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(54) Dispersed catalyst cracking with methanol as a coreactant.

(57) A catalytic cracking process is described in which an oxygenate, e.g., methanol, is a coreactant with an oil, e.g., a gas oil in combination with an acidic catalyst, preferably finely divided ZSM-5. The exothermic methanol conversion reaction is approximately heat balanced by the endothermic catalytic cracking reaction.

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DISPERSED CATALYST CRACKING WITH METHANOL AS A COREACTANT

This invention relates to fluid catalytic cracking of a mixture of hydrocarbon oils and methanol in the presence of a dispersion of fine zeolite particles, exemplified by ZSM-5.

The use of zeolite catalysts based on rare-earth exchanged zeolites X and Y has become widely accepted by the petroleum industry for cracking gas oil to make gasoline and fuel oil. Most known or proposed processes which involve zeolite catalyzed hydrocarbon reactions utilize a fixed bed reactor with particles of 2 mm or more diameter or a fluidized bed of catalyst, as in FCC cracking, with particle sizes from 1 to 140 microns, with an average particle size of about 60 microns. In all of these processes the reaction is conducted with a relatively large amount of catalyst in contact with the feed at any given instant.

U.S. Patent 3,951,781 teaches mixing a hydrogen donor (e.g., CH_3OH, C_2H_5OH, ethers, and the like) with de-asphalted resid before fluid catalytic cracking. The ratio of methanol to hydrocarbon charge is 0.01 to 5, preferably 0.05 to 0.30 on a stoichiometric basis but is varied as a function of the hydrogen deficiency of a raffinate obtained from solvent deasphalting a vacuum tower bottoms, the amount of sulfur, nitrogen, and oxygen in the raffinate, the amount of polycyclic aromatics, the catalytic composition employed, and the level of conversion desired. It is significant that it is preferred to avoid any considerable or significant excess of methanol with the charge because of methanol's tendency to react with itself under some conditions.

U.S. Patent 3,974,063 teaches the conversion of nitrogen-containing oil stock, such as shale oil syn crudes, by cracking in the presence of C_2-C_5 hydrocarbons and/or methanol with an acidic zeolite cracking catalyst. Co-cracking of the high nitrogen stock with the carbon-hydrogen contributors provides appreciable denitrogenation of the charge, thus decreasing the need for further hydroprocessing. The reactions are promoted by a mixture of large and small pore zeolites in the presence of hydrogen donors at (900-1000°F) 482-593°C, a hydrocarbon residence time of 0.5 seconds to 5 minutes, using 2-15 wt.% faujasite and/or mordenite zeolite, dispersed in a matrix. Pressure is generally less than 800 kPa (100 psig). The ratio of methanol to hydrocarbon in the charge is 0.01 to 5, preferably 0.05 to 0.30 on a stoichiometric basis.

U.S. Patent 4,002,557 describes mixing an H_2-rich, H_2-donor, or H_2-generating material, such as methanol, with gas oil, and then preheating, admixing with catalyst, and reacting in an FCC unit. It is preferred to avoid providing any considerable or significant excess of methanol with a charge because of its tendency to react with itself under some conditions.

U.S. Patent 4,263,126 is directed to converting waxy or viscous hydrocarbon oils to lower the pour point or provide less viscous oils. Reactive dispersions of zeolites, such as HZSM-5, HZSM-11, HZSM-12, HZSM-23, HZSM-35, and HZSM-38, are used as an extremely fine powder having a particle size of less than 0.01 to 5 microns. It is preferred to use the as-formed powder since this is convenient and least expensive if no separation or reuse of the particles is required. The reactive dispersion is heated to 200-500°C for a time effective to induce conversion, usually from 0.1 to 72 hours.

U.S. Patent 4,328,834 teaches conversion of methanol, or a mixture of lower alcohols and related oxygenates such as ethers, aldehydes, and ketones, in the presence of a special type of zeolite catalyst maintained in an upflowing fluid condition and comprising a dispersed catalyst phase riser contact zone discharging into a more dense upflowing fluid mass of catalyst particles. The riser residence time is 1-10 seconds, and in the more dense phase is 5 to 80 seconds. The catalyst density in the riser is 0.016 to 0.24 g/cc (1-15 pounds per cubic foot) and in the dense phase is 0.32 to 0.64 g/cc (20 to 40 pounds per cubic foot). Heat exchangers limit temperature rise to 195°F (108°C) and the dense fluid bed temperature to (427°C) 800°F , preferably below 765°F (407°C). The reactor pressure at the bottom of the dense bed is restricted to 2-2.5 atmospheres. The catalyst is a zeolite having high silica-to-alumina mol rations and high activity, even when the silica-to-alumina mol ratio exceeds 30.

Activity is generally defined in terms of an alpha value. Alpha activity is defined in U.S. Patent No. 3,354,078 and the Journal of Catalysis, Vol. IV, pages 522-529, August 1965.

Generally, ZSM-5 zeolites are activated by calcining to remove water and organic templates. Calcination is achieved by heating the zeolite in air, hydrogen, or an inert gas such as nitrogen so that the desired activity is obtained. Typically, the heat treatment proceeds for at least 1 hour, although heating may last between 1-24 hours. The heat treatment is dry (no water) although up to 3% by weight of steam may be included in the calcining atmosphere.

Catalytic cracking is an endothermic process which, at relatively high reaction rates, can become thermally self-quenching. The catalyst is regenerated by burning off coke to create maximum temperatures of about (730°C) 1350°F. The hot catalyst is then recirculated for admixture with the incoming oil. Preferably, the catalyst is a zeolite embedded in a matrix of relatively inert material which acts as a heat sink for transporting heat from the regenerator to the cracking unit. All amorphous catalysts are also used.

Since the discovery of highly active zeolite cracking catalysts, the use of such zeolite crystals without the accompaniment of a large amount of inert materials has long been sought as a major improvement of the catalytic cracking process. However, it has been impractical to do so without a means of supplying heat to the reactor.

A reverse difficulty has arisen with highly exothermic reactions of Fischer-Tropsch synthesis, the oxo process, and oxygenate conversions. Attempts have been made to balance such exothermic and endothermic reactions by transferring heat through heat exchangers, but a method for achieving a more sensitive heat balance therebetween is needed.

A way has now been discovered to balance the endothermic FCC cracking reaction with the exothermic reactions discussed above, and simultaneously improve the cracking reaction by minimizing coke make.

Accordingly, the present invention provides a process for catalytic cracking of a hydrocarbon without catalyst regeneration, characterised by contacting in a reactor a hydrocarbon, a carbon oxygenate, and a finely divided and highly active zeolite catalyst capable of cracking the hydrocarbon and exothermically converting the carbon oxygenate to a hydrocarbon of increased carbon content and wherein at least a majority of the heat of reaction of the endothermic catalytic cracking reaction is supplied by the exothermic conversion of oxygenates to hydrocarbons.

Fig. 1 is a schematic flow sheet for a catalytic heat balanced cracking/conversion process.

Fig. 2 is a graph showing first order relationships for hexadecane cracking.

Fig. 3 is an Arrhenius plot for hexadecane cracking.

Fig. 4 is an Arrhenius plot for hexadecane cracking in reactors of different diameters.

Fig. 5 is a graph for the ratio of propane/methane, on a weight basis, versus temperature for hexadecane cracking.

Fig 6 is an Arrhenius plot for cracking of hexadecane and hexadeane/methanol mixtures.

The intimacy of the two reactions effects minutely localized balancing of temperatures at the catalyst surfaces, as indicated by the small coke make, provided that the oxygenate, e.g., methanol is in the proper proportion to the oil. Preferably, the methanol is mixed with the catalyst upstream of the cracking unit and before admixture with the oil. This protects the catalyst from adsorption of poisonous compounds (e.g., nitrogenous compounds) during the initial stages of the reaction, particularly if the methanol is insoluble in the non-polar hydrocarbon feed.

It is preferred that the catalyst be a zeolite in the as-made crystal form and finely subdivided, of a very high acid activity preferably above 500, more preferably above 1000, (e.g., an alpha equal to 1600), and that the quantity of catalyst be very small in proportion to the oil (approximately 0.02 wt.% of the oil or at a ratio of catalyst/oil of less than 0.01). The catalyst particle size is preferably less than 50 microns.

Balancing the methanol exotherm against the hydrocarbon oil endotherm requires a heat balance within the catalytic cracker that is based upon the weight ratios of methanol to oil. Preferably, the weight ratios are within the range of 1:20 to 2:1 of methanol:oil. More methanol is used when the feed comes in at a temperature below the reaction temperature. This is based on the fact that each gram of methanol converted gives off 300-400 calories of heat and each gram of oil cracked absorbs 100-170 calories of heat.

Such a relationship enables the cracking reaction to be sustained substantially entirely by the highly exothermic conversion of methanol in the presence of a small concentration of high activity zeolite catalysts, whereby the cracking reaction is prevented from quenching itself thermally.

It has specifically been found that if a highly active zeolite catalyst, having an activity, alpha, of about 1600, is used in a very highly divided state, such as a mean particle size of $3x10^{-4}$ cm, it is possible to volatilize a hydrocarbon, such as a gas oil, and an oxygenate, such as methanol, and then to crack the gas oil while simultaneously converting the methanol at temperatures in the range of 450 to 650°C during a reaction period of 1 to 60 seconds, preferably 6 to15 seconds, without having to add a significant amount of additional heat and without significant production of coke or of gas and while producing an increased quantity of lower-boiling and unsaturated hydrocarbons. The quantity of the catalyst can be up to 5.0 wt.% and preferably is no more than 1.0 percent by weight and more preferably, no more than 0.02% by weight of the oil. The catalyst need not be regenerated because, at the 0.02% level, the quantity of catalyst consumed is about the same as that usually lost during regenerating operations.

As shown in Fig. 1, the process of the invention comprises admixing a preheated hydrocarbon such as a gas oil in line 12, a catalyst in line 14, an oxygenate such as methanol in line 13 to form a mixture in line 21 which, with recycled hydrocarbons in line 49, forms a feed mixture in line 23 which enters heater 25. The feed is heated to 500-650°C (932-1202°F), and charged via lines 26, 28, 29 to riser reactor 31. Products, unreacted feed and catalyst are discharged via line 33 to a heat exchanger 35, in which the incoming gas oil in line 11 is preheated. The cooled riser effluent is fed through line 37 to a fractionator 41. CO_2 and CO are removed by line 43, C_1-C_5 products are removed by line 45, C_6-C_{15} products and water are removed by line 47, and unreacted hydrocarbons, such as gas oil, are removed via line 49. The materials in line 47 are fed to decanter 51 from which C_6-C_{15} products are discharged by line 53 and water and catalyst are discharged to waste disposal through line 55.

Riser reactor 31 is conventional except that there is no need for a cyclone separator nor catalyst stripping section.

The feed in line 26 is heated to near the reaction temperature before entering reactor 31. Temperature in the reactor is controlled by balancing the ratio of oxygenate to hydrocarbon in the feed mixture against the conversion level that is desired. Reactor 31 has a built-in temperature control mechanism which is effective and automatic because the exothermic methanol conversion is always 100% complete, while the oil conversion, which is endothermic, is limited by the quantity of heat given off by the methanol conversion.

If the feed has a high nitrogen content, heater 25 may separately heat a mixture of oxygenate and catalyst which enters the heater through line 17. The separately heated oxygenate/catalyst mixture is fed to line 26 through line 27 and enters reactor 31 through lines 28, 29. In addition, the hydrocarbon and the oxygenate may be heated, as a mixture which moves through lines 21, 23, 26 or separately by moving through lines 21, 23, 26 for the hydrocarbon and through lines 17, 27 for the oxygenate, while catalyst is sent through line 14 to join line 28.

EXAMPLE 1

Cracking reactions were carried out in an isothermal empty plug flow reactor, using feeds of n-hexadecane containing 0.02 wt.% to 1.0 wt.% ZSM-5 powder. The mean crystal size was 0.02 to 0.05 microns. The catalyst particle size was less than 44 microns.

Tables 1 and 2 summarize the results from these hexadecane cracking runs. Being a pure compound, hexadecane should show a first-order cracking rate dependent on hydrocarbon concentration, regardless of whether the cracking proceeds by carbonium ion or by a free radical rate. Plots of 1n (1-conversion) vs $LHSV^{-1}$, for several catalyst concentrations and two temperatures, are shown in Fig. 2 and confirm these first-order kinetics. Activation energies derived from these data are shown in Fig. 3.

For the uncatalyzed hexadecane reactions, the observed 50.1 kcal/mol and 46.5 kcal/mol activation energies fall close to the 50-60 kcal/mol range that is frequently cited for free radical cracking reactions of pure hydrocarbons. Similarly, for cracking runs using a catalys-to-oil ratio of $2x10^{-4}$, the measured activation energies of 20.5 kcal/mol and 23.6 kcal/mol fall within the 15 to 30 kcal/mol range that is often cited for the carbonium ion catalyzed reaction of other normal parafins. That these measured activation energies are on the low side may be explained by the non-isothermality occurring at the entrance to the reactor where the feed is volatilized. The lower temperatures at the outsets of the reactions, where the catalyst is most active, would conceivably produce artificially low conversions and therefore artificially low activation energies if isothermality is assumed.

As the catalyst concentration was increased to a catalyst-to-oil ratio of $1x10^{-2}$, the activation energy dropped to approximately 2.5 kcal/mol. Although such a drop in activation energy suggests the onset of a mass transfer limited regime, mathematically derived criteria which have been developed indicate that mass transfer limitations (both interphase and intracrystalline) should not be encountered under these reaction conditions.

In brief, these experimental runs 1-12, as shown in Table 1 and as analyzed in Figures 2-5, verify a theoretical model which was designed to predict the conditions required for cracking with low concentrations of a finely dispersed catalyst by applying the model to the cracking of a hexadecane with dispersed, small crystal ZSM-5. At high conversions, the reaction becomes heat transfer limited because of the large cracking endotherm and the high intrinsic activity of the catalyst.

An important finding is that small quantities (approximately 0.02 wt.%) of a high activity (alpha equals 1600) ZSM-5 can produce significant levels of conversion when dispersed in a hydrocarbon stream fed to a riser-type reactor. The plot shown in Figure 4 is particularly significant because it shows that operation in a smaller tube produces a higher surface area-to-volume ratio than a larger tube and therefore provides better heat transfer to the reaction from the heated exterior wall of the reactor.

Other conclusions are that nearly 50% of the n-hexadecane is converted by as little as 0.02 wt.% of catalyst ZSM-5 at 610°C (1130°F) and at a gas residence time of less than 1.5 seconds. No intracrystalline or interphase mass transfer limitations were observed under these conditions. Another important conclusion is that the endothermic hexadecane cracking reaction becomes heat transfer limited as the concentration of the highly acidic ZSM-5B catalyst (alpha equals 1600) is increased to 1.0 wt.%.

EXAMPLE 2

Another series of 12 runs, numbers 13-24, was made to study the cracking behavior of hexadecane alone, the conversion behavior of methanol alone, and the conversion behavior of mixtures of hexadecane and methanol (80% n-C_{16}:20% CH_3OH) with the same catalyst used in runs 1-12 while furnishing information on the heat balance between the two reactions at four selected temperatures and at an LHSV of 18.6. These runs were carried out in an empty tubular reactor immersed in a heated isothermal fluidized sand bath. LHSV was based on the heated empty volume of the reactor.

The data for Runs 13-24 are summarized in Table 2 and are particularly interesting for the detailed product analyses. With respect to LHSV, these runs 13-24 were therefore between the high LHSV runs 1,2, 5, 6, 9, 10, and the low LSHV runs 3, 4, 7, 8, 11, and 12. Runs 13 and 19 used no catalyst and are therefore similar in this respect to runs 9-12. Runs 15, 18, 21, and 24 were heat-balance runs at each of the four temperatures for a feed mixture of 80% n-hexadecane and 20% methanol by weight. The two runs 15 and 18 at higher temperatures, 607°C (1125°F) and 588°C (1090°F), respectively, show that the conversion of hexadecane to substantially lower boiling materials was excellent while producing negligible quantities of methane.

These runs with a feed mixture of hexadecane and methanol are also interesting because they show that all methanol was converted at least to dimethyl ether (DME) and that most of the DME was broken down into methane and water, thereby liberating a significant amount of water. It would also seem that the methane in these runs was then combined into more complex products such as propene for Runs 15 and 18 at higher temperatures of 607°C (1125°F) and 588°C (1090°F), respectively, with significant additions being made to the C_5's and C_6's. For Run No. 15 at 607°C (1125°F) important additions were also made to the C_7's, C_8's, and C_9's. For the two runs at lower temperatures, Nos. 21 and 24, there was some additional production of propene over methanol alone and over hexadecne alone. Furthermore, for Run 21, additional amounts of C_6+ were produced.

It is further of interest that Run 15, in comparison to Run 16, produced less than 2/3 as much water, presumably indicating that DME reacted to produce other products than methane and water. However, Run 18 showed that lower temperatures produced even less water, particularly in contrast to the high production of water for Run 21 at 521°C (970°F), in comparison to the low production of water for Run 22 at the same temperature. These runs also show that the conversion of hexadecane was above 90% for the two higher temperatures and that the conversion of methanol was 100% for the three higher temperatures.

The data in Table 2 are summarized in Figure 6 which is an Arrhenius plot for cracking of hexadecane and hexadecane/methanol mixtures. This figure shows that methanol, when added to the hexadecane feed in the proportion of 20 wt.% methanol:80% n-hexadecane and subsequently mixed with high activity ZSM-5 catalysts (1% by weight on total feed), does increase the conversion of hexadecane above those conversion levels obtained with pure hexadecane as the feed and with pure methanol as the feed. At the lowest temperature 482°C (900°F), methanol in the reaction products diluted the hexadecane and, because methanol's reaction rate is lower, reduced the hexadecane conversion below that achievable with pure hexadecane. The high conversion in the hexadeane-methanol mixture at higher temperatures is thus primarily due to the fact that the cracking reaction becomes reactor heat transfer limited. In consequence, the exothermic methanol reaction is able to contribute heat to the hexadecane reaction throughout the reaction zone and thereby maintain the reaction temperature uniformly at the selected level, not merely along heat transfer surfaces.

Table 3 is a thermodynamic analysis of the methanol:hexadecane runs. This table shows that adding methanol to hexadecane drives the hexadecane reaction to a greater conversion to the extent that the net heat liberated by the methanol to DME to parafins + aromatics reaction is very nearly equivalent to the heat taken up in the now more extensive endothermic cracking reaction of the hexadecane.

Table 1

DISPERSED CATALYST CRACKING OF HEXADECANE OVER ZSM-5B CATALYST

	1	2	3	4	5	6	7	8	9	10	11	12
LHSV, hr^{-1}	25	25	10	10	25	25	10	10	25	25	10	10
Temperature, °C	498.9	600.6	500.3	601.1	499.4	599.7	497.8	610.1	498.9	606.1	496.7	602.2
Feed Rate (cc/hr)	100	100	40	40	100	100	40	40	100	100	40	40
Catalyst-to-Oil Ratio (x 10^2)	1	1	1	1	0.02	0.02	0.02	0.02	0	0	0	0
Net Liquid Fed (gms)	43.7	55.5	37.3	23.2	32.2	51.9	19.6	30.2	47.9	18.5	52.0	9.1
Net Liquid Out (gms)	36.8	42.82	24.32	15.33	30.66	46.44	17.94	21.43	46.11	17.95	51.73	7.41
Net Hexadecane in Prod. (gms)	30.31	33.96	16.45	9.20	29.95	41.73	16.86	15.98	46.07	16.93	51.63	6.24
Net Gas Out (gms)	6.2	8.18	12.98	8.32	0.420	3.39	1.41	8.80	0.10	0.72	0.292	1.63
Gas (cc)	3400	4270	5300	4150	230	1900	540	670	100	490	180	1100
% Liquid	85.6	83.96	65.19	64.82	98.65	93.20	92.71	70.89	99.59	96.14	99.44	81.97
% Gas	14.4	16.04	34.81	35.18	1.35	6.80	7.29	29.11	0.41	3.86	0.56	18.03
Analysis of Converted Liquid												
IBP-148°C (IBP-300°F)	0.505	0.608	0.469	0.608	0.443	0.12	0.677	0.398	0.716	0.244	0.768	0.147
148-176°C (300-350°F)	0.361	0.265	0.330	0.243	0.446	0.871	0.084	0.275	0.265	0.231	0.230	0.265
176-204°C (350-400°F)	0.072	0.055	0.101	0.068	0.029	0.009	0.077	0.102	0.010	0.144	0.002	0.172
204-232°C (400-450°F)	0.035	0.038	0.062	0.048	0.014	0	0.067	0.099	0.009	0.145	0	0.164
232-260°C (450-500°F)	0.019	0.010	0.029	0.025	0.005	0	0.054	0.089	0	0.205	0	0.171
260-282°C (500-540°F)	0.008	0.024	0.009	0.008	0.063	0	0.041	0.037	0	0.031	0	0.081

Table 1 (Cont.)

DISPERSED CATALYST CRACKING OF HEXADECANE OVER ZSM-5B CATALYST

	1	2	3	4	5	6	7	8	9	10	11	12
Gas Analysis (wt.%)												
Methane	0.080	1.12	0.114	2.664	1.114	4.835	1.862	6.700	4.923	14.608	14.721	13.81
Ethane + Ethylene	1.99	4.98	3.72	18.01	6.18	23.50	9.63	37.38	21.45	52.38	46.45	52.10
Propane	25.39	11.98	20.69	13.59	17.65	7.79	11.60	3.48	16.53	4.05	7.26	3.29
Propene	24.86	21.31	31.79	46.62	43.11	36.87	44.50	37.56	37.93	19.79	23.56	21.37
Isobutane	7.59	3.31	3.96	1.90	3.35	0.75	2.21	0.28	1.074	0.133	0.25	0.15
n-Butane	17.35	11.50	9.66	4.21	8.71	3.41	4.67	0.98	5.17	0.736	1.20	0.69
Other Butanes	22.74	45.80	30.07	13.01	25.62	22.85	25.48	11.62	12.92	8.29	6.56	8.59
C_3H_8/CH_4 (wt. basis)	322.6	10.7	181.8	5.10	15.87	1.61	6.23	0.400	3.36	0.277	0.493	0.238
$i\text{-}C_4/n\text{-}C_4$	0.438	0.287	0.411	0.450	0.394	0.219	0.473	0.282	0.209	0.180	0.208	0.218
Conversion on Liquid (%)	17.64	20.70	32.37	39.98	2.32	10.14	6.02	18.03	0.07	5.68	0.200	15.79
Conversion Liq + Gas (%)	29.50	33.42	55.91	61.10	3.66	16.94	13.31	47.14	0.21	9.54	0.760	30.97
Gas/Liquid	0.168	0.191	0.534	0.542	0.014	0.073	0.079	0.411	0.004	0.040	0.006	0.220
Mass Balance	0.984	0.919	1.001	1.010	0.965	0.964	0.999	1.000	0.967	1.009	1.000	1.016

Table 2

SUMMARY OF CRACKING DATA FOR REACTION OF HEXADECANE, METHANOL, AND HEXADECANE/METHANOL MIX OVER A ZSM-5 CATALYST DISPERSED IN THE FEED AT LHSV = 18.6 HR^{-1}

Run No.	13	14	15	16	17	18	19	20	21	22	23	24
Feed	n-$C_{16}H_{34}$	n-$C_{16}H_{34}$	Mix*	MEOH	n-$C_{16}H_{34}$	Mix*	n-$C_{16}H_{34}$	n-$C_{16}H_{34}$	Mix*	MEOH	n-$C_{16}H_{34}$	Mix*
Temperature, °F	1125	1125	1125	1125	1090	1090	970	970	970	970	900	900
Temperature, °C	607	607	607	607	588	588	521	521	521	521	482	482
Wt.% ZSM-5	None	1.0	1.0	1.0	1.0	1.0	None	1.0	1.0	1.0	1.0	1.0
Wt.% Hexadecane	100	100	80	-	100	80	100	100	80	-	100	80
Wt.% Methanol	-	-	20	100	-	20	-	-	20	100	-	20
Total gms charged	30.4	36.1	30.9	23.6	38.6	34.0	45.8	22.0	14.8	30.7	20.0	20.0
Total gms recovered	30.4	35.2	29.9	23.5	37.1	33.1	45.4	21.9	14.4	30.7	18.9	20.16
Mass Balance	100	97.5	96.8	99.6	96.1	97.4	99.2	99.5	97.3	99.7	95.0	100.2
Product Analysis												
Methanol	-	-	-	45.97	-	-	-	-	-	82.50	-	10.16
DME	-	-	6.17	31.57	-	9.83	-	-	0.29	3.41	-	2.75
CO	-	-	0.27	5.61	-	-	-	-	0.05	2.47	-	-
CO_2	-	-	0.54	1.24	-	0.43	-	-	0.20	0.94	-	-
H_2O	-	-	8.12	13.50	-	6.82	-	-	10.94	4.94	-	4.46
CH_4	0.19	0.17	0.81	0.69	0.095	0.94	0.07	0.024	0.92	4.46	0.012	0.28
$C_2+C_2^=$	10.77	3.15	3.12	0.06	1.814	3.42	0.22	0.47	0.11	0.14	0.072	0.20
C_3	0.08	6.07	4.14	0.24	5.40	3.75	0.04	3.81	3.52	0.08	0.53	0.97

Table 2
(Continued)

SUMMARY OF CRACKING DATA FOR REACTION OF HEXADECANE, METHANOL, AND HEXADECANE/METHANOL MIX OVER A ZSM-5 CATALYST DISPERSED IN THE FEED AT LHSV = 18.6 HR^{-1}

Run No.	13	14	15	16	17	18	19	20	21	22	23	24
$C_3^=$	0.48	12.91	18.47	0.06	8.57	15.82	0.09	4.22	9.88	0.19	0.53	2.08
$I\text{-}C_4$	0.08	1.53	1.99	0.34	1.13	1.89	0.08	1.45	2.75	0.08	0.22	0.64
$N\text{-}C_4$	0.22	3.72	1.79	0.05	1.71	1.63	0.04	3.08	2.15	0.09	0.47	0.59
$C_4^=$'S	2.97	13.11	12.19	0.49	15.89	12.80	0.25	7.87	8.82	0.32	2.49	1.88
C_5'S	6.35	8.72	11.27	0.33	10.44	12.10	0.48	19.70	12.30	0.40	14.21	2.85
C_6'S	1.40	4.15	6.34	-	5.61	8.71	-	4.43	8.74	-	3.47	7.81
C_7'S	-	3.12	5.01	-	2.85	3.54	-	0.95	4.13	-	1.93	1.48
C_8'S	-	2.97	5.62	-	2.87	4.10	-	2.20	2.17	-	1.25	0.89
C_9'S	-	2.83	4.35	-	2.78	3.15	-	2.26	4.14	-	0.91	0.55
C_{10}'S	-	1.19	1.79	-	1.20	1.54	-	1.07	0.94	-	0.78	0.48
C_{11}'S	-	0.19	0.24	-	0.21	0.21	-	0.63	0.52	-	0.56	0.43
C_{12}'S	-	0.14	0.20	-	-	0.21	-	-	0.41	-	0.51	0.31
C_{13}'S	-	0.83	1.07	-	0.95	1.13	-	0.33	0.59	-	0.36	0.31
C_{14}'S	0.19	1.13	0.15	-	1.15	0.20	-	0.22	0.83	-	0.26	0.18
C_{15}'S	0.63	0.26	0.39	-	0.26	0.30	-	0.68	0.40	-	0.36	2.10
Hexadecane	86.11	33.81	5.58	-	37.07	6.72	98.73	45.91	25.20	-	64.46	58.63
Higher Boilers	0.53	-	0.43	-	-	0.76	-	0.69	-	-	1.62	-
Conversion of $C_{16}H_{34}$	13.89	66.19	93.02	-	62.93	91.60	1.27	54.09	69.50	-	35.54	26.71
% HC From MEOH	-	-	4.90	2.26	-	2.92	-	-	8.52	5.76	-	2.63
Conversion of MEOH	-	-	100	54.03	-	100	-	-	100	17.50	-	49.20

*Mix: All $n\text{-}C_{16}H_{34}$:MEOH Mixtures are 80 wt.% $n\text{-}C_{16}H_{34}$ and 20 wt.% MEOH

Table 3

THERMODYNAMIC ANALYSIS OF MEOH - HEXADECANE DISPERSED CATALYST RUNS

Run No.	FEED		PRODUCT					QMEOH	Qn-$C_{16}H_{34}$
	gMEOH	g$C_{16}H_{34}$	g$C_{16}H_{34}$	gMEOH	gDME	gH_2O	gMEOH HC*	kcal/mole	kcal/mole
16	100	-	-	45.97	31.57	13.50	2.26	-4.07	-
17	-	100	37.07	-	-	-	-	-	+13.33
18	20	80	6.72	-	9.83	6.82	2.92	-2.01	+15.52
14	-	100	33.81	-	-	-	-	-	+14.02
15	20	80	5.58	-	6.17	8.12	4.90	-2.20	+15.76

*Note: Remainder is CO and CO_2. MEOH conversion to CO and CO_2 is ignored in heat balance.

Q = Net heat liberated (-) or consumed (+) by each reactant

Although the example used ZSM-5 to catalyze both the exothermic conversion of oxygenates and the endothermic catalytic cracking reaction, it is possible to use other zeolites, or other acidic catalysts to promote these reactions.

Large pore zeolites, such as type X and Y zeolite or mordenite, can be used, so long as they have sufficient acid activity to promote both the cracking reaction and the oxygenate conversion. Amorphous materials such as alumina, silica alumina, clays, etc., may also be used providing they have the requisite acid activity. Many times, acid activity can be added to amorphous materials by contacting them with other acidic compounds, e.g., impregnating a relatively inert material with a solution of a strong soluble mineral acid, or contacting an alumina with a Friedel Crafts metal halide.

In some circumstances, the strong mineral acids, such as HF acid and HCL, H2SO4, may be used neat, or in aqueous or non aqueous solution to provide the desired acidity. Solid phosphoric acid is another material which can be used to promote this reaction.

The preferred materials are those with an acid activity, as measured by the alpha test of 100 to 100,000, preferably above 500, and most preferably above 1000.

Shape selective zeolites, those having a Constrait Index of 1-12, are especially preferred because of the desirable products formed from the oxygenates over the zeolites. The shape selectivity of these zeolites may also make them resistant to aging (usually by coke deposition) which rapidly occurs on conventional large pore zeolites.

It is possible to obtain a desired acid activity by mixing together two dissimilar materials, e.g., a relatively high acidity ZSM-5, or other zeolite, could be mixed with a much more inert material such as alumina or clay.

It is also possible to use less active materials, as long as a compensating increase in the amount of the acid acting material is made. Similar conversions will be obtained when adding 0.02 wt % of 1600 alpha ZSM-5 or with 0.2 wt % ZSM-5 with an alpha activity of 160.

In general, higher temperatures make both catalytic and non-catalytic reactions go more quickly. Thus at higher temperatures less catalyst is needed, because small amounts of catalyst that are there are very effective. This must be balanced against the generally undesirable thermal cracking that occurs spontaneously at these higher temperatures.

Residence time too is an important variable. An increase in catalyst residence time (e.g., a longer riser reactor) permits use of a lower acid activity catalyst, or less catalyst.

In general terms, it requires more energy to achieve high reaction temperatures, so attempts may be made to minimize the reaction temperature by providing more catalyst, more acidic catalyst materials, or longer residence time.

Sometimes it will be most beneficial to operate at higher temperatures, particularly when reforming like reactions are desired. To shift reaction conditions to stable, roughly heat balanced operation at high temperatures, it may be desirable to resort to lower acid activity catalysts, shorter residence times, or less catalyst, so that a heat balanced reaction can be obtained at higher temperatures which favor reforming.

It is also possible to run a heat balanced reaction, without catalyst regeneration, by using relatively large amounts of low acidity materials. In such a mode of operation a very high silica ZSM-5 (or other stable acid acting material) could be contained in a fixed bed, or preferably in a fluidized bed, through which feed oil and oxygenates pass. Lower activity catalysts could be tolerated because there would be so much more catalyst present, e.g., LHSVs, based on total liquid feed, equivalent to 0.1-10, preferably 0.5-5, provide large volumes of catalysts of relatively low activity which will carry out the desired catalytic cracking and oxygenate conversion reactions. A large, dense phase fluidized bed operation would have some additional advantages in that the catalyst acts as a heat sink and minimizes temperature variations if any problems in mixing oxygenates and oil occur. Such problems may occur when the two feedstocks are incompatible or difficult to mix. It is also hard to mix together oxygenates (which vaporize readily at low temperatures) with relatively heavy hydrocarbons (which are more difficult to vaporize).

In this mode of operation, which could be considered as a CSTR, or continuous stirred tank reactor operation, high acid activity of the zeolite is not as important as the long term stability of the zeolite which will minimize the need for continuous regeneration.

Of course regeneration is a possibility, and a catalyst regneration facility may be closely associated with the reactor. The catalyst regenerator would not function as a means of heat balancing the unit, its primary purpose would be to remove deactivating coke from the catalyst. It is likely that coke yield would be so low in such a process that catalyst regeneration would provide no more than a minimal amount, perhaps 10%, or less, of the normal heat requirements of the process. Of course heat of coke combustion may be recovered by heat exchange of hot regeneration exhaust gas with incoming feed.

Another mode of operation which is possible is use of a moving bed reactor. Such a design would work, but is considerably more complicated than either a fluidized dense phase reactor, or a simple packed bed reactor.

The process of the present invention frees the catalytic cracking process from its dependency upon catalyst regeneration to keep the unit heat balanced. Heat balanced operation without regeneration can be achieved in two ways, either by using small amounts of dispersed highly active catalysts (and this operation was used in the example) or by providing large amounts of catalyst of great stability, although perhaps of somewhat lesser activity.

Prior art workers came very close to this concept, in that they added methanol to FCC feeds, see e.g., U.S. Patents 3,974,062 and 3,974,063. In both of these patents the FCC reaction relied upon hot regenerated catalyst to keep the unit heat balanced. Addition of methanol did not bring about profound changes in conversion of feed to lighter products. The catalyst in the prior art unit continued to accumulate about 1% coke, representing a loss of valuable liquid products. Perhaps the large amounts of catalyst present, 3 weights of catalyst per weight of oil caused premature conversion of methanol to something else. In contrast, in the process of the present invention, as disclosed in the example, there is almost no catalyst present. Put in more concrete terms, the prior art processes wherein methanol was added to the FCC feed required 3 kilograms of catalyst per kilogram of oil feed. The process of the present invention requires only 0.2 grams of catalyst per kilogram of oil feed. The prior art process used 15,000 times as much catalyst as the present invention.

By freeding the catalytic cracking process from its dependency upon catalyst regeneration as a means of heat balancing the reaction, the significant capital and operating costs of FCC regenerators, air compressors, etc. are eliminated. The heat balanced process of the present invention will not produce SO_x, which is inherently produced in FCC regenerators when sulphur (present in the coke deposited on the catalyst) is burned to SO_x. Thus the process of the present invention eliminates the substantial air pollution problem associated with conventional catalytic cracking units, namely the production of SOX and the regenerator flue gas.

It is believed that the products of the process of the present invention have properties which are superior to those conventionally obtained via catalytic cracking of hydrocarbons. One reason for this is that conversion is no longer tied to reactor temperature as it was in the past. Conversion can be adjusted by increasing or decreasing the amount of catalyst added. The temperature of the reaction zone can be largely determined by the amount of feed preheat, as opposed to the temperature and amount of hot regenerated catalyst added to the reactor.

Claims

1. A process for catalytic cracking of a hydrocarbon with an acidic catalyst to lighter products characterized by contacting in a reactor a hydrocarbon, a carbon oxygenate, and an acidic catalyst capable of cracking the hydrocarbon and exothermically converting the carbon oxygenate to a hydrocarbon of increased carbon content and wherein at least a majority of the heat of reaction of the endothermic catalytic cracking reaction is supplied by the exothermic conversion of oxygenates to hydrocarbons.

2. The process of Claim 1 wherein the reactor is a riser reactor.

3. The process of Claim 1 or 2 wherein the hydrocarbon is a gas oil.

4. The process of any preceding Claim wherein the carbon oxygenate is selected from the group of lower alcohols, ethers, aldehydes, and ketones.

5. The process of Claim 4 wherein the carbon oxygenate is methanol.

6. The process of any preceding Claim wherein the catalyst is a zeolite.

7. The process of Claim 6 wherein the zeolite is HZSM-5.

8. The process of preceding Claim wherein the zeolite is present in an amount equal to 0.01 to 5 wt.% of the oil.

9. The process of Claim 8 wherein the zeolite is present in an amount equal to 0.02 to 1.0 wt.% of the oil.

10. The process of any preceding Claim wherein the reaction occurs at 450-650°C and oil residence time in the reactor is 1 to 10 seconds.

11. The process of any preceding Claim wherein the carbon oxygenate to oil ratio is 1:20 to 2:1 by weight.

12. The process of any preceding Claim wherein the oxygenate and catalyst are premixed, for dispersion of catalyst in the oxygenate, prior to admixing with the oil.

13. The process of any preceding Claim wherein the catalyst is ZSM-5 with an alpha activity above 500 and the catalyst particle size is less than 50 microns.

Fig.1

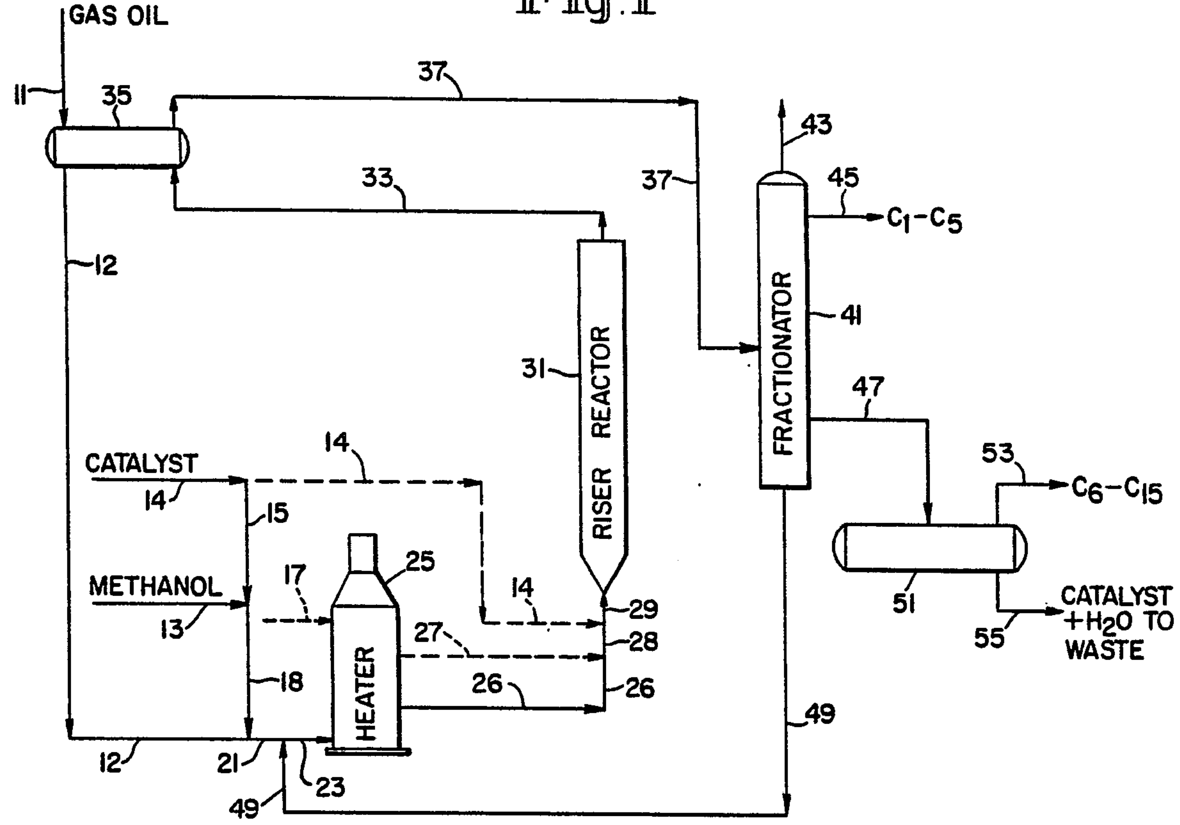

GAS OIL
11
35
37
33
37
43
45
C1-C5
12
31
RISER REACTOR
FRACTIONATOR
41
47
CATALYST
14
15
METHANOL
13
17
25
HEATER
14
29
28
27
26
26
18
12
21
23
49
49
53
C6-C15
51
55
CATALYST +H2O TO WASTE

Fig.2

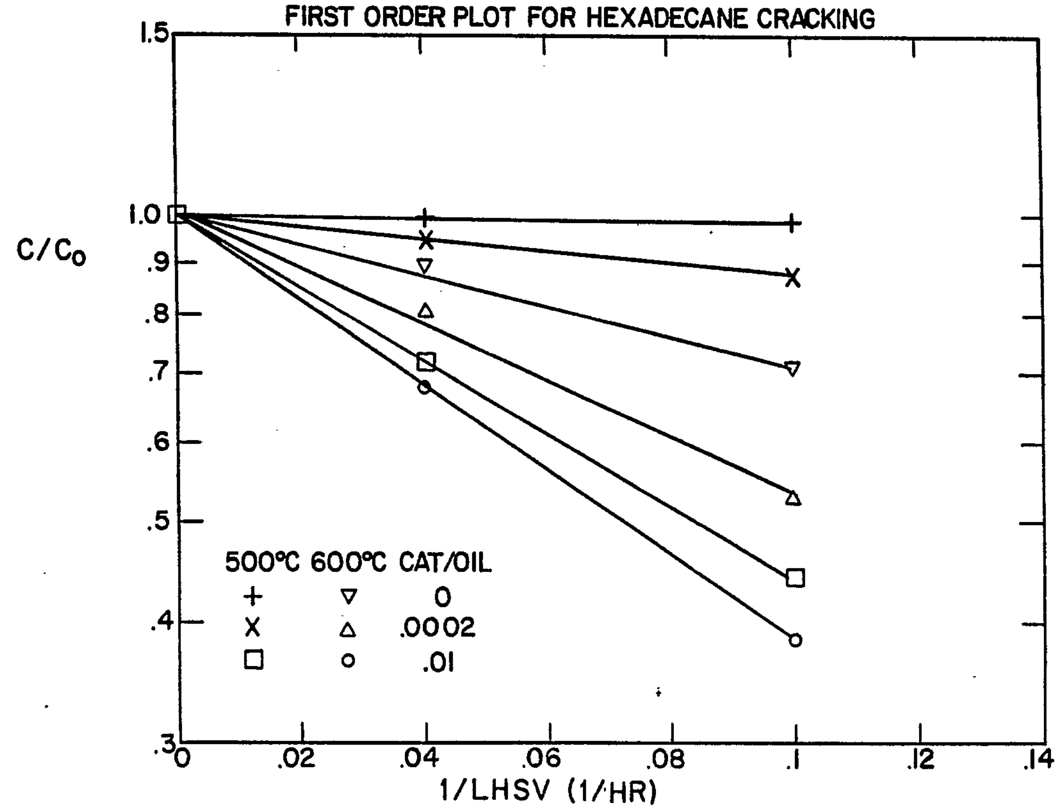

FIRST ORDER PLOT FOR HEXADECANE CRACKING
C/C0
1.5
1.0
.9
.8
.7
.6
.5
.4
.3
0
.02
.04
.06
.08
.1
.12
.14
1/LHSV (1/HR)
500°C 600°C CAT/OIL
+ ▽ 0
X △ .0002
□ ○ .01

Fig.3

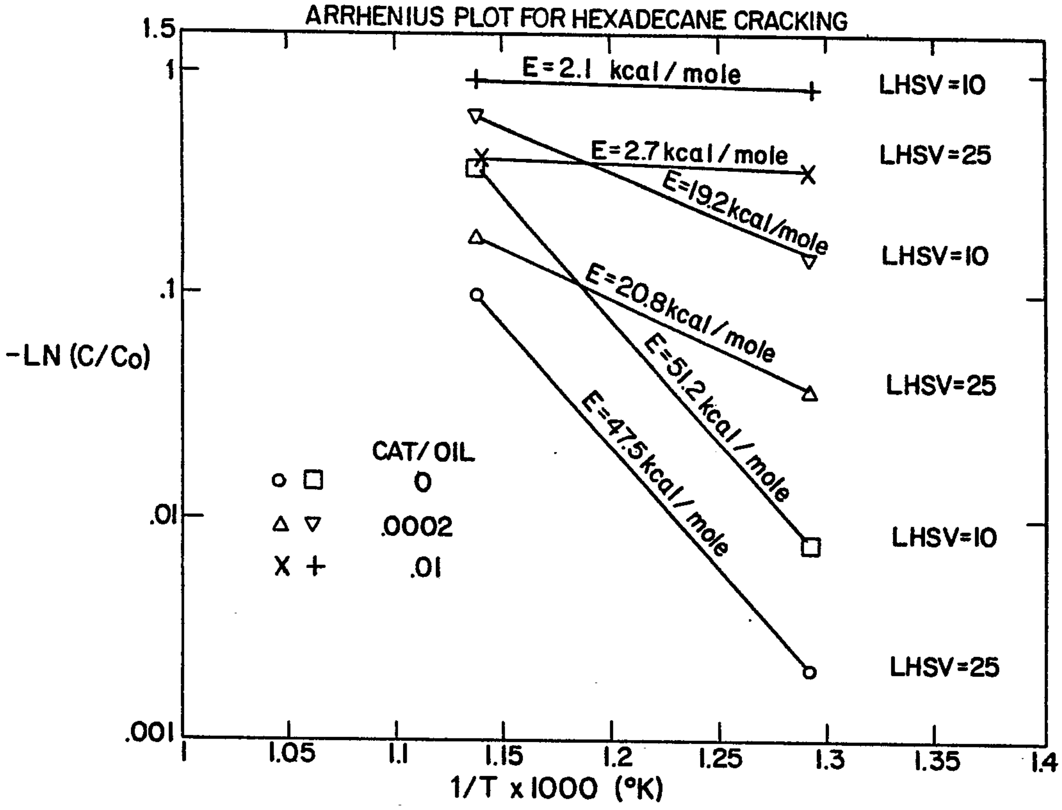

ARRHENIUS PLOT FOR HEXADECANE CRACKING
1.5
1
.1
.01
.001
-LN (C/Co)
1
1.05
1.1
1.15
1.2
1.25
1.3
1.35
1.4
1/T x 1000 (°K)
E=2.1 kcal/mole
E=2.7 kcal/mole
E=19.2 kcal/mole
E=20.8 kcal/mole
E=51.2 kcal/mole
E=47.5 kcal/mole
LHSV=10
LHSV=25
LHSV=10
LHSV=25
LHSV=10
LHSV=25
CAT/OIL
○ □ 0
△ ▽ .0002
X + .01

Fig.4

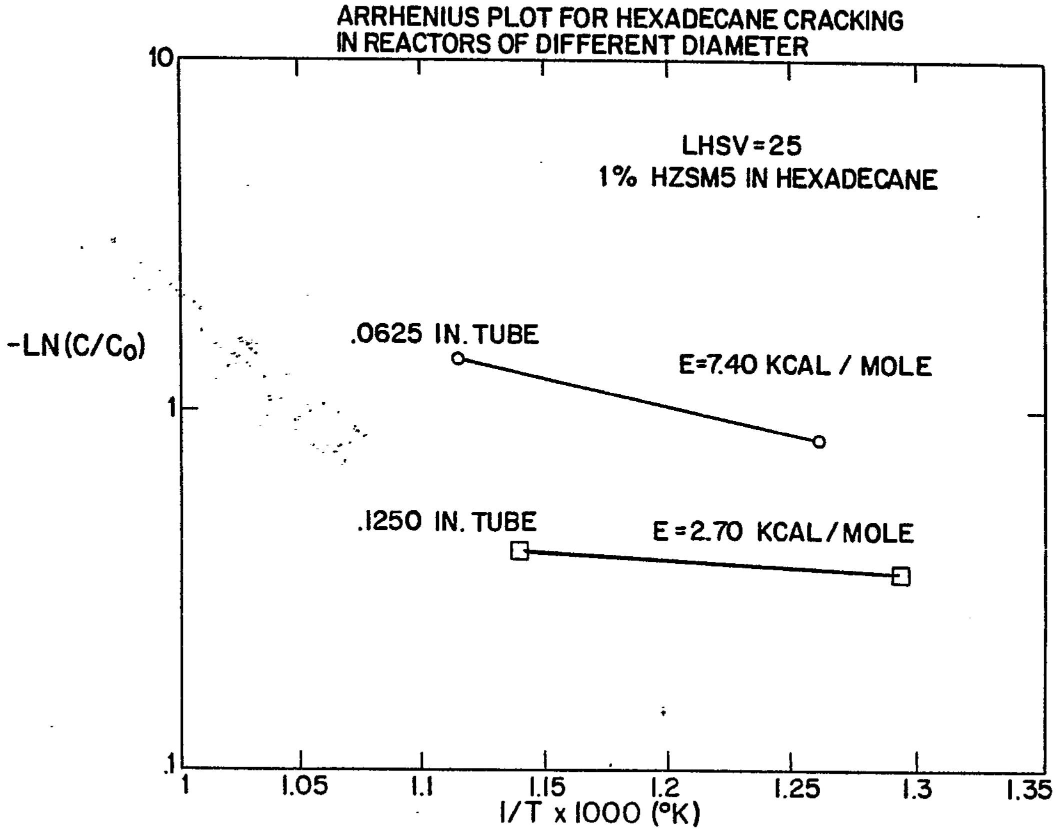

ARRHENIUS PLOT FOR HEXADECANE CRACKING
IN REACTORS OF DIFFERENT DIAMETER
10
1
.1
-LN (C/Co)
1
1.05
1.1
1.15
1.2
1.25
1.3
1.35
1/T x 1000 (°K)
LHSV=25
1% HZSM5 IN HEXADECANE
.0625 IN. TUBE
E=7.40 KCAL / MOLE
.1250 IN. TUBE
E=2.70 KCAL / MOLE

Fig. 5

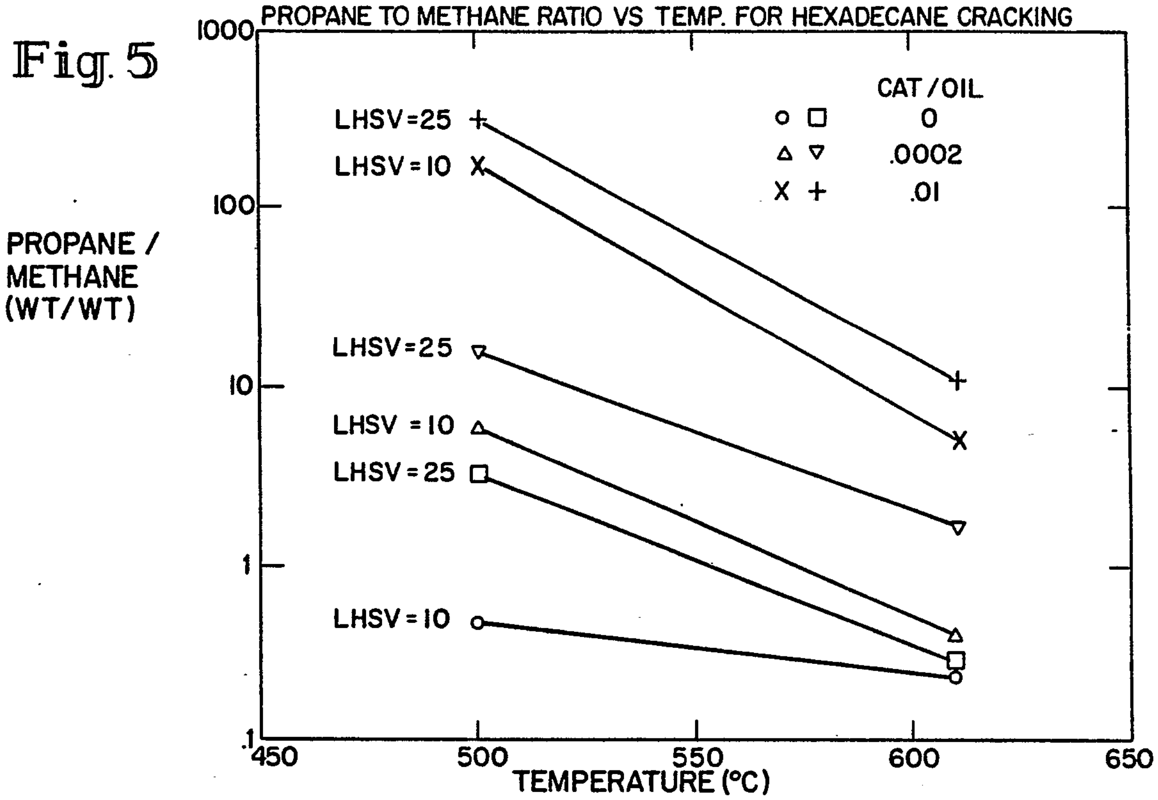
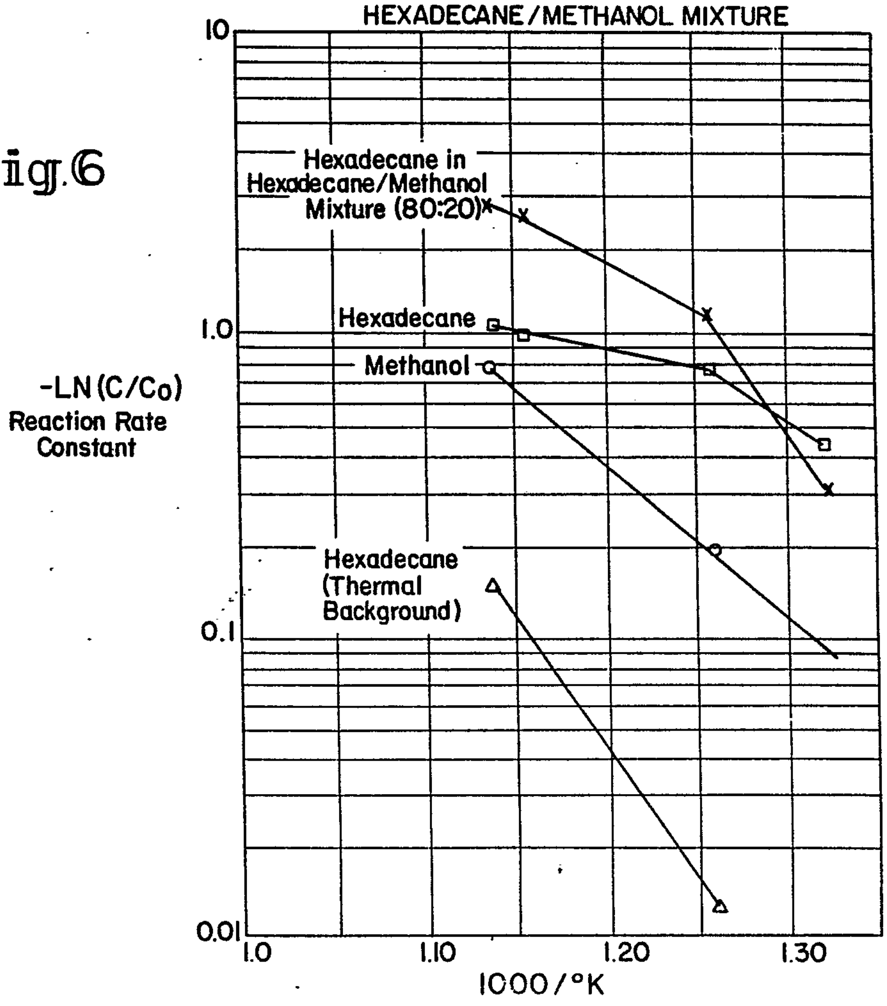

PROPANE TO METHANE RATIO VS TEMP. FOR HEXADECANE CRACKING
PROPANE / METHANE (WT/WT)
1000
100
10
1
.1
450
500
550
600
650
TEMPERATURE (°C)
CAT / OIL
○ □ 0
△ ▽ .0002
X + .01
LHSV=25
LHSV=10
LHSV=25
LHSV=10
LHSV=25
LHSV=10

Fig.6


HEXADECANE / METHANOL MIXTURE
10
1.0
0.1
0.01
-LN (C/Co)
Reaction Rate Constant
Hexadecane in Hexadecane/Methanol Mixture (80:20)
Hexadecane
Methanol
Hexadecane (Thermal Background)
1.0
1.10
1.20
1.30
1000/°K

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 86 30 0225

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	FR-A-2 441 599 (PETROLEO BRASILEIRO) * Claims 1,2; page 1, lines 1-4 * ---	1,3,4,10,11	C 10 G 11/05 C 10 G 3/00 C 10 G 11/18 // B 01 J 29/28
A	US-A-4 012 455 (OWEN et al.) * Claim 1; column 2, lines 21-39; example 1; column 5, lines 32-52 * ---	1-7,10,11	
A	US-A-4 112 056 (CHEN et al.) * Claims 1,2; column 8, lines 16-24 * -----	1,4-7	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 10 G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	11-08-1986	DE HERDT O.C.E.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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L : document cited for other reasons

& : member of the same patent family, corresponding document