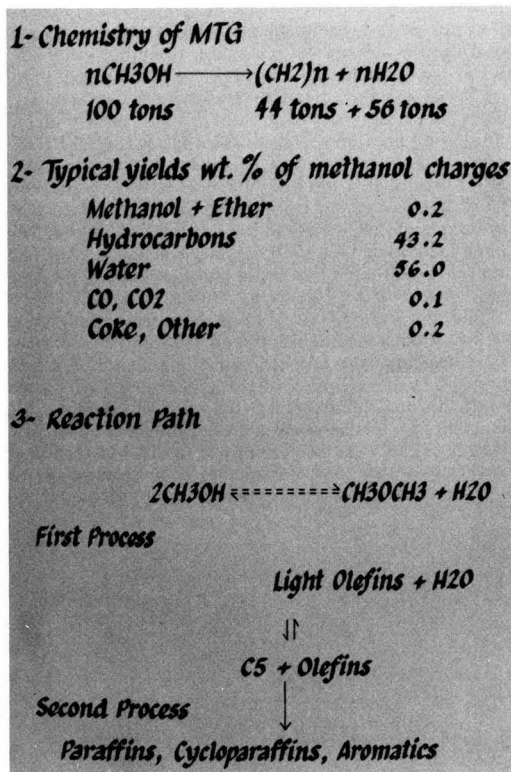*Theory of process parameters:* This enables SABIC's team to understand fundamentals of the process where the critical areas are found. It is an aid in comparing competing processes and provides awareness regarding the strong and weak points of the technology.

Competitive position: The licensor will no doubt have his views about competitive positioning. Therefore, the SABIC team should have its own survey data to be aware about the share-of-market for competing processes.

Strong points of proposed process: Normally, the licensor will not be slow to sell the attributes of his process. The SABIC team must be capable of distinguishing sales talk from hard technical facts. Therefore, SABIC's team will include in their discussion the guarantees, as well as achievements of operating plants. This area is pursued in more depth at a later stage.

Product quality specifications: Although this is self-explanatory, a matter sometimes overlooked is the possibility that the product quality is better than the real commercial requirements. This is only an asset if there is no significant and unnecessary cost.

Reliability, simplicity, safety, ease-of-operation and operating experience: This is an extremely important aspect of the overall assessment and one which has to be carefully balanced against those processes which are new and unproven and which may appear to give a better promise of higher efficiency or less capital. Visits to operating plants of the licensees where the most up-to-date technology of the licensor is being used should be made without the licensor being present. The SABIC team should prepare a check-list of questions related to operating costs, feedstock utilization, catalyst requirements, operating problems, maintenance requirements, control systems, improvements and modifications, safety records and environmental impact.

Experience and competence as a licensor and worldwide use of the process: This is to help the SABIC team's overall awareness of the licensor's position and reputation worldwide.

Relationship with engineering contractors and restrictions on use of contractors: Some engineering contractors have competitive technology of their own and a licensor may be unwilling to accept such a contractor to carry out the engineering for fear of losing proprietary know-how. Therefore, a good relationship between the

contractor and licensor may yield greater efficiency during the engineering phase.

Licensing conditions: The SABIC team must ascertain from the licensor the following:
a. Scope of grant of license and exclusivity.
b. Performance guarantees.
c. Liability of licensor for failure to meet the guarantees of capacity, product quality and yields.
d. Guarantee of catalyst life and supply.
e. Protection against patent infringement for process and product sales.
f. Future exchange of technical know-how, plant expansion and process improvements.
g. Checking of engineering designs.
h. License fees, terms of payment and royalties.
i. Transfer of research and development packages.

Economics and all necessary data for assessment of production cost: The licensor should provide the SABIC team all required information to enable it to generate the capital cost, and the operating and production costs.

Features with specific relevance to Saudi Arabia: The SABIC team should take in consideration the safety, environmental aspects, reliability, simplicity and operational facility, in addition to the general and specialist staff training which may be needed. Also, maintenance, engineering, manufacturing resources and spare parts supply should be considered in more depth. The licensor's experience, capability and willingness to train SABIC's Saudi personnel must also be given careful evaluation.

UNPROVEN TECHNOLOGY

It is worthwhile to mention the question of novel and yet unproven technology. In general, the aim in Saudi Arabia should be to avoid unproven technology, but a too rigid philosophy on this point should be avoided, as well. Any assessment team must be flexible in outlook and properly balance the risk against the advantages of novelty. It is not uncommon that a technology is unproven, but has considerable similarity to proven technology for the manufacture of a different product. The risk in such cases is therefore reduced. Again, some new technologies may have very significant cost savings and potential for ease of operation, minimum environmental impact, etc. It may well result in commercial disaster to reject such technology out of hand because it is unproven. The potential gain may well justify the risk.

APPENDIX I

Saudi Basic Industries Corporation (SABIC), with headquarters in Riyadh, Saudi Arabia, was established in 1976 to develop, operate and market the products of its 15 basic industries, and other downstream and support industries. These have been created to gain maximum utilization of Saudi Arabia's vast natural resources of hydrocarbons and minerals and to reinforce the foundation of Saudi Arabia's industrial and economic growth.

During the past decade, on opposite sides of the country, two new industrial cities have been literally carved out of the desert where hydrocarbon resources are plentiful. Al-Jubail on the Arabian Gulf, and Yanbu on the Red Sea include complete industrial, port shipping, residential housing, shopping and recreational facilities. Here SABIC has already invested over $10 billion to establish, construct and operate its new industries.

An international joint venture company, SABIC had two primary objectives: to develop Saudi Arabia's non-oil hydrocarbon resources and to develop the country's manpower into a trained workforce capable of assuming the responsibilities of national industrialization.

The company chose the joint venture approach to man-

ufacture basic petrochemicals of a quality to compete effectively in the world marketplace. SABIC co-owns most of the plants, usually on a 50-50 basis, with major multinational chemical corporations that will market and consume internally a percentage of the Saudi Arabian product. Among SABIC's partners are Exxon, Mobil, Shell, Celanese, Texas Eastern, Mitsubishi, Lucky Goldstar, Enichem and Neste Oy.

SABIC selected these partners on the basis of their ability to meet several strategically important criteria: their proven experience; a record of profitable operations; ability to market their products worldwide; access to state-of-the-art technology; and their willingness to train Saudi personnel both in-kingdom and at the partners' plants, offices and laboratories worldwide.

In exchange, SABIC's partners gain the opportunity to build new capacity where long-term feedstock availability is assured. Natural gas is supplied to the SABIC plants from Saudi Arabia's Master Gas Gathering System, built to collect, transport and separate natural gas and its extracted liquids into methane, ethane, LP-gas and other components.

In addition to its joint venture, SABIC has also established licensing agreements with other companies to integrate their latest technologies within SABIC's new industries.

APPENDIX II
PETROCHEMICAL INDUSTRIES

Saudi Methanol Co. (AR-RAZI)

Established in 1979 as a joint venture between SABIC and a Japanese consortium led by Mitsubishi Gas Chemical Company. The plant, on stream since mid-1983, produces 600,000 MTPA of Chemical Grade Methanol.

National Methanol Co. (IBM SINA)

A joint venture between SABIC, Celanese and Texas Eastern, incorporated in 1981. The plant began production of 700,000 MTPA of Chemical Grade Methanol in 1984.

Saudi Petrochemical Co. (SADAF):

A joint venture between SABIC and Pecten Arabian Company, a subsidiary of Shell, U.S.A. The company was established in 1980 and began production of Ethylene in late 1984. Other units came on-stream in early 1985 with annual capacities of:

656,000 tons	— Ethylene
454,000 tons	— Ethylene Dichloride
295,000 tons	— Styrene
281,000 tons	— Crude Industrial Ethanol
377,000 tons	— Caustic Soda

Al-Jubail Petrochemical Co. (KEMYA):

Incorporated in 1980 as a joint venture between SABIC and Exxon. It began full production in 1985 with an annual capacity of 270,000 tons of Linear Low Density Polyethylene.

Saudi Yanbu Petrochemical Co. (YANPET):

Established in 1980 as a joint venture between SABIC and Mobil. Operations began in 1985 with annual capacities of:

455,000 tons	— Ethylene
220,000 tons	— Ethylene Glycol
205,000 tons	LLDPE
91,000 tons	HDPE

Arabian Petrochemical Co. (PETROKEMYA):

Wholly owned by SABIC, the company was established in 1980, and came on-stream in 1985 with production of 500,000 MTPA. In 1988 PETROKEMYA will add additional capacity of 100,000 MTPA of Polystyrene and 50,000 MTPA of Butene-1.

Eastern Petrochemical Co. (SHARQ):

Incorporated in 1981 as a joint venture between SABIC and a Japanese consortium led by Mitsubishi. Operations began in 1985 with annual capacity of 130,000 tons of LLDPE and 300,000 tons of Ethylene Glycol.

FERTILIZER INDUSTRIES
Saudi Arabian Fertilizer Co. (SAFCO):

Formed in 1965, SAFCO ownership is divided between SABIC, SAFCO employees and public shareholders. The plant came on-stream in 1969 with annual capacities of:

330,000 tons	— Urea
20,000 tons	— Melamine
100,000 tons	— Sulphuric Acid

Al-Jubail Fertilizer Co. (SAMAD):

A joint venture between SABIC and the Taiwan Fertilizer Co., established in 1980. Production of 500,000 MTPA of Urea began in 1983.

National Chemical Fertilizer Co. (IBN AL-BAYTAR):

A joint venture between SABIC and SAFCO, formed in 1985. The plant, scheduled to go on-stream in 1988, will have a capacity of 500,000 MTPA of Ammonia.

MINERAL INDUSTRIES
Saudi Iron & Steel Co. (HADEED):

Formed in 1979 as a joint venture between SABIC and DEG of West Germany. On-stream in 1983, the plant produces 800,000 MTPA of steel rods and bars.

Jeddah Steel Rolling Mill Co. (SULB):

Wholly owned by HADEED, SULB came on-stream in 1981 with an annual capacity of 140,000 tons of steel rods and bars.

National Industrial Gases Co. (GAS):

Established in 1983 as a joint venture between SABIC and a group of Saudi companies already involved in the production of industrial gases. The plant's first stage went into operation in 1984. Nitrogen capacity is 146,000 MTPA. Oxygen production began in 1985 with a capacity of 438,000 MTPA.

INTERMEDIATE COMPANIES
National Plastic Co. (IBN-HAYYAN):

This joint venture between SABIC and the Lucky Goldstar Group of South Korea was incorporated in 1983. The plant came on-stream in early 1986 with an annual capacity of 300,000 tons of Vinyl Chloride Monomer and 200,000 tons of Polyvinyl Chloride.

Saudi European Chemical Co. (IBN ZAHR):

Established in 1984 as SABIC's first Euro-Saudi joint venture. The participants include the Arabian Petroleum

Investment Corp. (APICORP), Neste Oy of Finland and Enichem of Italy. An agreement for construction of the plant was signed in 1985 with Snamprogetti of Italy. It is scheduled to go on-stream in 1988 to produce 500,000 MTPA of Methyl Tertiary Butyl Ether (MTBE), a high-octane oxygenated gasoline additive to replace lead tetraethel.

MARKETING COMPANIES

SABIC Marketing Ltd., and SABIC Marketing Services Ltd.:

Provide an effective worldwide, regional and local marketing network, technical and customer services, and logistical systems for product transportation and storage.

SABIC Regional Joint Ventures

The Company is involved in three intra-Arabian Gulf manufacturing projects, and a marketing operation (all located in Bahrain).

LITERATURE CITED

1. Ehrler, J. L., J. Barry, "The Future of C_1 Chemistry", Chemtech, March, 1983, p. 188.
2. Ehrler, J. L., J. Barry, "The Future of C_1 Chemistry", Chemtech. March, 1983, p. 191.
3. Tadashi, S. A., (Mitsubishi Gas Chemical) US patent 3,971,735, Canadian Patent No. 1032523 and British Patent 1,488,042.
4. Gallagher, J. T., "Imperial Chemical Industries". British Patent 1,159,035.
5. Kollar, J., "Ethylene Glycol from Syngas", Chemtech, August, 1984, pp 506-509.
6. The UBE/UCC Process for Synthesis Gas to Ethylene Glycol, "The Go-Process".
7. Ehrler, J. L., J. Barry, "The Future of C_1 Chemistry", Chemtech., March 1983, p. 190.
8. Courty Ph., J. P. Anlie, A. Convers. P. Kikitenko, A. Sugier, Institut Francias du Petrole, "C_1—C_6 Alcohols from Syngas Hydrocarbon Processing, November, 1984,
9. "Davy Offers Process for Ethanol from Natural Gas". European Chemical News, March 25, 1985.
10. "Getting Mixed Alcohols from Synthesis Gas". Chemical Week, November 7, 1984.
11. "Dow Develops Catalytic Method to Produce Higher Mixed Alcohols". Chemical & Eng. News, November 12, 1984.
12. Snamprogetti/Haldor Topsoe, "Methanolo ed Alcoli Superiori (MAS) Process".
13. "Bi Metallic Catalysts Boost C_1 Chemistry". Chemical & Eng. News. **63**, 46, (January 7, 1985).
14. Kobayashi, K., "International Trends in Methanol". Chemical Economy & Eng. Rev., May, 1985.
15. Meisel S. L., J. P. McCullough, C. H. Lechthaler, P. B. Weisz, "Gasoline from Methanol in One Step", Chemtech., February, 1976.
16. Gierlich, H. H., K. H. Keim, N. Thiagarajan, E. Nitschke, N. Daviduk, A. Y. Kam, "Successful Scale-up of the Fluidbed". Second E PRI Conference, San Francisco, USA. April 15-19, 1985.
17. Miller, B. J., J. Drummond, "The Mobil Methanol to Gasoline Process", Petroleum Review, April, 1981.
18. Hwu, F. S., J. W. Hightower, "Radioactive (14C) Tracer Studies of Methanol Conversion over a Ni-ZSM-5 Zeolite", American Chemical Society, Washington, D. C. Meeting, August 28, 1982, p. 1165.
19. Berry, R. I., "Gasoline or Olefins from an Alcohol Feed". Chem. Eng., April 21, 1980.
20. "How Shell Hopes to Turn Shut-in-Gas into Light Liquids". International Gas Report, May 24, 1985.
21. A. Quilo, A., J. S. Alder, Freeman D. H., Voorhoeve, R. J. H., "Focus on C Chemistry". Hydrocarbon Processing, March, 1983, pp. 61-62.
22. Haggin, J. "Progress in C_1 Chemistry Aired" Chem. & Eng. News, June 28, 1982.

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Saudi MTBE Plant and Its Role in The Lead Phasedown in The Country

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A description of the Saudi methyl tertiary butyl plant which is scheduled to start up in late 1987.

INTRODUCTION

Due to the abundant supplies of natural gas and crude oil, Saudi Arabia has established large number of petrochemical industries in the past few years. Saudi Arabian Basic Industries Corporation (SABIC) embarked on a number of joint venture projects with major international oil companies. Table I shows the Saudi petrochemical projects on operation or on the study stage. By these projects Saudi Arabia will become a major petrochemical producer accounting for more than 5% of the total world petrochemicals. Nearly 11% of the total petrochemical production will be used locally.

The production of the unleaded gasoline has opened up opportunities for some petrochemicals, mainly the oxygenates. In this respect, methyl tertiary butyl ether (MTBE) received worldwide interest a high octane blending agent for motor gasoline. Its blending research octane number ranges from 115 to 133 and is largely independent of lead content.

Currently gasoline is produced in Saudi Arabia by the addition of the maximum allowable lead compounds, 0.84 gm/litre [1]. Although the adaption of no-lead gasoline is not yet planned, the production of low-lead gasoline is now required since lead pollution had reached a dangerous level in the country [2].

The following is a brief description of the Saudi MTBE plant. The present status of the Saudi refineries is also described as well as the possible ways of reducing the lead content in gasoline. The role of the MTBE plant on the phasedown is also discussed.

MTBE SYNTHESIS

MTBE is produced by the catalytic reaction of isobutylene and methanol. It is manufactured on a commercial scale in Italy and West Germany as well as small plants in the United States. Table 2 shows the existing and planned worldwide MTBE plants. MTBE was first produced in Western Europe in 1976. By the end of 1979, MTBE capacity in Western Europe was about 25,000 tons per year. US started the production of MTBE in the early 1979.

The MTBE synthetic process contains two fixed bed water cooled reactors. In these reactors, isobutylene is reacted with an excess amount of methanol in the liquid phase according to the following reaction:

$$\underset{CH_3}{\overset{CH_3}{C}} = CH_2 + CH_3OH \longleftrightarrow CH_3O - \underset{CH_3}{\overset{CH_3}{C}} - CH_3$$

The reaction is exothermic and takes place at 30 to 100°C (86-212°F) and pressure of 7 to 14 atms (100-200 psig). The activation energy is about 17 Kcal/mole. The catalysts are fixed beds of acidic ion exchange resin, such as Amberlyst® [15]. The resin typically consists of sulfonated polystyrene cross-lined with divinylbenzene. The reactors' output is distilled to recover MTBE product. The spent C_4-methanol is usually recycled.

In the distillation steps as shown in Figure 1, the two methanol azeotropic mixtures, MTBE-methanol and C_4-methanol azeotropes, are separated at the first column. C_4 azeotrope contains little methanol which can be recovered for recycle by water extraction plus fractionation of the extract. While the MTBE-methanol mixture is redistilled to produce MTBE-methanol mixture is redistilled to produce MTBE as a bottom product, methanol recovered at the top of this column is recycled to the reactor.

Properties of MTBE are listed in Table 3. Production grade MTBE has a minimum purity of 98% wt with a small amount of methanol and byproducts as indicated in Table 4. The process can be simply modified for the production of more nearly pure MTBE, of the order of 99% and higher [3].

AN INTEGRATED COMPLEX

Since isobutylene will be manufactured in site from the C_4 portion of liquified petroleum gas (LP-gas), the MTBE plant will be part of an integrated complex. The complex will have the following process steps as illustrated in Figure 2:

1. Isomerization
   (include a deisobutanizer to separate normal and isobutane)
2. Dehydrogenation
   (for the formation of isobutylene)
3. MTBE plant

Methanol will be supplied from the Saudi Methanol Company (Al-Razi) at a rate of 178,000 tons/year. It is also estimated that the butane content of LP-gas will be about 687,000 tons/year, for the production of 500,000 tons/year of MTBE. Table 5 shows the necessary utilities from the proposed plant. The estimated capital investment required for such a plant is about 270 million US Dollars in 1980 basis at the middle east conditions [4]. Table 6 illustrates the economics of this process.

By this integrated plant, MTBE is produced by utilizing the available feed stocks. The plant will start up in late 1987. On Dec. 16, 1984, in Riyadh, Saudi Arabia,

Project	Product	Capacity (tons/year)	Start-Up
Saudi Arabian Fertilizer	Urea	330,000	1969
CO. (SAFCO), SABIC	Sulfuric acid	40,000	
	Melamine	20,000	
Saudi Methanol Co. (ARAZI)	Methanol	600,000	1983
(SABIC-Japanese)			
AlJubail Fertilizer (SAMAD)	Ammonia	300,000	1983
(SABIC-Taiwan)	Urea	500,000	
National Industrial Gases	Nitrogen	146,000	1984/85
(SABIC-Saudi Private Sector)	Oxygen	438,000	
National Methanol Co.	Methanol	650,000	1984
(IBNSINA)			
(SABIC-Celanese-Texas East)			
Saudi Yanbu Petrochemical	Ethylene	450,000	1985
(YANPET)	Ethyleneglycol	200,000	
(SABIC-Mobil)	low density polyethylene	200,000	
	high density polyethylene	90,000	
Arabian Petrochemical Co.	Ethylene	500,000	1985
(PETROCHEMA), SABIC			
Al-Jubail Petrochemical	low density polyethylene	260,000	1985
(KEMA), (SABIC-Exxon)			
Saudi Petrochemical Co.	Ethylene	685,000	1985
(SADAF)	ethylene dichloride	456,000	
(SABIC-Shell Oil)	Styrene	295,000	
	Ethanol	281,000	
	Caustic Soda	377,000	
Eastern Petrochemical Co.	low density polyethylene	130,000	1985
(SHARQ), (SABIC-Japanese)	Ethylene glycol	300,000	
National Plastic Co.	Benzene	245,000	1986
(IBN HAYYAN)	Vinyl Chloride Monomer	300,000	
(SABIC-Lucky Goldstar)	Polyvinylchloride	200,000	
Saudi European Petrochem.	MTBE	500,000	1987
(IBN ZAHAR)	Butene-1	80,000	
(SABIC-Nest Oy-Agip-Apricrp)	Butadiene	124,000	
	Polystyrene	70,000	Under Study
	Acetic Acid	80,000	Under Study
	Vinyl acetate	112,000	Under Study
	Polyvinylacetate	40,000	Under Study
	Compound fertilizer	200,000	Under Study

SABIC signed a joint venture project with the following companies:

APICORP   10% (Arabian Petroleum Investment Corp)
AGIP   10% (Italy)
NESTE OY   10% (Finland)

Three commercial licenses will be responsible for the build up of this plant. UOP will construct the isomerization unit, Air Products will construct the dehydrogenation unit and Snamprogetti will construct the MTBE unit.

The main product of this complex is MTBE, although butadiene and butene-1 will be produced in significant amounts. It is estimated that about 124,000 tons/year of butadiene and 80,000 tons/year of butene-1 will be manufactured. There are other benefits of this integrated system besides the production for some byproducts. Integration affords the optimization of numerous process recycle streams between units as well as the utilization of off-gas stream for use as fuel or feed stock [4]. It enhances the energy efficiency and product yield.

RAW MATERIAL AVAILABILITY

The main raw materials for the production of MTBE are isobutylene and methanol. As mentioned before, methanol will be available from the existing methanol plant, while isobutylene is manufactured from butane. Table 7 shows the prices of raw materials and products on US Gulf Coast on mid 1984.

The only imports required for the MTBE complex are butane and methanol. Those materials are produced in large amounts in Saudi Arabia. There are no environmental pollution or waste streams for disposal from this complex. An area about 172 meters by 326 meters is required for the process units.

THE MTBE ROLE

MTBE is an effective octane booster for unleaded gasoline. Sinc it has a low boiling point (55°C), the increase of the octane number is concentrated in the front end of the gasoline. This increases the engine efficiency in the low speed phase. MTBE has no adverse effect on automobile performance. In fact, carbon monoxide and hydrocarbon emissions are reduced by the blending of MTBE in the gasoline as shown in Figure 3 [5].

The United State EPA has approved the use of MTBE up to 10% in unleaded gasoline since 1973. For the following reasons MTBE is considered an excellent gasoline blender:

1. It possesses a very high road octane number.
2. It improves the engine efficiency of automobiles in the low speed acceleration.
3. It is uneffected by the lead level in the gasoline.
4. It is soluble with hydrocarbons.
5. It does not have a vapor lock tendency, icing problem, or corrosion problem.
6. It shows no difference in the evaporation losses of gasoline.

TABLE 2. WORLD-WIDE MTBE PLANTS

Country	Company	Capacity tons/year	Start up date
U.K.	Highland Hydrocarbon	200,000	1983
	ICI	75,000	1986
	Petrofina	150,000	1986
	Lindsay Oil Ref.	100,000	planned
Ireland	Carbohyde Ireland Ltd	500,000	planned
ECC			
Belgium	SIBP	100,000	1983
Italy	Anic	60,000	1973
	Anic	40,000	1977
Netherlands	Dutch State Mines	75,000	1981
	Shell	75,000	1982
W. Germany	Huls	120,000	1978
	Texaco	12,500	1980
	Erdolchemic	30,000	1986
W. Europe			
Austria	OEMV	50,000	1983
Finland	Nest Oy	80,000	1980
Greece	Motoroll Hellas	34,000	planned
Norway	Saga Petrokjemi	120,000	1984
Portugal	Co Natl Petroquimica	40,000	1982
Spain	Petronor	45,000	1986
E. Europe			
Bulgaria	Neftochin	80,000	1985
Czechoslovakia	Techno export	90,000	1981
Hungary	Chemokomplex	30,000	1983
E. Germany	Industric Analgen	45,000	1982
Yugoslavia	Fabrika SKO	38,000	1980
	Fabrika SKO	35,000	1984
E. Asia			
Taiwan	China Synthetic Petrochem	75,000	1984
Japan	Tonen Petroch	1,700	1980
	Mitsui Petrochemical	5,000	1983
	Idemitsu Kosan	10,000	1987
Middle East			
Kuwait	Kuwait National Ind	150,000	planned
Saudi Arabia	SABIC	500,000	1987
Libya	Pasco	60,000	planned
USA	AMCO	100,000	1985
	AMCO	34,000	1987
	ARCO	200,000	1979
	Champlin Petroleum	105,000	1982
	Charter Int	50,000	1981
	Exxon	105,000	1982
	Exxon	40,000	1983
	Good Hope Refinery	20,000	1980
	Good Hope Refinery	70,000	1984
	Petrotex	280,000	1980
	Phillips	20,000	1979
	Phillips	100,000	1980
	Schenectady Chemical	50,000	1981
	Shell	160,000	1983
	Sohio	100,000	1987
	Tenneco	100,000	1978
	Tenneco	180,000	1981
	Texaco	250,000	1982
	Union Pacific	70,000	1980
Canada	Alberta National Gas	500,000	planned
	Gulf Canada	100,000	1986
Colombia	Empressa Columbia Pert	120,000	planned
Mexico	Petroleos Mexicanos	60,000	1984
Argentina	Petroguimica General	40,000	planned
USSR	Techmashimport	250,000	1984
		1,000,000	planned

7.   It has no adverse health effect.

The total world production of MTBE in 1983 was about 2.1 million tons/year. By 1990, the production rate will reach an estimated 5.3 million tons/year. The gasoline consumption in Western Europe, USA and Japan was 108, 282 and 26 million tons respectively in 1983 (6). By 1990, the total consumption of those countries will be about 384 million tons/year. If MTBE is added at the max-imum allowable percentage of 10% to those gasoline pools, MTBE demand would be 38.4 million tons. This is far above the expected world production of 5.3 million tons at that time. As you can see, the MTBE market will be significantly effected by the following factors:

1.   Octane requirements in automobiles.
2.   Antipollution legislation.
3.   Gasoline demand.

Figure 1. MTBE synthesis.

Figure 2. Route to MTBE using butane feed.

4. Modification in the refineries processes.

MTBE BLENDING IN SAUDI REFINERIES

In the United States, EPA ordered a gradual reductions in gasoline lead content beginning in 1973. The following schedule has been adapted for the maximum addition of lead into gasoline in USA:

Step 1.   Late 1973, 0.45 gm/liter.
Step 2.   Mid 1974, introduction of lead free gasoline.
Step 3.   July 1985, 0.13 gm/liter.
Step 4.   January 1986, 0.03 gm/liter.
Step 5.   January 1988, 0.01 gm/liter.
Step 6.   By 1990, lead will be eliminated from all US motor gasoline.

Western European countries and Japan also reduced the lead concentration in their gasolines. By January 1, 1986, almost all Western European countries had reduced the lead contents in gasoline to 0.4 gm/liter [7]. A further reduction to 0.15 gm/liter is planned. In Japan about 96% of the gasoline pool is already lead free.

In some Saudi refineries, the maximum allowable level of 0.84 gm/liter, of lead is added. The average lead content of gasoline in Saudi refineries is 0.60 gm/liter as shown in Table 8. This figure is considered high as compared to the other countries in the world [1]. The lead content of gasoline must be reduced soon due to its dangerous environmental impact [2].

Lead is introduced into gasoline blends to increase the octane number of the fuel. The reduction of lead content in gasoline will increase octane requirements to maintain the current production rate and quality of gasoline. Since engine performance is a function of octane, if lead is withdrawn from the gasoline blend, alternative sources of octane must be accessed. These include:

1. Operational changes in existing refinery process. (e.g. increase reformer severity and catalyst change)
2. Introduction of high octane blend stocks, such as MTBE
3. Investment in new refinery processing equipment. (e.g. isomerization and continuously regenerated catalytic reformers)

Lead content of Saudi Arabian gasolines could be reduced below current levels fairly quickly at relatively low cost. Elimination of lead from gasoline would require major expenditure totalling an estimated 2 billion US Dollars over a 10 year period. However, the lead content of Saudi gasoline could be reduced to approximately 0.35 gm/liter by operational changes in the existing refineries. A further reduction in lead content to 0.25 gm/liter could

TABLE 3. PHYSICAL PROPERTIES OF MTBE

Chemical Formula	C5H120
Molecular weight	88.14
Specific gravity 4°C	0.7405
Boiling temp at 760 mmHg	55.2°C
Vapor pressure at 30°C	313 mmHg
Freeze point	−108.6°C
Specific heat at 25°C	0.51 cal/gm C
Latent heat of vaporization at 25C	81.7 kcal/kg
Lower heating value	8395 kcal/kg

Source: Snamprogetti, MTBE Report: MTBE As Alternative Motor-Fuel, Technical Brochure

TABLE 5. MTBE PLANT UTILITIES

Electricity	17,653	kWh
Cooling Water	31,982	m3/hr
Fresh Water	81	m3/hr
Fuel	236.7 × 10E6	kcal/hr

TABLE 6. ECONOMICS OF MTBE FROM BUTANE, 1980

Capacity	500,000	tons/yr
Investment	270	mm$
Total Production Cost	36	¢/kg
Total MTBE Cost	40	¢/kg
	113	¢/gal

Source: Ref 4 and Oil and Gas Journal, Dec 22, 1980.

TABLE 4. MTBE PRODUCT CHARACTERISTICS

MTBE	min 99.0% wt
C4 hydrocarbons	max 0.1% wt
Methanol	max 0.1% wt
Di-isobutene	max 0.5% wt
Terteriay Butyl alcohol	max 0.5% wt
Water	max 50 ppm wt
Temperature	40°C
Pressure	4 bar(g)
Physical state	liquid

Source: Snamprogetti, MTBE Report: The Snamprogetti-Anic MTBE Technology, Technical Brochure.

TABLE 7. RAW MATERIALS AND PRODUCT PRICES, 1984, US GULF COAST

	¢/gal	$/metric ton
Butane	77	340
Isobutylene	64	280
Methanol	59	197
Unleaded Gasoline	87	320
MTBE	136	483

Source: Bitar, L. S., Hazbun, E. A., and Piel, W. J., Hydrocarbon Processing 63, 63, Oct 1984.
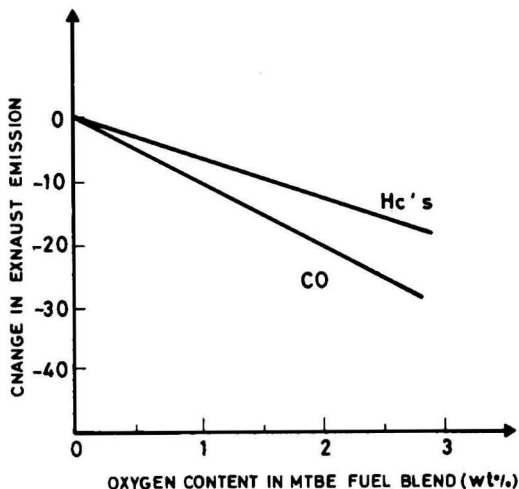
Figure 3. Reduction in tailpipe emission vs. wt% oxygen in fuels blended with MTBE. Source: ARCO, MTBE Octance Enhancer, technical brochure.

be achieved by the MTBE blends. Table 9 shows the ability of Saudi refineries to reduce lead content. About 350,000 tons/year of MTBE would be required.

Nevertheless, the ability of Riyadh and Jeddah refineries to meet the prementioned lead level depends on their continuing to produce regular (83RON) gasoline.

TABLE 8. LEAD CONTENT IN SAUDI ARABIA REFINERIES

Refinery	Production (thousand barrels/day)	Current lead content (grams/liter)
Ras Tanura	64.9	0.84
Jeddah	13.6	0.84
Riyad	43.4	0.30
Yanbu	37.6	0.49
Total	159.5	0.60

TABLE 9. CAPACITY OF SAUDI REFINERIES TO REDUCE LEAD CONTENT WITH CURRENT GRADE STRUCTURE

Lead Content, gm/liter

	Current Operation	Operational Changes	With MTBE Blending
Ras Tanura	0.84	0.60	0.42
Jeddah	0.84	0.74	0.28
Riyad	0.30	0.10	—
Yanbu	0.49	0.15	0.12
Total	0.60	0.37	0.25

TABLE 10. CAPACITY OF SAUDI REFINERIES TO REDUCE LEAD CONTENT IF ONLY PREMIUM GASOLINE MANUFACTURE

Lead Content, gm/liter

	Current Operation	Operational Changes	With MTBE Blending
Ras Tanura	0.84	0.60	0.42
Jeddah	0.84	0.35	0.15
Riyad	0.72	0.33	—
Yanbu	0.49	0.15	0.12
Total	0.72	0.40	0.31

This grade represents about 15% of the total gasoline produced. If this grade is eliminated, then the average lead level would increase to 0.72 gm/liter. The lead level could be reduced to 0.40 gm/liter by operational changes and to 0.31 gm/liter with the addition of MTBE. Table 10 shows the lead levels required to meet this changed grade structure.

CONCLUSIONS

This appreciable reduction in the lead content of gasoline with the addition of MTBE will decrease lead emissions. It is considered as a step toward the production of lead free gasoline in the future. However, the control of the other automotive emissions, namely carbon monoxide, unburned hydrocarbons and nitrogen oxides required lead free gasoline. To date all catalysts used for this purpose are intolerant of lead.

Currently about 80% of vehicles imported into Saudi Arabia are from Japan, 15% from USA and the remainder from Europe and other locations. The gasoline currently produced is 95 RON. This satisfied about 99% of the vehicle fleet. It may be possible to reduce the octane quality of gasoline and still achieve an acceptable level of 94 RON that would satisfy about 98% of the vehicle fleet. Only 92% of vehicle fleet will be satisfied by 93.4 RON. It is probably wishful thinking to request the imported Japanese vehicles to operate at a lower octane requirement. If 99% of the vehicle fleet were satisfied by 91 RON gasoline, a shift to a new process alternative in the reduction of lead content in the gasoline could be considered.

In retrospect, the average lead level in Saudi gasoline can be reduced fairly quickly from 0.60 gm/liter to 0.37 gm/liter by only operational changes in the existing refineries. If MTBE is used the lead level could be reduced to 0.25 gm/liter. Until that time, lower octane requirements must be imposed on the imported vehicles, before any investment on new refinery processes could be started. The production of lead free gasoline could then be investigated.

LITERATURE CITED

1. Al-Mutaz, I. S., and T. F. Al-Fariss, "Impact of Lead Phase-down On Saudi Refineries", Hydrocarbon Processing, 65, 66B (May 1986).
2. Al-Mutaz, I. S., "Automotive Emission Problem In Saudi Arabia", Submitted for Publication (1987).
3. Pecci, G., and F. Telemaco, Hydrocarbon Processing, 56, 98 (Dec. 1977).
4. Muddarris, G. R., and M. J. Pettman, Hydrocarbon Processing, 59, 91 (Oct 1980).
5. ARCO MTBE Octane Enhancer, Technical Brochure.
6. "Worldwide Survey of Motor Gasoline Quality", The Associated Octel Co. Ltd., London (May 1984).
7. Valais, M., and R. Malmaison, "Lead Phaseout in Western Europe", Chemical Engineering Progress, 82, 34 (March 1986).

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Syngas: A Promising Feedstock in the Near Future

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A rapid survey of most promising syngas-based processes within the framework of some near-future objectives.

INTRODUCTION

The conclusion of an editorial dated March 1981 and entitled "Return to syngas" was "Yes, syngas from non-petroleum raw materials has arrived and the future looks bright indeed" [1]. At the same time, it was predicted that crude oil prices could reach $100 per barrel by 1990, routes from natural gas and coal to chemicals via syngas were projected to supplant the existing olefin based processes [2]. For these reasons, priority objectives have been stated:

1. Spare energy
2. Diversify its sources [3]

Syngas, the so-called mixture of carbon monoxide, carbon dioxide and hydrogen can be produced from several sources, such as, coal, shale oil, sand oil, heavy residue, biomass and natural, fatal or associated gas.

Nevertheless, syngas production will almost entirely come from natural gas since gasification of coal, heavy residue or biomass is less economical and natural gas resources get more important. Combined purification of syngas for pure CO or hydrogen production will also develop.

Although crude oil prices have not yet increased as foreseen, just after the petroleum crisis of 1973, petrochemicals from syngas remain an attractive objective. Petrochemistry is estimated to significantly increase within the next 20 years and some new or improved processes, yet emerging, may use syngas as a starting material especially in countries having large resources of associated gas at their disposal [4]. The objective of this article is a rapid survey of most promising syngas-based processes, within the framework of some near-future objectives.

SYNGAS PRODUCTION PROCESSES:
THEIR ADEQUACY TO SYNGAS CONSUMING ONES

Table 1 summarizes the relationship between available feedstocks, their H_2/C molar ratio and the adapted syngas process to be used and the resulting syngas composition. The greatest diversity is offered to natural and associated gas since syngas with large range of compositions (H_2/CO ranging from 1.5 to 6), can be produced from it, using steam reforming, partial oxidation or the new combination of both processes [5, 6]. Heavy residue and coal, through partial oxidation [7, 8] or gasification [9] processes yield rich-CO syngas which can be used directly

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TABLE 1. ADEQUACY OF SYNGAS PRODUCTION PROCESS TO FEEDSTOCKS

Feedstock	H_2/C (mol)	Syngas Production Process	Typical Syngas Composition	
			H_2/CO (mol)	$H_2/(2CO+3 CO_2)$
Natural Gas	1.5-2	Steam-Reforming	5-7	1.3-1.5
		Partial Oxidation	1.5-2	0.6-0.8
Associated Gas		Steam Reforming Autothermal reforming	2.5-2.8	1-1.1
Naphtha	1	Steam-reforming	4-7	0.9-1.1
Heavy residue	0.6	Partial oxidation	0.9	0.4
Coal (Biomass)	0.25-0.40	Gasification*	0.6-2	0.2-0.5*

* Fixed, fluidized or moving bed technologies.

TABLE 2. SYNGAS STOICHIOMETRY REQUIRED FOR SOME PROCESSES

Process	$\dfrac{H_2}{CO}$	$\dfrac{H_2}{2CO + 3CO_2}$	Syngas Production Process
Methanol	$\geqslant 2$	$\geqslant 1$	a-b-c
Methanol-Higher alcohols	1-2.5		b-c (removal of CO_2) d-f and/or H_2 in some cases)
Glycol	1.5-1	/	d-f (or b with H_2 part.removal)
(direct-indirect synthesis)			
Oxosyntheses	1		f (" " ")
Hydrocarbonylations	1 (aldehyde)		d-f
	2 (alcohol)		b (or c with H_2 part.removal)
Carbonylations (Acetic acid Acetic anhydride)	0 (pure CO)		ALL (Selective CO Extraction)

Process		Feedstock
a:	Steam-Reforming	
b:	Partial oxidation	
c:	Steam-Reforming Autothermal Reforming	NATURAL GAS
d:	Partial Oxidation	Heavy Residue
f:	Gasification	Coal, Biomass

in most reductive carbonylation processes (Table 2).

Table 2 deals with different syngas composition required for certain processes [2], most of which use substoichiometric compositions ($H_2/CO \leqslant 2$). This means that some competition will appear between syngas production processes and related feedstocks (heavy residue, coal), directly yielding the desired stoichiometry, and those based on gas (a, b, c processes of Table 2) which uses cheaper feedstocks, but require a further H_2 removal before use.

It must be emphasized that most syngas consuming processes require a very high feedstock purity. A few sulphur resistant catalysts, often based on molybdenum, tungsten and other metals, have been claimed for sulphur-resistant methanation and, very recently, for direct synthesis of alcohols from syngas [10]. In the latter case, H_2S, added to the feed gas, is said to promote the chain-growth mechanism.

Adjusting syngas composition is often a great challenge since most syngas based processes operate at partial conversion, with recycle of most untransformed $(CO + H_2)$. Furthermore, some of them need CO_2 removal in recycled syngas before further use. This implies some changes of inlet reactor composition with respect to the make-up one. The optimum syngas composition is related to many parameters, including reaction stoichiometry, reaction kinetic parameters, required level of reduction of catalysts, and build up of "inert" gases.

Proven commercial processes have been developed for the selective removal of CO, CO_2 and H_2 (COSORB, PSA, PRISM . . .). For some reductive carbonylation processes, recovered H_2 is necessary either to reduce acid, aldehyde function to alcohols, or to hydrogenate esters to alcohols. For the other processes (such as methanol synthesis) excess of hydrogen is consumed as fuel-gas. Recovered CO_2 can be recycled to syngas production section [11] (steam-reforming, partial oxidation) since the reverse shift reaction transforms $(H_2 + CO_2)$ into $(CO + H_2O)$ at high temperature (700-900°C) in the presence of nickel based catalysts. CO_2, the fatal by-product of syngas production processes as well as of many syntheses based on $(CO + H_2)$ can only be upgraded to petrochemicals in a few cases; the main ones are urea and methanol synthesis. A strong incentive for the near future should be to develop new processes yielding petrochemicals from $(CO_2 + H_2)$.

THE PRESENT ECONOMICAL APPROACH OF SYNGAS PRODUCTION

Methanol synthesis being one of the biggest syngas-consuming processes, it is worthwhile, therefore, to approach syngas production economics within the specific case of methanol production, depending on origin and cost of the raw material to be used. Figure 1 [3] presents some methanol production costs from different carbon sources: natural gas, naphta, heavy oil residue and coal (TEXACO gasification technology). This comparison deals with production capacities of 1800 t/day, except for naphta (500 t/day).

For most producing countries, natural gas represents the most attractive type of feedstock, since it yields the best production costs. Whereas naphta, heavy oil residue and coal give methanol production costs which are always higher than 200 $/t. Figure 1 also shows that 150 $/t methanol can be produced from heavy residue at 0.4 $/MMBTU, naphta at 1.5 $/MMBTU (not available) natural gas at 2.4 $/MMBTU (available in Canada, USA . . .). It also explains why most world methanol production units operate with natural gas as a primary feed, as can be seen in Table 3 (1982 data). In consequence, it can be predicted that most near future syngas will be produced from associated or natural gas. Independently, specific
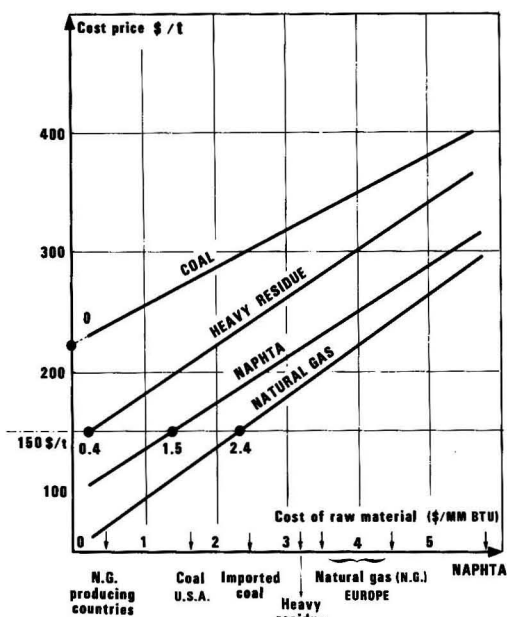

Figure 1. Compared cost prices of methanol (Variable feedstocks and related costs, W. Europe, early 1984).

situations such as coal to syngas based industrial complexes, located in Sasol (South Africa) and Tennessee (USA) will pursue and, eventually, diversify.

THE WIDE RANGE OF SYNGAS BASED SYNTHESIS

Figure 2 sums up the diversity of organic synthesis which can be achieved from syngas and its first and second generation intermediates. Direct synthesis yields methane, hydrocarbons, (Fischer Tropsch), methanol, methanol-higher alcohol mixtures or ethanol. In the presence of nitrogen compounds, synthesis of nitriles, amines and amides is also feasible. Indirect synthesis concern reaction of syngas, CO alone and $CO + H_2O$; O_2 then CO (oxycarbonylation) with methanol, formaldehyde, olefins and acetic acid. As described in Figure 2, several oxygenated products (alcohols, aldehydes, acids, esters, glycol) can be produced in this way.

Last but not least, a new chemistry using methanol as a feed, with zeolites, is developing. Gasoline, aromatics and olefins can also be indirectly produced from syngas, avoiding broad distribution of chain-growth mechanism because of the geometrical selectivity of the zeolites to be used. The significant interest devoted to these new technologies together with the diversity of the R & D objectives, points out the outstanding possibilities of syngas chemistry, susceptible to prevail over classical petrochemical processes as soon as the economics are sufficiently attractive. Acetic acid synthesis constitutes a very good example of shutting-down existing capacities, which were based on ethylene from petroleum sources.

TABLE 3. BREAKDOWN OF WORLD PRODUCTION CAPACITIES OF METHANOL (1982)

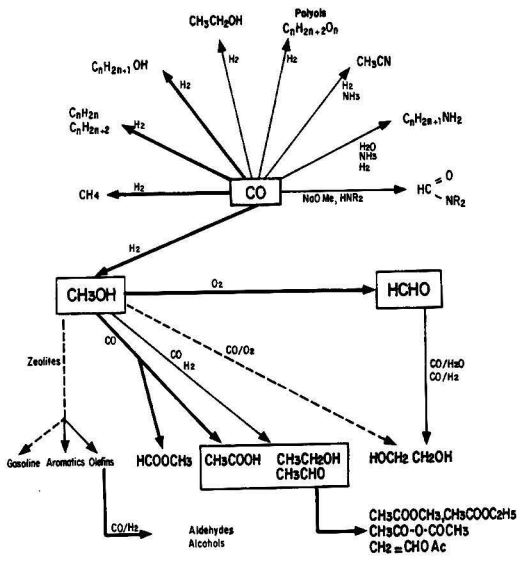|	
Natural gas	71
LPG, refinery gases	6
Naphtha	10
Residues	13
Coal	negligible
	100%

Figure 2. Direct and indirect synthesis from syngas.

Figure 3 already widely published induces some differentiation between metals which chemisorb CO nondissociatively (Cu, Ag, Pd); these metals will mainly produce one carbon oxygenated molecule (e.g. methanol) and the others (dissociative chemisorption) which induce—CH_2 intermediates susceptible to chain-growth (CO insertion) yielding C_2^+ compounds, as well as CH_4 and other hydrocarbons. Rhodium holds an outstanding position: very expensive and rather scarce, it acts as a key-compound of many synthesis, mainly those dealing with acetic derivates production. Replacement of Rhodium by non-precious metal (Co, Ni, . . .) is a very promising challenge for the future [12].

DIRECT SYNTHESIS FROM SYNGAS

Besides substitute "natural" gas production, yet forgotten [13] *Fischer-Tropsch* process has been of prime importance, in Germany, during the last World war. This di-
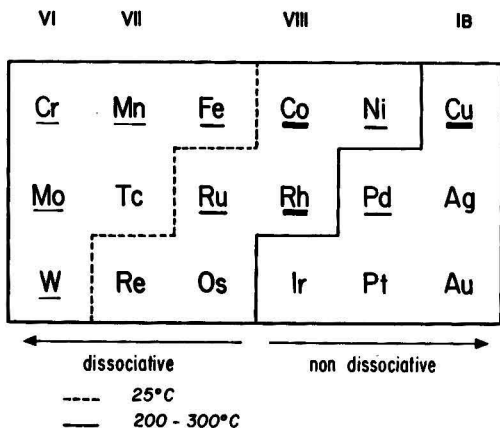

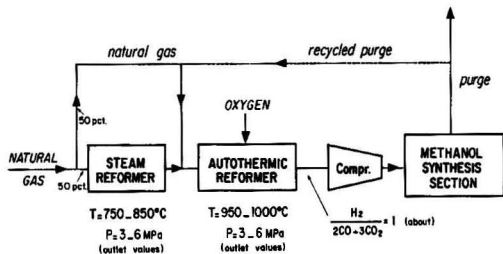Figure 3. Dissociative or nondissociative CO chemisorption on transition metals.

rect synthesis process, yields a very broad product distribution, ranging from 80% CH_4 up to 50% waxes, containing more than 35 carbon atoms per molecule. Product distribution depends on catalyst and process conditions; high $C_{12}+$ fraction for the ARGE fixed bed technology, high C_5-C_{11} fraction for the SYNTHOL fluidized bed technology [14].

Due to the particular situation of South Africa (the cost ratio of oil to coal today is even higher than it was in Europe before 1945 [2]), three industrial plants, whose total capacity, is 4,850,000 t/y, produce most of the olefins, gasoline, diesel oil, kerosene and other hydrocarbons locally consumed.

The extensive distribution of products together with the low maximum yields for petrochemical cuts, Table 4, have to be related to the Schultz-Flory distribution, a major drawback of this process. R & D efforts in the near future will be pursued in order to find positive ways to deviate from the Schultz-Flory mechanism. Shape selective zeolites have been used in this way [15, 16]. The use of cheap associated gas, together with shape-selective catalysts, could be a major incentive for near future developments.

Methanol synthesis: Table 5 shows the world-wide predicted increase of methanol installed capacities. 34-35 10^6 tons are expected to be produced by the years 2000 [17]. Typical performances detailed in the same table [17] explain why old high pressure technologies have been replaced by low-pressure based processes. Provided that available feed-syngas is free from sulfur, chlorine and carbonyl metals, impressive performances are yielded.

The increase of single-train capacities of large methanol units as well as significant improvements of energy recovery and carbon balances (syngas production section included) leads to about 18% savings on previous energy balances of plants designed in the 1970's [18]. A significant contribution to these savings arises also from the new high-pressure-combined process (Figure 4) for syngas production [5, 6]. A new plant, based on this tech-

TABLE 4. FISCHER-TROPSCH SYNTHESIS OF HYDROCARBONS

		Max. yield	
• Maximum yields for	CH_4	100	(wt pct)
complete S.F. mechanism	LPG	55	
	Gasoline	38	
	Diesel	40	
	Waxes	80	

TABLE 5. METHANOL SYNTHESIS

World-wide Increase
of Methanol Installed Capacities
(10^6t)

1985	1990	2000
18.5	25	34-35

	Typical performances	
Process	High-Pressure	Low-Pressure
Temperature (°C)	330-400	230-270
Pressure (MPa)	25-35	5-10
Catalysts	ZnO-Cr_2O_3	CuO-ZnO (+ Al_2O_3,Cr_2O_3, Others)
Duration of Life (years)	2-3	3-8
Products (pct)		
Methanol	≥97	98-99
Hydrocarbons	≤ 3	1- 2

Figure 4. The new technology of production of stoichiometric syngas.

CIRCULATING SLURRY   **EBULLATING BED**   **TRICKLE BED IFP TECHNOLOGY**

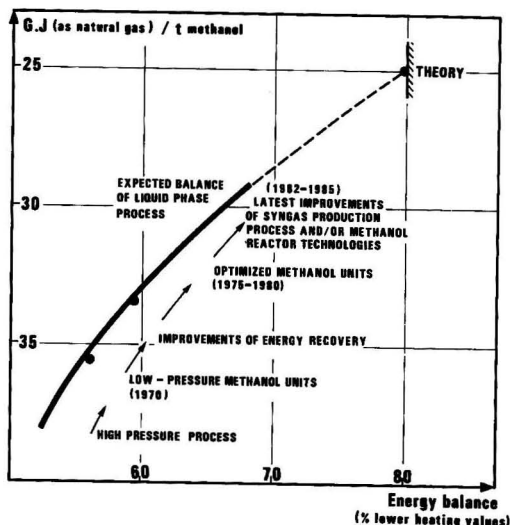Figure 5. Liquid phase methanol synthesis, the different approaches.

Figure 6. Methanol synthesis, recent progresses in energy balance and N. G. consumption.

TABLE 6. ALCOHOLS PRODUCTION (DIRECT SYNTHESIS)

Prospective Study of Oxygenated Motor-Fuel Demand for Western Europe (1985—datas)

	10^6 Tons
● Annual consumption	100
● Available market for oxygenates	7
Average content of oxygenates, 7 pct (wt)	
● Breakdown:	
— Ethers	1
(Limitation due to olefins resources)	
Methanol-TBA Mixt.	2.5
(60-40)	
● Open market for syngas	3.5
to alcohols route	

nology (2000 t/day of methanol) has just been started-up in Malaysia [15]. Another improvement (bench or demonstration unit stage) concerns liquid-phase technologies. This new technology allows careful control of reaction temperature, optimized heat recovery, high flexibility in production capacity and a simplified design of fixed bed reactors (Figure 5) [18].

Lastly, Figure 6, illustrates the successive energy balance improvements of industrial methanol plants. Latest expected figure [18] 29 GJ/t methanol corresponds to an energy balance (pure CH₄, lower heating values) of 68%; an 85% energetic yield with respect to the theoretical figure (25 GJ/t) of stoichiometric reaction:

$$CH_4 + 1/2\ O_2 \xrightarrow{(H_2O)} CO + 2H_2 \rightarrow CH_3\ OH$$

Methanol and higher alcohols synthesis: The production of methanol-higher alcohols mixture from syngas is justified with the open market created in many countries (mainly Western Europe, USA) by the lead suppression in gasoline; Table 6 illustrates the situation for Western Europe [19]. Table 7 summarizes the different approaches for producing such mixtures from syngas [10, 18, 20, 21]. Most of these processes also obey to a chain-growth mechanism; the heavier the average molecular weight of alcohols, the bigger the proportion of

heavy compounds and, more often than not, the lower the alcohol selectivity. In fact a drawback for most of these processes is the coproduction of hydrocarbons. Some such processes operate with CO-rich feed gas, since this favors chain-growth. Lastly most of them need CO₂ removal of recycled gas; this is a traditional way to partially remove water from alcohols, through shift-conversion, in order to simplify alcohol dehydration step.

Tables 8 and 9 deal with the use of alcohols for motor-fuel blending. Table 8 shows that the best octane numbers are yielded with *low-carbon alcohols* (n = 2 - 4) although (Table 9) better compatibilizing properties correspond to C_3-C_5 alcohols. The C_2-C_6 alcohols mixture produced by the process (18-21), under R & D program of IFP and Idemitsu, represents a good compromise between octane and compatibilizing properties.

Preliminary economics of previous alcohol-producing processes have already been published [6, 10, 18, 21]. Since accurate data are not always given, it seems premature to make any economical comparison between them. For example, cheap fractionation technologies do not necessarily consider the removal of undesirable oxygenates, as being as indispensable as that of heavier compounds (Boiling point 180⁺°C) for motor-fuels blending; this significantly hampers the first published economics. Furthermore, with regard to methanol production, the syngas to alcohol complex constitutes a whole ensemble in which the overall economics result from the overall

Catalyst (basic formula)	T(°C)	P_{MPa}	make-up required H_2/CO	CO_2	C_2+OH content (wt%)
Cr Zn K	370 430	20-28	3-3.5	No	10-20
Cu Zn K (+Al, Cr . . .)	350 400	10-15	~2	Opt.	20-30
Cu Co based catalysts	270 320	6-10	1.5 ± 0.5	No	25-50
Modified methanol catalysts	290	5-10	1	No	17-45
Mo K(S) catalysts	240* 325	10-28*	~1*	No (+H_2S)	20-70*

* patent datas EP 119609

TABLE 8. TYPICAL OCTANE BLENDING VALUES OF VARIOUS
ALCOHOLS (LEAD-FREE GASOLINE R.O.N. 91.4, M.O.N. 83.3)

Alcohols	C_1	C_2	iC_3	nC_3	nC_4	tC_4	nC_6	nC_8
R.O.N.								
addn. 5% Vol.	134	135	122	117	94	108	56	18
addn 10% Vol.	132	132	120	118	96	110	56	28
M.O.N.								
addn. 5% Vol.	98	100	96	92	80	94	41	21
addn. 10% Vol.	100	104	96	90	78	93	46	27

TABLE 9. COMPATIBILIZING PROPERTIES OF VARIOUS ALCOHOLS

(premium lead-free gasoline—38 pct. aromatics—T −20°C)
methanol added : 5.3 wt. pct
water : 0.1-0.3 pct
colsolvent : variable

	0.1	0.2	0.3
H_2O			
Cosolvent			
nC_4OH	1.58	3.40	5.27
T.B.A.	1.98	4.04	5.80
C_2-C_6 alcohols	2.01	4.17	5.70
A.B.E.	2.27	4.46	6.65
C_2OH	2.29	4.85	7.49
nC_5OH	1.61	3.80	5.51

optimization of each material and energetic balance of each unit step associated to each other. Such overall data are very seldom available. Generally speaking, direct synthesis of alcohol from syngas is considered to be promising, as soon as we are able to dispose of attractive priced gas, providing that the resulting price of alcohol produced is competitive with those of conventional motor-fuels.

Direct synthesis of ethylene-glycol [22]: Ethylene-glycol can be prepared directly from CO and H_2. Despite its rather high selectivity to ethylene glycol, this approach which implies formyl-species as intermediates, is inevitably penalized. Extremely high pressures are required to allow favorable thermodynamics; hence indirect synthesis is more attractive, as will be seen later.

INDIRECT SYNTHESIS

Considering the wide range of feasible synthesis from syngas and petrochemical intermediates, our analysis will be restricted to a few specific cases. Figure 7 compares the predicted cost prices of some raw materials to those of rank products [2]. It can be seen that the production of ethylene glycol and acetic acid are synthesis with a high

potential. Alkanes, olefins, fall into the low potential category [2].

Commercial and Near-Future Commercial Processes

These processes are mostly related to acetic derivates chemistry and Figure 8 gives details on the production of C_2 and C_2+ oxygenated molecules from CO, syngas and methanol. Acetic acid produced from methanol carbonylation becomes itself an intermediate for synthesis of methyl acetate, the dual precursor for acetic anhydride and vinylacetate synthesis.

Acetic acid: Since 1974, carbonylation of methanol has been replacing the conventional ethylene—acetaldehyde—acetic acid route (Waker process). The first methanol carbonylation process utilized cobalt based systems, operating under severe conditions (210-250°C, 70 MPa). The discovery of rhodium based systems which yield impressive performances in much milder conditions (175-190°C, 2 to 4 MPa) [23] have overthrown the situation. Despite the use of iodine (the cocatalyst of most of indirect synthesis) which requires Hastelloy and Zirconium metallurgy, this process has outstanding economics [3, 4] as can be seen in Figure 9 (economics for Western Europe early 1984). This comparison deals with the following flow-schemes [3, 4]:

1. Steam-cracking of ethane to ethylene (450,000 t/y), further oxidation to acetaldehyde (WACKER-HOECHST process), then, to acetic acid (80,000 t/y).
2. Steam-reforming of natural gas; methanol (600,000 t/y) and carbon monoxide (40,000 t/y) production, this latter one being based on cryogenic fractionation. Acetic acid synthesis; Monsanto process (80,000 t/y).

It is easy to understand why acetic acid synthesis has become exclusively carried out from methanol and CO; i.e. syngas. The future objective is to replace the rhodium of present day catalysts with non-precious metals such as nickel or cobalt [12, 23]. This implies further improvements of related selectivities.

Acetic anhydride: Because of Tennessee-Eastman's location, near substantial high-grade coal deposits and, perhaps, because of previous prospective analysis predicting 1990's oil prices as high as 100 $/bbl, this coal-based acetic anhydride process (240,000 t/y) has just started. Since traditional process uses ketene and acetic acid (ex. syngas route) the challenge deals with a 100% syngas route to acetic anhydride. The two-step process uses methyl-acetate as an intermediate. Rhodium catalysts are also used. Very high yields under moderate operating conditions (170-210°C, 4-8 MPa) are obtained. This makes this process promising, even though the predicted drawback of its development would be the low-growth of acetic anhydride demand.
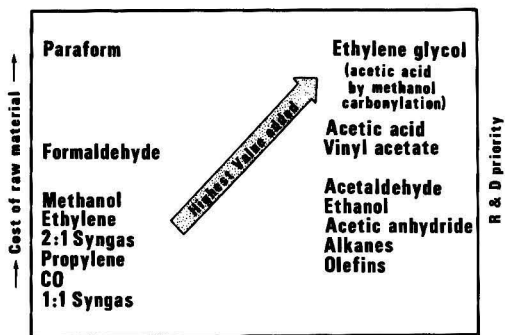
Figure 7. Tendencies for R & D objectives in syngas chemistry (Gulf Coast prices projection to 1990).
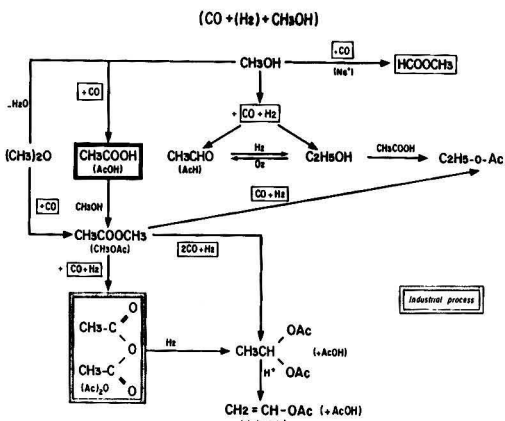

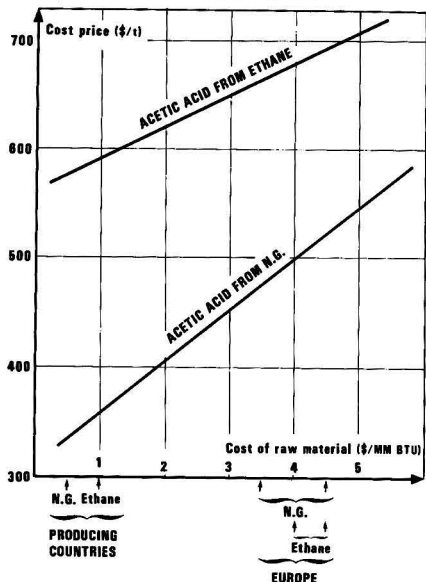Figure 8. Production of C_2 and C_2 + molecules through indirect synthesis.

Figure 9. Compared cost prices of acetic acid.

Oxo synthesis: This process, born around the year 1938, produces at present 5.5 Mt/y of various C_4, C_4^+ aldehydes, alcohols, ketones and carboxylic derivatives. The late developments, concerning rhodium phosphine homogeneous catalysts (Union Carbide) have led to significant improvements of performances compared to those of homogeneous cobalt based catalysts (Ruhrchemie-Shell), such as, milder operating conditions (90-120°C, 3 MPa) and higher n/iso ratios (> 10) for products [24]. Furthermore recent catalyst developments of Rhone-Poulenc and Ruhrchemie [25] dealing with rhodium-trimeta sulphonato-triphenyl phosphine (Rh-TPPTS) allows the hydroformylation to proceed in a two-phase system which separates catalysts (water-rich phase) from products (organic phase). This process yields n butyraldehyde from propylene and syngas under mild conditions (5 MPa) with very high activity (440 lb C_3H_7CHO h^{-1} · m^{-3}) and 95% linear selectivity [25].

Other Developments

Vinylacetate: The industrial proven process, based on ethylene acetoxylation, already uses acetic acid, a syngas produced reagent, for 70% of its raw material balance [2]. The new process, not yet of economical value, deals with ethylidene diacetate route (Figure 8).

Acetaldehyde, ethanol: Reductive carbonylation of methanol has been extensively studied [23]. Although significant progress has been made, such processes cannot yet compete with the ethylene route.

Ethylene glycol: The proven industrial process, which uses the ethylene—ethylene oxide—glycol route, is based on 100% petroleum chemistry. This proven process is said to be vulnerable [2] with regard to syngas based ones, since its overall yield is less than 70%, on ethylene feed. Figure 10 deals with several syngas to glycol routes. Apart from direct synthesis and radical-initiated condensation of methanol and formaldehyde which indirectly concern syngas chemistry, several others have been studied. The oldest one, the glycolic acid production from formaldehyde by acid catalysis H_2SO_4-70 MPa has been used commercially by Du Pont until 1968 [26]. Recent acid catalysis improvements have led to substantial lowering of severity of reaction conditions. The two other main ways are the oxidative carbonylation route [23-26], it is said that a 20,000 t/y plant, producing oxalic acid according to this technology, is still operating in Japan [26], and the formaldehyde—paraformaldehyde reductive carbonylation route whose interest is hampered by the need of use of anhydrous formaldehyde [26].
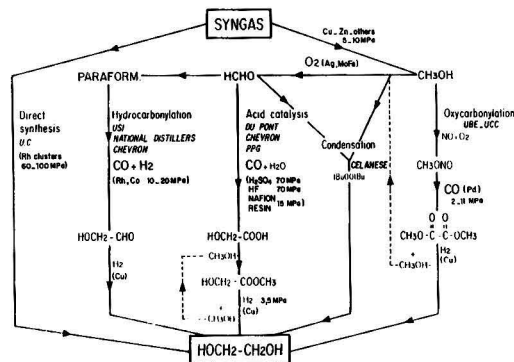

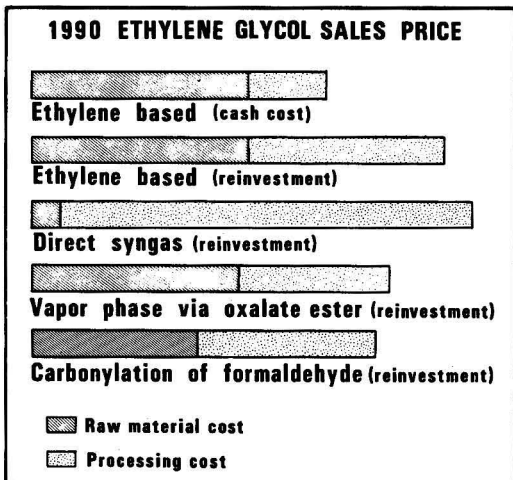Figure 10. Main routes from syngas to ethylene glycol.

1990 ETHYLENE GLYCOL SALES PRICE

Ethylene based (cash cost)

Ethylene based (reinvestment)

Direct syngas (reinvestment)

Vapor phase via oxalate ester (reinvestment)

Carbonylation of formaldehyde (reinvestment)

▨ Raw material cost

▨ Processing cost

Figure 11. Comparative economics for $C_2^=$ and syngas-based ethylene glycol routes, US Gulf Coast, 1983. (R. J. H. Voorhoeve et. al.—Celanese—H. P. 03/83 pp. 57-65).

Figure 11, [2] sets out some economical comparisons. With regard to oil-based processes, some of these technologies are competitive, when direct synthesis which correspond to the cheapest raw material cost is penalized for its huge processing cost. Oxalate esters and formaldehyde reductive carbonylation routes appear promising even though further progress is required to take the place of the present process.

OTHER METHANOL-BASED PROCESSES

These processes deal with gasoline, ethers, and light olefins production from methanol, they all use methanol, whose precursor is syngas, but *not* syngas itself. *Gasoline* production from methanol is a promising process when compared to the direct synthesis approach (Fischer-Tropsch), since the use of shape selective zeolites allows escape from the chain-growth mechanism. Meanwhile, the high rate of coking implies future industrial development of moving bed regenerative technology, which is under demonstration in Wesseling (W. Germany) [26]. Furthermore, this process is bounded to the use of cheap methanol, allowing local production of motor fuels at reasonable cost.

Strong incentives for *Ethers* production comes from present day low methanol prices as well as the progressive lead suppression in motor fuels in Western Europe and USA. Ethers have the emerging advantage to provide high octane blending values, together with a low oxygen content. The drawback is their poor compatibilizing properties which prohibits the coaddition of pure methanol to ether-blended motor-fuels.

Last but not least, *Light Olefins* can be selectively produced from methanol in the presence of molecular sieve based catalysts. Despite their still impressive performances (with respect to the direct synthesis of olefins from syngas), lower raw material costs are required in order to bring attractive economics to these processes.

CONCLUSION

Table 10 [3] deals with some predictive analysis of the importance of world syngas chemistry by the end of the century. With regard to overall petrochemistry, it can be

TABLE 10. WORLD-WIDE PREDICTED WEIGHT OF SYNGAS CHEMISTRY (EXPRESSED AS 10^6 TEP)

	1980	2000
Petrochemistry	140	270-320
Methanol + Acetic Acid (Main products)	7	20
% of petrochemistry	5%	6-7.5%
Ammonia + Urea	73	120
Petrochemistry + Ammonia + Urea	213	390-440
Methanol-Acetic acid Ammonia-Urea	80	140
% of Petrochemistry + Ammonia + Urea	38%	32-35%

predicted that both syngas and petrochemical increases of capacity will be of the same order. Up to the years 2000, the share of conventional, petroleum issued processes, will represent a leading part, as long as a new Petroleum crisis will not modify this situation. Major syngas developments will concern methanol, acetic acid and their derivates, as well as ammonia and urea (fertilizers industry) which, in fact, constitute the majority of syngas chemistry applications, as pointed out in the same table.

It must also be emphasized that syngas chemistry developments will mainly concern natural gas; mostly associated gas, available at a very low cost in oil/gas producing countries (Middle-East, Far East, Eastern countries, Canada, . . .) Syngas-based chemical complexes should develop in most industrialized oil producing countries although the lesser ones will produce methanol [19]. The expected growth of chemical uses of natural gas will range from the present day 1.5 to approximately 2 TEP (1 TEP ≃ 16 MMBTU) by the end of century. Since these two billions of TEP will only represent 7% of the overall natural gas consumption to be expected by the year 2000, large natural gas resources will remain available for further increase of syngas uses.

In conclusion, chemical upgrading of Natural Gas is of prime importance. Direct transformation of methane can be a valuable long-term target [27] but the significant progresses in syngas chemistry which have been gained in catalysis developments, energy recovery and energetic yields, reactor technology etc. makes us feel sure that significant short-term goals are obtainable (e.g. acetic acid and its derivates) and to a lesser extent ethylene glycol, alcohols production, although the present decrease in petroleum prices has led to some retrenchments in R & D for syngas chemistry. It can be strongly expected that all the chemical industry will consider syngas as a promising feedstock, and therefore of major strategic importance, in the near future.

LITERATURE CITED

1. Ponder, T. C., Editorial. *Hydrocarbon Processing*, p. 67 (March 1981).
2. Voorhoeve, R. J. H., et al., *Hydrocarbon Processing*, p. 57-65 (March 1983).

3. Balaceanu, J. C., XIIIe Mendeleev Congress of Applied Chemistry, Leningrad, (May 1984).
4. Chauvel, A., IFP, Unpublished data (1984).
5. Banquy, D., Brit. Patent, 1,569,014 (1977).
6. Supp, E., *Hydrocarbon Processing*, p. 34C-34J (July 1984).
7. Marion, C. P., J. R. Muenger, *Energy Progress*, **1**, p. 27-32 (1981).
8. Ter Haar, L. W., *Chem. Ec. & Eng. Review*, **5**, 12 (nr 68), p. 22-28, (December 1973).
9. Eleventh World Petroleum Congress—Coal Liquefaction and Gasification—RTD5 (E. J. Parente—G. F. I. Roberts *et al.*—R. A. Cardello *et al.*, A. E. Sheindlin *et al.*, Proceedings—J. Wiley & Sons, London 1983.
10. Dow Chemical, E. P. 119 609—Priority 18th March 1983. W. J. Mintz, G. J. Quarderer, Alcohols as an octane enhancer (Alcohol week's seminar)—Saint-Antonio (U.S.A.) (March 27, 28, 1985).
11. I. C. I. F. 2.207.392 (1969). I.F.P.G.B. 2139 224 (1983).
12. RHONE-POULENC, E.P. 35 458, 1981 and F. 2496 644, 1982; MITSUBISHI E. P. 65817 (1982).
13. I.F.P., F. 2546 879 (1983).
14. Dry, M. E., Catalysis Science and Technology, Vol. 1, p. 160-255. J. R. Anderson, M. Boudart, Ed. Springer Verlag (1981).
15. USP. 4, 261, 864, 4 261 865 (1981), 4294 725 (1981), 4 338 089 (1981).
16. Bussemeir, B., C. D. Frohning, B. Cornelis, *Hydrocarbon Processing*, (November 1976).
17. I.F.P.—Proprietary data.
18. Alcohol Fuel Technology Symposium Ottawa, Proceeding II, W. Hilsebein, E. Supp, p. 140-146, M. E. Franck, p. 425-433, P. Courty et al., p. 92-99 (May 1984).
19. Chauvel, A., Unpublished data (1985).
20. I.F.P., F. 2 523 957, Priority data, 26/03 (1982).
21. Courty, P., et al., 11th World Petroleum Congress—London, Sept. 1983, Proceedings (PD9), J. Wiley & Sons (1983).
22. Union Carbide, USP, 4 199 520 (1980).
23. Chaumette, P., F. Hugues, *Revue de l'I.F.P.*, **40**, (1), p. 91-111, and references therein (1985).
24. Tkachenko, I., *Inf. Chimie*, **249**, p. 115-121 (May 1984).
25. Waller, F. J., *J. Mol. Cat.*, **31**, (2), 123-136 (1985).
26. Sauby, J. B.—Oxygen and the Conversion of Future Feedstocks, London, Third BOC. Priestley Conference Proceedings, p. 221-237 (1983).
27. Lunsford, J. H., et al. *J. Am. Chem. Soc.*, **107**, 1052 (1985).

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Design & Operation of a Selective Sweetening Plant Using MDEA

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Operating data were collected from the Signalta gas sweetening plant.
The plant has had an interesting variety of
feed gas and operating conditions. The design and operation of the facility for
CO_2 slippage are discussed.

INTRODUCTION

The Signalta Resources Forestburg Gas Plant was constructed during the winter of 1983 and placed on stream in April of 1984. A design outlet gas specification of 1/4 grain H_2S/100 scf was requested to ensure meeting the contract commitment of 1 grain/100 scf. The design gas flow-rate was 30 MMSCFD containing 0.5% H_2S and 3% CO_2 at 415 psia and 70°F.

The overall plant is configured as shown in Figure 1. Inlet separation facilities are followed by a feed gas heater. The gas stream then flows through a filter separator followed by the amine contactor. Another filter separator is used as a sweet gas scrubber. After sweetening, the gas is routed to a dew point control refrigeration unit. Finally, a single stage of compression is required to boost the gas to 1200 psig maximum pipeline pressure.

The sweetening chemical selected for the Forestburg Plant was methyldiethanolamine (MDEA). This was chosen due to its capability to remove H_2S and leave a portion of the CO_2 in the residue gas. At the time of plant commissioning it was one of the first operating MDEA facilities in Western Canada.

The inlet gas comes from 20 wells and is located in various pipelines up to 6″ diameter with a total length of more than 50 miles. Some of the wells produce as much as 2% H_2S and occasionally some oil and asphaltene. The actual feed stream reaching the plant normally contains 0.2 to 0.4% H_2S. Due to demand the flow rate has varied from 6 to 27 MMSCFD.

Several tests of the plant were undertaken to determine the effects of changes in feed point on the contactor. This information can be used to improve the methods and assumptions used in the design of MDEA sweetening systems. Considerable interest is expressed by production companies in the adjustability of CO_2 slippage that can be obtained using MDEA. This opportunity is also used to describe the initial calculation procedures used to develop an MDEA design.

Figure 1. Block flow diagram for Forestburg Facility.

PROCESS CHEMISTRY

The methyldiethanolamine (MDEA) process as used for natural gas treating utilizes the selectivity of the chemical

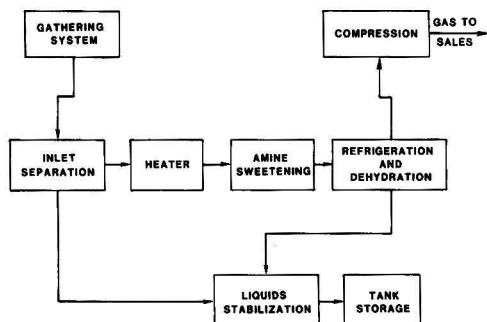for H_2S in preference to CO_2 in a nonequilibrium situation. Several sources of published material are available describing the various reactions that may take place [1-6]. The most significant observation from a plant design perspective is relatively simple. H_2S chemically reacts with MDEA almost instantaneously by proton transfer as is the case with other commonly used amines.

$$H_2S + R_2 NCH_3 \leftrightarrows R_2NHCH_4^+ + HS^-$$
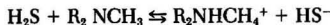
Since MDEA is a tertiary amine and does not have a hydrogen atom attached to the nitrogen atom, the CO_2 reaction can only occur after the CO_2 has formed bicarbonate with water.

$$CO_2 + H_2O \leftrightarrows HCO_3^- + H^+$$
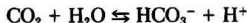
It is the formation of the bicarbonate which is generally considered to be the slow reaction which limits the CO_2 reaction to less than equilibrium values at short contact times. The bicarbonate then undertakes an acid-base reaction with the amine to yield an overall CO_2 reaction:

$$CO_2 + H_2O + R_2 NCH_3 \leftrightarrows R_2 NHCH_4^+ + HCO_3^-$$
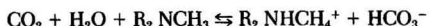
Because of the slow intermediate step required for the CO_2 and water it may be assumed that H_2S reaction with MDEA is gas phase limited while the CO_2 reaction is liquid phase limited [2]. It is obvious that to utilize MDEA effectively in selective situations it is necessary to keep the liquid phase contact time for the reaction to a minimum so that less CO_2 will be absorbed by the amine solution. Several mechanical design considerations must be taken into account in proper absorber vessel design to ensure that this will occur. The mechanical design requirements have an effect on the process operation. Therefore, it is necessary to properly allow reasonable first order estimates of the mechanical influence on the process.

A computerized approach to the process design calculations is a necessity in order to optimize the design in any reasonable time frame. The program used for the design of the Signalta MDEA process was TSWEET from Bryan Research & Engineering of Bryan, Texas. This program does rigorous tray by tray calculations for the contactor and stripper columns by the Ishii-Otto method and contains a kinetic model to simulate the effects of contact time and the MDEA selectivity. A modified Kent and Eisenberg equilibrium model is used to calculate the vapor pressures of H_2S and CO_2 above the amine solutions. This program also contains the ability to simulate multiple feed points to the absorber, which is one method of control over the selectivity.

PRELIMINARY DESIGN CONSIDERATIONS

Several preliminary considerations should be examined for each sweetening application. These include:

Circulation Rate

The ratio of CO_2 to H_2S in the feed gas is of considerable importance in the selection of MDEA as the sweetening agent. The more CO_2 in relation to H_2S, the more attractive economically it will appear to remove only the H_2S. The original CO_2 to H_2S ratio for the Forestburg plant was 6:1 which was the initial indication that MDEA was worth considering. In addition, preliminary simulations indicated that 1/4 grain/100 SCF specification with slightly less than 2% CO_2 in the outlet gas was readily achievable.

When initially designing an MDEA facility, a first estimate of the circulation rate is required. A good approximation is to calculate the amine rate required to remove all the H_2S and half of the CO_2.

$$GPM = \frac{.206 \times MM \times (H_2S + CO_2) \times MWT}{ML \times WT}$$

where

MM	= gas flow MMSCFD
H_2S	= mol % of H_2S to be removed
CO_2	= mol % of CO_2 to be removed
MWT	= mole WT of MDEA = 119.9
ML	= mol loading, moles acid gas/mole
WT	= amine solution weight percent circulated

Using the design feed gas analysis for the Forestburg Plant from Table 1 as an example case, this is calculated as follows:

$$GPM = \frac{0.206 \times 0.30 \times (0.5 + 1.5) \times 119.9}{0.3 \times 50}$$

Thus, a preliminary circulation rate of 100 USGPM is selected. It is worth noting that the 0.3 mol loading was selected due to the relatively low 415 psi operating pressure of the Forestburg contactor. At higher pressures a mole loading of 0.4 to 0.5 would be a more representative initial estimate.

Tray Residence Time

The next step is to determine the residence time in the contactor. Because multiple feed points or parallel feeds and drawoffs are often used for selective applications, it is necessary to calculate this value on a stage by stage basis for use in kinetic modeling. The exact tower and tray geometry is not known at the start of the design. The most straightforward procedure is to initially assume two seconds residence time on the trays which receive full amine flow. If multiple feed points are used, the residence time up the column can be calculated by the inverse ratio of the amine flow rates. Thus, no initial determination of the contactor diameter is required.

Designers who require a closer approximation of the residence time must estimate the contactor diameter by calculating the bubbling area and downcomer area [7, 8] as shown in Figure 2. The required active bubbling area on a tray is primarily dependent on gas flow and secondar-
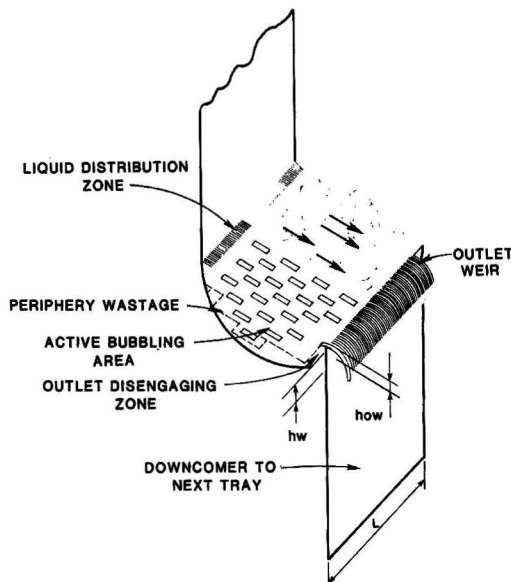

Figure 2. Typical contactor tray arrangement.

ily on liquid flow rate. The required bubbling area can be calculated by neglecting the liquid effect and using Souder's and Brown's correlation [7]:

$$U_{al} = \frac{K(\rho_L - \rho_G)\,0.5}{\rho_G^{0.5}}$$

where

K = 0.25 for valve trays, 0.20 for bubble cap trays

U_{al} = allowable velocity of gas through bubbling area, ft./sec.

ρ_L = density of the amine solution, lb./cu. ft.

ρ_G = density of the gas at tray conditions, lb./cu. ft.

The downcomer area can be calculated from the liquid flow rate assuming a downflow velocity of 0.25 ft./sec. The bubbling area plus two downcomers plus 15% for liquid distribution zone and wastage are used as the total tower cross sectional area. Using the data from Table 1.

$$U_{al} = 0.25 \left(\frac{64.4 - 1.41}{(1.41)^{0.5}} \right)^{0.5} = 1.67 \text{ ft./sec.}$$

Actual Volumetric Flow of Gas = 11 ft.³/sec.

$$\text{Bubbling Area} = \frac{11}{1.67} = 6.6 \text{ sq. ft.}$$

Area of Downcomer =

$$\frac{100 \text{ GPM}}{0.25 \text{ ft./sec} \times (7.48 \text{ gal/ft}^3 \times 60 \text{ sec/min})}$$

$$= 0.9 \text{ sq. ft.}$$

Total Required Tower Area =

$$(6.6 + .9 + .9)\,1.15 = 9.66 \text{ ft.}^2$$

This results in a tower I.D. of 42 inches

The next step in determining the residence time on an actual tray is to calculate the depth of liquid on the tray. The assumption that the weir length is 0.7 times the tower diameter is normally satisfactory for initial calculations. The height of liquid over the weir is calculated using the Francis straight weir relation [7].

$$h_{ow} = .48\,(\text{GPM/L})^{0.67}$$

where L = weir length in inches
For the design case;

$$h_{ow} = .48\,(100/(.7 \times 42))^{0.67} = 1.1 \text{ inches}$$

The standard weir height used by most tray manufacturers is 2.0 inches for a total from depth of 3.1 inches at the tray outlet. The hydraulic gradient across the tray can also be calculated. However, the error incurred by ignoring it at this point is relatively minor.

The so-called clear liquid residence time can now be calculated.

Clear Liquid Residence Time =

$$\frac{\text{Bubbling Area} * \text{Froth Depth}}{\text{Liquid Flow Rate}} * \text{Froth Gravity}$$

Design Case:

$$\text{CLRT} = \frac{6.6 \text{ ft.}^2 * (3.1/12) \text{ ft} * 0.3}{100 \text{ GPM}/(7.48 \times 60)} = 2.3 \text{ secs.}$$

The product of the froth depth and froth gravity, yields the depth of the clear liquid on the tray. These factors must be used since the fluid flowing across the bubbling area is froth of low density due to the contained gas bubbles. The 2.3 second valve is quite close to the 2.0 second residence time recommendation at the beginning of this section. If the designer had used the 2.0 second estimate, the contactor size could be generated by the computer program

TABLE 1. DESIGN & TEST DATA FOR SIGNALTA PLANT

| Gas Stream | Design | Test A 85/12/16 | | | Test B 86/02/27 | | | Test C 86/02/27 | | |
		Inlet	Acid G.	Outlet	Inlet	Acid G.	Outlet	Inlet	Acid G.	Outlet
CO₂ Mole %	3.00	2.99	66.59	2.05	3.08	74.72	1.95	3.02	70.68	2.13
H₂S Mole %	.50	.43**	29.33	2.8 ppm	.31	20.29	.6-1.5 ppm	.31	23.46	3.2-3.7 ppm
Flow Rate, MMSCFD	30.00	22.0	.32*	20.8	14.09	.21	12.98	14.16	.19	13.22
Fuel Gas, MMSCFD		By Difference		.88	By Difference		.90	By Difference		.75
Contractor:										
Gas In Temp, °F	70	59			60			60		
Gas Out Temp, °F	125	85			86			86.5		
L. Amine In Temp.	110	74			79			77.		
R. Amine Out Temp.	106	80			77			83		
Gas In Press, PSIA	428	432			393			393		
Avg. Gas #/ft³	1.41	—			—			—		
Amine Rate, GPM	100	72			70			70		
% to Tray 1	100	36			39			11		
% to Tray 7	—	64			61			24		
% to Tray 13	—	0			0			65		
Reboiler:										
Steam, lb/gal	1.2	1.5			1.55			1.55		
Press, PSIA	27.7	22			23			23		
Amine Wt. %	50	36.2			32.4			32.25		
Stripper:										
Feed Temp, °F	220	204			205			204		
O/H Cond. Temp.	120	88			87			93		
Residence Time:										
Seconds										
Tray 1-6	2.3	6.7			6.5			20.3		
Tray 7-12	2.3	2.9			2.9			7.1		
Tray 13-20	2.3	2.9			2.9			2.9		

* Calculated by CO₂ Balance
** Calculated from Acid Gas Composition

and the Francis weir equation [7] used to refine the residence time calculations.

Equilibrium Stages

The number of actual trays per theoretical stage is always a point of discussion amongst equipment designers. The situation is made more complex when entering the realm of nonequilibrium contact, where one of the components is achieving only a certain percentage of equilibrium. A significant amount of research work has been done and there is more to be done in this area. Rather than belabor the topic with a discussion of point efficiencies, Murphree tray efficiencies and so on, a value of three actual trays per theoretical stage gives realistic comparisons between calculated and actual results. A test of this simplification is the prediction of temperature profiles for absorbers. Prior information published by Daviet, et al. [3] shows reasonable correlation between calculated and actual temperature profiles using the three actual trays per stage approach.

Contactor Feed Points

The primary method of adjusting the MDEA system performance with regard to H_2S removal and CO_2 slippage is the location and quantity of amine delivered to different feed points on the contactor. In general, if the amine is totally supplied to only the bottom few trays, the CO_2 slippage will be quite high, possibly over 80%. Unfortunately, this may also result in inadequate contact to achieve H_2S specification. The H_2S requirement can be achieved by flowing a lesser amount of amine into a higher feed point in the tower. Some care must be taken with regard to feed temperature and CO_2 absorption heat of reaction. It is possible to create a temperature profile that will not improve the absorption of H_2S due to the elevated temperature and CO_2 content of the amine. Fortunately, this type of problem becomes apparent when the calculations are rigorously performed by computer. A reasonable level of adjustability is provided by using three feed points. Sour gas entering the Forestburg Plant contacts all the amine on the bottom eight trays followed by a lower amine rate for the next six trays and a final section of six trays at the top of the contactor. Thus the amine feed points are on trays 1, 7 and 13 by process numbering convention. Different feed points could be selected based on the three actual trays per theoretical stage rule and calculations showing a process benefit for the change. Some applications will show that 20 trays are not required, however it is very difficult to convince an experienced amine plant purchaser of this, probably with past bitter experience as justification.

Stripping Rates

Amine plants have been designed for many years using a rule of thumb of one lb. of steam per gallon of amine circulated. The final requirements for stripping steam rate must be determind from the rigorous computer calculations. The stripping rate required is highly variable depending on CO_2/H_2S ratio and may be as low as .8 to meet a 1 grain/100 SCF H_2S specification and as high as 1.5 to meet 1/4 grain/100 SCF H_2S specification. In general, MDEA is easier to strip than other amines and an operating rate of less than one lb. steam/gallon will meet 1/4 grain requirements. The design of the stripper and reboiler is conventional with respect to other amine system designs. In the stripper, the trays have been found to be more efficient and two actual trays per theoretical stage should be used. Packed towers are often used in stripping applications and an HETP of three feet is a conservative value.

Design Optimization

The previous sections have outlined some basic assumptions and methods of calculating first trials for the various design parameters. The design is then finalized by providing the data to the computer program for rigorous calculation. When the initial simulation results are obtained they can be inspected and some of the parameters modified accordingly. For example, the stripping rate can be reduced if H_2S content of the outlet gas is significantly below 1/4 grain per 100 SCF. The circulation rate can be reduced to improve the CO_2 slippage. Residence times on the trays can be changed within the limits of contactor diameter by a factor of about -50 to $+100$ percent by selecting alternate weir heights. Changing the quantity of amine supplied to different feed points will show changes in CO_2 slippage and H_2S sweetness. More H_2S and CO_2 are removed from the gas stream by increasing amine flow rates to more contact stages. It should be noticed that it is necessary to revise the contact times for each new amine flowrate tested. This process of making slight alterations to the calculations is a valuable exercise for the designer to perform so that critical limitations in the final design can be avoided. Selection of a process design which has some flexibility will simplify the selection of the mechanical equipment.

MECHANICAL EQUIPMENT

The selection of heat exchange and mechanical equipment is often specific to a given plant process design however some discussion of the equipment used at the Forestburg Plant is of some interest.

Lean Rich Exchanger

A plate/plate exchanger was used as the lean/rich amine exchanger. This type of exchanger offers large surface areas and high transfer rates in a small volume. The designer should be careful to allow for acid gas breakout on the rich amine side of the exchanger. This factor is important for both pressure drop and heat exchange considerations. The pressure drop through the lean side should be kept below two psi to prevent pumping problems associated with reducing the lean amine below its vapor pressure at the exchanger inlet nozzle. On the other hand it is advisable to keep velocities high enough that the exchanger does not collect dirt. A single pass configuration on both sides of this exchanger is advisable. The plates should be 316 SS, EPDM gaskets are recommended. A few years ago, gasket leaks were the plague of plate/plate exchangers. In general, this situation has been corrected. It is still necessary to have a spare set of gaskets readily available.

Booster Pumps

The common practice of placing the booster pumps downstream of the lean/rich exchanger was not followed in the Forestburg design. Sufficient NPSH was available to allow these pumps to operate properly with the hot lean amine directly from the reboiler. This was done in an attempt to overcome the problem mentioned in the previous paragraph. It also allowed the use of higher pressure drop in the plate exchanger and subsequent reduction in size of that unit. The use of high temperature seals and seal cooling were required, however. Although there have been no problems with the selected arrangement, the more common practice is probably less expensive and less prone to design oversights which might cause pump cavitation. It is interesting to note that some amine plants have no booster pumps on the basis that sufficient NPSH is available for the charge pumps without using a booster. Very often these designs ultimately have cavitation problems. The reason for this is the presence of hydrocarbons

in the amine which can reduce the NPSH available to half of what would be expected from the amine solution vapor pressure calculations.

Filtration

A full flow amine filter was incorporated into the Forestburg Amine Plant. A 5% flow charcoal filter was also installed in the amine stream. Directly ahead of the amine contactor in the gas stream a large filter separator removes any particulate or liquid mists that might be present after inlet separation. Even with all of the above filters and a double system wash before start-up, the Forestburg Plant encountered foaming problems for the first several weeks after start-up. As this problem has almost entirely disappeared without any mechanical modification, it is presumed that well completion fluids or oil entrainment were the culprits. An asphaltene dispersant of unknown chemical composition injected at some of the wellheads seems to have helped eliminate this problem as well. The use of antifoam agents in the plant has been reduced to nil.

Air Coolers

The overhead condenser and the lean amine cooler were mounted in a common unit. Air recirculation and two speed fan motors were also used to prevent freezing problems at low ambient conditions. This is also the reason that a 50% MDEA solution was used in the original design.

Charge Pumps

The highest maintenance items on the amine plant are generally the charge pumps. The Forestburg Plant operating pressure was sufficiently low that high speed centrifugal pumps could be economically used to pump the amine solution up to contactor pressure. This type of pump is highly recommended from a maintenance viewpoint. Most of the inherent problems with the more commonly used plunger pumps in amine service are a result of the packing glands filtering iron sulfides out of the amine solution. Build-up of these particles results in abrasion of the plungers and frequent replacement. The drawback of the centrifugal pump is its relatively low pumping efficiency which increases the horsepower consumption by a factor of approximately two. At high operating pressures the plunger pumps are still the best choice due to the high comparative cost of multistage centrifugal pumps. The acceleration head requirements and possible use of pulsation dampening should not be overlooked when using plunger pumps.

DISCUSSION OF PLANT TEST

The design considerations and methods previously discussed were used to design an MDEA facility for the Signalta Forestburg Plant. The design information as determined by final computer simulation is shown in the first column of Table 1. The process flow diagram for the amine process is shown in Figure 3.

Inlet, residue and acid gas samples were analyzed by gas chromatograph. During test A, discrepancies were found between the inlet H_2S measurements and the acid gas flow rates. Investigation into this problem uncovered acid gas metering errors and variance between chromatograph and Tutweiler H_2S measurements. Therefore, it was necessary to calculate the acid gas rate based on the CO_2 concentration (a relatively large number) and then back calculate the inlet H_2S from the acid gas flow rate. This corresponded with Gastec sample tube readings taken during the test. For the subsequent B and C tests, H_2S readings were taken by gas chromatograph, Tutweiler ap-
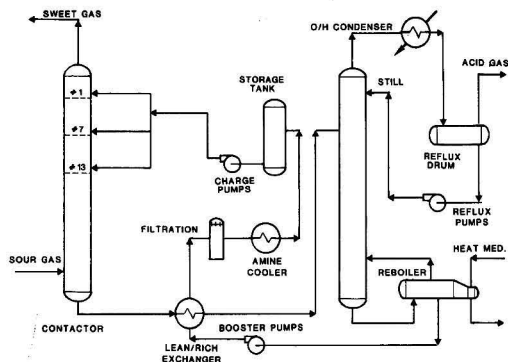

Figure 3. Process flow diagram for Forestburg Sweetening Plant.

paratus and Gastec indicator tubes. Due to variations in the different methods, the low and high readings were discarded and the remaining readings were averaged to show the results in Table 1.

As with most operating facilities of this type, the final operating conditions are never quite the same as were estimated in the original design. As can be seen from the Test Data columns of Table 1, the plant operating pressures, temperatures and flow rates were quite different from the original design.

This type of disparity in the design and test conditions is probably the best test of the simulation program used to design the plant. Table 2 shows that the TSWEET program results conformed very closely to the test data when actual operating conditions are simulated. The primary effect for investigation was the influence of feed point and contact time on the CO_2 slippage and H_2S sweetness. Thus the tests were conducted using a high stripping rate to minimize the effects of changes in lean amine loadings. It is important to vary as few parameters as possible to obtain meaningful data. The simulation results proved to be very accurate within 5% for the CO_2 slippage and were conservative for the H_2S calculations. It is difficult to quantify the results concerning the H_2S content in the outlet gas as the H_2S monitor at the site sampled the residue gas every few seconds and variations of 1 ppm were not unusual between consecutive readings. We were pleased that the prediction was slightly conservative.

CONCLUSION

The use of basic design parameters outlined earlier in this paper allows the designer of an MDEA plant to ap-

TABLE 2. COMPARISON OF TEST DATA & SIMULATION RESULTS

	Test	Predicted by TSWEET
Test A		
CO_2 out	2.05%	2.14%
H_2S out	2.8 ppm	3.2 ppm
CO_2 mass balance	*	—
H_2S mass balance	*	—
Test B		
CO_2 out	1.95%	1.92%
H_2S out	.6-1.5 ppm	1.94 ppm
CO_2 mass balance	−1.5%	—
H_2S mass balance	−2.5%	—
Test C		
CO_2 out	2.13%	2.01%
H_2S out	3.2-3.7 ppm	4.5 ppm
CO_2 mass balance	+1.0%	—
H_2S mass balance	+1.5%	—

* Test A meter errors required CO_2 and H_2S be used to calculate acid gas flowrate.

proximate the required circulation rates and heat loads. Subsequent use of a computerized simulation model, which accounts for kinetic effects and performs rigorous equilibrium calculations enables a large degree of refinement in the final design. The capability of modifying several parameters allows the designer to identify potential limitations in the overall scheme and avoid deficiencies in the final plant equipment selection.

ACKNOWLEDGMENTS

LITERATURE CITED

1. Savage, D. W., and E. W. Funk, "Selective Absorption of H$_2$S and CO$_2$ into Aqueous Solutions of Methyldiethanolamine," paper presented at AIChE meeting, Houstin, Texas, April 5-9, 1981.

2. Danckwerts, P. V., "Gas Liquid Reactions," McGraw Hill, New York, 1970.

3. Daviet, G. R., R. Sundermann, S. T. Donnelly, J. A. Bullin, "Dome's North Caroline Plant Conversion to MDEA" Proceedings of Gas Processors Association Convention, New Orleans, LA, p. 69 (March, 1984).

4. Ammons, H. L., and D. M. Sitton, "Operation Data From a Commercial MDEA Gas Treater," paper presented at the Gas Conditioning Conference, Norman, Oklahoma, March 2-4, 1981.

5. Pennwalt Chemicals, "Methyldiethanolamine for Gas Sweetening," publication S-282.

6. Jou, F. Y., D. Lal, A. E. Mather, and F. D. Otto, "Solubility of Acid Gases in Methyldiethanolamine Solutions" paper presented at Canadian Gas Processors Association meeting, Calgary, March 12, 1981.

7. Perry & Chilton, "Chemical Engineers Handbook," Chapter 18, 5th Edition, McGraw Hill, New York (1973).

8. Smith, B. D., "Design of Equilibrium Stage Processes," McGraw Hill, New York, 1963.

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R&D Opportunities in the Use of Natural Gas As a Chemical Feedstock

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The results of a technical, economic and market assessment of the use of natural gas as a chemical feedstock.

MARKET OVERVIEW

The U.S. petrochemical industry, which includes SIC 28 (Chemicals and Allied Products) and SIC 29 (Petroleum and Coal Products), has historically accounted for about one-half of total industrial gas consumption, or about 3.0 to 3.2 quads per year. Natural gas consumed by the petrochemical industry is used either for fuel and power, or as process feed material for conversion to other intermediate or finished-product chemicals. Of the 3,125 billion cubic feet (bcf) (88 bcm, billion cubic meters) of natural gas sales to the petrochemical industry in 1980, fuel uses, excluding fuels for feedstock conversion, accounted for 63.4% (1,982 bcf; 56 bcm). The remaining 36.6% (1,143 bcf; 32 bcm) was used as a chemical feedstock and as fuel associated with the conversion of methane to commodity chemicals.

As shown in Figure 1, the largest volume chemicals produced in 1980 from methane feedstock included ammonia, hydrogen, methanol and carbon black. Production of these four chemicals accounted for about 98% of the 1,143 bcf (32 bcm) of gas use cited above. Production of other chemicals such as ethylene, acetylene, hydrogen cyanide and chlorinated methanes comprise the remaining 2% of gas use. In 1980, a peak production year for bulk chemicals from methane, nearly 60% of the feedstock and associated fuel was used for the production of ammonia. Methane for ammonia feedstock accounted for 267 bcf (10 bcm), while an additional 300 bcf (8.5 bcm) of natural gas was used as fuel in the methane-to-ammonia conversion

process. Hydrogen accounted for just over 300 bcf of methane consumption, 205 bcf (6 bcm) as feedstock and an estimated 100 bcf (3 bcm) as fuel. Methanol production consumed another 132 bcf (3.7 bcm) of natural gas, 77 bcf (2 bcm) as feedstock and 55 bcf (1.5 bcm) as fuels. Carbon black production consumed 22 bcf (0.6 bcm) of natural gas as feedstock and an additional 2 bcf (0.05 bcm) as fuel. Production of other chemicals made up the remainder, accounting for 15 bcf (0.4 bcm) of natural gas consumption for use as feedstock and conversion-related fuel.

MAJOR COMMODITY CHEMICALS

Ammonia

Ammonia is produced by catalytic reaction of nitrogen from air and hydrogen from natural gas. Consumption of ammonia in the United States is dominated by its application in nitrogenous fertilizers, which accounts for 80% of the end-use demand. Resins, fibers and plastics used primarily in the construction and automotive industries account for an additional 15% of ammonia demand, with the remaining 5% used in the production of explosives for mining and military applications.

As noted earlier, production of ammonia is the largest consumer of feedstock methane. U.S. ammonia production grew steadily from 13.8 million metric tons in 1973 to a peak of 17.8 million tons in 1980. Domestic production declined 25% between 1980 and 1983, falling to a 10-year low of 13.1 million metric tons. Industry estimates in 1985 of ammonia production for the remainder of the decade forecast a recovery to production levels of 14.5 to 15.0 million tons. Increased agricultural fertilizer use could boost ammonia demand, since lower grain inventories and an end of the government's payment-in-kind program may lead to the restoration of a sizable portion of the agricultural acreage previously held out of production.

Reduced demand for ammonia products coupled with rising natural gas prices has led to the permanent or temporary closing of nearly a quarter of the U.S. ammonia production capacity that was operating in 1976. Of the plants operating at the end of 1982, 61% (11.3 million metric tons per year) of capacity was located in major gas-producing states including Texas, Louisiana, Oklahoma, New Mexico and Alaska. By contrast, two-thirds of the 5.0 million metric tons per year of plant capacity closures since 1976 have occurred in states served primarily by interstate pipelines.

High U.S. gas prices (until the recent drop in crude oil prices), low-cost imported ammonia, and reduced domes-
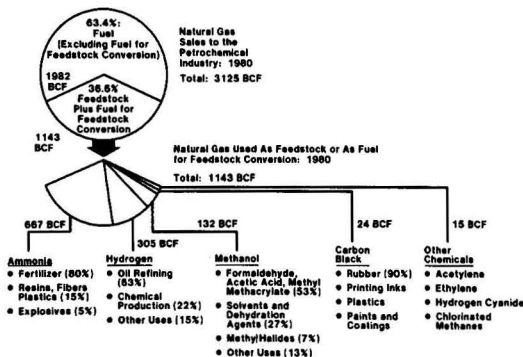

Figure 1. Natural gas use in the production of petrochemicals (Note: 1 bcf = 28.3 million cubic meters).

tic demand for nitrogen fertilizers are the major factors contributing to ammonia plant shutdowns as well as to the reduced profitability of those plants still operating. In mid-1982, the average price paid for natural gas by U.S. ammonia producers was $2.80 per thousand cubic feet (mcf), contributing to over 60% of the total production cost for a typical plant.

In 1982, the U.S. imported 2.2 million metric tons of ammonia primarily from the USSR, Mexico, Canada and Trinidad. In contrast to U.S. producers, Mexican ammonia producers pay an average of $0.44/mcf of gas, which contributes only $16.50/metric ton to ammonia production cost. Until recently, the U.S. exported about 1.0 million metric tons of ammonia annually. Exports have dropped sharply in the last few years and now amount to only about half the historic levels.

Historically, U.S. ammonia production has been somewhat cyclic as producers respond to agricultural fertilizer demands. The cyclic nature of this market will likely continue in the future, but it is doubtful that domestic ammonia production will ever exceed the peak production levels of 1980. World ammonia production, on the other hand, is projected to grow from just over 100 million metric tons per year in 1980 to 120-125 million by 1990. The long-term outlook for U.S. production will depend primarily on the worldwide demand for nitrogen fertilizers and the future of domestic natural gas prices.

Hydrogen

Excluding hydrogen already accounted for in ammonia and methanol synthesis, U.S. industry consumes approximately 1,120 bcf (32 bcm) of hydrogen annually. Although difficult to determine from available data sources, it is estimated that currently about 70-75% of this amount is the product of steam reforming of natural gas. Much of the remainder is produced by purification of hydrogen in by-product streams from various chemical conversion processes. In 1980 an estimated 820 bcf (23 bcm) of hydrogen was produced from natural gas, which accounted for the consumption of 205 bcf (6 bcm) of feedstock methane, second only to that of ammonia. On a Btu basis, steam reforming of natural gas requires equivalent amounts of feedstock and fuel. Fuel is used primarily for steam generation. The largest users of hydrogen from natural gas are refineries and large chemical producers, many of whom have waste steam and by-product fuels available to reduce their natural gas fuel requirement. Thus, it is estimated that only an additional 100 bcf (3 bcm) of natural gas is consumed as a reformer fuel.

Of the 820 bcf (23 bcm) of hydrogen produced from natural gas in 1980, about 520 bcf (15 bcm), or 63%, was consumed in oil refining processes. In the past, many refiners had excess by-product hydrogen, which was often burned to satisfy process heater fuel requirements. This situation is now changing, and as U.S. refiners move toward processing lower quality crudes, many are running into a hydrogen deficit. While refiners obtain vast quantities of hydrogen from the crude oil they process, many still find this insufficient to meet demand. The net balance, however, is a function of the type of crude being processed and the slate of products produced by the refiner. As such, the future demand for hydrogen in refining operations is extremely difficult to project because of the many variabilities in crude quality, product slate and geographic location.

While steam reforming of natural gas is now the preferred method of making supplemental hydrogen in refineries, partial oxidation of heavier feedstocks may offer operational advantages in some cases. Partial oxidation is a controlled combustion process that burns hydrocarbons in an oxygen-deficient atmosphere, converting the hydrocarbon to carbon monoxide and hydrogen. The technique requires the capital and operating costs of an air-separation plant to provide the oxygen. Although partial oxidation may not currently be economical on a widespread basis, it does offer the advantage of being able to handle a range of feedstocks including crude oil and residuum. Given the dynamic nature of refinery economics, the flexibility of partial oxidation may be beneficial at some locations.

The situation for large chemical facilities that use hydrogen produced from natural gas is similar to that of the refineries. In 1980, large chemical producers consumed 22% (180 bcf; 5 bcm) of the hydrogen manufactured from natural gas. Many of these firms also consumed as process feed or fuel additional amounts of hydrogen generated as a by-product in a variety of processes. By-product hydrogen is worth $2.00-$3.00/mcf, depending on its source. As a fuel it has only one-third the Btu value of natural gas and so is equivalent to natural gas priced at $6.00-$9.00/mcf.

The future of the hydrogen market, particularly that part of the market produced from steam reforming of natural gas, is highly uncertain. The complexities of the largest segments of the market — refineries and large chemical producers, which account for 85% of the hydrogen demand — make it difficult to project meaningful forecasts. The merchant hydrogen market is probably safe from the threat of advanced electrolysis, and many of the high-value-added industries that it serves are expected to continue to grow. Some of the natural gas reforming, which supplies most of this market segment, however, could be displaced by by-product hydrogen now used as fuel. But this loss could also be buffered if natural gas is substituted for the hydrogen fuel.

Methanol

Methanol is produced by a reaction of carbon monoxide and hydrogen made by steam-reforming natural gas or heavier hydrocarbons. As of early 1985, there were 13 methanol plants in the United States with a combined production capacity of nearly 1,955 million gallons (7.5 billion liters) per year. Natural gas is used as a feedstock in ten plants representing 1,595 million gallons (6 billion liters) per year of capacity. Two plants use oil or refinery by-product, while the remaining facility, operated by Tennessee Eastman, uses a coal-conversion process to produce methanol that is further processed onsite to acetic anhydride. The ten natural-gas-based facilities are located exclusively in Texas, Louisiana and Florida.

Except for 1981, when domestic methanol production peaked at 1.3 billion gallons (5 billion liters), annual production over the past decade varied between 0.85 and 1.1 billion gallons (3.2 and 4.2 billion liters). Production in four of the last five years has been 1.1 billion gallons (4.2 billion liters), which accounted for consumption of 77 bcf (2 bcm) of natural gas feedstock and 54 bcf (1.5 bcm) of natural gas fuel annually. Similar to the situation faced by the ammonia industry, foreign producers of methanol from inexpensive gas sources will become an increasing threat to domestic production. World capacity by 1990 is expected to reach 10-11 billion gallons (38-42 billion liters) per year, more than doubling the 1980 capacity of 4.6 billion gallons (17.5 billion liters).

The greatest demand for methanol is as a chemical intermediate for further processing into formaldehyde, acetic acid and methyl methacrylate, which together compose 53% of the methanol market. Formaldehyde, used in the production of adhesives for plywood and particle board, insulation, and plastics, represents the largest single share (37% in 1981) of methanol demand. Acetic acid is a rapidly growing market for methanol and currently accounts for about 12% of demand. The market demand for acetic acid includes applications in construction materials and paints as well as textile and paper coatings. Although demand for acetic acid has been relatively stable at 1.3 to 1.5 billion

pounds (590,000 to 681,000 metric tons) per year over the past decade, methanol's growing share of this market has resulted from development of a methanol carbonylation process that has proved to be more economical than the existing ethylene oxidation route. Production of methyl methacrylate accounts for an additional 4% of methanol use and ultimately finds market outlets as acrylic sheets and various surface coatings.

Industrial solvents and other uses, primarily dehydration agents, represent 27% of total methanol demand. Methyl halides, which represent 7% of the methanol market, are used in the manufacture of silicon rubber and various pesticides and herbicides.

The newest market outlet for methanol, and the only end use with a potential for high growth in the future, is the fuel-use market, which consumed about 150 million gallons of methanol in 1982. The high octane quality of methanol makes it an attractive blending component for gasoline. From 1980 to 1985, the use of methanol and methanol-derived cosolvents for gasoline blending increased significantly. The gasoline additive methyl tertiary butyl ether (MTBE), made by an acid-catalyzed reaction of methanol and isobutylene, has consumed significant quantities of methanol as its use grows as an octane booster for unleaded gasoline. More recently, a 1:1 blend of methanol and gasoline-grade tertiary butyl alcohol (GTBA) has been marketed by ARCO under the trade name Oxinol as an octane-enhancing gasoline additive. The decision by the Environmental Protection Agency to phase out leaded gasoline completely by the 1990's should increase this use of methanol.

Carbon Black

Carbon black is a very finely divided, essentially nonporous carbonaceous material, produced in a precisely controlled pyrolytic process. Carbon black ranges from fine particles such as those used in tire treads to the coarser particles used in the main body of tires.

Almost 90% of carbon black produced goes into reinforcing and compounding agents for rubber. Motor vehicle and aircraft tires account for roughly 60-65% of carbon black consumption in a given year. Carbon black increases strength, resilience and abrasion resistance of rubber, as well as adding color. The rubber compound in modern tires contains perhaps 30-40% carbon black. Carbon black is also used in printing inks, plastics, coatings and paints.

Carbon black is produced from both oil and natural gas feedstocks. Oil is by far the dominant feedstock, accounting for more than 90% of the 1.2 to 1.5 million metric tons per year of carbon black production. Natural gas feedstock makes up the remainder and in 1980 accounted for the consumption of 22 bcf (0.6 bcm) of natural gas feedstock and an additional 2 bcf (0.05 bcm) natural gas fuel. Sixteen of the 23 carbon black plants in the United States are located in Texas and Louisiana.

Carbon black is currently produced by two basic conversion processes, partial oxidation and cracking. Cracking is used by only one natural-gas-based plant in the United States with a capacity of 50 million pounds (22,700 metric tons) per year. Partial oxidation is used in all other oil- and gas-based facilities. During the 1960's and 1970's, partial oxidation of oil gained popularity because of better product quality and superior economic performance relative to partial oxidation of natural gas.

Carbon black production reached a peak in 1978, when 1.7 million metric tons were produced in the United States. By 1981, production had declined by roughly 18% and by 1982, production had declined more than 25% from the 1978 level. The decline in output of carbon black is due to reduced consumption in motor vehicle tires and mechanical rubber goods, a decline in exports, and inventory reductions on the part of carbon black producers and tire manufacturers. Although overall tire shipments increased slightly in 1982 relative to 1981, tire production declined by almost 10% as tire manufacturers reduced inventories built up in anticipation of a rubber workers' strike early in 1982. Exports of carbon black declined by 40% between 1981 and 1982 due to the worldwide recession.

The lower level of demand for carbon black in the face of general overcapacity resulted in a number of plant closings during the early 1980's. Nearly 500,000 tons of carbon black capacity have been permanently shut down since 1979 as producers sought to reduce costs. Operating rates in 1982 averaged roughly 70-75% of capacity. In addition to overcapacity and reduced demand, rising feedstock and energy costs affected profitability as actual selling prices were heavily discounted.

As a result of these factors, natural gas consumption as a feedstock in the production of carbon black will fall dramatically from its 1980 level of roughly 22 bcf (0.6 bcm) as reported by the Bureau of Census. Residual oil is clearly the preferred feedstock. Oil-based processes offer greater advantages in controlling product quality, which led carbon black producers to switch to oil over the past two decades even in the face of relatively low gas prices. This being the case, it is difficult to envision natural gas being used as a feedstock to produce carbon black in the declining and more competitive market of the future.

Other Chemicals

As noted earlier, ammonia, hydrogen, methanol and carbon black are the four major commodity chemicals produced from methane or natural gas. The following brief comments describe the market outlook for several other chemicals that are also produced from methane but in much lower quantities than the four cited above — ethylene, acetylene, hydrogen cyanide and chlorinated methanes.

Ethylene ranks first in importance as a raw material for the petrochemical industry. Ethylene derivatives — polyethylene, propylene, ethylene oxide, vinyl chloride, styrene, propylene and butadiene — are used in the production of fabricated plastics, antifreeze, fibers and solvents. Traditional commercial production involves the thermal and catalytic cracking of natural gas liquids (ethane, propane and butane) or other hydrocarbons ranging from naphtha to heavy gas oil. The availability of large quantities of low-cost ethane feedstock prompted the 1985 construction of new ethylene plants in Saudi Arabia and Canada. It is expected that these plants will export ethylene to countries that traditionally have been served by U.S. producers, aggravating the existing gap between U.S. ethylene production (projected to be 30 to 31.7 billion pounds — 13.6 to 14.4 million metric tons — in 1985) and nameplate capacity [about 36 billion pounds (16.3 million metric tons)] in 1985.

Other feedstocks for ethylene production are also being explored, including ethanol and — of greater interest to the gas industry — methane itself. The Benson Process (developed by Dr. Sidney Benson at the Hydrocarbon Research Institute at the University of Southern California in Los Angeles) involves the net reaction of two molecules of methane plus one of oxygen to yield one molecule of ethylene and two of water. KTI reportedly prepared in 1985 a conceptual design for a commercial system, said to be competitive with ethane cracking when the cost differential between methane and ethane is in the range of $1 to $2 per/mcf.

Worldwide demand for ethylene derivatives is expected to remain high through the early 1990's. For example, increased use of low- and high-density polyethylenes is anticipated in making products ranging from packaging and films to housewares. U.S. producers are expected to focus on upgrading existing facilities to boost energy efficiency

and feedstock flexibility and on exploring innovative ethylene production techniques such as the Benson Process.

Acetylene can be produced from a variety of hydrocarbons — including methane, ethane, propane, butane and ethylene — as well as from calcium carbide. Of the nine major U.S. acetylene production plants in operation in 1984, seven (representing about 76% of U.S. production capacity) used natural gas or ethylene feedstock; the other two used calcium carbide. Acetylene production in 1983 and 1984 totalled about 286 million pounds (130,000 metric tons) per year.

Acetylene production decreased between 1974 and 1983 at an annual rate of about 7% as producers of such high-volume acetylene derivatives as vinyl chloride, 1,4-butanediol, and vinyl acetate switched from acetylene-based to ethylene-based processes. Only a few specialty applications for acetylene offer growth potential. Ethylene-based vinyl chloride production is expected to rise in coming years, and predictions suggest acetylene production may grow at only about 0.5% per year through 1988.

Methane is a feedstock in each of the three major processes used to produce hydrogen cyanide. There were 14 hydrogen cyanide production plants in the U.S. in 1984, with a total nameplate capacity of 1.32 billion pounds (599,300 metric tons) per year; demand amounted to 976 million pounds (443,100 metric tons) in 1984 and was projected to increase to 1.19 billion pounds (540,300 metric tons) in 1988.

The major uses of hydrogen cyanide include the production of adiponitrile, methyl methacrylate, cyanuric chloride, chelating agents and sodium cyanide. Hydrogen cyanide can also be used as a gaseous disinfectant, and cyanides are widely used in ore processing and metal treating. Substantial global overcapacity for acrylonitrile production has led to depressed prices for hydrogen cyanide, and the cyclical nature of most uses has affected demand. Demand is expected to rise 5% per year through 1988, due largely to the projected strength of the auto industry (which uses methyl-methacrylate-based surface coating resins) and to substantial exports of cyanuric chloride to the Far East.

Chlorinated methanes comprise a family of four chemicals: methyl chloride, methylene chloride, chloroform and carbon tetrachloride. Through the process of oxychlorination, methane can be reacted with hydrogen chloride and oxygen to yield the four chlorinated methanes. The proportions of each of the four can be varied somewhat, but a typical yield would be 24 units of methyl chloride, 12 of methylene chloride, four of chloroform and one of carbon tetrachloride. The only effluents from the process are nonpolluting nitrogen, carbon dioxide and water.

Methyl chloride is used primarily in the production of silicones; methylene chloride is used to make aerosols, paint removers and degreasers; chloroform and carbon tetrachloride are chiefly used to produce fluorocarbons (in turn used in refrigerants and fluoropolymers). Production of chloromethanes peaked in 1981, slackened in 1982-83, then recovered substantially in 1984-85. Moderate growth in production of methyl chloride and chloroform is projected into the late 1980s; growth for methylene chloride and carbon tetrachloride is expected to be somewhat slower, due primarily to overcapacity of U.S. production facilities.

SUMMARY—MAJOR COMMODITY CHEMICALS

The early 1980s saw a dramatic decline in interstate natural gas sales for feedstock (and associated fuel) purposes. Most of the impact felt by interstate pipelines was a result of the shutdown of a quarter of the U.S. ammonia industry as demand fell and gas prices rose to uneconomic levels.

At best, the market outlook for major bulk commodity chemicals — ammonia, hydrogen, methanol and carbon

black — produced from feedstock methane is uncertain. In the near term, possible increases in methanol and hydrogen production, which represented just over 35% of 1980 feedstock and associated fuel uses, may tend to offset anticipated further declines in ammonia and carbon black production, which make up most of the remaining use of methane feedstock.
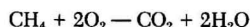
Beyond the near term, even with the potential for a large growth in methanol demand as a fuel additive, domestic production of ammonia, methanol and carbon black is significantly threatened by foreign producers who have access to natural gas at prices one-tenth those of new contract U.S. natural gas prices. International market and gas cost factors so dramatically influence the future outlook of U.S. bulk chemicals produced from methane that incremental improvements to existing processes offer little optimism for changing the near-term outlook.

Because of transportation costs, hydrogen is the only bulk chemical produced from methane that is not threatened by foreign competition. However, the future of the majority of hydrogen production from natural gas depends heavily upon intricate supply, demand and process balances inherent in the U.S. refining and chemicals industries.
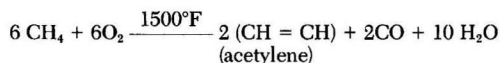
NEW ADVANCES IN METHANE CHEMISTRY

The fundamental problem in converting methane (and most paraffinic hydrocarbons) into other commercial products is the chemical stability of the methane molecule. The bonds in methane are among the most unreactive in hydrocarbons, with its tetrahedral geometric and electronic structure making it difficult to react with other molecules. Reactions that methane does undergo are usually irreversible and difficult to control. Typically, it reacts only with highly active substances, or under very vigorous conditions. Examples of such reactions include:
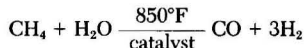
Combustion or complete oxidation—

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

Controlled oxidation—

$$6\ CH_4 + 6O_2 \xrightarrow{\quad 1500°F \quad} 2\ (CH = CH) + 2CO + 10\ H_2O$$
$$\text{(acetylene)}$$

Hydrolysis or steam reforming—

$$CH_4 + H_2O \xrightarrow[\text{catalyst}]{850°F} CO + 3H_2$$

Halogenation—

$$CH_4 + X_2 \longrightarrow CH_3X + HX;\ \text{where } X = F, Cl, Br$$

After many years of neglect, there has been a recent worldwide interest in C_1 chemistry — reactions of methane, carbon oxides and other single-carbon compounds. For example, the Japanese government and industry is supporting a multimillion dollar R&D effort in this field. Various petrochemical companies in the United States are also looking for new and dependable feedstocks.

Other new processes have been proposed to make useful commercial products from methane without reforming to carbon monoxide and hydrogen. The Benson Process (described earlier), for example, involves the chlorination of methane to chloromethane, followed by decomposition of the chloromethane to ethylene and acetylene.

Controlled activation of carbon-hydrogen bonds is an important area of growing interest in catalytic research. The goal of this research has been to activate paraffinic carbon-hydrogen bonds selectively by catalytic means and to substitute or insert another molecule into the paraffin.

Researchers hope that such selective modification may provide routes to further hydrocarbon conversions that avoid the high energy requirement of oxidation while also providing greater selectivity and control of conversion. Thus far there has been very limited success with carbon-hydrogen bond activation. Researchers at DuPont have used lutetium complexes to exchange hydrogen atoms on the methane molecule. Other researchers have successfully added an iridium complex to various normal, cyclic, and isoparaffins. Although none of the reactions thus far achieved have any industrial application for petrochemicals, they are significant in a basic research context and may help focus further research in catalytic hydrocarbon reactions.

Biotechnology is another important area of long-term research. Recent demonstrations that specialized organisms can be "bred" to perform a myriad of tasks have propelled the science of biotechnology to the forefront. Further development of this technology is likely to have significant impacts on the energy industry. Although no bioconversion process currently exists based on methane, biotechnology has practical applications in the pharmaceutical and agricultural industries. Enzymes have also been developed that aid in the clean-up of oil spills. Bioconversion processes for methane could, in the long term, replace the more energy-intensive, thermally driven chemical conversion processes currently used.

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Integrating Microcomputers into Engineering/Technology Curricula

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*The importance of increasing microcomputer usage in
engineering/technology curricula and several potential problems
that pose significant challenges to faculty.*

MICROCOMPUTER USAGE IN ENGINEERING

The computational nature of engineering activities has always created a need for increasing computing power and resources. This is especially true for engineering design which calls for routine experimentation, iteration and innovation. Previously, this computing power was available only on the mainframe and mini computers. But these types of computing resources are not easily affordable; especially by small and medium sized engineering companies. Even in large companies, these resources are not easily accessible to everyone who needs it. In the past, this lack of access to computing power, has lead to delays in completion of engineering projects and to lower levels of productivity. Of course, the end result of all this has been reduced profit margins and increasing threats from stiff foreign competition.

This situation is changing because of the rapid advancements in chip technology. Now, microcomputers and their associated peripherals and software are providing affordable, dependable and easy access of computing resources to professionals in the engineering world. Microcomputers are being used in increasing numbers in engineering activities primarily because of their low cost, personal nature and expanding capabilities.

The same factors mentioned above have also spawned an enormous growth in the number of companies in the business of writing and producing engineering software for microcomputers. This growth has resulted in a healthy competition which has resulted in relatively low cost software packages that are sometimes amazing in quality and capability. Universities are also beginning to do a significant amount of research in the generation of engineering software for microcomputers. In many companies, projects have been undertaken for converting many software packages that run on the mainframes and minis to enable them to work on the microcomputers.

The predictions for the future call for a continued decrease in the costs accompanied by an increase in the capabilities of microcomputers. Industry experts predict an annual growth rate of 25-30% in the use of computers in the engineering profession. It is reasonable to expect a large portion of this growth to occur because of microcomputers. Thus, the potential clearly exists for continued phenomenal growth in the use of microcomputers by the engineering industry and profession.

IMPORTANCE OF MICROCOMPUTER USAGE

In light of the factors mentioned above, there are several clear and compelling reasons for engineering and technology programs to plan for increasing usage of microcomputers in their curricula. Engineering educators should be aware of these reasons and increase microcomputer usage in their curricula; otherwise, the universities will be producing graduates with inadequate skills who will not fit into the rapidly changing work environment. It is quite clear that the future engineers should not only know the fundamentals of engineering design and calculations but also should know how to perform these activities using application software packages at engineering workstations, which will probably be microcomputer-based. A basic objective of a good educational program, especially at the undergraduate level, is to keep pace with the industry and to produce graduates who will fulfill the practical needs of the industry. Looking at the trends in the industry, it is quite clear that any engineering/technology education will be incomplete and unsatisfactory unless there are sufficient opportunities for students to use microcomputers and a variety of engineering software packages. In the future, the microcomputer may become as indispensable to the engineer as the calculator is today and the slide rule was in the past. Because of the versatile nature of the microcomputer, it is also important to note that they could be used for purposes other than calculation and design in the work-place. They could be used for inventory analysis, word processing, report generation, preparation of work orders, specifications, invoices, accounting and a variety of other tasks. Information flow in the engineering industry could very well be through a network of microcomputer based stations. Clearly this is the beginning of a revolution in the work environment of the engineering profession. Many engineering companies have already provided a microcomputer at every engineer's desk. Considering the benefits in terms of increased productivity, tremendous opportunities for innovation, and the pressures of foreign competition, this is a reasonable and desirable response. Undoubtedly, the universities have a major responsibility in training the future engineers for this changing work environment so that they can use a powerful tool like the microcomputer in an optimal and effective manner. Besides, there are additional reasons

for engineering/technology programs to increase microcomputer usage in their curricula. Agencies like the Accreditation Board for Engineering and Technology (ABET) are exerting pressures for increased computer usage in engineering and technology curricula and justifiably so. Organizations like CACHE (Computer Aids for Chemical Engineering Education) are also calling for an increase in computer usage in engineering curricula. Another strong argument in favor of increasing microcomputer usage in engineering/technology curricula is the extent to which they are being used today in the universities. Considering the current trends in the industry, their use is not at a satisfactory level. In many engineering and technology programs computer usage consists of taking only the required courses in FORTRAN programming and introduction to computers. Clearly, this will not be sufficient to meet the needs of the future. Students should be exposed to extensive use of engineering software that run on microcomputers. In addition, they should also be exposed to other uses of the microcomputer like information handling, simple accounting and word processing. The challenge for the universities is to start thinking ahead and plan for increasing microcomputer usage in engineering/technology curricula.

CHALLENGES FOR THE ENGINEERING/TECHNOLOGY FACULTY

The process of increasing microcomputer usage in engineering/technology curricula requires considerable thought and careful planning. This process poses some significant challenges to the faculty and administrators of engineering/technology programs.

Since this process is equipment intensive, it is totally different from modifying program content. Plans will have to be made to acquire the required resources, that is, the microcomputers and their associated peripherals and software packages. In many cases, a large number of microcomputer based workstations will have to be acquired to provide adequate terminal time to students. This cannot be accomplished over a short span of time considering the limited developmental budgets in many departments. Getting funds from the university developmental budgets could be a very difficult task during times of decreasing enrollments in some engineering/technology programs. Nevertheless, faculty and administrators in engineering/technology programs should take upon themselves the task of convincing the university officials the desperate need for acquiring such resources. They should present the argument that without these resources there is a real danger of the programs becoming obsolete and losing recognition or even accreditation. They should also point out that this could ultimately lead to the program becoming unattractive to prospective students and a further drop in enrollments. In many places, because of the lack of sufficient funds, microcomputers and the associated software and peripherals may have to be acquired in a phased and carefully planned manner. Another challenge for the engineering/technology faculty and administrators is to get the engineering companies involved in this endeavour to modernize the curricula. Another factor to be considered is the lack of expertise in some faculty in the use of microcomputers. This makes the task of selection of equipment and setting them up quite difficult. The faculty will have to train and educate themselves in this new area of technology. This is especially a difficult task considering the pace at which things change in this area. Faculty should be able to communicate in clear terms to the vendors their hardware and software needs. They should also be familiar with the technical jargon and the language of the vendors. This

can be a difficult task in an unfamiliar subject area. This process of gaining familiarity places additional burdens on a faculty member's time and resources.

Once the microcomputers are acquired and set up, their maintenance and day to day operation can require significant amount of resources in terms of lab personnel and funds to maintain the hardware and software. In cases where the number of workstations are limited, the optimal use of these resources require careful planning and the microcomputer labs will have to be kept open for extended periods of time. Faculty cannot be present to monitor the use of hardware and software at all times when the labs are open. Careful selection of student lab assistants who have familiarity with the use of the hardware and the applications software packages may provide some solutions to the problem. Hiring full-time lab assistants and lab technicians presents a serious problem where funds are limited. In any case, staffing of the microcomputer labs could pose significant problems.

Maintenance agreements for hardware and software have to be studied carefully. During the planning process, it is important that funds be identified and designated for the maintenance and staffing of such labs. If these expenditures are not planned and budgeted, it could lead to ineffective use of sophisticated and costly equipment. Of course, as far as maintenance, operation, and facilities are concerned, microcomputers offer significant advantages over mainframe and minicomputers.

Traditionally, the university computing centers take care of maintenance and operation of computer resources; especially if they are being used campus-wide. The microcomputer labs mentioned here do not have campus-wide user base; they cater to the needs of a specific academic discipline. Naturally, questions could arise regarding the location of these labs and the responsibility for their operation and maintenance. Should it rest with the department or with the university computing center? Pros and cons of this issue need to be studied carefully. If such facilities are located in the department and are further operated and maintained by the department, it provides much needed independence and flexibility to the faculty and students. But, this could tax departmental resources. Also, the expertise of the computing center personnel in operating and maintaining such facilities is something very valuable and should be sought after by the engineering/technology faculty. Perhaps a committee consisting of department faculty and computing center personnel should be responsible and should periodically review the maintenance and operation of such labs.

Advisory committees consisting of experts in the field of microcomputer usage for engineering activities could provide valuable input in the areas of equipment selection and set up, planning of facilities and planning for maintenance and operation. The composition and selection of such a committee requires some thought. Such a committee should consist of a group of dedicated individuals from engineering companies who are committed to the cause of increasing the use of state-of-the-art equipment and ideas in the teaching of engineering principles and practice. It could also include faculty from other campuses who have had significant experiences in similar kinds of activities. Such input is especially crucial in an area where some faculty themselves lack expertise and experience and have a lot to learn. Because of the evolutionary nature of this equipment and software and the lack of familiarity with it, many faculty initially may have a lot of resistance to overcome in learning to use them. Often, such learning experiences can be time consuming and frustrating for people who are not familiar with computers. But there is very little choice for the faculty other than to face these challenges and frustrations and gain expertise and experience in using microcomputers for engi-

neering applications. During the planning process, it is very important that a few workstations are dedicated exclusively for faculty use so as to provide an environment that is peaceful and conducive to learning.

CHANGES TO THE CURRICULUM

Considering the existing pressures of satisfying core requirements in humanities, mathematics, science and basic engineering, engineering/technology curricula hardly have enough room to accommodate additional required courses. This will only cut into the choice that the students have in selecting free and technical electives. Nevertheless, ways should be found to fit microcomputer based applications into engineering and technology curriculum. One can think of two distinct approaches.

One possible approach could be a steady infusion of microcomputer usage in all the relevant engineering/technology courses. Another approach might be to have courses like Material and Energy Balances, Fluid Mechanics, Mass Transfer, Thermodynamics, Heat Transfer and Reaction Engineering. They could also be required to use these packages during their senior design projects. Another idea might be to put together Computer Aided Instruction (CAI) packages or modules that will serve as tutorials to students in the solution of homework problems. This will enable the students to gain a great deal of familiarity and confidence in the use of the microcomputer. In any case, it is important that the exposure to the use of these software packages must come only after the fundamentals and basic principles are taught in the classroom as they are being done today and further only after the students have had sufficient practice and drill in the use of these fundamentals by solving a good number of classroom and homework problems. An idea worth trying would be to ask the students to solve the classroom and homework problems using the applications software packages and verify the results of the output from these packages. Thus, they experience the differences between the approaches. This way, while the student has the fundamentals firmly entrenched, he/she also realizes how the computer could be used as a powerful tool in the solution of the same problems. The student also gets a better understanding and feel for these applications software packages and does not view it merely as a "black-box." The students also begin to realize the potential these packages have in design experimentation and innovation. The infusion approach is naturally going to place some pressures on the time available for covering syllabi of existing courses. It is also going to place enormous responsibility on the instructors. However, the infusion approach should be viewed as a steady and gradual process which provides opportunities to use applications software packages in a phased manner during different stages of the curriculum.

The approach of having separate courses at the junior or senior level certainly provides exposure to applications software in a concentrated and dedicated manner but one of the disadvantages could be that the students may not be learning the fundamentals and basic principles during the same time frame. But there could be distinct advantages in trying to teach the use of applications software packages in a concerted effort by means of spe-

cialized courses. There is certainly more dedication and commitment on the part of the faculty teaching such courses. This could produce better results.

Whatever may be the approach, the opportunities are exciting and challenging for faculty desirous of introducing microcomputer usage at the undergraduate level. At the graduate level, several projects could be designed to solve problems being addressed in graduate research work. It is also quite important that the students are taught a programming language like FORTRAN or BASIC at the undergraduate level but certainly the emphasis in these courses should be in the writing and designing of programs that have useful engineering applications.

COMPUTER INTENSIVE EDUCATIONAL ENVIRONMENT

The Engineering Technology department at UH-Downtown offers undergraduate degree programs in Process and Piping Design, Structural Analysis and Design and Electrical/Electronics Design. Considering the applied nature of its degree programs, the department is committed to extensive computer usage in its courses. As a first step, the department worked towards the goal of establishing a Computer Aided Design and Drafting (CADD) laboratory. An Industrial Advisory Committee established for this purpose was very helpful in not only guiding and advising the faculty but also in fund raising efforts. About 35 different systems including PC-based systems, were examined during this search process. However, at that time CADD software for microcomputers had not advanced to a satisfactory degree. This factor coupled with the availability of a VAX 11/750 and an attractive educational discount from the vendor led to the selection of an Auto-Trol system which included four CC-80 CADD workstations and GS-5000 software. Courses in CADD have been offered since Fall 1983 and have been very popular creating a need for more workstations and additional sections. But since the selection and purchase of Auto-Trol equipment in 1983, things have changed dramatically in the area of CADD. Powerful and inexpensive software packages (like Auto-Cad) which can run on microcomputers have been developed. Therefore, as far as the future is concerned the department will enhance its CADD program by acquiring microcomputers for use in the introductory courses and use the Auto-Trol system for advanced courses. The department is further committed to the extensive use of engineering software in its courses. During Fall 1982, the department initiated a policy of requiring the students to successfully complete a computer assignment in each junior and senior level course. As part of the university's Computer Intensive Educational Environment (CIE) drive, the department acquired two DEC PRO-350 personal computers through two internal funding proposals submitted during 1983-84. The associated peripherals and several applications software packages like Design Graphix, TK! Solver and Mechanical Engineering TK! Solver were also acquired through these proposals. Faculty in the department have used the PROSE software for generating memos and storing tests and assignments. By using the system, they have gained familiarity and that crucial degree of comfort and confidence necessary for working with computers.

The Mechanical engineering TK! Solver package contains several applications software that could be used in Fluid Mechanics, Heat Transfer and Engineering Mechanics. Students have been exposed to the use of this software in the analysis of fluid flow through piping systems and conduction and convection heat transfer problems. They have used this to verify the solutions to the classroom and homework problem assignments. Thus,

they have looked at a different and faster way of solving the same problem after they have had exposure to the fundamentals and the theory behind the solution to the problem. This approach has enabled them to gain a better understanding of the applications software package and can modify their use to suit their needs, if necessary. Illustrations of output from this applications software package are shown in Table 1. In addition, students are required to write applications programs in many of the engineering and technology courses. The future plans are for the use of applications software packages in appropriate engineering and technology courses. As an example, students in the basic drafting course are given a demonstration of the CADD package. Students in the Piping design courses are exposed to the use of McAuto's Pipeline and AAA Technology's Triflex software. Extensive use of the TK! Solver package is also planned. Senior students could be expected to formulate applications software modules using the TK! Solver package. Funding proposals have been submitted for the acquisition of IBM PCs. IBM PCs were chosen because of the extensive availability of applications software in engineering for them. Many other microcomputer based engineering software

packages are also being considered. Hopefully, the students will be exposed to the use of applications packages at a satisfactory level in all of the three degree programs.

Thus, the plans for creating a Computer Intensive Educational Environment in the department call for extensive use and integration of microcomputers into the curricula. At this point of time, funding for the acquisition of the required hardware and software is a major problem but the department is currently addressing this issue. Also, the department is basically pursuing the infusion approach with the exception of the CADD courses. Specialized courses in other areas of microcomputer applications may evolve later.

CONCLUSIONS

The engineering industry and profession is increasing microcomputer usage at a very rapid rate. It is envisioned that in the future most of the engineering work will be routinely performed at computer-based engineering workstations. For the reasons of cost-effectiveness and personal nature, these workstations will in all probability be microcomputers. Hence it is imperative that the future

TABLE 1. ILLUSTRATIONS OF OUTPUT

St Input	Name	Output	Unit	Comment
				** CYLINDRICAL WALL HEAT TRANSFER **
1	L		ft	axial length of cylindrical body
1.034	r1		in	radius of inside cylindrical surface
30	h1		Btu/(ft²	convective coefficient (inside wall)
27	k1		Btu/(ft*h	conductive constant (1st layer)
1.187	r2		in	radius of intermediate interface
.023	k2		But/(ft*h	conductive constant (2nd layer)
1.687	r3		in	radius of outside surface
2	h2		Btu/(ft²	convective coefficient (outside wall)
0	epsi			radiation emissivity (outside wall)
	Q	81.675491	Btu/h	total heat transferred across wall
320	T0		°F	inside fluid temperature
	T1	314.97135	°F	inside wall temperature
	T2	314.90491	°F	intermediate interface temperature
	T3	116.23257	°F	outside wall temperature
70	T4		°F	outside environmental temperature
	Rh1	.06156864	°F*h/Btu	therm. convect. resistance (inside)
	Rk1	.00081343	°F*h/Btu	therm. conduct. resistance (1st layer)
	Rk2	2.4324597	°F*h/Btu	therm. conduct. resistance (2nd layer)
	Rh2	.56605196	°F*h/Btu	therm. convect. resistance (outside)
	Rr		°F*h/Btu	therm. radiation resistance (outside)
1.713E-9	sigma		Btu/(ft²	Stefan-Boltzmann constant

St Input	Name	Output	Unit	Comment
				** FLUID FLOW IN PIPES **
	valid	'accurate		model validity
	flow	'turbulen		flow type
150	L		m	length of pipe
.3	D		m	pipe inside diameter
.2	Q		m³/s	volume flow rate of fluid
	V	2.8294212	m/s	linear speed of fluid in pipe
	f	.01934305		friction factor of pipe
	Re	84882.636		Reynolds number of pipe flow
940	rho		kg/m³	fluid mass density
	w	9221.4027	N/m³	fluid weight density
	u	.00940000	kg/(m*s)	fluid viscosity
.00001	v		m²/s	kinematic viscosity
	dP	134248.49	N/m²	pressure drop across pipe of length L
1.5	C			sum of orifice coefficients for pipe
10	Z		m	vertical height of end #2 avove end #1
	power	26849.701	W	pump output power
.000046	epsilon		m	pipe roughness
	hf	4.5583613	m	head loss
	Area	.07068583	m²	cross-sectional area of pipe
9.81	g		m/s²	acceleration of gravity

engineers/technologists be familiar with the use of these workstations. This means that they must have had some exposure to the use of microcomputers and engineering applications software during their undergraduate education. Currently, students are not being exposed to the use of computers in solving engineering problems in general and in particular to the use of applications software packages at a satisfactorily level in universities. So, the engineering and technology curricula have to start integrating extensive use of microcomputers into their curricula. There are bound to be significant challenges associated with this process. These could be in the areas of funding, selection and acquisition of hardware and software, training of faculty, and operation and maintenance of such labs. Nevertheless a beginning has to be made and these challenges have to be faced; the time is very opportune now with the enormous amount of fairly powerful software being available for the microcomputers. Curricula and programs which do not make a start now, face the risk of becoming obsolete and falling way behind in this evolutionary and rapidly changing field. Faculty in engineering and technology departments should take a lot of initiative in this direction and think of innovative approaches to solve the problems they face in this area. At first, they might consider steady infusion of microcomputer usage into the curricula; perhaps even considering borrowing equipment for this purpose. Later they could plan on specialized courses involving applications of the microcomputer. In any case, the faculty should emphasize the use of the microcomputer only as a powerful tool in solving engineering problems. The best way to drive home this point is to expose the students to the use of applications software packages only after they have had enough background in the subject matter by the fundamentals being covered in the classroom and also by solving homework problems.

At the Engineering Technology department, UH-Downtown a modest beginning has been made in integrating microcomputer usage into the curriculum. There is still a long way to go and efforts are continuing in this direction. The ultimate goal is to have a good and smoothly operating Computer Intensive Educational Environment in the department that effectively educates the future engineers/technologists in the use of microcomputers as a powerful and versatile tool in engineering activities.

The engineering profession and industry will have to cooperate in a large measure for the universities to achieve their goals in this area. Efforts made by universities, industry, and professional societies in this direction could very well determine the future of the engineering industry and profession in the United States.

LITERATURE CITED

1. Nandagopal, N. S., "Computer Aided Engineering: Why and How should the Universities Get Involved?" South Central Regional ACM Conference (November, 1985).
2. Edgar, T. F., et al., "Use of Computers in Chemical Engineering Education", *Chemical Engineering Progress*, 81, No. 9 pp. 9-13 (1985).
3. Israni, H. and N. S. Nandagopal, "PC-Based CAD Systems *vs* Industrial Grade CAD Systems in University Education", Proceedings of the Technical Conference on CAD/CAM/CAE/Piping sponsored by the Society of Piping Engineers and Designers (SPED), (September, 1985).
4. Israni, H., and N. S. Nandagopal, "Implementation of an Undergraduate CAD Program", National Computer Graphics Association (NCGA) Conference Proceedings (April, 1985).
5. Sutton, I., "Converting Software for Microcomputers", *Chemical Engineering (USA)* (January, 1985).
6. Carnahan, B., and C. Jeager, "The MicroCACHE system for Computer Aided Instruction", AIChE Meeting, Anaheim, California, May, 1984.
7. Finlayson, B. A., "Impact of Computers on Undergraduate Education," *Chemical Engineering Progress*, 80, No. 2, 70-74 (1984).

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An Economic Assessment of Using Surfactants in Cleaning Coal By the Oil Agglomeration Method

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The oil agglomeration process has been used in various forms to affect a separation of coal and shale and to produce waterproof, easy to handle pellets. The process of separation may be terminated early, as in the Olifloc process, or may be continued to the pelletizing stage as in the case of the Shell Pelletizing Separator System. Regardless of which process is used, it would appear from the reported work [1, 2, 3, 4, 5] that in order for the obvious technical advantages of the process to be obtained it is necessary to reduce the operating costs in the form of reduced oil consumption. Recent work has indicated that this could be achieved by the use of surfactants [6]. Hence, the work evaluated in this paper is to be concerned with reduction of the excessive oil (up to 20% w/w) requirements by the use of surfactants.

INTRODUCTION

In any evaluation of a separation process, the quality of the product is of paramount importance. For coal this will vary with the application. If the product is feed stock to a coke works then the specification will be a material containing less than 8.0% ash (as received). Assuming a mean moisture content of 30.0% then the ash content increases to approximately 12.0% on an air dried basis, the basis upon which this work has been expressed. At the same time, power generation is concerned with a feed stock less than 18.0% ash overall on an air dried basis [6]. A product of inferior quality will attract financial penalties or possibly result in contract cancellations.

While the quality of the product determines the market, the yield from any particular process will determine the financial rewards. Hence in any appraisal both properties should be considered.

The assessment of this work is, therefore, made on the basis of combustible recovery and upon ash content.

MATERIAL AND EXPERIMENTAL PROCEDURE

A bulk sample was collected from a large coal rich tailings lagoon (containing 54% ash) at Blidworth Colliery, Nottinghamshire Area, United Kingdom. The major portion of it (60%) to be found in the minus 45 μm fraction used for the agglomeration tests. A binder of proven efficiency [7, 8] diesel oil, appears to have been employed universally and as a consequence this was selected as the standard binder. It was a light diesel oil of specific gravity 0.013 lbs/cu. ft. The emulsifying agents used in this work were Duomeen "T" and Oleic Acid. Duomeen "T" is a cationic bitumen emulsion where "T" refers to tallow. It is a diamine emulsifier, with the organic group R contacting the bitumen phase and the amine group NH_3^+ protruding into the water phase. Hence to a large extent it is very similar to diamine compounds which have their basic from and may be expressed as:

$$R- NH\ CH_2\ CH_2\ NH_2$$
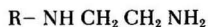
(R = hydrocarbon chain)

Following sample preparation, process variables have been investigated. These resulted in the establishment of the standard conditions for the oil agglomeration basic process which are listed in Table I.

These conditions do not specify the results. They will depend mainly upon the diesel oil dosage. The basic re-

TABLE 1. BASIC PROCESS CONDITIONS

Variable	Value	Variable	Value
Stirrer speed	6000 rpm	Conditioning Time	5 minutes
Sold concentration	20 (w/w)	Agglomeration Time	2 minutes
pH	7.2		

TABLE 2.

% diesel oil	3	5	7	9	11	13	15
% ash	18.8	18.8	15.3	15.3	14.80	13.20	15.50
% yield	48.2	50.0	49.2	51.0	51.70	51.30	53.50
% recovery	80.8	83.9	86.0	89.0	90.8	91.80	93.00

TABLE 3. RESULTS OF DIESEL OIL/OLEIC ACID

Oleic Acid Dosage lbs/ton	Diesel Oil (% wt.)	Yield (% wt.)	Efficiency Ash Content	Combustible Recovery (%)
0.28	5	45.4	10.9	83.5
0.54		46.2	12.0	84.0
0.82		49.0	13.0	88.0
1.08		48.0	13.6	85.6
0.28	7	48.0	10.6	88.5
0.54		49.0	11.0	89.8
0.82		50.7	13.0	91.0
1.08		48.4	9.4	90.6
0.28	9	48.2	9.4	90.0
0.54		49.3	8.7	93.0
0.82		51.1	10.7	94.7
1.08		49.0	9.1	91.7
0.28	11	48.0	7.7	91.0
0.54		50.0	8.0	94.4
0.82		52.0	8.0	98.7
1.08		50.2	8.7	94.6

TABLE 4. RESULTS OF DIESEL OIL/DUOMEEN "T"

Duomeen "T" Dosage lbs/ton	Diesel Oil (% wt.)	Yield (% wt.)	Efficiency Ash Content (% wt.)	Combustible Recovery (%)
5.2	3	46.7	13.5	83.3
10.6		46.2	11.5	84.6
16.0		47.1	10.9	86.6
26.0		46.2	7.3	88.4
37.2		47.1	8.2	89.2
48.0		47.6	8.3	90.0
5.2	5	49.0	12.5	88.3
10.6		47.0	9.6	88.7
16.0		47.6	7.8	90.5
26.0		48.2	8.5	91.0
37.2		47.3	6.7	91.0
48.0		49.0	8.1	92.7
5.2	7	49.0	8.2	92.6
10.6		49.3	8.2	93.4
16.0		50.0	9.0	93.8
26.0		49.3	7.5	94.1
37.2		50.2	7.6	95.7
48.0		50.0	7.3	95.6
5.2	9	49.7	8.0	94.5
10.6		49.7	7.6	95.0
16.0		50.0	7.5	95.4
26.0		50.0	7.2	95.7
37.2		50.2	7.0	96.2
48.0		51.0	7.0	97.0
5.2	11	50.2	8.5	95.0
10.6		50.2	8.2	95.0
16.0		51.1	8.0	97.0
26.0		51.1	7.7	97.3
37.2		51.1	7.2	98.0
48.0		50.7	6.3	98.0

sults relating to various oil dosages are given in Table 2 below.

The procedures and standard conditions established above were followed throughout. The total initial conditioning period was five minutes and the surfactants were added after three minutes and the mixture conditioned for a further two minutes. The object was to maintain the procedures adopted for the standard test work and to assure the emulsification of binder (diesel oil). The results for the surfactants are shown in Tables 3 and 4.

PRESENTATION OF THE RESULTS

Examination of Table 3 and 4 reveals two important factors. First, for the system using oleic acid, the major effects of the surfactant addition, i.e. ash reduction, occur at low dosage levels. Secondly, at these additions, the corresponding yield remain approximately constant. Combustible recovery gives a single measure of efficiency without reference to the financial consideration of yield. The yield for the Dumeen "T" addition remains almost constant throughout the range of dosage levels. Combustible recovery offers a single variable assessment of system.

The method of the assessment used is to superimpose the effects of the surfactant addition onto the combustible recovery/oil dosage graphs. The resulting curves are shown as Figures 1 and 2. Considering Figure 1 for Oleic Acid, the horizontal lines represent the recoveries at various diesel oil dosages with no surfactant. The diesel oil dosage is shown in the right hand margin. The corre-
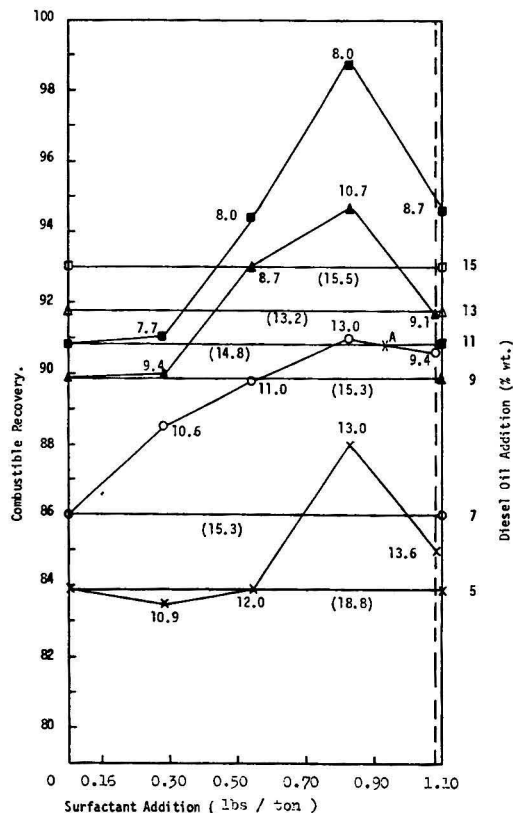

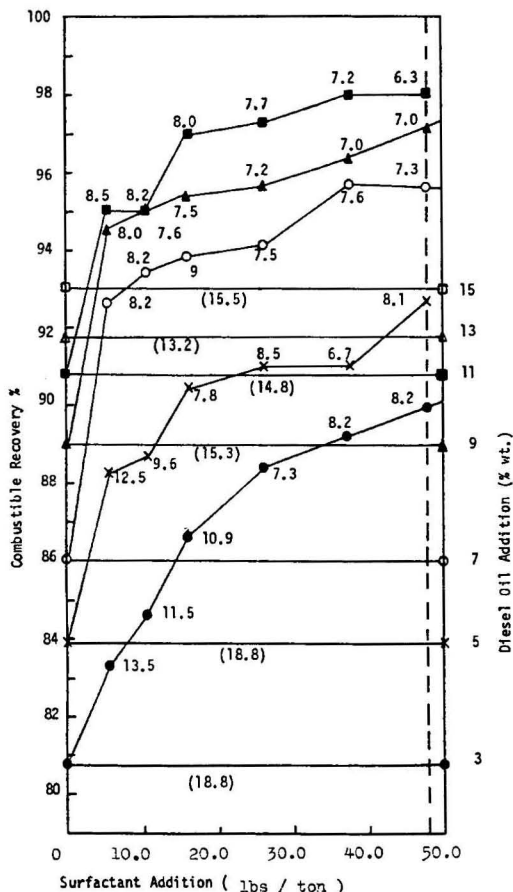Figure 1. Reduction of diesel oil with Oleic acid addition.

Figure 2. Reduction of diesel oil with Duomeen "T" addition.

The ash contents of the two systems at the point of the intersection will not, however, be the same. Thus considering point "A" in Figure 1, 90.8% recovery could be obtained either by 11.0% diesel oil, or by 7.0% diesel oil with 0.90 lbs/ton Oleic Acid. Assuming a constant yield over the ranges surfactant considered, approximate ash contents may be obtained by the interpolation, i.e. point "A" produces an ash content of around 10.8% compared with 14.8 for the straight 11.0% diesel oil addition. For clarity and ease of reference, extracted data from Figures 1 and 2 relating to the benefits of the surfactant use are shown in Table 5 and 6.

THE RELATIVE ADVANTAGE OF SURFACTANT USE
Oleic Acid

The possible savings to be obtained with oleic acid are shown in Table 5. Maximum diesel oil reduction of the order of 6.0 percentage points (40%) is indicated for the highest diesel oil dosage (15% w/w). With one exception all ash contents are the standard specification. Using an untaxed cost of $1.2 per gallon for diesel oil this gives an approximate cost of $3 per percentage point of addition [2]. Assuming a figure of $1165/ton for Oleic Acid, then for the 11.0% straight diesel oil system a saving in oil consumption of $12.00 treated (4 × $3) could be obtained by the addition of Oleic Acid to the value of $0.46 (0.78 lbs/ton). Again considerable benefits are to be obtained. Ash contents, with one exception, (13%) are well within the general specification.

Dumeen "T"

The improved efficiency curves for the bitumen emulsion are shown in Figure 2. The most significant difference between these curves and those for Oleic Acid (see Figure 1) is that a peak value of recovery is not obtained, the recovery curves continue to rise with increased Dumeen "T" addition. This is a reflection of constant yields, but generally decreasing ash content with increasing surfactant addition. The resulting projections relating to reduction in diesel oil dosage are therefore more pronounced with maximum savings of the order of 8.0 percentage points (61.50%) being indicated. For example, if one is considering a reduction of 6.0 percentage points (46%) then operating at 9.0% diesel oil allows this to be achieved at 4 lbs/ton of emulsion, on the other hand operating at 3% diesel oil requires 35 lbs/ton to achieve the same results (reduction).

It is estimated that the cost of Dumeen "T" emulsion would be comparable or less than diesel oil. Hence all cases, in spite of the relatively high consumption of the emulsion, it is apparent that significant cost reductions are to be obtained.

ponding ash contents of the produced agglomerates are printed directly below the horizontal line. For the 7% diesel oil dosage, a recovery of 86.0%, at an ash content of 15.3%, is obtained. The curves superimposed upon these horizontal lines are those relating to the surfactant additions and the figures adjacent to the experimental points are the ash content from that particular test. Again referring to the 7% diesel oil addition, a recovery of 90.8 at an ash content of 10.8% will be obtained for 0.92 lbs/ton Oleic Acid addition. Consequently wherever a curve intersects a horizontal line the combustible recovery at that point may be obtained by either straight forward diesel oil addition or by reduced diesel oil with a surfactant.

TABLE 5. OIL REDUCTION OBTAINABLE WITH OLEIC ACID

| | Standard System | | | | Alternative System(s) | |
Diesel Oil % wt.	Recovery % wt.	Ash % wt.	Diesel Oil % wt.	Surfactant lbs/ton	Ash % wt.	Diesel Oil Reduction %
15.0	93.0	15.5	11.0	0.46	8.9	4.0
			9.0	0.54	8.7	6.0
13.0	91.8	13.2	11.0	0.34	7.8	2.0
			9.0	0.44	8.9	4.0
11.0	90.8	14.8	9.0	0.34	9.1	2.0
			7.0	0.78	12.9	4.0
9.0	89.0	15.3	7.0	0.56	11.1	2.0
7.0	86.0	15.3	5.0	0.68	12.5	2.0

Standard System			Alternative System(s)			
Diesel Oil % wt.	Recovery % wt.	Ash % wt.	Diesel Oil % wt.	Surfactant Dosage lbs/ton	Ash % wt.	Diesel Oil Reduction %
15.0	93.0	15.5	11.0	3.0	11.6	4.0
			9.0	4.0	10.4	6.0
			7.0	8.0	8.2	8.0
13.0	91.8	13.2	11.0	1.5	13.2	2.0
			9.0	3.0	11.6	4.0
			7.0	4.8	9.3	6.0
			5.0	42.0	7.4	8.0
11.0	98.8	14.8	9.0	2.0	12.9	2.0
			7.0	4.0	10.0	4.0
			5.0	22.0	8.2	6.0
9.0	89.0	15.3	7.0	2.6	12.0	2.0
			5.0	12.0	9.2	4.0
			3.0	35.0	8.0	6.0
7.0	86.0	15.3	5.0	2.6	14.0	2.0
			3.0	14.0	11.1	4.0

SUMMARY

On the basis of combustible recovery, it has been shown that the levels of diesel oil (9 – 15% w/w) required for the basic process developed within this work, can be reduced by the addition of surfactants. Ash levels are also generally improved. The system is, however, very sensitive to overdosing and strict monitoring of these additions must be maintained.

LITERATURE CITED

1. Bogenschneider, B and W. Erdmann, Industrial-Scale Exam. of Olifloc Process at Ruhrkhole A. G., *Aufbereitung-TechniK.*, **22**, No. 4, pp 188-198 (1981).
2. Brookes, G. F. et al., The Selective Flocculation of Coal/Shale Mixture Using Commercial and Modified Polyacrylamide Polymers. XIV Int. Proc. Congress, Toronto, Canada, Paper VIII- 7, (1982).
3. Verschuur, E and G. R. Davis, The Shell Pelletizing Separator. Key to a Novel Process for Dewatering and Deashing Slurries of Coal Fines, Symposium on Pellets and Granules, Australian Inst. Min. Met., Newcastle N. S. W. Paper 41 (1976).
4. Bensley, C. N. et al., The Effect of Emulsification on the Selective Agglomeration of Fine Coal. *Int. Journal of Min. Processing*, 4, 1977, pp. 173-184 (1977).
5. Capes, C. E. et al, Application of Spherical Agglomeration to Coal Preparation. Proceedings of Symposium on Pellets and Granules, Newcastle, N. S. W. Australian Inst. Min. Metall., Paper 49 (1976).
6. Abdelrahman, A. A., Spherical Agglomeration of Coal by Diesel Oil, Ph.D. Thesis, University of Nottingham, Nottingham, U. K., (1983).
7. Leininger, G. et al., Application of Olifloc Process for a Selective Agglomeration of Ultra Fine Hard Coal Slurries. Germ. *Chem. Eng.*, **5**, pp. 53-58 (1982).
8. Capes, C. E., Agglomeration in Coal Preparation, ed. Leonard, J. W. et al., The AIMMPE, Baltimore, Maryland, U.S.A. Port City Press Inc., pp. 10-105/10-116 (1979).

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Characteristics of a New Methanol Synthesis Reactor

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A new type of synthesis reactor which has the rate of the one-pass reaction increased. The required power of the unreacted gas recycle is reduced from an energy saving point of view as well as larger-scale production, which is excellent in the recovery of both sensible heat of reacted gas and heat of reaction.

INTRODUCTION

Methanol was mainly used as chemical feedstock until around ten years ago, since then, it has gradually widened its fuel use as an alternative energy in consequence of the repeated oil crises. Along with this trend, development activities for the improvement of methanol plants are being carried out, aiming at energy saving and larger-scale production. In methanol plants, one of the most important key techniques is a catalyst of high-activity, high-selectivity type. Another is a synthesis reactor which can allow such catalyst to bring its performance into full play. As previously reported [2], a catalyst showing high activity at low temperature and low pressure has been developed. A more accurate equation of the reaction rate has been defined by reviewing the reaction mechanisms so far proposed.

In this article, the authors propose a new type of synthesis reactor, which has the rate of the one-pass reaction increased, hence the required power of the unreacted gas recycle reduced from an energy saving point of view as well as larger-scale production, which is excellent in the recovery of both sensible heat of reacted gas and heat of reaction. It has an advantage also in terms of manufacturing, operation, inspection and maintenance.

The concept and features of the new reactor are first described in comparison with conventional types of reactors. Then, the flow, heat transfer and reaction characteristics of the new reactor determined by one-dimensional and two-dimensional analysis are presented. Finally, the results of real gas tests in a pilot plant having a methanol production capacity of 10 tons/day are reported. The results of the pilot plant tests with real gas confirm the characteristics as expected through the analysis.

BASIC CONCEPT OF NEW REACTOR

The Methanol synthesis from the synthetic gas takes place in the presence of a catalyst at a temperature from 200 to 300°C and under a pressure from 50 to 150 atm. The reaction releases a relatively large quantity of reaction heat. In view of these facts, a reactor for methanol synthesis must meet the conditions given in Table 1. In

TABLE 1. CONDITIONS OF A METHANOL SYNTHESIS REACTOR

Category	Item		Description
Performance	Flow	1.	Uniform distribution of gas in catalyst bed
	Heat transfer	2.	Low pressure drop
	Reaction	3.	High conversion
	Controllability	4.	No occurrence of hot spot
	Durability	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
Construction	Internal construction	1.	Simple and compact
	Tightness	2.	No leakage between gas/coolant/outside
	Thermal expansion	3.	High space factor
	Support	4.	Absorption of thermal expansion
		5	Stable support of catalyst bed, boiler, etc.
Material	Strength	1.	Combination of materials with little differential thermal expansion
	Corrosion resistance	2.	Resistance to carbonyl, and Resistance to hydrogen embrittlement
	Catalytic activity	3.	Prevention of impurities formation
Maintenance	Inspection	1.	Easy charging and discharging of catalyst
	Repair	2.	Inspection and repair possible

terms of performance in particular, the reactor must present a good controllability of the catalyst bed temperature. In terms of thermo-stability, 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 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 Figure 1. Type V in Figure 1 is the new, double-tube type reactor discussed in this paper. The characteristic features of each type are outlined below:

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. As a result, the reactant gas temperature rises while the gas is flowing 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 temperature at the inlet, but also the concentration of methanol is lowered.

Type II

In this reactor, the reaction proceeds adiabatically in each catalyst bed, like in Type I. However, the inlet temperature of each bed is controlled by the steam pressure of waste heat boilers independently, so that the concentration of methanol at the inlet does not decrease. The heat of reaction is recovered by the waste heat boilers to a larger extent.

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". In this type, the tubes packed with catalyst are externally cooled by boiler water and a nearly isothermal temperature profile is formed in the catalyst bed. 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.

Type IV

In contrast with Type III, Type IV is comprised 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. In addition, it is necessary to pack the catalyst between the water tubes and the arrangement pitch is limited by the particle diameter of the catalyst. As a result, the heat exchange surface per unit volume of catalyst is in general, considerably smaller as compared with Type III and the heat recovery is reduced accordingly. The temperature goes up and its profile in the catalyst bed peaks near the inlet.

Type V

This type is a methanol synthesis reactor based on the new concept discussed in this paper. It is a simple, double-tube type vertical heat exchanger. The catalyst is packed in the annual space of each double tube and the boiler water circulates in 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. 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 low 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 Figure 1. In a Type V reactor, 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.

All reactors so far proposed as devise to ensure that the reaction proceeds while approaching such maximum reaction trajectory, but the real operational line is only made closer to the ideal one as a whole, and deviates from the maximum reaction rate trajectory.

Other types of reactors than those given in Figure 1 have been proposed, for example, in the radial flow type reactor, the reactant gas flows radially to minimize the pressure drop of gas in the catalyst bed. A three-phase fluidized-bed reactor, which is still in the stage of development, has also been proposed. However, these types are not taken into consideration for the above comparison because the advantageous features of Type V herein proposed can be well defined without comparison.
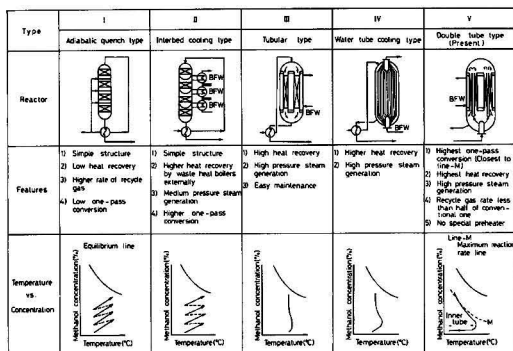
ANALYSIS
Mathematical Model and Calculation Procedure

One-dimensional Analysis: In this section, the procedure for the analysis of flow, heat transfer and reaction,

Figure 1. Types of methanol synthesis reactors.

TABLE 2. CALCULATIONAL CONDITIONS USED FOR ONE-DIMENSIONAL ANALYSIS

Inner tube	: inside diameter	16		mm
	: outside diameter	19		mm
Outer tube	: inside diameter	75		mm
Tube length	:	10,	20	m
Feed gas	: composition	A gas,	B gas	(See Table 3)
	inlet temperature	50,	150	°C
Space velocity	:	3000,	4500,	6000 1/h
Pressure	:	5.9,	7.8,	9.8 MPa
Saturation temperature of boiler water:		200,	215,	250 °C

* The values underlined are reference points for the parameter survey.

which only takes into account the fluid flow direction in the reactor, is described. As reported in the preceeding presentation [2], the methanol synthesis reaction is chemically formulated as follows:

$$CO + 2H_2 \rightarrow CH_3OH \qquad \text{(reaction 1)}$$

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad \text{(reaction 2)}$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad \text{(reaction 3)}$$

The concept of the new reactor herein proposed is modeled for the purpose of numerical analysis. The model obtained is shown in Figure 2. The feed gas flows upwards through the inner tube while being preheated. The reactant gas flows downwards through the catalyst bed while being subjected to the reaction. These two gas flows then exchange heat counter-currently. The reactant gas and the cooling water also exchange heat counter-currently through the outer tube wall. The temperature profile of each fluid in the axial direction of the reactor is schematically represented in Figure 3. The gas phase material balance of each component, heat balance and pressure drop in a steady state are expressed by the differential equations, for an increment, dl, extending over an axial distance, l, from the top of reactor tube as shown 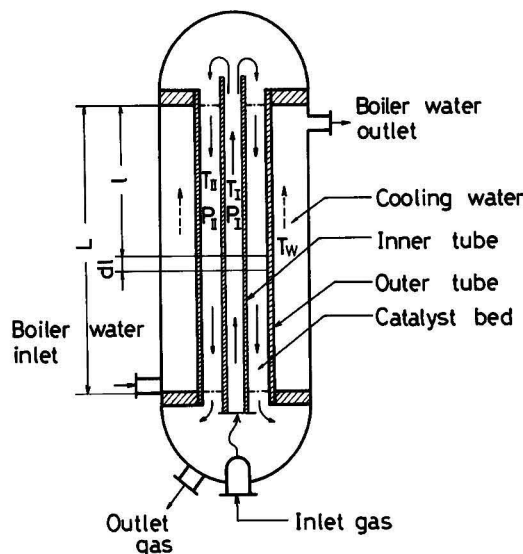in Figure 2, where the over-all heat transfer coefficient is determined by considering boiling, subcooling and transition zones on the outside wall of the outer tube.

Two-dimensional Analysis: With a view of seeing the radial direction temperature profiles of gas and catalyst bed packed in an annular space and, more specifically, whether any hot spot may occur or not, a two-dimensional analysis is made by considering a particular point of the reactor tube in terms of the temperature profile.

In this analysis, the catalyst bed is considered to consist of two phases, namely, solid phase (catalyst) and gas phase. The partial differential equations for pressure balance and heat balance are solved by FEM (finite element method) to determine the temperature profiles of both phases.

Calculation Results and Discussion

One-dimensional Analysis: The calculation conditions are given in Table 2 and 3. In determining the diameter of a double tube, the charging and discharging of the catalyst as well as flow and heat transfer must be taken into account. In order that the catalyst can be charged and discharged smoothly without bridging, the annular gap in the double tube must be at least several times as large as the catalyst particle diameter. From the viewpoint of heat transfer, however, if the diameter of outer tube is too large, heat dissipation of the catalyst will be insufficient. This may result in thermal damage of the catalyst and intensification of the secondary reaction leading to an increase of impurities. The diameters of the inner and outer tubes are given in Table 2 as those taken the optimum values after having made a case study for a copper based catalyst (in the cylindrical form with diameter of 6.1 mm and height of 5.0 mm).

Figure 2. Concept of new methanol synthesis reactor. Note: A reactor for practical use is provided with multi-double tube.
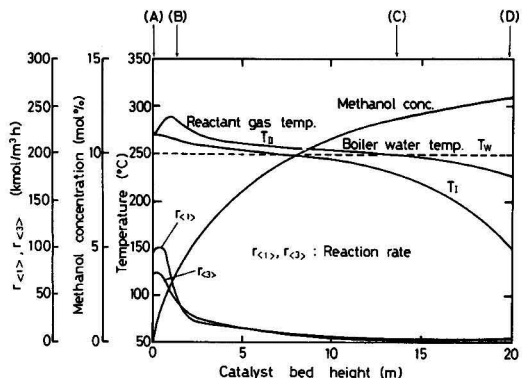
Figure 3. Results of one-dimensional analysis: Profiles of temperature, methanol concentration and reaction rate (Base case).

TABLE 3. FEED GAS COMPOSITION AT REACTOR INLET USED FOR ONE-DIMENSIONAL ANALYSIS

Component	A gas (mol %)	B gas (mol %)
CO	9	8
CO_2	8	5
H_2	65	80
CH_4	13	6
N_2	5	1
H_2O	0	0
CH_3OH	0	0
Total	100	100

As for feed gas composition, the separation of crude methanol from the reactor outlet gas as well as the recycle, with a partial purge, of unreacted gas into the reactor were considered and as shown in Table 3, two cases of feed gas composition are taken into consideration: one is a typical case of the combination of steam reforming and partial oxidation for natural gas reforming (gas A), and the other, a typical case of steam reforming of natural gas (gas B).

The calculation results are shown in Figure 3 to 9. A typical result shown in Figure 3, which is corresponding to the calculation conditions as reference points indicated in Table 2, explains the general characteristics of the new reactor proposed by the authors. First, the feed gas is preheated while flowing through the inner tube, and the preheated gas changes its direction of flow at the outlet of the inner tube and flows into the catalyst bed in the outer tube. Near the catalyst bed inlet, the reaction proceeds at the maximum rate, also the gas temperature reaches its peak almost simultaneously. The gas can then flow down to the reactor outlet while being cooled on both sides of the inner tube and outer tubes thereby increasing the concentration of methanol as a reaction product.

The effects of the reactor length as a constructional parameter can be explained by taking two different values of reactor length, 10m and 20m. When the reactor length is made longer, the cooling effect becomes better. The feed gas temperature at the turn-back point and the peak temperature of gas being reacted in the outer tube are both slightly decreased. The temperature of the reacted gas at the outer tube outlet is somewhat reduced and the methanol concentration is increased.

Consider the effects of the feed gas temperature at the reactor inlet. When the feed gas inlet temperature is
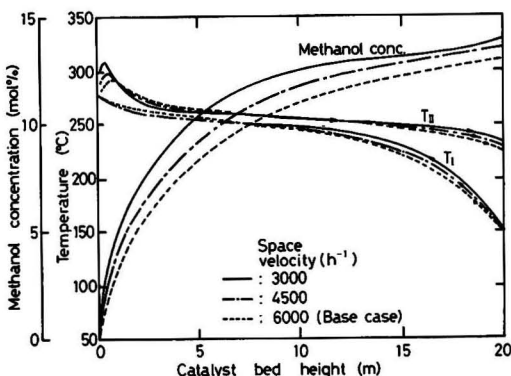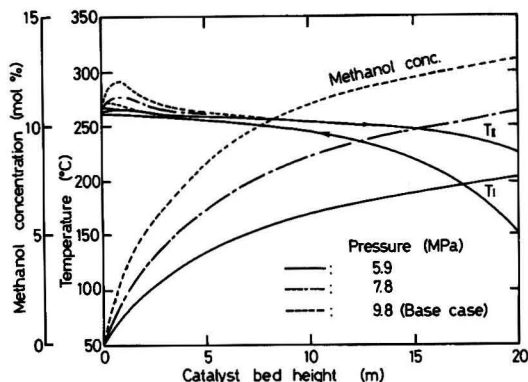

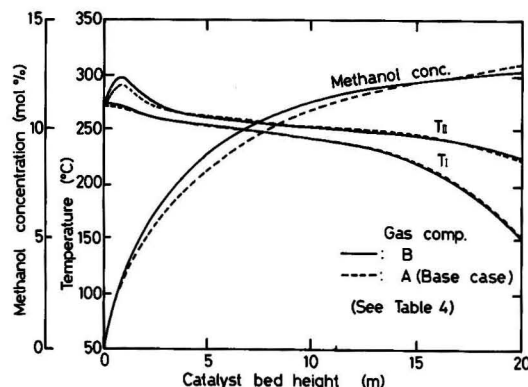Figure 5. Effect of pressure on gas temperature profiles and methanol concentration.

Figure 6. Effect of gas composition on gas temperature profiles and methanol concentration.
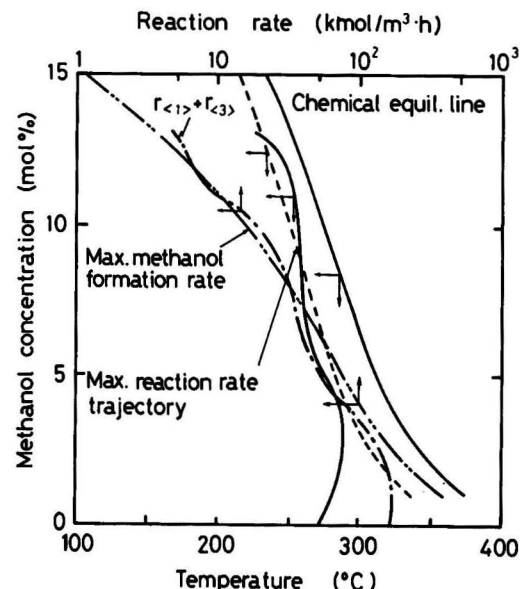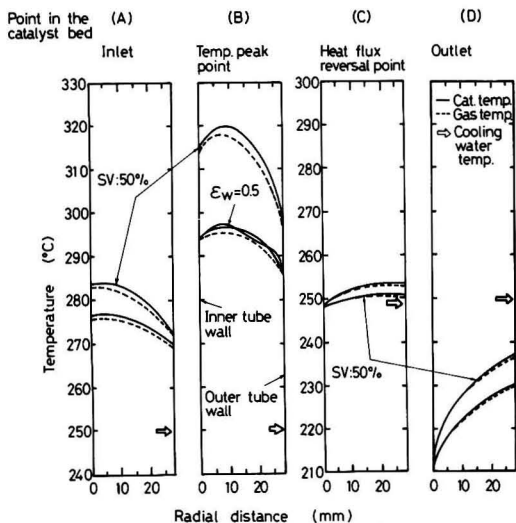

Figure 7. Methanol formation trajectories.

Figure 4. Effect of space velocity on gas temperature profiles and methanol concentration.

Figure 8. Temperature profiles in the catalyst bed.

Figure 10. Schematic flow diagram of pilot plant using a new methanol synthesis reactor.
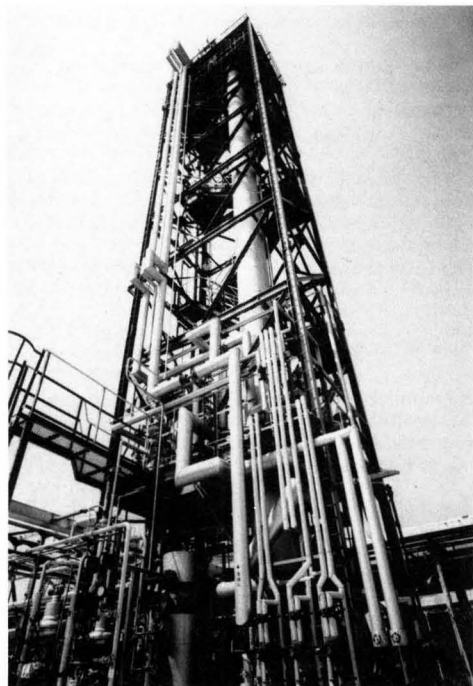

Figure 9. 10T/D pilot plant of new reactor constructed in MGC's Niigata Plant.

raised from 50°C to 150°C, the whole temperature profile of gas being reacted in the outer tube is also raised slightly and the reaction rate increases accordingly, so that the methanol concentration may be increased slightly. However, the effects of the feed gas inlet temperature can be considered minor because the quantity of sensible heat required for preheating the feed gas is sufficiently small as compared with the reaction heat.
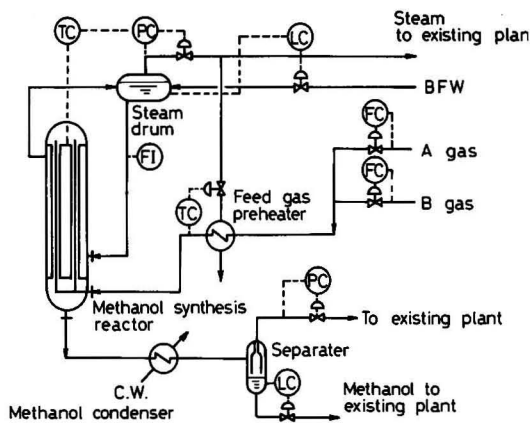
The calculation results for different space velocities of feed gas are shown in Figure 4. Since the fluid film heat transfer coefficients between particles and gas and within the tubes depend largely upon the space velocity, the effects of this space velocity are remarkable on the heat transfer characteristics, that is, catalyst cooling. As is clear from Figure 4, according as the space velocity is lowered, the heat transfer rate becomes poorer and the temperature in the catalyst bed in the outer tube becomes higher. As a result, methanol concentration at the outlet also becomes higher. However, since the flow rate of the feed gas is reduced, an increase in the total production of methanol can not be expected. Moreover, because the temperature rise is remarkable particularly at the temperature peak point, an extremely low space velocity may result in thermal damage of the catalyst.

Figure 5 shows the calculation results for three different synthesis pressures, 5.9, 7.8 and 9.8 MPa. Increased synthesis pressure directly leads to an increase of the reaction rate, with scarcely any improvement of the heat transfer rates. Therefore, as the synthesis pressure is increased, the removal of the reaction heat becomes more difficult. As can be seen in Figure 5, a sharp rise of the reaction rate takes place around the inlet of catalyst bed particularly in the outer tube. Such a sharp rise of the reaction rate naturally entails a rise in temperature. However, if the thermal damage of the catalyst can be tolerated, especially around the temperature peak point, as well as the formation of impurities resulting from secondary reactions brought about by the temperature rise, the production of methanol can be improved by increasing the synthesis pressure.

The temperature of boiler feed water governs the reaction temperature level in the outer tube. Since the saturation temperature of boiler feed water can easily be raised or lowered through the boiler pressure control, the reaction temperature can also be controlled to the proper value according to the degree of catalyst activity.

For different gas compositions a case of high hydrogen content (gas B) shows a steeper temperature peak at the early stage of reaction than that of a low hydrogen content (gas A) as shown in Figure 6. But, the final value of methanol concentration for gas A case is somewhat higher than for gas B, because of the high content of carbon oxides in gas A.

The relation between the real reaction trajectory and the ideal one of the maximum reaction rate is shown in Figure 7. In the temperature-methanol concentration

plane, the reaction trajectory in the reactor proposed almost coincides with the ideal trajectory over a wide range. In the reaction rate-methanol concentration plane, the overall reaction rate in the reactor $r_{<1>} + r_{<3>}$ also coincides with the ideal one.

Two-dimensional Analysis: To estimate the radial temperature profiles at certain particular point in the catalyst bed, a two-dimensional analysis was made. The points in the catalyst bed taken for the two-dimensional analysis are shown in Figure 3. These were obtained by the one-dimensional analysis:

(A) Catalyst bed inlet
(B) Temperature peak point
(C) Heat flux reversal points, that is, the point where cooling water and catalyst bed temperatures are reversed.
(D) Catalyst bed outlet

At these points, the two-dimensional analysis were carried out under the conditions indicated in Table 2. Figure 8 shows the radial temperature profile at each point considered. As can be seen in the figure, the radial temperature profiles at the bed inlet and those at the temperature peak point present gentle gradients at the center of the catalyst bed, while those gradient are steep on the cooling water side. On the contrary, the temperature gradient at the bed outlet is steep on the inner tube side. This trend corresponds to the direction of heat flow.

The smaller space velocity case (SV = 50%) is also shown in Figure 8. At the temperature peak point the effect of the gas flow bypassing along the tube wall is also examined by setting to an equivalent value (ϵ_w = 0.5) the void fraction of the catalyst bed near the tube wall. From these analytical results, the following are deduced:

a. The difference in temperature between gas and catalyst particles is maximum and in the order of a few degrees at the temperature peak point. Therefore, this fact verifies the approximation in the one-dimensional analysis that the temperature profile of the gas in the outer tube and that of the catalyst bed are approximately equal in the longitudinal direction of the reactor tube.
b. When the flow rate of gas is reduced to half or less, the maximum temperature at the temperature peak point becomes high (over 300°C).
c. The effect of the gas bypassing flow in the catalyst bed along the tube wall on the temperature profile is negligible.
d. Radial pressure and flow velocity profiles are practically uniform.

PILOT PLANT OPERATION
Specifications of the Pilot Plant and Experimental Procedure

The pilot plant used for this study is represented in Figures 9 and 10. The specifications are given in Table 4.

In this pilot plant, the length of the catalyst tube was 20m for the purpose of imposing severe conditions, especially from a mechanical point of view. In practice, however, any optimum length can be selected. This will depend on plant size and process conditions.

Although the longitudinal size of the pilot plant was comparable to that of a commercial plant, the transversal size was reduced to the minimum permitting to reproduce the behavior of a commercial plant with six catalyst tubes arranged circumferentially in the reactor. On each catalyst tube, 10 thermometers of the thermo-couple type were provided. This permitted the catalyst bed temperature profile to be determined at 60 points.

After preheating, the gas was fed into the synthesis reactor and subjected to a synthesis reaction. After the reaction, the gas was cooled to condense crude methanol.

TABLE 4. SPECIFICATIONS OF PILOT PLANT

Methanol synthesis reactor
- Catalyst tube length : 20 m
- Outer tube diameter : 85 mm o.d.
- Inner tube diameter : 19 mm o.d.
- Number of catalyst tubes : 6
- Tubes material : Carbon −0.5 Mo
- Shell material : Carbon Steel
Performance
- Capacity : 10 t/d
- Pressure range : 45-110 kg/cm²

Then, it was fed into a separator to separate the liquid from the gas. The flow rate of the feed gas was measured before preheating and the feed gas temperature at the reactor inlet was controlled through the flow regulation of steam fed into the preheater.

The reactant gas pressure in the reactor was set at the desired value by controlling the gas pressure at the outlet of the crude methanol separator. For the catalyst bed cooling, a natural circulation boiler having a steam drum on top was installed and the boiling water temperature was set to be desired value by controlling the steam pressure.

The following factors were measured and analyzed at the steady state:
1. Flow rate and composition of feed gas.
2. Temperature and pressure of feed gas at the reactor inlet.
3. Composition and pressure of gas at the reactor outlet.
4. Composition and flow rate of crude methanol.
5. Flow rate and temperature of circulating boiler water.
6. Flow rate and pressure of saturated steam produced.

For instrumentation, a distributed control system was adopted. All operational data were logged and analyzed by an on-line computer system.

The catalyst used was copper based type. It was cylindrical with a diameter of 6.1 mm and height of 5.0 mm.

EXPERIMENTAL RESULTS AND DISCUSSIONS

Operational conditions and experimental results for each run are given in Table 5 and a comparison of observed and calculated values for the case of Run P-1 are shown in Figure 11.
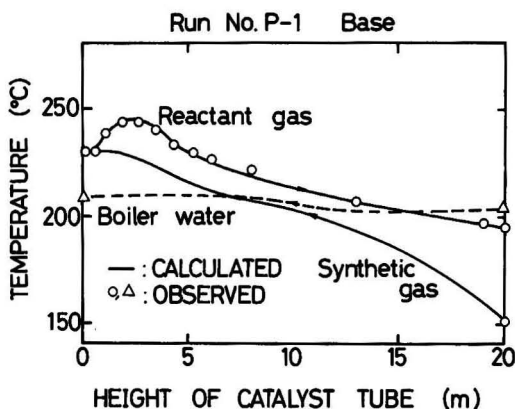

Figure 11. A comparison of observed and calculated values for the pilot plant operation of new reactor.

Run No. Operation Mode.		P-1 Base		P-2 High Space Velocity		P-3 Low Pressure		P-4 High Temperature	
Gas Condition		Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
Pressure	(kg/cm²)	83.55	81.07	86.37	81.07	63.79	56.11	63.56	56.06
Temperature	(°C)	150.0	187.1	150.0	187.1	150.0	199.6	150.0	215.5
Composition	(mol %)								
CO		10.65	1.13	10.09	2.24	11.23	2.85	8.93	2.37
CO_2		6.87	6.69	5.70	5.51	6.62	6.91	5.78	5.39
H_2		67.60	55.69	72.24	64.24	69.31	60.22	72.06	65.01
CH_4		13.56	17.61	10.86	13.40	11.67	14.60	12.06	14.44
N_2		0.86	1.12	0.69	0.85	0.70	0.88	0.69	0.83
H_2O		0.09	2.34	0.09	1.63	0.11	1.51	0.09	1.64
CH_3OH		0.37	15.42	0.33	12.13	0.36	13.03	0.39	10.32
Total		100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Space Velocity[1]	(l/h)	4158		6400		6098		6260	
Space Time Yield	(t/m³h)	0.416		0.818		0.825		0.703	
Boiler Steam									
Pressure	(kg/cm²)	19.46		19.46		28.53		46.03	
Temperature	(°C)	210.0		210.0		230.0		258.0	
Boiler Feed Water									
Flow rate	(t/h)	5.46		6.24		5.48		4.02	
Temperature	(°C)	204.0		204.0		222.0		250.0	

[1] Space velocity is defined by the ratio of normal volumetric flow rate at the catalyst bed inlet to catalyst bed volume.

To review Run P-1, it can be well seen from the observed data that the gas reaches its temperature peak at a point of 2.5m near the catalyst tube inlet. Thereafter, it cools while flowing toward the reactor outlet in a counter-current relative to both cooling water and feed gas. The observed temperature profile agrees well with the one calculated. The mean difference is within ±5°C.

Further, in this case, the boiler water is fed into the shell side of the reactor bottom at a temperature of 204°C. It is in a somewhat subcooled state, relative to its saturation temperature of 210°C. While flowing upwards, the boiler water is first cooled down by preheating the feed gas, and then heated by the reacted gas to reach its saturation temperature. As a result, subcooling and boiling zones exist on the shell side, where the cooling water flows.

As for the quantity of steam generated in the boiler, this is determined by heat balance in the reactor, the difference between observed and calculated values is in the order of ±15%.

As for the pressure loss of gas flowing through the inner and outer tubes, the observed value in the case of Run P-1 was 2.48 kg/cm² while calculated value was 2.55 kg/cm². Thus, a close agreement between observed and calculated values was obtained. Table 5 shows the space velocity for Run P-2 increasing when compared to Run P-1.

From the calculation results, it was expected that the catalyst bed peak temperature could be reduced, the gas temperature at the turn-back point would be reduced slightly, the outlet concentration of methanol decrease and the loss of gas pressure increased. The observed tendency and values were practically as expected.

Also for other similar cases, where the synthesis pressure was reduced (Run P-3) and the boiler steam temperature was increased (Run P-4), a comparison between the observed and calculated values was made. These comparisons also show a close agreement between values. It can therefore be considered that the reaction model as well as the flow and heat transfer model used in this study are reasonable and are well applicable for commercial plant design, performance estimation of a commercial plant and other purposes of practical use.

CONCLUSION

The main advantages of the new methanol reactor herein discussed are listed as follows:

1. The reaction trajectory closest to the maximum reaction rate line gives a higher one-pass conversion by more than twice that of a conventional reactor such as the adiabatic quench type, so that the rate of recycle gas decreases by more than half. For example, at a space velocity of 5000 h⁻¹ and synthesis pressure of 7.85 × 10⁶ Pa (80 kg/cm²), a methanol concentration of 14.0 mol% or more can be obtained at the reactor outlet.

2. High-level energy can be recovered. For example, one ton or more of steam at 3.92 × 10⁶ Pa (40 kg/cm²) is generated with each ton of methanol.

3. The catalyst bed temperature is controlled by steam pressure in the shell of the reactor.

4. Preheating the feed gas in the reactor and the inner tubes will replace the feed gas preheater.

NOTATION

l	= distance from top of catalyst tube
L	= catalyst bed height
$r_{<j>}$	= the jth reaction rate
T_w	= cooling water temperature
T_I	= gas temperature in inner tube
T_{II}	= gas temperature in outer tube
ϵ_w	= void fraction in the vicinity of a wall

LITERATURE CITED

1. Takase, I. and K. Niwa, "Mitsubishi Methanol Process," *Chem. Economy & Eng. Review*, 17 (5), 24 (1985).
2. Takagawa, M. and M. Kuwa, "Kinetic Study on New Methanol Synthesis Model for Advanced Converter Design," Paper presented at the AIChE's Spring National Meeting, New Orleans, April 6-10, 1986, (in Group 16, Session 15).
3. Makihara, H., H. Horizoe, K. Kobayashi, C. Kuwada, K. Niwa, H. Nagai and K. Morita, "Characteristics of a New Methanol Synthesis Reactor," Paper presented at the AIChE's Spring National Meeting, New Orleans, April 6-10, 1986, (in Group 16, Session 15).

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All-Hydroprocessing Route for High-Viscosity Index Lubes

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*Combines hydrocracking with catalytic dewaxing to produce
high quality neutral oils from very low quality
feedstocks such as Alaskan North Slope distillates.*

INTRODUCTION

Chevron's Richmond Lube Oil Project (RLOP) is the first commercial process to combine hydrocracking, catalytic dewaxing, and hydrofinishing for the manufacture of high-V.I. lubes. (The V.I., or Viscosity Index, is defined by ASTM Method D2270.) The project, which includes the world's largest lube hydrocracker, came onstream in late 1984 and is designed to produce 9000 BPOD of light, medium, and heavy neutral basestocks. This all-hydroprocessing route produces basestocks with exceptional oxidation stability and low-temperature properties.

The decision to build a grass-roots lube plant was based on the following factors:

Aging Facilities: The previous Chevron lube facility at the Richmond, California refinery was very old and badly in need of repair. The cost of upgrading it was a substantial fraction of the cost of a grass-roots plant.

Feed Flexibility: The old lube plant was based on Duo-Sol solvent extraction technology and, like all solvent-based lube plants, was energy-intensive and dependent on high-V.I. feedstocks. Newer hydrocracking technology promised much greater feed flexibility, a vital factor to reduce Chevron's dependence on foreign crudes. To maximize yield and product quality, the old lube plant required a special segregation of Arabian Light resid shipped from Chevron's Pascagoula, Mississippi refinery. The new lube plant's design basis feed was a blend of two domestic crudes: Alaskan North Slope and a California blend called Waxy Light Heavy.

West Coast Supply Balance: Although nationwide lube supply and demand were in balance, the West Coast was extremely short on high-V.I. lube oil manufacturing capacity. Besides Chevron's plant, which produced about 3500 BPCD of lube basestocks, there was only one other plant—Unocal's Duo-Sol plant in Rodeo, California, which produced about 4000 BPCD of lube basestocks. Chevron's capacity was well below our internal demand, making us the nation's largest net purchaser of lube basestocks. A new plant would make Chevron self-sufficient in supply in a supply-short West Coast market.

WHY HYDROCRACKING?

The selection of hydrocracking technology was clear cut in view of the following advantages:

Feed Flexibility: Solvent extraction upgrades V.I. by a physical separation—low V.I. components are removed as extract and high-V.I. components remain in the raffinate.

Hydrocracking is a chemical separation process which upgrades V.I. in two ways:

(1) Removing low-V.I. components by cracking them to lower boiling ranges, and

(2) Rearranging low-V.I. components to higher-V.I. ones by reactions such as aromatics saturation and naphthenic ring opening.

Because of its ability to create higher V.I. components, hydrocracking offers much greater feedstock flexibility, allowing the use of lower-V.I. domestic crudes that are unimaginable for a solvent extraction plant.

Lower Feed and Operating Costs: Although hydrocracking's capital costs are somewhat greater than solvent extraction, feedstock and operating costs are much lower. Solvent refiners are forced to pay a premium for higher V.I. "lube crudes" whereas hydrocrackers can accept less expensive feeds. Hydrogen is the major operating cost for a hydrocracker; however, its cost is offset by the roughly 10% volume expansion resulting from hydrogen processing.

Byproduct Credits: The byproducts of hydrocracking include valuable transportation fuels such as gasoline, jet and diesel. The byproduct of solvent refining is a highly aromatic extract which can be used in fuel oil or FCC feed.

Process Flexibility: An additional benefit of hydrocrackers is that these units can be readily adapted to other refinery objectives. For example, during times of low lube oil demand hydrocrackers can produce transportation fuels and prepare premium FCC feeds.

Chevron Research Company, a recognized leader in hydroprocessing technology, has been doing research in lube oil hydrocracking since the early 1960's. Although the Corporation had no commercial experience with lube hydrocracking, there was great confidence that the process could be successfully piloted, scaled up, designed and built using proprietary technology, and that it would produce base oils superior to current solvent extracted oils.

DESIGN BASIS

Chevron's Richmond Lube Oil Project (RLOP) is designed to produce three grades of neutral oils: Light, Medium and Heavy Neutral. Table 1 lists the specifications for these oils. The Saybolt viscosities at 100°F are about 100, 240, and 500 for the light, medium and heavy grades, respectively.

TABLE 1. SPECIFICATIONS FOR RLOP NEUTRAL OILS

	Light	Medium	Heavy
Viscosity, cS, 40°C	18.8-20.9	44.0-48.0	—
Viscosity, cS, 100°C	—	—	10.7-11.4
Viscosity Index, min.	95	95	95
Flash Point, °F, min.	380	435	475
Pour Point, °F, max.	15	15	15
ASTM D1500 Color, max.	1.0	1.5	2.5

The product base oils had to satisfy a number of rigid internal specifications including bulk oxidation stability (as measured by an oxygen uptake test) and long-term storage stability (as measured by long-term storage in air at elevated temperatures). The base oils also had to be equal or superior in performance to our existing solvent refined oils when blended into Chevron's product line of crankcase oils, transmission fluids, hydraulic fluids, industrial oils and greases.

The design basis feed is a blend of Alaskan North Slope and California crudes because these crudes are readily available on the U.S. West Coast. The hydrocracking reactors are designed to use commercially available Chevron hydrocracking catalysts and to have a service life of at least two years before regeneration.

USE OF V.I. AS A LUBE OIL SPECIFICATION

One of the design criteria is that the lube oil products have a minimum V.I. of 95. This constraint had a profound influence on the process flow scheme.

Viscosity Index is the primary control parameter for most commercial lube manufacturing processes, whether solvent extraction or hydrocracking. We feel that there is an undue emphasis on V.I. as a measure of basestock quality and performance. The V.I. scale was defined in 1929 using unrefined reference oils and remains essentially unchanged except for patchwork extensions. The quality criteria and refining technology for today's lube oils are vastly different than when V.I. was first introduced.

Zakarian [1] reviewed the haphazard history of the ASTM V.I. standard and called for an industrywide reassessment of its use. Other recent appeals for change have come from D. W. Murray et. al. [2] of Imperial Oil Company who showed a shotgun correlation between V.I. and engine oil performance and from J. H. Roberts [3] of Mobil Oil Corporation.

The fundamental assumption defining V.I. is that "the viscosity indexes of all lubricating fractions, separated or refined by conventional methods from any given crude, ordinarily are approximately constant [4]." When the V.I. scale was first proposed in 1929, the lubricating fractions from Pennsylvania crude were chosen to represent 100 V.I. When the proponents of V.I. extended the scale in 1940 to cover oils lighter than 40 SUS @ 210°F, they violated their fundamental premise by selecting different reference crudes to represent 100 V.I. for low-viscosity oils. Thus, light and heavy oils are not compared on the same basis. Light oils are underrated and the scale is extremely sensitive to viscosity measurement in the low-vis regions.

IMPACT OF V.I. ON HYDROCRACKER DESIGN

The inconsistent definition of V.I. is apparent when the products from a lube oil hydrocracker are examined. Figure 1 plots the V.I. against the viscosity measured at 40°C for the products hydrocracked in a pilot plant from Alaskan North Slope feedstock at different conversions. The feed boiling range was 700-1000°F and the products were cut into five lube fractions. At any given refining severity (i.e., conversion), the V.I. is far from constant for the lube
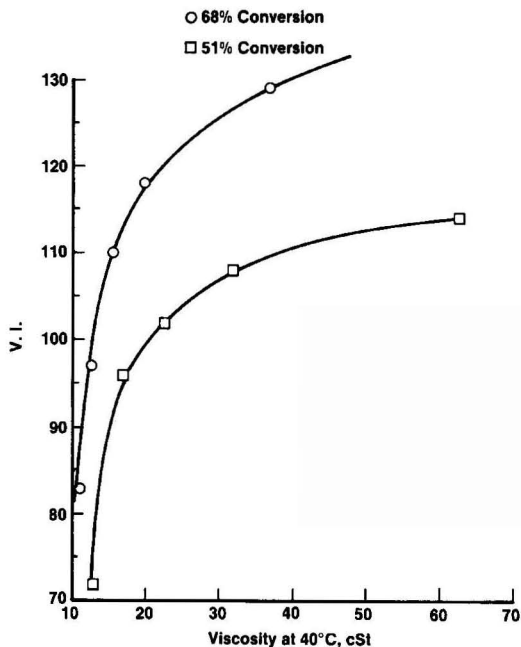

Figure 1. V.I. versus viscosity at 40°C Alaskan North Slope feed.

oil fractions. As the product viscosity increases, the V.I. increases—contrary to the fundamental assumption defining V.I. This phenomenon, which occurs often in lube hydrocracking studies, has been termed 'V.I. droop.' The principal reason for V.I. droop has little to do with the actual viscosity-temperature response of the products; rather, the droop results mainly from the V.I. rating system which, as previously mentioned, rates low-vis oils with a different scale than high-vis oils.

V.I. droop had a profound effect on RLOP plant design because the three neutral oil products were required to meet the same minimum V.I. specification. The most convenient way of hydrocracking lubes is to do so in one reactor; but this approach is uneconomic because of V.I. droop. If one reactor were operated to meet the minimum V.I. specification of the lightest product, the heavier products would have V.I.'s much higher than the minimum. This severe overprocessing would result in a loss of valuable lube oil product. The RLOP flow scheme, described in the next section, uses two lube oil hydrocrackers to maximize the yield of all products and to minimize V.I. giveaway.

An alternative approach is to build one hydrocracker, and to run in blocked operation; that is, to run for a period of time with light feed and then to switch and run for a period with heavy feed. This approach is used in many commercial hydrocrackers; however, blocked operation was not favored for the following reasons:

1. Product downgrade and lost operating time between feed switches.
2. More complex operation and refinery-wide impact on other units.
3. Increased feed and intermediate tankage requirements.
4. Increased energy costs by reheating feeds from tankage instead of using hot feeds direct from a crude distillation tower.

The Sun Oil hydrocracker in Puerto Rico gets around V.I. droop by pretreating the heavy portion of the feed in a furfural extraction unit. This pretreatment removes
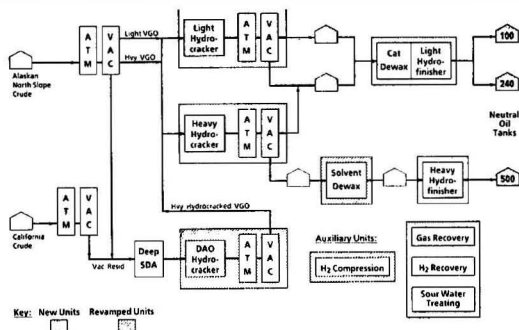
Figure 2. RLOP project flow diagram.

uum column added to an existing deasphalted oil (DAO) hydrocracker.

As its name implies, the Light Hydrocracker uses a light feed to produce the waxy light neutral product as well as a portion of the waxy medium neutral. The catalyst temperature is adjusted to maintain the light neutral V.I. specification. Because of V.I. droop, this produces medium neutral oil with very high V.I. The Heavy Hydrocracker uses a heavy feed to produce the waxy heavy neutral product and a portion of the waxy medium neutral. The catalyst temperature is adjusted to maintain the heavy neutral V.I. specification. This yields a medium neutral oil with below specification V.I.; however, on-specification medium neutral is made by blending the waxy medium neutral cuts from each hydrocracker. The blend ratio is carefully monitored to meet not only the medium neutral V.I. specification but also the viscosity and flash point specifications.

Each lube hydrocracker includes its own atmospheric and vacuum distillation columns. Table 3 lists typical properties from the hydrocracker distillation columns. The vacuum columns are controlled to meet the flash point and viscosity specifications of the final neutral oil products. Table 4 shows typical product yields from the lube hydrocrackers. The examples in Tables 3 and 4 come from a period when the hydrocrackers were running 100% Alaskan North Slope feed.

RLOP uses two different dewaxing technologies: catalytic dewaxing and solvent dewaxing. Light and medium neutral oils are blocked through a catalytic dewaxer, while heavy neutral oil is solvent dewaxed in an existing solvent dewaxer. Chevron chose catalytic dewaxing because of its lower operating and capital costs. Revamping the existing solvent dewaxer for heavy neutral represented the lowest cost design for RLOP.

The catalytic dewaxing reactor is followed immediately by a hydrofinishing reactor to stabilize the light and medium neutral oil products. This close integration avoids the cost of a separate reaction and distillation section for hydrofinishing. The temperature of the dewaxing reactor is adjusted to meet the product pour point specification. The temperature of the hydrofinishing reactor is adjusted

low-V.I. components in the heavy feed thereby preventing them from cracking to a lighter lube oil boiling range and depressing the V.I. of the light lube cuts. Another way around droop is to reprocess the lighter lube fractions.

PROCESS FLOW AND CONTROL

Figure 2 shows the RLOP flow diagram. An existing crude unit supplies two hot vacuum gas oil feeds directly to two lube hydrocrackers. As mentioned previously, this direct, non-blocked operating mode saves the cost of storing and reheating the feedstocks. However, crude unit operation requires careful monitoring to ensure steady operating conditions for the hydrocracking reactors and the lube distillation columns downstream of the reactors.

Table 2 displays the properties of the hydrocracker feeds while running 100% Alaskan North Slope crude. The Light Hydrocracker feed is a blend of 2/3 light vacuum gas oil (VGO) and 1/3 heavy VGO from the crude unit. The Heavy Hydrocracker feed is a blend of 2/3 heavy VGO and 1/3 heavy hydrocracked VGO. The heavy hydrocracked VGO is the 900-1010°F cut from a new vac-

TABLE 2. PROPERTIES OF FEEDSTOCKS

	Light VGO from Crude Unit	Heavy VGO from Crude Unit	Blend of 67% LVGO + 33% HVGO (LC feed)*	Heavy VGO from DAO cracker (33% of HC feed)**
API Gravity	21.4	18.6	20.4	22.8
Sulfur, wt.%	1.21	1.31	1.26	0.065
Nitrogen, ppm	1220	2030	1700	1015
Viscosity, cS, 100°C	5.765	14.51	7.662	16.72
Pour Point, °F	+85	+105	+95	+110
D1160 Distillation				
St/5	681/708	737/801	676/738	807/871
10/30	726/755	823/866	751/782	905/939
50	780	896	815	954
70/90	801/840	934/984	852/924	972/1000
95/EP	862/910	1006/1040	960/1013	1013/1029
% recovery	99	99.5	99	98
Dewaxed Oil				
Wt.% Wax	6.2	6.3	6.6	6.3
Pour Point, °F	+15	+5	+15	+5
Vis, cS, 40°C	54.84	327.2	86.42	281.9
Vis, cS, 100°C	6.208	16.76	8.107	17.88
V.I.	32	18	38	58

* LC = Light Hydrocracker
** HC = Heavy Hydrocracker.

TABLE 3. TYPICAL INSPECTIONS OF PRODUCTS
FROM LUBE HYDROCRACKERS

	Light Hydrocracker	Heavy Hydrocracker
Gasoline		
API Gravity	64.0	63.5
Jet Fuel		
API Gravity	40.0	38.2
Flash Point, °F	110	110
Freeze Point, °F	−65	−65
Smoke Point, mm	21	20
Diesel		
API Gravity	33.4	30.6
Pour Point, °F	−10	−10
Cetane Index	52	47
FCC Feed		
API Gravity		30.4
Sulfur, ppm		<3
Nitrogen, ppm		<1
Light Neutral		
API Gravity	34.6	
Flash Point, °F	405	
Dewaxed Oil		
Vis, cS, 40°C	18.11	
Vis, cS, 100°C	3.846	
V.I.	103	
Medium Neutral		
API Gravity	34.2	31.4
Flash Point, °F	440	440
Dewaxed Oil		
Vis, cS, 40°C	31.44	47.37
Vis, cS, 100°C	5.639	6.812
V.I.	119	97
Heavy Neutral		
API Gravity		31.6
Flash Point, °F		515
Dewaxed Oil		
Vis, cS, 40°C		90.73
Vis, cS, 100°C		10.70
V.I.		101

to meet internal oxidation stability and long-term storage specifications. Because the stability tests require more than one day to complete, the hydrofinishing reactor, in practice, is controlled by a UV absorbance measurement that correlates to both tests. Finished light and medium neutral products are sent directly to storage tanks.

Heavy neutral oil is solvent dewaxed and then stabilized in the Heavy Hydrofinisher. This reactor is controlled in the same manner as the Light Hydrofinisher.

TABLE 4. TYPICAL YIELDS FROM LUBE HYDROCRACKERS

	Light Hydrocracker	Heavy Hydrocracker
H2 Consumption, SCF/B	1100	1050
Yields, LV%		
LPG	2.6	2.3
Gasoline	12.7	7.5
Jet Fuel	33.9	20.9
Diesel	22.3	16.3
FCC Feed	—	17.6
Waxy Light Neutral	23.0	—
Waxy Medium Neutral	18.0	29.6
Waxy Heavy Neutral	—	15.6
Total	112.5	109.8
Controlling Product	Light Neutral	Heavy Neutral
Controlling Dewaxed V.I.	103	101

TABLE 5. TYPICAL PROPERTIES OF RLOP NEUTRAL OILS

	Light	Medium	Heavy
Viscosity, cS			
@ 40°C	19.1	46 0	93.3
@ 100°C	3.94	6.82	10.9
Viscosity, SUS			
@ 100°F	100	237	485
Viscosity Index	100	102	101
API Gravity	34.9	32.8	31.0
Flash Point, COC, °F	400	455	505
Pour Point, °F	15	10	10
Color, ASTM D1500	<0.5	<0.5	<1.0
n-d-M Analysis			
Refractive Index, 20°C	1.4675	1.4731	1.4773
Density, g/cc, 20°C	0.8470	0.8594	0.8679
Molecular Weight	375	454	495
% C paraffinic	69.7	68.8	68.0
% C naphthenic	30.3	31.2	32.0
% C aromatic	0.0	0.0	0.0
Clay Gel Chromatography			
Saturates, wt.%	98.0	99.3	99.4
Aromatics, wt.%	2.0	0.7	0.8
Polars, wt.%	0.1	0.1	0.1
Aniline Point, °F	225	241	255

PRODUCT QUALITY

RLOP is the first commercial process to combine hydrocracking, catalytic dewaxing, and hydrofinishing. This all-hydrogen approach to lube oil manufacture makes lube oil products superior in several ways to many oils produced by the industry. Among the excellent chemical and physical properties of RLOP base oils are: nearly water-white color, excellent response to oxidation inhibitors, excellent response to pour point depressants, extremely low levels of sulfur and nitrogen, and extremely high saturates content.

Table 5 summarizes some of the more important physical and chemical characteristics of Chevron Light, Medium and Heavy Neutral. The most apparent difference between these stocks and solvent-refined base oils is the much reduced level of aromatics. This is seen in the n-d-M analysis (ASTM D3238), in clay-gel chromatography (ASTM D2007), and in aniline points.

Two areas that are substantially improved because of processing methods are the responses to oxidation inhibitors and to pour point depressants.

Oxidation Tests: Hydroprocessing produces basestocks with excellent response to oxidation inhibitors. This has been demonstrated in a variety of bench oxidation tests, as well as in full-scale engine tests.

Chevron Research Company uses a proprietary bench-scale oxidation test, named Oxidator BN, to measure the high temperature oxidation stability of fully formulated lubricants in a simulated engine environment. Base oil is

TABLE 6. CHEVRON OXIDATOR BN TEST RESULTS

Basestocks	Hours to 1-liter Oxygen Uptake
Chevron 100 Neutral	22+
Chevron 240 Neutral	22+
Chevron 500 Neutral	22+
Solvent Refined 100 Neutrals	6 to 8
Sovlent Refined 600 Neutrals	6 to 8
Naphthenic Basestocks	2 to 5
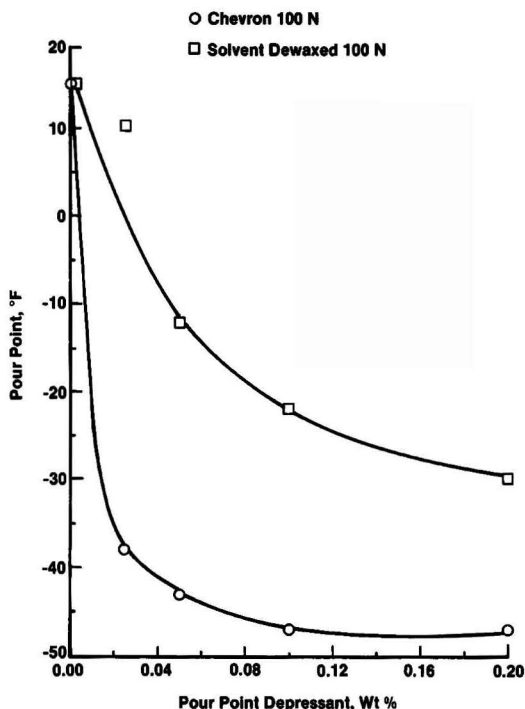
Figure 3. Response to pour point depressants.

This type of excellent oxidation performance is also seen in the ASTM D943 Turbine Oil Oxidation Stability Test (TOST). With Chevron neutrals and commercial additive packages, oxidation lifetimes (hours to a total acid number of 2.0) of more than 4000 hours are typical. With the same additive package, solvent refined stocks of turbine oil quality show lifetimes of 2000-3000 hours.

Low Temperature Properties: As described earlier, the Light and Medium Neutral are catalytically dewaxed. The consequences of this type of dewaxing are superior low temperature properties for these two viscosity grades.

Even though the pour point of the Light Neutral is about the same as other commercially available 100 Neutral basestocks (+15°F), its response to pour point depressants is dramatically superior. Relatively small amounts of pour point depressants are necessary to depress the pour point to −45°F. Figure 3 shows the pour point with increasing amounts of a common polymethacrylate pour point depressant. To obtain a −30°F pour point requires about one-eighth the amount of additive as does the solvent refined, solvent dewaxed 100 Neutral.

The primary reason for the dramatic difference in response to pour point depressants is the lower wax content in the Chevron neutrals. Catalytic dewaxing is selective for wax structure whereas solvent dewaxing is selective for wax melting point. In order to reach a +15°F pour point, more wax is removed in catalytic dewaxing than would otherwise be necessary using solvent dewaxing.

mixed with both oxidation promoters (metal catalysts) and oxidation inhibitors, placed in a glass tube, and heated to 340°F while stirring. The oxygen uptake is measured as a function of time. The catalyst package is a solution of mixed metal naphthenates (mainly lead naphthenate, but also copper, iron, manganese, and tin naphthenates), and the oxidation inhibitor is an additive commonly used in engine oil formulations. Table 6 shows Oxidator BN results of Chevron neutral oils compared to other basestocks. The hydroprocessed Chevron oils show excellent resistance to high-temperature oxidation.

SURVEY OF COMMERCIAL LUBE HYDROCRACKERS

Lube hydrocracking is a relatively recent commercial development and hydrocracked base oils occupy a small, but growing, share of the high-V.I. market. Table 7 lists the capacities and locations of commercial lube hydrocrackers operating in the non-Communist world. The first hydrocracker came onstream in 1966 and nearly half of the capacity was started up in the 1980's.

Chevron's Richmond Lube Oil project includes the world's largest lube hydrocracker. Gulf Research and Development Company is the predominant licensor of hydrocracking technology. Following the 1985 merger between Gulf and Chevron corporations, Chevron became both the largest licensor and operator of lube hydrockers.

TABLE 7. LUBE HYDROCRACKING PLANTS

Company	Location	Onstream	Licensor	Feed, BPOD
Empresa Nacional Calvo Sotelo	Puertollano, Spain	1966	I.F.P.	2,500
Idemitsu Kosan	Chiba, Japan	1969	Chevron*	10,500
Pennzoil	Rouseville, Pennsylvania	1972	Chevron*	2,700
Quaker State	Congo, West Virginia	1972	U.O.P.	1,600
Sun Oil	Yabucoa, Puerto Rico	1972	Chevron*	12,200
Shell France	Petit-Couronne, France	1972	Shell	5,600
Petro Canada	Clarkson, Ont., Canada	1979	Chevron*	10,000
Ssangyong Oil	Onsan, Korea	1980	Chevron*	6,000
Pennzoil-Atlas	Shreveport, Louisiana	1983	Chevron*	5,000
Chevron	Richmond, California	1984	Chevron	18,500(HNC) 12,000(LNC)

* Licensed originally by Gulf Research and Development Company.

LITERATURE CITED

1. Zakarian, J. A., NPRA Fuels and Lubricants Meeting, Paper FL-82-85, Houston, Texas, Nov. 4-5, 1982.
2. Murray, D. W., J. M. MacDonald, A. M. White, and P. G. Wright, *Pet. Rev.*, **36** (2), 36 (1982).
3. Roberts, J. H., NPRA Annual Meeting, Paper AM-85-21C, San Antonio, Texas, Mar. 24-26, 1985.
4. Dean, E. W. and G. H. B. Davis, *Chem. Met. Eng.*, **36**, 618 (1929).
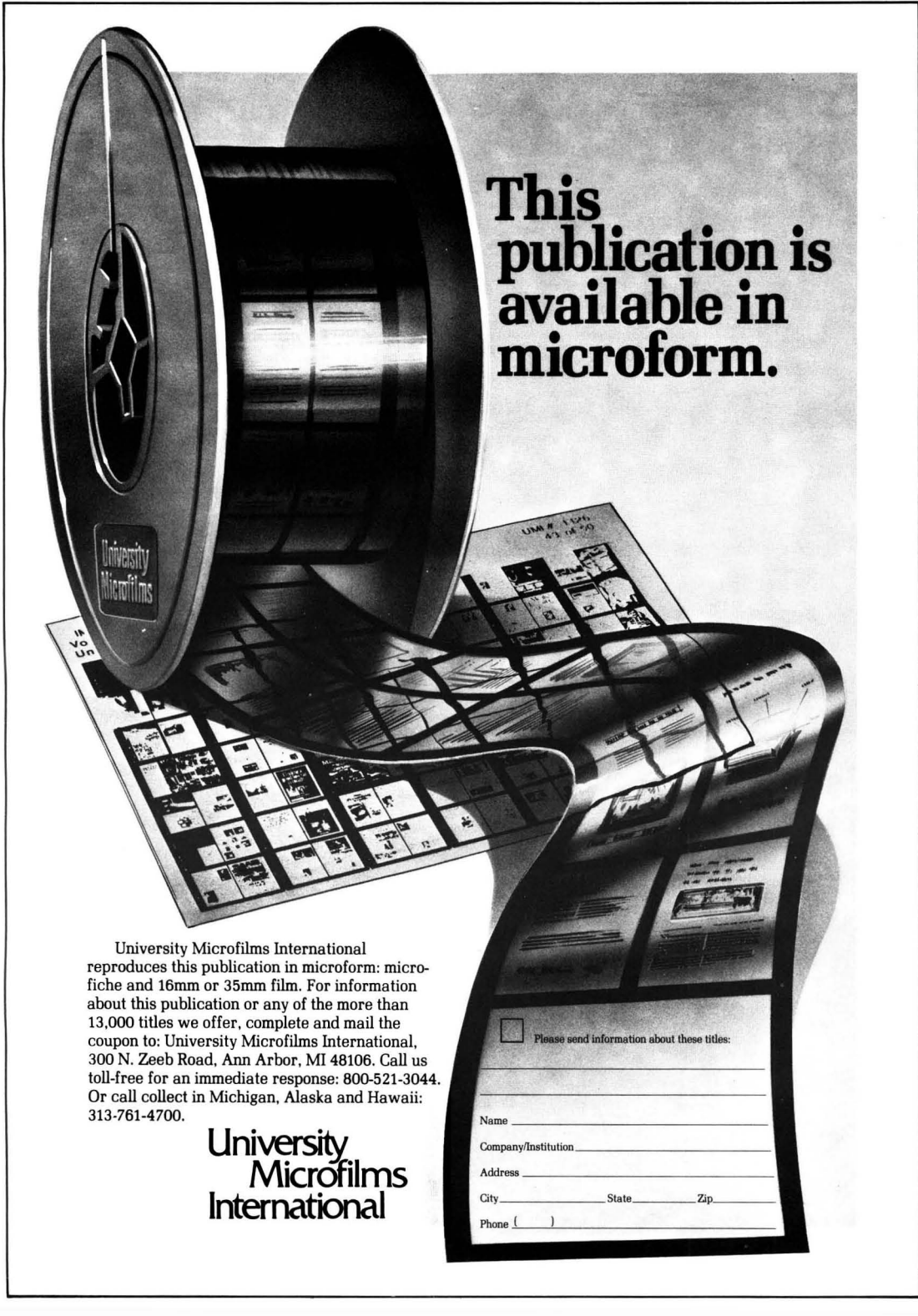
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