Olefins and BTX-Production by Thermal Cracking of Hydrotreated Vacuum Gas Oil and Related Fractions

Aramco vacuum gas oil was catalytically hydrotreated to conversions of 20, 40 and 60%, and subsequently fractionated into naphtha, kerosene, gas oil, and hydrotreated vacuum gas oil. These fractions were thermally cracked to test their potential as feedstock for olefins and BTX production. The olefin yields from the hydrotreated vacuum gas oil obtained from hydrotreating with 40 and 60% conversion favorably compare with those of straight-run naphthas. Cracking in conventional naphtha/atmospheric gas oil units becomes possible. The naphtha, kerosene and gas oil fractions are preferably added to standard refinery streams.

P. J. CLYMANS and
G. F. FROMENT
Laboratorium voor Petrochemische
Techniek
Rijksuniversiteit, Gent, Belgium

M. BERTHELIN and
P. TRAMBOUZE
Centre d'Etudes et de Développement
Industriels
Institut Français du Pétrole
Solaize, France

SCOPE

Rising naphtha prices have increased the interest in higher boiling petroleum fractions as feedstock for olefin production. An interesting candidate is vacuum gas oil in particular, since the demand for this fraction on the fuel market is decreasing. Vacuum gas oil is not a particularly appropriate feedstock for olefin production, however, because of its high naphthenic and polycondensed aromatics content.

Cracking vacuum gas oil also creates problems because of its high sulfur content, and excessive tar and coke formation. Most of the drawbacks mentioned above can be eliminated by catalytic hydrotreating or by extraction (Korosi et al., 1979; Goetzmann et al., 1979; Wernicke et al., 1979; Rhoé, 1981; Schneider et al., 1981). The present work compares product yields from several fractions derived from the hydrotreating of vacuum gas oil with these obtained from the original vacuum gas oil and from a raffinate of the furfural extraction of aromatics.

CONCLUSIONS AND SIGNIFICANCE

Extensive data have been collected on the thermal cracking of various fractions resulting from the hydrotreatment of a virgin vacuum gas oil. The potential of the various fractions as feedstock for olefins production has been evaluated. The heavy hydrotreated fraction, HVGO, is a valuable alternative for straight-run naphtha. The light fractions are acceptable feedstocks for thermal cracking, but would preferably be added to standard refinery streams.

The experimental results verify a number of advantages with respect to the cracking of virgin vacuum gas oil. The thermal cracking of the pretreated feedstocks leads to higher yields of ethylene, propylene and butadiene. Consequently, for a given ethylene production, the number of cracking furnaces is reduced. The fuel oil yield is drastically lowered, while its quality is improved, because of the hydrodesulfurization. Due to the lower fouling rates a transfer line heat exchanger can be used for the effluent cooling, so that high-pressure steam is produced and the thermal efficiency of the unit is increased. The lower coking rates lengthen run lengths and/or increase cracking severity.

Since the hydrotreated vacuum gas oil can be cracked in a naphtha/atmospheric gas oil furnace it has to be considered as a valuable alternative for naphtha as a cracking feedstock. The cracking of a full-range straight-run naphtha leads to ethylene yields which are typically 3 to 4 wt. % higher than those of HVGO-40 and HVGO-60, the maximum propylene yield is comparable, the butadiene yield is about 2% lower, while the methane yield is between 5 and 7 wt. % higher. An economic evaluation of hydrotreatment based on the present data base has been carried out by Kaiser et al. (1982). It was found to be attractive, but the environment and type of operation are important factors.

I.F.P. HYDROTREATING PROCESS

I.F.P. developed a hydrotreating process based on a weakly acidic bimetallic silica-alumina catalyst. The process operates at pressures between 50 to 150 bar and space velocities between 0.5 and 1.0 vol./vol. catalyst/hour, depending on the feedstock and the desired conversion. The hydrotreating increases the paraffinic content and reduces the (poly)aromatics content. The feedstocks required for the present investigation were prepared in a number of pilots containing up to 30 L of catalyst in the Centre d'Etudes et de Dêveloppement Industriels of I.F.P. The effluent was fractionated into naphtha, kerosene, gas oil, and vacuum gas oil. These fractions were then evaluated as feedstock for thermal cracking units.

STEAM CRACKER PILOT UNIT

The Laboratorium voor Petrochemische Techniek designed, built and operates a pilot unit for the study of thermal cracking. The unit has been described in previous papers (Van Damme et al., 1981a). The furnace is fired with natural gas by means of radiant burners. The cracking section proper consists of five cells which can be fired at different intensities. The length of the coil is 21.75 m in the cracking section proper; the internal diameter is 1 cm. The hydrocarbon feed flow rate can be set between 0.5 and 10 kg/h by means of electronically controlled pumps. The residence time can be varied between 0.15 and 0.75 s. The feed system for heavy feedstocks, with pour point above ambient temperature, is electrically heated. The process gas temperture is measured in 12 locations and the external wall temperature in 14 locations. Pressure gages and transducers allow measurement and registration of the pressure profile along the reactor. Five on-line gas chromatographs enable the effluent to be analyzed up to C_{20} components (Van Damme et al., 1981b; Van Camp et al., 1982a). The pilot plant is connected with a PDP-8E process computer which has several on-line functions:

(1) *Data Acquisition*. Temperatures, pressures, weights of hydrocarbon and water vessels on the strain gage balances and chromatograph outputs.

(2) *Data Treatment*. Integration of the chromatograph peaks and calculation of the product yields and feed rates.

(3) *Control of the Unit*. Switching of the valves in the gas chromatographs, stabilization of temperature profiles in the cracking coil by adaptation of the firing; stabilization of a given ethylene/propylene ratio, control of the feed flow rates.

REACTOR EFFLUENT ANALYSIS

Figure 1 shows a schematic view of the sampling and analysis section. The pressure is recorded (1) and controlled by means of a restriction valve (2). A constant nitrogen flow (3), metered by a mass flow controller, is mixed with the effluent gas and used as an internal standard for the gas chromatographic analysis. A sample for C_5^+ analysis is taken at 350 to 400°C. The sampling system is contained in an oven (4) heated at 300°C and consists of a cyclone (5), a high-temperature injection valve (6) and a glass splitter (7). The sample is led to the gas chromatograph through a capillary line, coated with OV-1 and kept at 200°C. The reactor effluent is then cooled to some 150°C by means of an oil cooler (8). Condensed hydrocarbons and coke particles are removed by a liquid separator (9) and a cyclone (10). A fraction of the product stream is withdrawn for on-line C_4^- analysis on four gas chromatographs, after removal of water in a glass cooler (11) at 45°C and separation of the condensed fraction (12). The effluent then flows through a tubular countercurrent heat exchanger (13) and is cooled to 5°C. The liquid from the liquid separators is collected to permit characterization of the pyrolysis fuel oil and pyrolysis gasoline fraction.

The complete separation of N_2 to C_4 hydrocarbons is performed by means of three gas chromatographs, equipped with precolumns to permit stripping, this reducing the total analysis time and fouling of the main column. The first gas chromatograph determines the N_2, CO and CH_4 content of the product stream on a Carbosphere column. All C_2 and heavier hydrocarbons contained in the sample are backflushed from the precolumn. The second gas chromatograph separates the N_2 + CO, CH_4, CO_2, C_2H_4, and C_2H_6 components on a Porapack N column. C_3 and heavier hydrocarbons are backflushed. All C_3 and C_4 saturates, monoolefins, diolefins and acetylenes are separated on the sebaconitrile column of the third gas chromatograph. The n-octane precolumn has a double function: it allows stripping off the C_5^+ fraction and it improves the separation between acetylene and propylene and between methylacetylene and cis-2-butene. A Carle gas chromatograph, model 357, gives the complete analysis of H_2 to C_4. The resolution in the C_4 range is not complete, however.

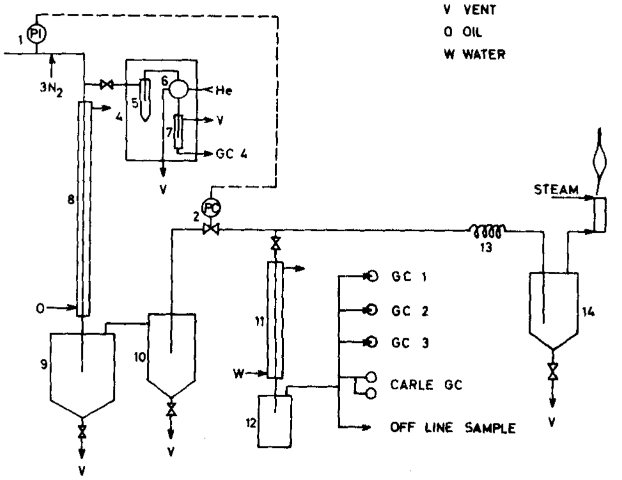

Figure 1. Reactor outlet line and sampling system.

The hot on-line gas sampling technique for the C_5^+ was developed to avoid the condensation method. Condensing a fraction of the effluent and analyzing two streams always involve material balances and recombination of the results, thus introducing errors. The separation of the C_5^+-fraction is performed on a 100 m capillary column coated with OV-101. The separation of the C_1–C_4 fraction on this column is improved by cryogenic operation. The identification of the peaks eluted from the 100 m OV-101 capillary was done by means of a GC-MS system, equipped with a computer for data processing.

The CH_4 mass flow is obtained from the N_2 to CH_4 ratio and the known mass flow of N_2. The other gas chromatographs then yield the mass flow of the C_2–C_4 components. The mass flow of the C_5^+ components is obtained by relating their responses from the C_5^+ GC with its OV-101 column to the sum C_1–C_4. This procedure, based on an internal standard, does not require any normalization. The total mass flow is obtained by summing up the individual mass flows. The mass balance can be checked. Any deficiency is caused by high boiling components which do not reach the GC detector and does not have to be spread out over all the components, as it is required in the normalization approach.

THERMAL CRACKING OF HEAVY FRACTION FROM HYDROTREATMENT

Virgin vacuum gas oil (VVGO) from Aramco was hydrotreated to various extents. The light ends were separated from the hydrotreated vacuum gas oil by distillation, leaving a heavy fraction with an initial boiling point close to that of the virgin vacuum gas oil. Gas oil HVGO-60, HVGO-40, and HVGO-20 are the heavy fraction of the hydrotreating of the virgin vacuum gas oil up to 60, 40 and 20% conversion, respectively. The hydrotreating conversion is defined as the percentage amount of hydrotreated product formed with a boiling point below the initial boiling point of the virgin vacuum gas oil.

Table 1 shows the characterization of these fractions. The feedstocks were cracked at a variety of conditions: steam dilution, 0.5 and 1.0 kg/kg; coil outlet pressure, 1.5 and 2.5 bar; coil outlet temperatures, 750, 785, 820°C. The experiments can be classified into four classes, Table 2.

The product distribution is a function of temperature, pressure, dilution and conversion. The methane yield was chosen as a measure of conversion. From the cracking of naphtha and kerosene it is known that the methane yield is a monotonically increasing

TABLE 1. FEED CHARACTERIZATION

	VVGO	HVGO-60	HVGO-40	HVGO-20	FVGO
Simulated Boiling Curve (°C)					
I.B.P.	271	230	268	270	285
5%	314	375	293	300	377
50%	428	425	404	413	433
95%	512	485	495	501	479
F.B.P.	586	513	546	553	505
d_4^{20}	0.912	0.8305	0.842	0.861	0.852
Pour Point (°C)	+30	+30	+33	+33	+36
Sulfur (wt. %)	3.01	0.001	0.001	0.007	0.76
Nitrogen (ppm)	595	5	10	10	30
H/C Molar	1.688	2.026	1.977	1.955	2.000
Mol. Wt.	345	400	359	350	392
PIONA Analysis (*wt.* %)					
N-Paraffins		6.90	8.37	6.04	
I-Paraffins	46.4	48.11	34.17	24.09	81.1
Naphthenes		38.27	49.42	47.72	
Aromatics	49.0	6.18	5.58	19.43	18.2
Resin	4.6	0.46	0.50	0.59	0.7
Loss	—	0.06	1.96	1.93	—
Structural Analysis (*wt.* %)					
C_P	62.0	80.5	70.0	64.2	73.1
C_N	18.2	18.7	30.0	31.5	22.1
C_A	19.8	0.8	0.	4.3	4.8

VVGO = virgin vacuum gas oil

HVGO-60; −40; −20 = heavy fractions of the hydrotreating of VVGO up to 60, 40 and 20% conversion

FVGO = raffinate of the furfural extraction of a vacuum gas oil

TABLE 2. CLASSIFICATION OF EXPERIMENTS

Class	Dilution (kg/kg)	Outlet Pres. (bar)	Gas Oil Partial Pres. at Inlet (bar)
1	0.5	1.5	0.14
2	1.0	1.5	0.07
3	0.5	2.5	0.23
4	1.0	2.5	0.12

function of conversion (Van Damme et al., 1981a; Van Camp and Froment, 1982b). The methane yield is also a monotonically increasing function of the equivalent space time V_E/F_o at constant dilution, whereby V_E is the equivalent reactor volume (1) and F_o the initial molar hydrocarbon flow rate (mol/s).

Froment et al. have extensively used the equivalent reactor volume concept in kinetic analyses (Van Damme et al., 1975; Froment et al., 1976, 1977). The equivalent reactor volume leads, at a given reference temperature and pressure, to the same conversion as the actual reactor volume, with its temperature and pressure profile. The dilution ratio of the feed is the same for both reactors. The following formula is obtained, for a first-order reaction:

$$V_E = \int_o^V \frac{p_t T_R}{p_{t_R} T} \exp\left[-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_R}\right)\right] dV \qquad (1)$$

The continuity equation for the equivalent reactor operating at T_R and p_R leads, after integration, to:

$$\frac{V_E}{F_o} = \frac{1}{A_o \exp\left(\frac{-E}{RT_R}\right)\left(\frac{p_{tR}}{RT_R}\right)} \int_o^x \frac{dx'}{\left(\frac{1 - x'}{1 + \delta + (\epsilon - 1)x'}\right)} \qquad (2)$$

Equation 2 clearly shows that, for a given dilution ratio, δ, the equivalent space time, V_E/F_o, completely defines the conversion. The equivalent space time is a useful concept in kinetic analysis and in scale-up. Since in industrial operation the conversion is generally not determined, an alternative measure of the severity, namely the methane yield, will be used here. Figure 2 shows that, for a given dilution (1 kg H_2O/kg HC) and total outlet pressure (1.5 bar abs.), the relation between the methane yield and the equivalent space time is practically identical for the hydrotreated vacuum gas oils and for the virgin vacuum gas oil. This justifies the use of the methane yield as a measure of severity in the comparison of product distributions obtained from the cracking of the different feedstocks.

Figures 3, 4 and 5 show the ethylene-, propylene- and butadiene yields obtained in the cracking of VVGO, HVGO-60, HVGO-40, and HVGO-20 for class 2 conditions. The ethylene yield increases with the hydrotreating conversion. The ethylene yield of VVGO is considerably lower. The propylene maximum and the butadiene yield also increase with the hydrotreating. These figures also show the yields obtained in the cracking of the raffinate of the furfural extraction of a vacuum gas oil (FVGO), which will be discussed later.

The influence of total and partial pressure on the yields of the most important products was determined in the cracking of HVGO-40, the most interesting product of hydrotreating. The relation of methane yield vs. V_E/F_o is shown in Figure 6. Two clearly distinct curves are obtained for the two dilutions, with the lowest dilution leading to the highest methane yield. A slight influence of total pressure is also observed.

When the conversion is plotted vs. V_E/F_o two curves related to the dilution are obtained, but there is no total pressure dependence, since the latter is accounted for by V_E/F_o. Pending a more appropriate factor as a substitute for conversion, the methane yield will still be retained as a measure of severity in what follows. Figures 7, 8 and 9 show the ethylene-, propylene- and butadiene yield plotted vs. the methane yield for HVGO-40. Figure 10 represents the aromatics yield. No influence of partial pressure on the BTX yield is observed. Notice the rapid rise of the benzene yield as the severity is increased. Table 3 summarizes the trends of the influence of partial and total pressure on the yields of the main products.

HYDROTREATED VACUUM GAS OIL *VS.* A RAFFINATE OF FURFURAL EXTRACTION OF A VACUUM GAS OIL

A raffinate of the furfural extraction of a vacuum gas oil (FVGO), characterized in Table 1, was cracked under the same conditions as the hydrotreated vacuum gas oils HVGO-60, HVGO-40, and HVGO-20. Figures 3, 4 and 5 contain curves showing the ethylene, propylene and butadiene yields from this furfural raffinate. The ethylene yield is lower than that from HVGO-40 and so is the propylene yield. The butadiene yield is

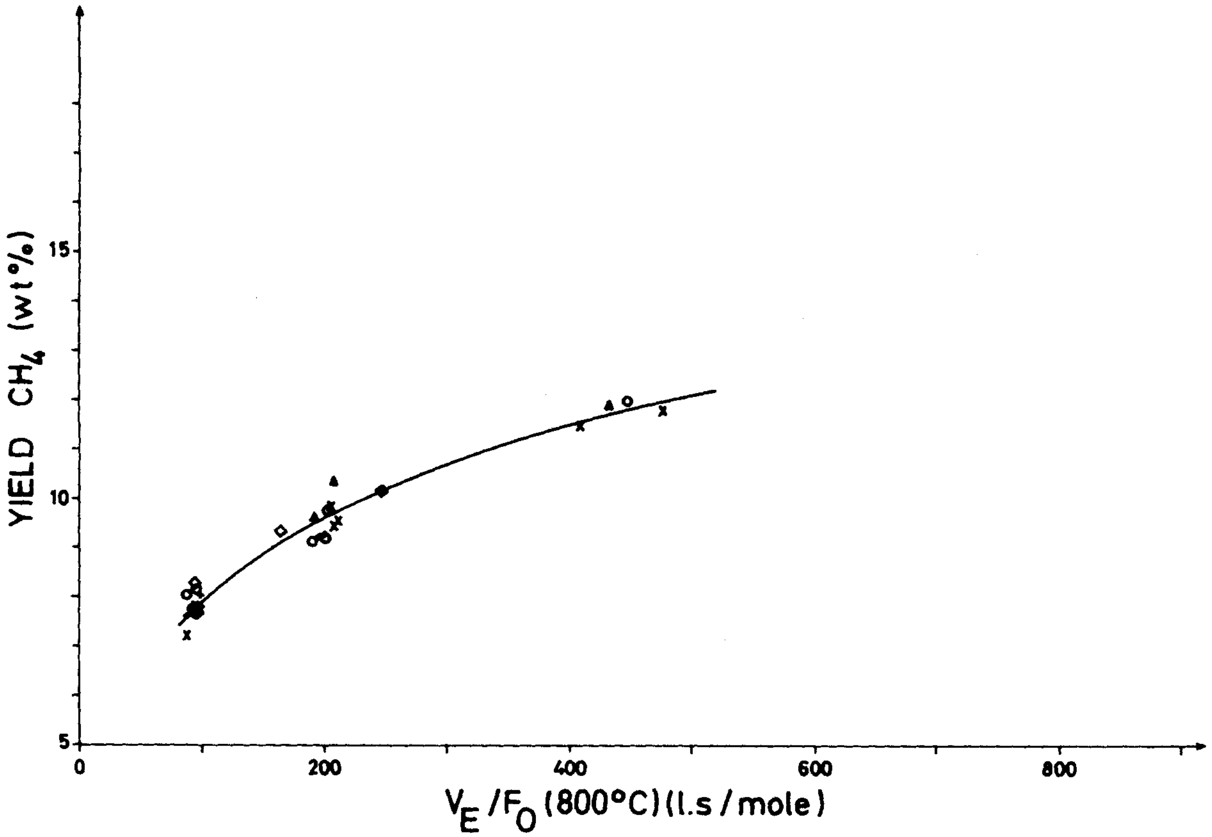

Figure 2. Methane yield vs. equivalent space time, V_E/F_o, for the different feedstocks (class 2 as defined in Table 2): ⏀ HVGO-60; △ HVGO-40; + HVGO-20; x FVGO; ◇ VVGO.

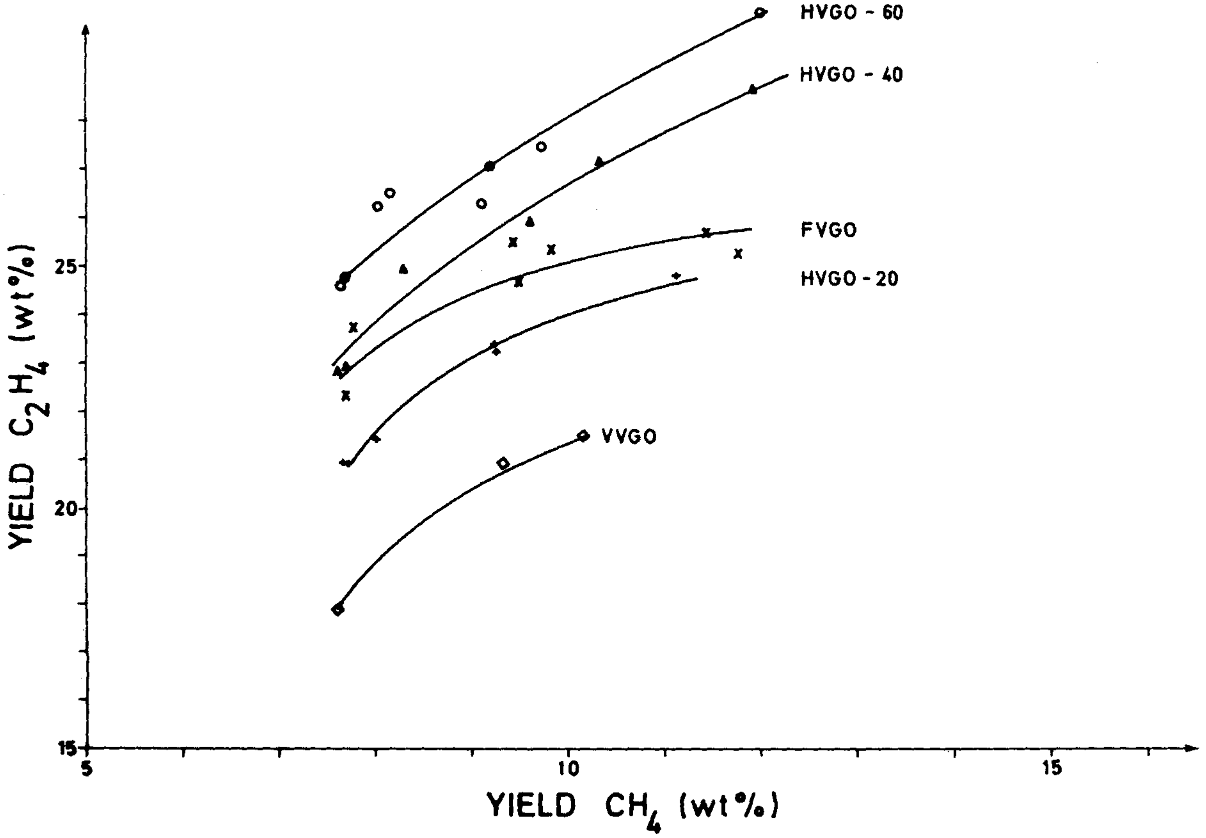

Figure 3. Ethylene yield vs. methane yield for the different feedstocks (class 2): ⏀ HVGO-60; △ HVGO-40; + HVGO-20; x FVGO; ◇ VVGO.

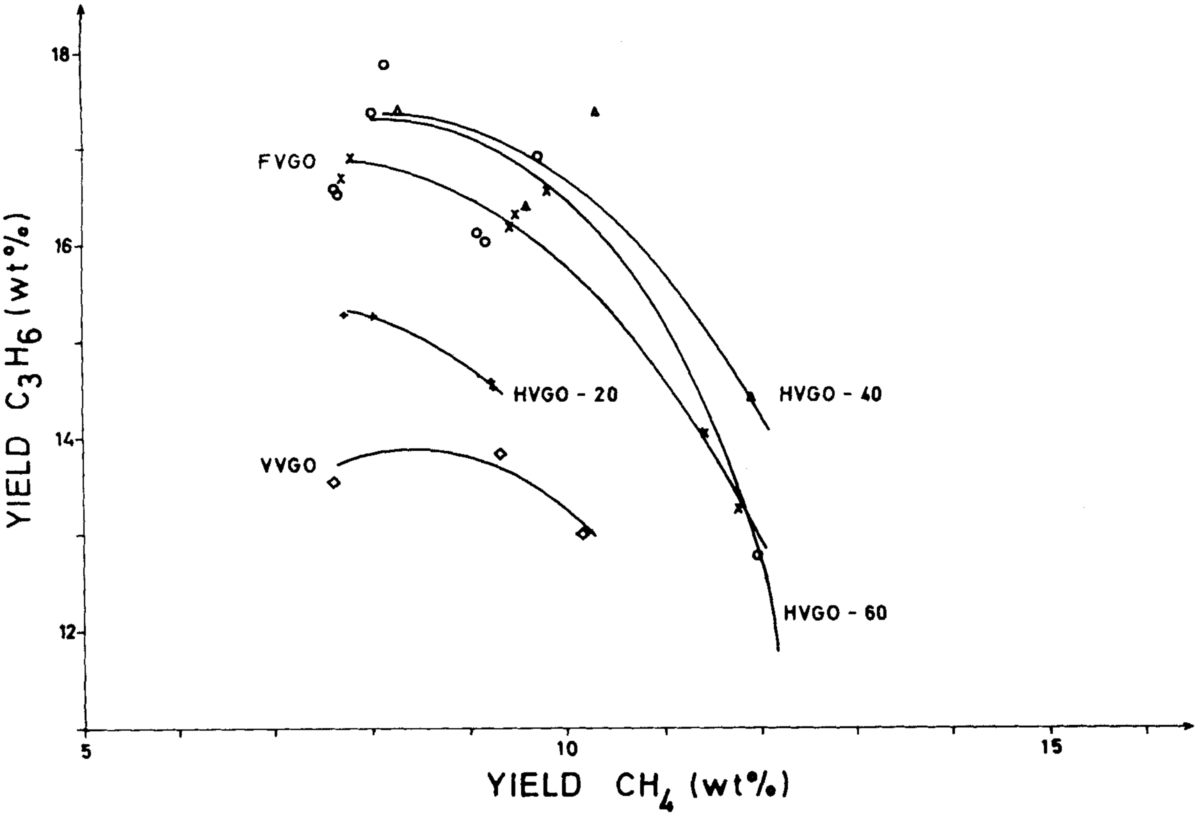

Figure 4. Propylene yield vs. methane yield for the different feedstocks (class 2): ⦶ HVGO-60; △ HVGO-40; + HVGO-20; x FVGO; ◇ VVGO.

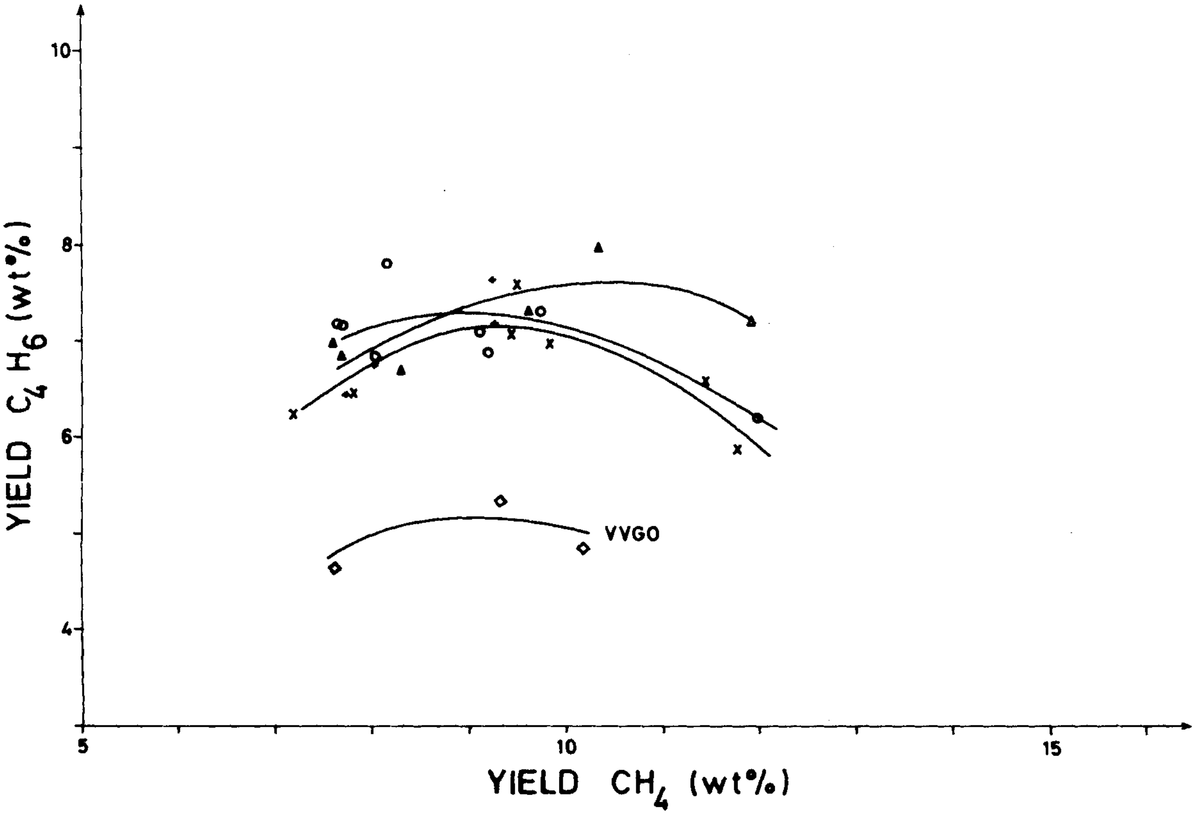

Figure 5. Butadiene yield vs. methane yield for the different feedstocks (class 2): ⦶ HVGO-60; △ HVGO-40; + HVGO-20; x FVGO; ◇ VVGO.

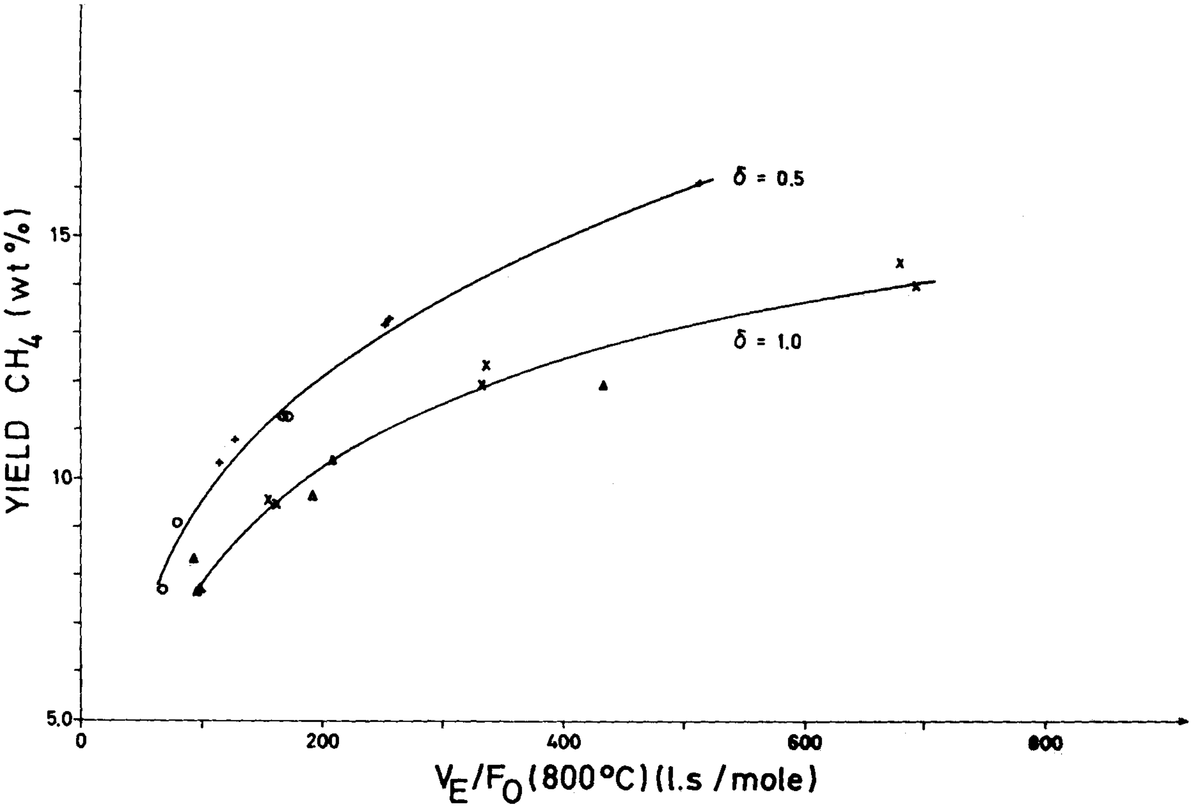

Figure 6. Methane yield vs. equivalent space time V_E/F_o for feedstock HVGO-40.

	Class ↓	p_t (bar)	Dilution (kg H_2O/kg HC)
○	1	1.5	0.5
△	2	1.5	1.0
+	3	2.5	0.5
x	4	2.5	1.0

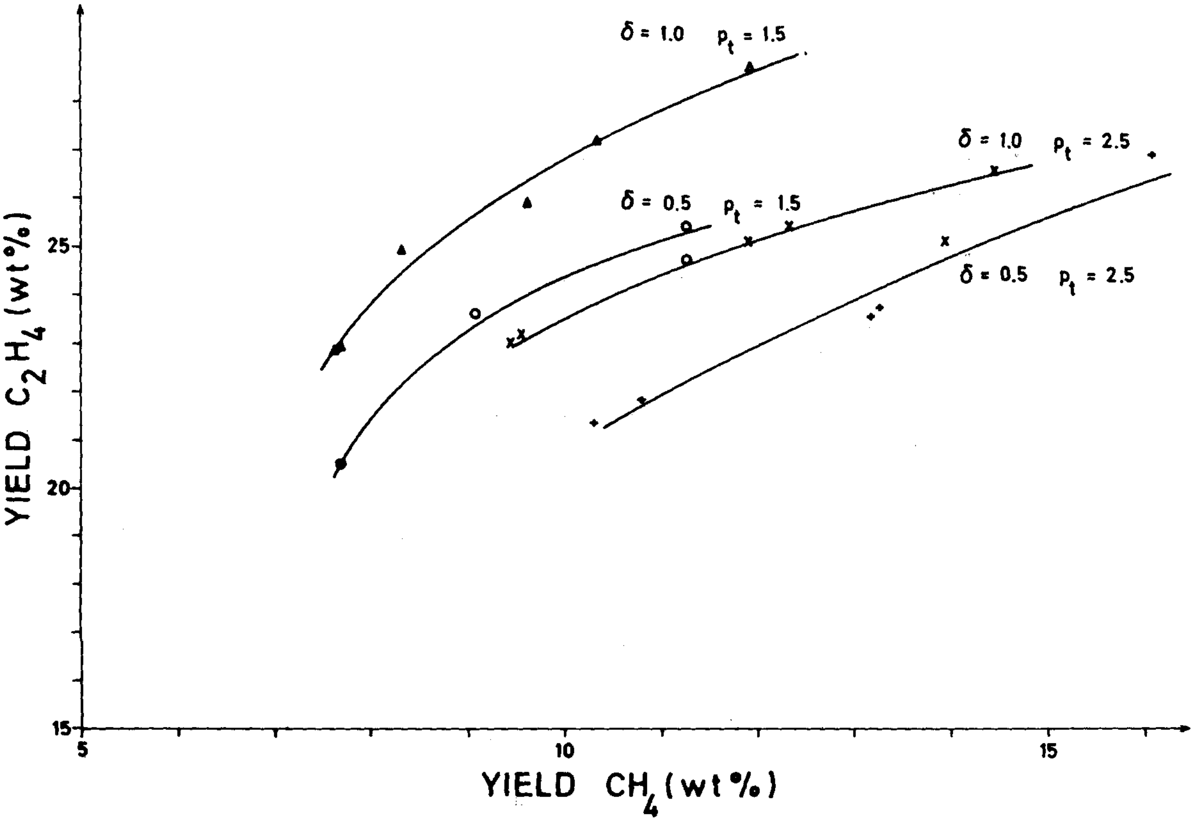

Figure 7. Ethylene yield vs. methane yield for feedstock HVGO-40: ○ class 1; △ class 2; + class 3; x class 4.

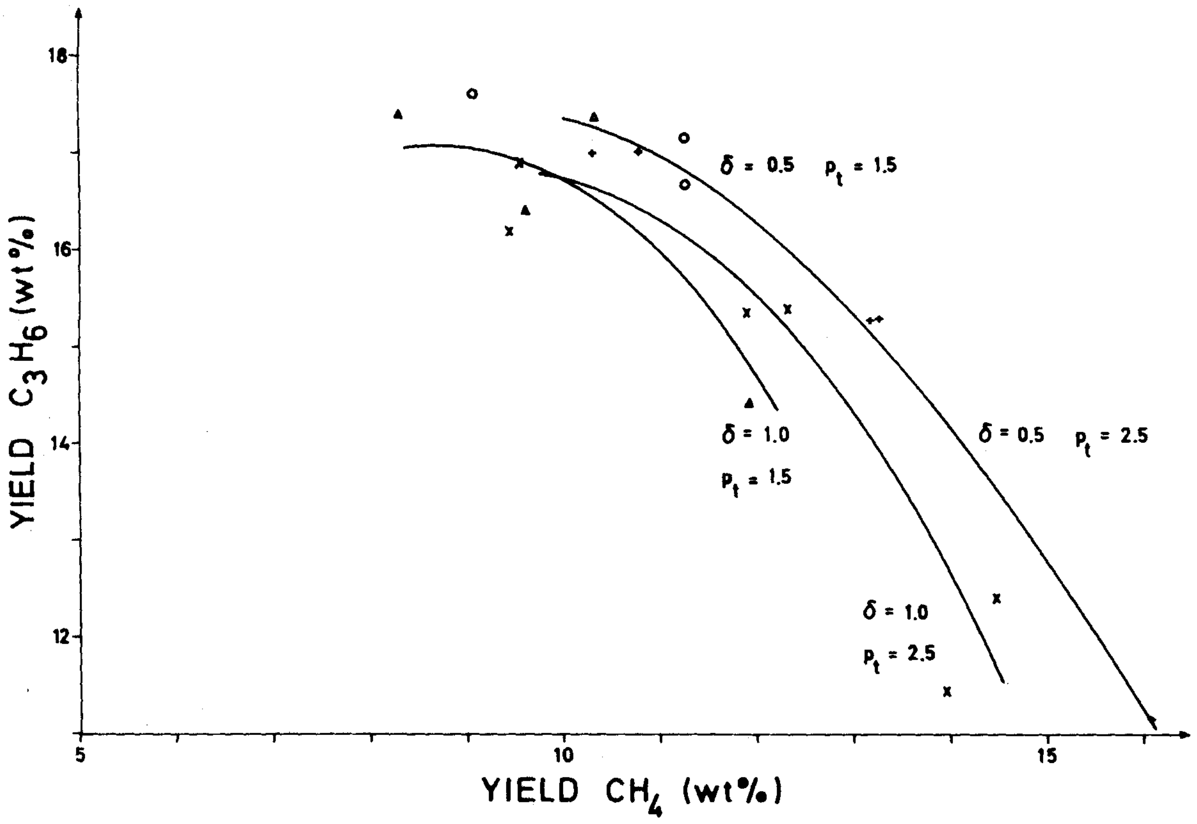

Figure 8. Propylene yield vs. methane yield for HVGO-40: ○ class 1; △ class 2; + class 3; x class 4.

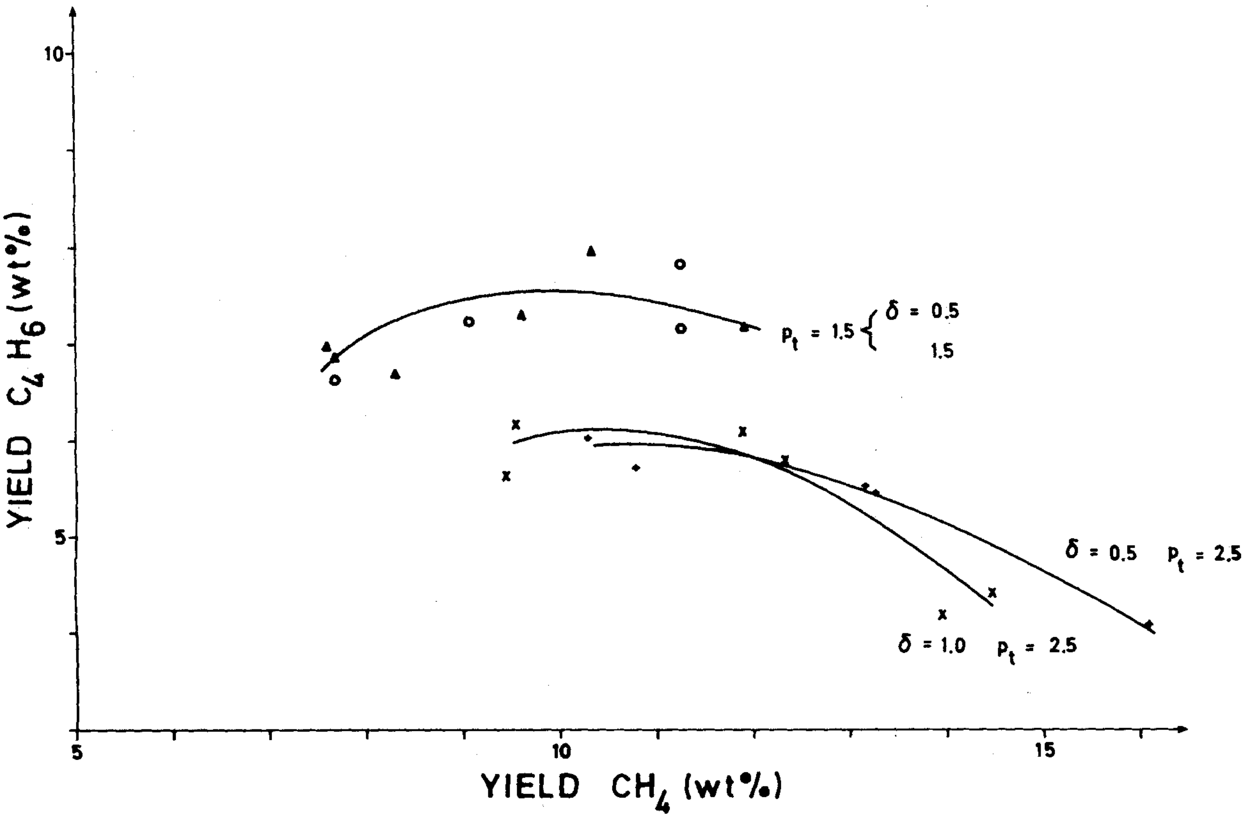

Figure 9. Butadiene yield vs. methane yield for HVGO-40: ○ class 1; △ class 2; + class 3; x class 4.

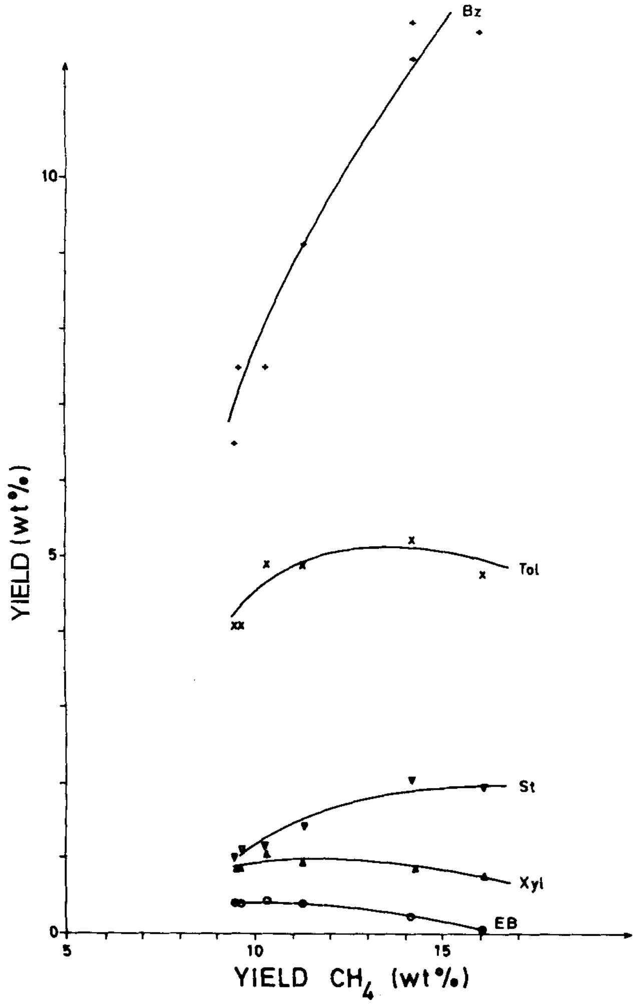

Figure 10. Aromatics yield vs. methane yield for HVGO-40: + Benzene; x Toluene; △ Xylene; ▽ Styrene; ○ Ethylbenzene.

close to that from HVGO-60. An important drawback of the selective aromatics extraction as compared with the hydrotreatment is the absence of an interesting application for the extracted polyaromatics.

TABLE 3. INFLUENCE OF PRESSURE ON THE PRODUCT DISTRIBUTION OF HYDROTREATED GAS OIL CRACKING

	Increase of Gas Oil Inlet Partial Pres.	Increase of Exit Total Pres.
H_2	−	−
CH_4	+	+
C_2H_2	−	−
C_2H_4	−	−
C_2H_6	+	+
C_3H_6		
Up to Maximum	0	0
Beyond Maximum	+	+
1,3-C_4H_6		
Up to Maximum	+	0
Beyond Maximum	−	−
1-C_4H_8 (Beyond Maximum)	+	+
2-C_4H_8 (Beyond Maximum)	+	+
i-C_4H_8 (Beyond Maximum)	+	+
C_5^+	+	+

+ = increase in yield; − = decrease in yield.

TABLE 4. CHARACTERIZATION OF THE FRACTIONS FOR A VVGO CONVERSION OF 43%

	(HN)	(HK)	(HG)	(350^+)
Yield (wt. %)	10	10	23	57
d_4^{15}	0.7615	0.8435	0.853	0.846
ASTM Boiling Range (°C)				
I.B.P.	53	202	272	312
5%	79	208	277	328
50%	127	219	301	417
95%	171	244	363	501
F.B.P.	179	259	369	520
Simulated Boiling Curve (°C)				
I.B.P.				281
5%				314
50%				414
95%				510
F.B.P.				560
Mol. wt.	104	200	228	363
PIONA (*wt. %*)				
N-Paraffins	13.9	20.7	14.5	89.9
I-Paraffins	21.6			
Naphthenes	40.7	58.3	66.4	
Aromatics	23.8	21.0	19.1	10.1
H/C, Molar	1.938	1.834	1.843	1.888

THERMAL CRACKING OF LIGHT FRACTIONS

The light end, formed in the hydrotreater, was separated into three fractions with a boiling range corresponding to full-range naphtha (I.B.P.–175°C), to kerosene (175–250°C) and to atmospheric gas oil (250–350°C). The fractions (I.B.P.–175°C), (175–250°C), (250–350°C) are called (HN), (HK), (HG) respectively. When the hydrotreater is integrated in a chemical complex and there is no refinery in the vicinity, it may be necessary to use these fractions as thermal cracking feedstocks.

The three light fractions considered here are products of the hydrotreating of virgin vacuum gas oil at 43% conversion. The heavy fraction (350^+) was also cracked for comparison. The feed characterization is summarized in Table 4. These fractions are more naphthenic than the usual straight-run naphthas, kerosenes and gas oils.

The fractions were cracked under Class 2 conditions (dilution, 1.0 kg/kg; exit pressure, 1.5 bar) and temperatures ranging from 785 to 880°C. The Figures 11–15 show the ethylene, propylene, butadiene and BTX yields from the four fractions as a function of the methane yield. The ethylene yields increase in the order: (HK) < (HN) < (HG) < (350^+). The fraction (HK) has the lowest yields for the main olefins. The fraction (350^+) leads to the highest olefin yields. The fraction (HG) has higher olefin yields than the fraction (HN), except for the butenes. The BTX yield decreases in the order (HN) > (HK) > (HG) > (350^+). This is explained by the fact that the BTX yield strongly depends on the amount of monoaromatics in the feed. The yield of pyrolysis fuel oil is highest for the heavy fractions.

The low ethylene yields of the light fractions can be explained by their high aromatics and naphthenes contents. For the fractions (HN) and (HK), the alkyl groups substituted on the aromatic and saturated rings are nearly exclusively methyl and ethyl side chains, so that the contribution of the side chains to the olefin yield is low. In spite of its high naphthene content, the (350^+) fraction is rich in paraffinic carbon atoms and therefore in paraffinic side chains. The comparison of (HG) with naphthenic atmospheric gas oils shows only small differences in the olefin yields. The thermal cracking of paraffinic gas oils clearly leads to higher ethylene yields. The benzene yield of the fraction (HG) exceeds that of straight-run atmospheric gas oils (2 wt. % and more), while the toluene and xylene yields are nearly the same.

The ethylene yield of (HK) is about 4 wt. % lower and the total C_4^- yield is about 5 wt. % lower than that obtained from straight-run kerosene cracking (Van Camp and Froment, 1983). The lower ethylene yield is caused by the lower paraffin content in the feed. The BTX yield is higher. The fraction (HN) leads to extremely low olefin yields. The BTX yields are higher than those observed in the

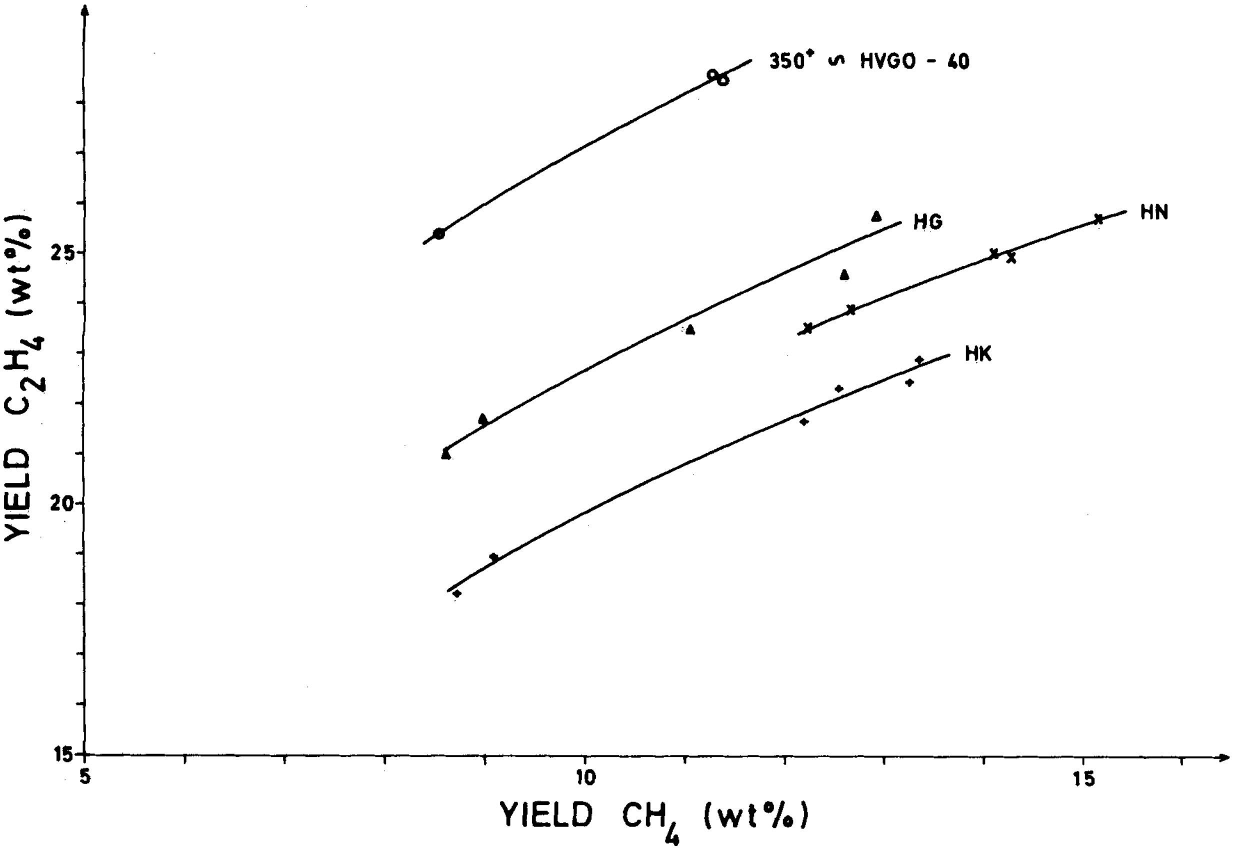

Figure 11. Ethylene yield vs. methane yield (class 2): Φ (350^+); △ (HG); + (HK); x (HN).

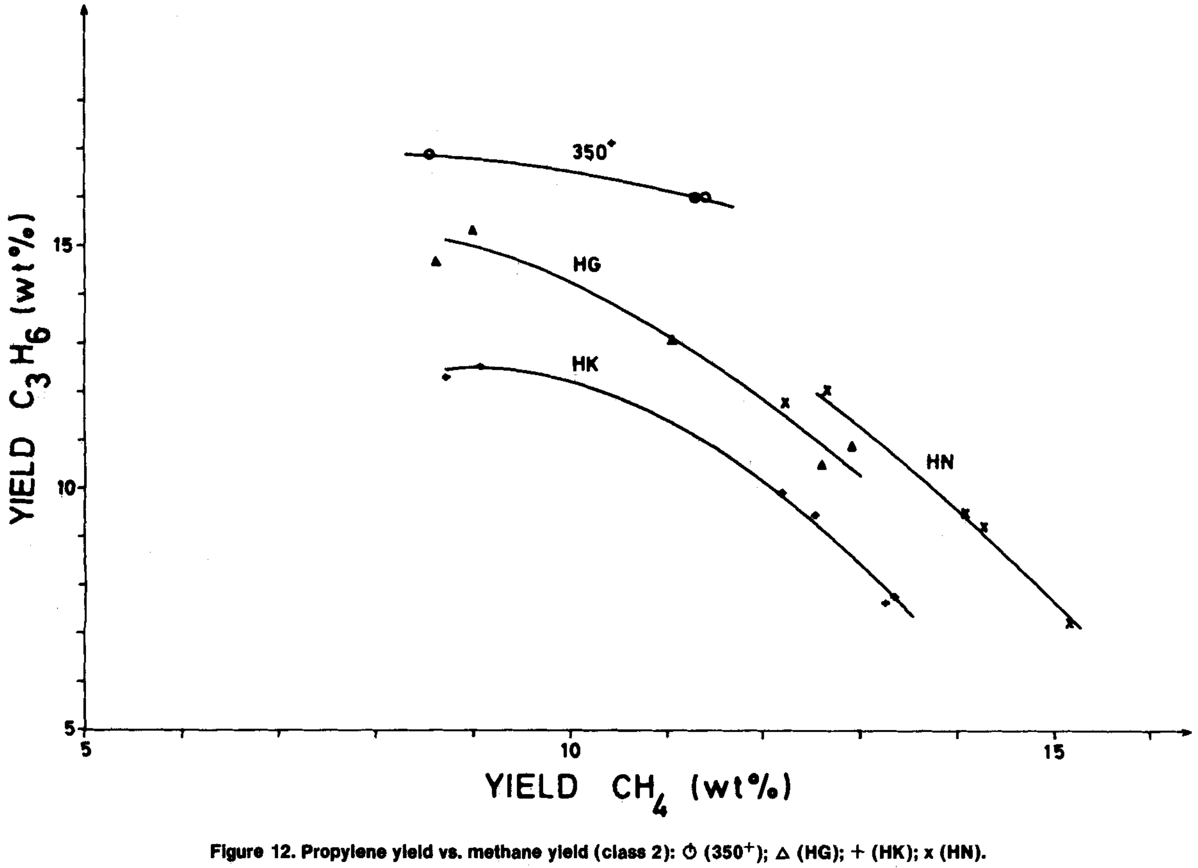

Figure 12. Propylene yield vs. methane yield (class 2): Φ (350^+); △ (HG); + (HK); x (HN).

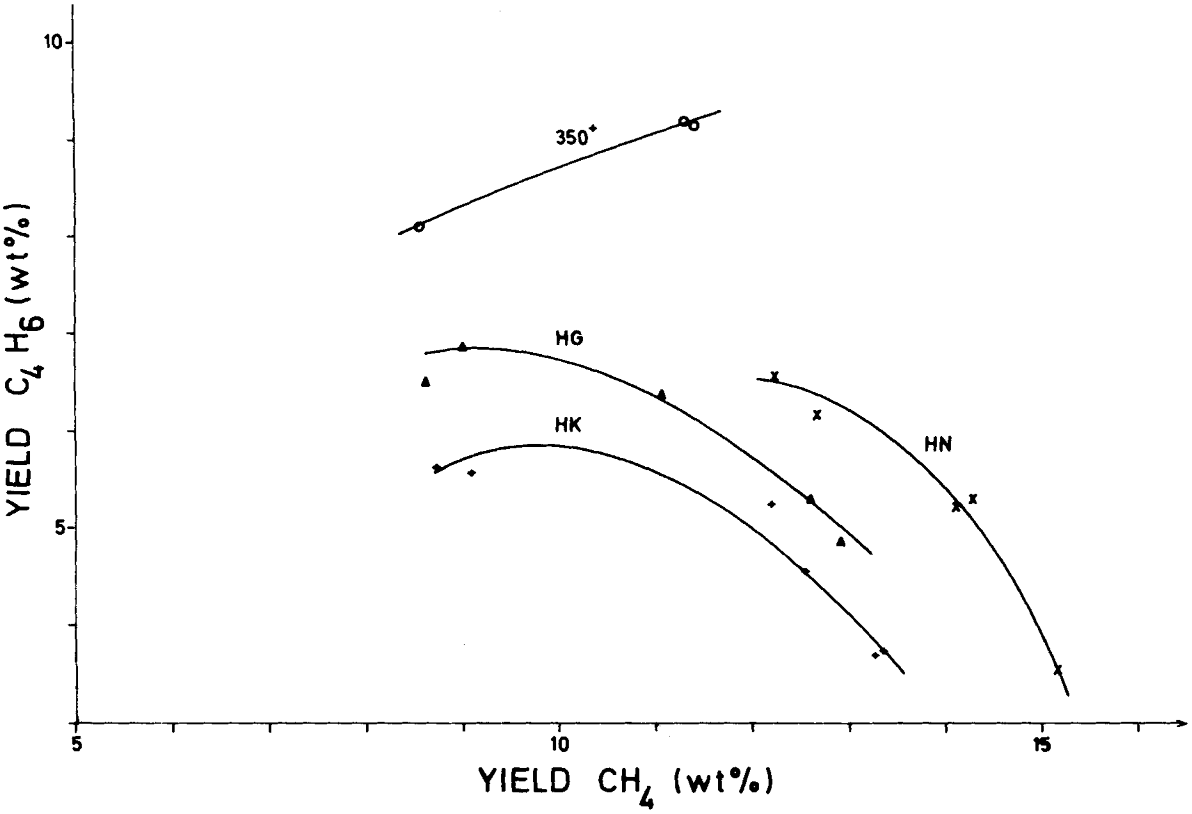

Figure 13. Butadiene yield vs. methane yield (class 2): ⌽ (350⁺); △ (HG); + (HK); x (HN).

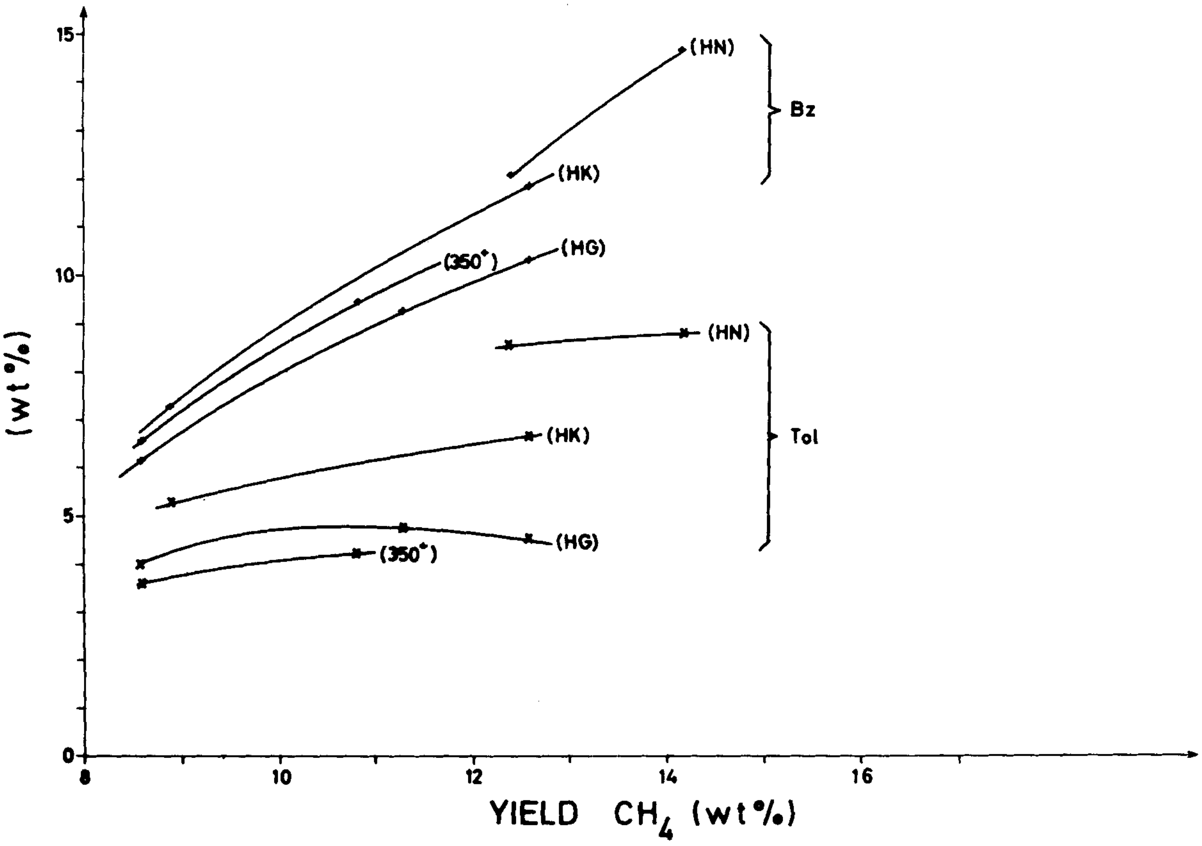

Figure 14. Benzene and toluene yields vs. methane yield for the four fractions (class 2): + Benzene; x Toluene.

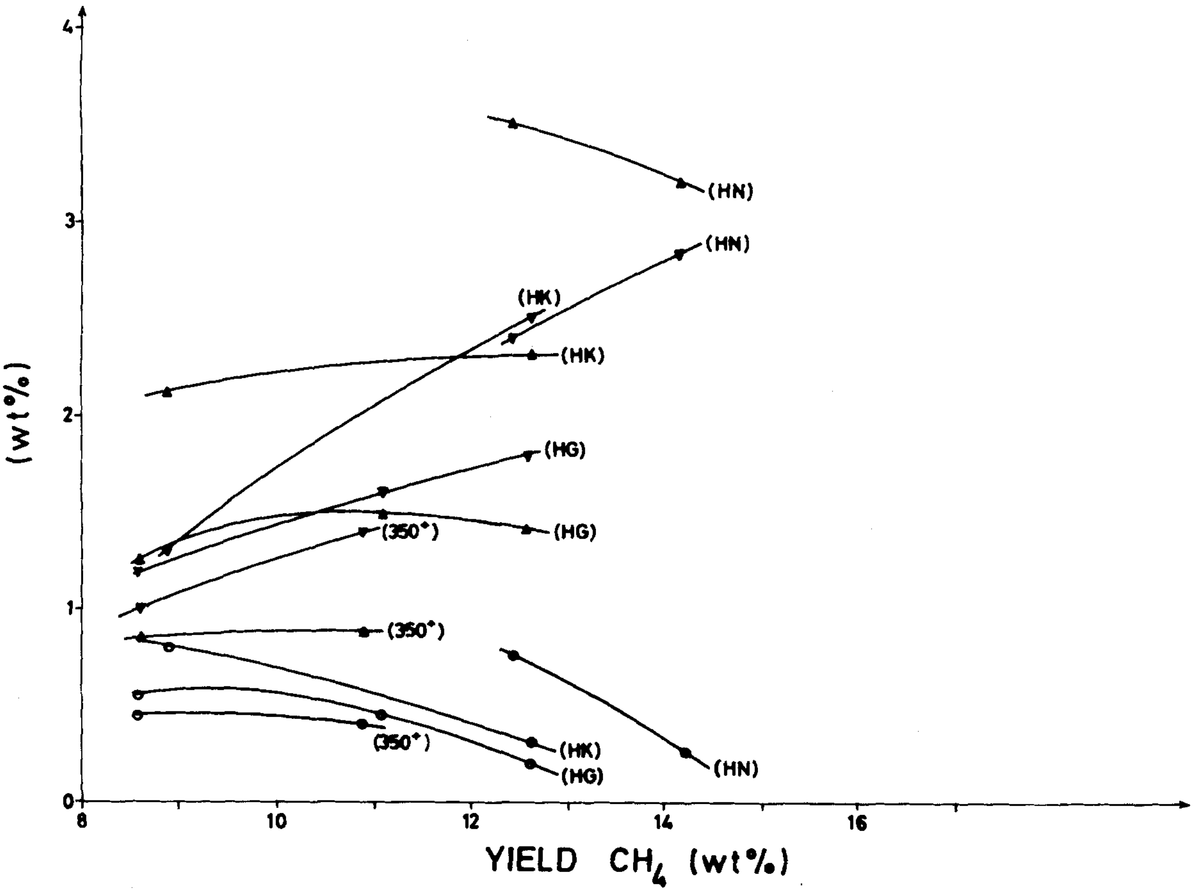

Figure 15. Xylene, styrene and ethylbenzene yields vs. methane yield for the four fractions (class 2): △ Xylene; ▽ Styrene; ○ Ethylbenzene.

thermal cracking of straight-run naphtha: the benzene yield increases to 15 wt. % and the toluene yield to 9 wt. %. The differences with straight-run naphtha can be explained by the high aromatics and naphthenes and the low paraffin content in the fraction (HN).

It can be concluded that the light fractions are notably poorer feedstocks for thermal cracking than the 350^+ fraction. The fraction (HG) is roughly equivalent to naphthenic atmospheric gas oil in this respect. The fraction (HK) is evidently less suitable than straight-run kerosene and (HN) is definitely a poor feedstock when compared with straight-run naphtha. In the appraisal of the values of these feedstocks the BTX fraction is important, because of the high yields (29 wt. % BTX for the fraction (HN) at high severity cracking).

From the above results it can be calculated that, for high-severity separate cracking of the fractions obtained from the hydrotreating, the once-through ethylene yield would be 27 wt. %, based on the total feed, for the conditions of Class 2. The cracking of the total liquid effluent of the hydrotreater would lead to much lower olefin yields, because the cracking severity has to be kept low, whereas in the first case each fraction can be cracked under specific optimal conditions.

Other possible applications of the light fractions can be more interesting; e.g., the fraction (HN) is an excellent feedstock for catalytic reforming.

ACKNOWLEDGMENT

P. J. Clymans is grateful to the Belgian Instituut ter Bevordering van het Wetenschappelijk Onderzoek in Nijverheid en Landbouw for a Research Fellowship.

NOTATION

A_o = frequency factor (s^{-1})
E = activation energy (kJ/kmol)
F_o = feed flow rate (kmol/s)
p_t = total pressure (bar)
p_{tR} = reference total pressure (bar)
T = temperature (K)
T_R = reference temperature (K)
V = reactor volume (m^3)
V_E = equivalent reactor volume (m^3)
x = molar conversion
ϵ = expansion (mol product/mol feed cracked)
δ = dilution (Eq. 2 in mol steam/mol hydrocarbon fed)

LITERATURE CITED

Froment, G. F., B. O. Van de Steene, and P. S. Van Damme, "Thermal Cracking of Ethane and Ethane Propane Mixtures," *I. & E.C. Process Design & Dev.*, **15**, 495 (1976).

Froment, G. F., B. O. Van de Steene, P. J. Vanden Berghe, and A. G. Goossens, "Thermal Cracking of Light Hydrocarbons and their Mixtures," *AIChE J.*, **23**, 93 (1977).

Goetzmann, S., W. Kreuter, and H. J. Wernicke, "Hydroconversion Upgrades Heavy Olefin Feedstocks," *Hydroc. Process.*, 109 (June, 1979).

Kaiser, V., P. J. Clymans, G. F. Froment, and S. Barendregt, "Hydrotreated Vacuum Gas Oil as a Feedstock for Olefins Production: A Technical and Economical Evaluation," *Proc. of Large Chem. Plants Symp.*, Ed., G. Froment, Antwerp, Belgium (1982).

Korosi, A., P. S. Virk, and H. N. Woebcke, "Pyrolysis of Virgin and Hydrogenated Gas Oil," *A.C.S.*, No. 183, 77 (1979).

Rhoé, A., "VGO Hydrogenation Reaps Benefits in Olefin Production," *Oil and Gas J.*, 164 (Jan. 26, 1981).

Van Camp, C. E., P. J. Clymans, P. S. Van Damme, and G. F. Froment, "Qualitative and Quantitative On-Line Analysis of Thermal Cracker Effluent by G.C.," *J. of Chromat. Sci.*, **21**, 259 (1983).

Schneider, W., E. Müller, R. Zschocke, and E. Onderka, "The LEUNA-Hydrocracking—Process for Vacuum Gas Oil," *Chem. Techn.* 508 (Oct., 1981).

Van Camp, C. E., P. S. Van Damme, and G. F. Froment, "The Thermal Cracking of Kerosene," *I. & E.C. Process Design & Dev.*, (1983).

Van Damme, P. S., S. Narayanan, and G. F. Froment, "Thermal Cracking of Propane and Propane-Propylene Mixtures: Pilot Plant vs. Industrial Data," *AIChE J.*, **21**, 1065 (1975).

Van Damme, P. S., G. F. Froment, and W. B. Balthasar, "Scaling-Up of Naphtha Cracking Coils," *I. & E.C. Process Design & Dev.*, **20**, 366 (1981).

Van Damme, P. S., C. E. Van Camp, P. S. Clymans, and G. F. Froment, "Hot On-line Sampling Improves Reactor Control," *Oil and Gas J.*, 124 (Sept. 7, 1981).

Wernicke, H. J., and W. Kreuter, "Pretread Feed for More Olefins," *Hydroc. Process.*, 137 (Oct., 1979).

Manuscript received April 27, 1983; revision received July 12, and accepted July 14, 1983.

Initial Value Approach to a Class of Reaction-Diffusion Systems

New sets of transformations that convert an original two-point boundary value problem into an equivalent initial value problem have been proposed and illustrated in the solution of the diffusion-reaction problem for a monodispersed catalyst pellet. The use of the transformations reduces the computational effort considerably. The method is especially useful in the analysis of more complex cases, such as bidispersed catalyst pellets, catalysts undergoing decay, and gas-solid noncatalytic reactions where the use of the conventional numerical techniques is quite involved and cumbersome. The method is applied to some known and to some yet-unresolved cases and the new results obtained are discussed.

A. N. NAMJOSHI,
B. D. KULKARNI, and
L. K. DORAISWAMY

National Chemical Laboratory
Poona 411 008, India

SCOPE

The literature is replete with solutions to a variety of reaction-diffusion problems (Aris, 1975; Carberry, 1976). Typically, in these problems one obtains a second-order differential equation with boundary conditions specified at two different locations leading to a boundary value problem. The solution to boundary value problems, specially nonlinear, is considerably involved and great attention has been devoted in the past to reduce the attendant numerical complexities (Kubicek and Hlavacek, 1970; 1971 a,b,c; Hanna, 1980; Michelsen and Villadsen, 1978; Finlayson, 1974; Jayaraman et al., 1982). Approximate methods leading to simple algebraic expressions for effectiveness factors have also been proposed in the literature (Churchill, 1977; Wedel and Luss, 1980; Sundaram, 1981; Gottifredi et al., 1980 a,b). While reliable methods of solution such as that of Weisz and Hicks (1962) exist for monoporous systems, their use in more complex cases such as for systems with mass transfer limitations, bidispersed catalysts, catalysts undergoing decay, or gas-solid noncatalytic systems, is fairly involved and cumbersome. General numerical methods that avoid trial and error to obtain solutions to similar complex cases have been proposed by Wendt et al. (1979), Hahn and Wendt (1982), and Hahn and Shadman (1983).

In most practical cases one has to deal with multicomponent reacting and diffusing species which lead to more than one nonlinear equation. Depending on the nature of coupling involved among the phenomenological equations describing the system, suitable methods that avoid trial and error have been devised. Thus when the coupling occurs in the rate terms, the general method proposed by Wendt et al. (1979), Hahn and Wendt (1982), and Hahn and Shadman (1983) can be employed. A suitable variant of these methods may be necessary when the governing equation involves additional coupling such as at the boundary conditions.

In the present work we propose new sets of transformations for several different rate forms, the use of which leads to an equivalent initial value problem. This makes it possible to gain computational advantage over the existing methods. In the first phase of this work, the intention being to develop and test these transformations, their use has been restricted to simple monodispersed catalyst pellets. Some known systems (rate forms) are therefore first studied and the results obtained are compared with the earlier (known) results. Some new rate forms have also been analyzed.

Subsequently the method is extended to the case where interphase diffusion is present and then to the case where all the three resistances—flow, interphase and intraphase—are present. Finally, the applicability of the method is demonstrated for more complex situations such as those encountered in bidispersed catalysts with Langmuir-Hinshelwood (L-H) kinetics, not analyzed before. The results obtained throw significant light on the behavior of such systems.

CONCLUSIONS AND SIGNIFICANCE

A vast body of literature exists on diffusion-reaction in a catalyst pellet. In spite of this, there is need for newer and simpler methods of solution, particularly applicable to more realistic situations than considered so far, such as reaction with complex kinetics in a biporous catalyst matrix. A few such situations have been considered in the present anlalysis, after confirming the validity of the proposed method of solution by first applying it to established situations. The method developed