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UPGRADING FUSED BENZENOID RING
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This invention relates to the reaction of fused benzenoid ring hydrocarbons with methylcyclohexane to produce compounds having a higher hydrogen content than said fused benzenoid ring hydrocarbon.

In the petroleum industry, large amounts of aromatic hydrocarbons containing 2 or more fused benzenoid rings are being produced. These materials are chiefly products of hydrocarbon conversion processes utilizing solid catalysts such as silica alumina, natural clays and silica magnesia; some are produced from the catalytic reforming operations. These fused benzenoid ring hydrocarbons are refractory materials and are difficult to crack further. When these compounds do break up, they tend to form coke and gas with low yields of the desired gasoline boiling range or light gas oil boiling range hydrocarbons. Hydrogenation of the compounds and/or alkylation of these compounds produce alkyl substituents which have a favorable effect on the cracking yields owing to the presence of added hydrogen. The continued large demand for high octane gasoline makes it imperative that the high boiling cycle stocks produced from the catalytic cracking of the virgin gas oils be made amenable to further catalytic cracking with yield of gasoline range aromatic hydrocarbons.

An object of the invention is a process for increasing the hydrogen content of fused benzenoid ring hydrocarbons. Another object is the treatment of hydrocarbon feeds, such as high boiling gas oils, to increase the hydrogen content. Yet another object is a method of upgrading heavy gas oils derived from catalytic cracking operations to make possible more usable catalytic cracking feed. Other objects will become apparent in the course of the detailed description.

In the process of this invention, a hydrocarbon feed containing an aromatic hydrocarbon having at least two fused benzenoid rings is contacted with a methylcyclohexane in the presence of liquid HF catalyst under conditions of temperature and time such that a reaction takes place between the methylcyclohexane and said aromatic hydrocarbon to produce a hydrocarbon product having a hydrogen content higher than said aromatic hydrocarbon.

The reacting aromatic hydrocarbon contains at least 2 fused benzenoid rings. In addition to the fused benzenoid rings, the aromatic hydrocarbon may contain hydrocarbon substituents such as alkyl, alkenyl, cycloalkyl and cycloalkenyl. Or, the aromatic hydrocarbon may contain fused ring substituents; these fused ring substituents may be naphthene or olefin in nature. Examples of various fused benzenoid ring aromatic hydrocarbons which are suitable for the process are: Naphthalene, anthracene, phenanthrene, pyrene, chrysene, pentacene, benzopyrene, perylene, coronene, picene and hexacene; the various methyl, ethyl, propyl, butyl, etc. derivatives of these; the ethenyl, propenyl and butenyl derivatives of these;

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acenaphthene, tetracene, hexahydropyrene, benzathrene, choloanthrene, rubicene, etc. These defined fused benzenoid ring hydrocarbons may be charged to the process as individual compounds or mixtures of individual compounds, in the absence of other types of hydrocarbons. Also, the defined charge hydrocarbons may be introduced into the reaction zone in admixture with mono-nuclear aromatic hydrocarbons, such as benzene, toluene or fused ring hydrocarbons such as the indanes or hydronaphthalenes. Also, the defined charge hydrocarbons may be utilized in combination with paraffinic hydrocarbons or olefinic hydrocarbons. Since the principal object of the invention is the upgrading of gas oils to make them suitable for catalytic cracking operation charge, the preferred feeds are cracked gas oils containing appreciable amounts of the defined fused benzenoid ring hydrocarbons. The cracked gas oils, either thermally cracked or catalytically cracked, contain particularly large amounts of these hydrocarbons. The so-called heavy gas oils which largely boil over the range of about 500° F. to 750° F., which have been derived from a catalytic cracking operation, are particularly suitable feeds to the process.

The other reactant is a methylcyclohexane.

The presence of some methylcyclohexane will result in an increase of the hydrogen content of the defined aromatic hydrocarbon charge. Theoretically about 2 moles of methylcyclohexane are required per mole of defined aromatic hydrocarbon in the hydrocarbon feed. In general, between about 1 and about 20 moles of methylcyclohexane are present in the reaction zone per mole of the defined fused benzenoid ring aromatic hydrocarbon present therein; preferably between about 3 and 5 moles of methylcyclohexane are used per mole of defined aromatic hydrocarbon present.

The reaction takes place in the presence of a liquid hydrogen fluoride catalyst. The reaction is carried out under substantially anhydrous conditions. Usually the hydrogen fluoride catalyst should not contain more than about 2 or 3 weight percent of water. Commercial anhydrous hydrofluoric acid is particularly suitable for use as the HF catalyst. The reaction requires the presence of liquid hydrogen fluoride and sufficient pressure must be maintained on the reaction zone to keep the HF in the liquid state.

The catalytic activity of the liquid HF is promoted by the presence of boron trifluoride. Small amounts of BF₃ will have some appreciable effect in increasing the catalytic activity. In general, between about 0.5 and 5 moles of BF₃ will be used per mole of defined aromatic hydrocarbon present in the reaction zone. Preferably between about 1 and 2 moles of BF₃ are present per mole of defined aromatic hydrocarbon present. The liquid HF is present in an amount between about 50 and 500 volume percent, based on defined aromatic hydrocarbon present in the reaction zone. More usually between about 100 and 200 volume percent, based on defined aromatic hydrocarbon, is utilized.

The reaction requires a time and temperature relationship which is dependent upon the activity of the catalyst system. When using liquid HF alone or liquid HF promoted with minor amounts of BF₃, the reaction is carried out at a temperature between about 75° C. and 200° C. The catalyst and the reactants are contacted at these temperatures for a time ranging between about 1 minute and about 8 hours. The higher temperatures permit shorter times of contacting or, conversely, the longer times correspond to the lower temperatures of contacting. When using liquid HF, under these condi-

tions, it is preferred to operate at a temperature between about 125 and 150° C.

When utilizing liquid HF and large amounts of BF₃ as the catalyst, the reaction is carried out at a temperature between about 15° C. and 100° C. The times of contacting at these temperatures are between about 5 minutes and 3 hours, with the longer times corresponding to the lower temperatures.

Prolonged times at higher temperatures or operation with temperatures much in excess of the upper limits set out results in excessive amounts of cracking and tar formation.

At the completion of the reaction, the liquid HF catalyst is separated, usually by decantation, from the hydrocarbon phase which contains the unreacted methylcyclohexane and the hydrocarbon product. The hydrocarbon product is characterized by a hydrogen content higher than that of the hydrocarbon feed to the reaction zone. Also, the catalyst may be separated from the hydrocarbon product and methylcyclohexane by distilling away the HF and BF₃, if any has been used.

The results obtainable with the process of the invention are illustrated by the following working examples. These examples were obtained by utilizing an autoclave provided with a mechanical stirrer. The reactants were introduced into the autoclave and the catalyst was then introduced therein. The contents of the autoclave were heated to the desired temperature and vigorously agitated for the selected contacting time. At the completion of this time, the contents were cooled and the acid phase separated. The acid phase was quenched in cold water. The hydrocarbon phase was neutralized. Any hydrocarbon recovered from the acid phase was added to the neutralized hydrocarbon phase. The total hydrocarbons were distilled to remove unreacted methylcyclohexane and were then cut up into narrow boiling range fractions. These narrow boiling range fractions were inspected for physical characteristics, such as refractive index, and were analyzed by infrared spectrometry for hydrocarbon class content.

In Table I there are set out the results of runs on the reaction of β -methylnaphthalene with methylcyclohexane and in one run without methylcyclohexane. In run No. A, the results show that the methylnaphthalene extensively cracked even at the low temperature of 20° C. Run No. B was carried out with methylcyclohexane as the isoparaffin. In run No. C, no BF₃ was used but a high temperature was used instead. The runs show that while the reaction was carried out considerable tar formation did take place under these conditions.

There is set out in Table II the results of reacting a heavy catalytic cycle oil derived from the cracking of gas oils over a silica alumina catalyst utilizing methylcyclohexane. Also, a run was made on the extract hydrocarbons obtained by the liquid SO₂ extraction of this heavy catalytic cycle oil. Runs No. D and E were carried out on the gas oil itself. Run No. D was carried out at 76° C.

TABLE I

Hydroalkylation of beta-methylnaphthalene

[Reaction time—4 hours.]

Run No.	A	B	C
Isoparaffin	None	Methylcyclohexane	Methylcyclohexane
HF, moles per mole Methylnaph	13	20	20
BF ₃ , moles per mole Methylnaph	1.4	1.5	0
Temperature, ° C.	20	20	100
Product Distribution, Wt. Percent (On isoparaffin-free basis):			
Methylnaphthalene	53	3	21
Alkylmethylnaphthalene	13	36	24
Tetralins, indanes, and alkylbenzenes	4	51	45
Tar	.80	10	23
Isoparaffin consumed, percent		75	30

TABLE II

Run No.	D	E	F
Petroleum Stock	HCCO	HCCO	HCCO-X
Wt. g.	124	121	131
Methylcyclohexane, Wt. g.	106	106	108
Wt. Percent MCH in Feed	46.1	46.7	44.6
HF, g.	400	400	400
BF ₃ , g.	64	73	86
Temp., ° C.	76	22	25
Time, Min.	180	300	180
Product Distribution, Wt. Percent:			
Butane	3	0	0
Methylcyclohexane	20	43.4	40.5
Gasoline	18	0	0
Gas Oil	59	56.6	59.5
Inspections:			
n _D ²⁰ of Petroleum Stock	1.5163	1.5163	1.5890
n _D ²⁰ of Gas Oil Fraction of Product	1.5230	1.5130	1.5848
n _D ²⁰ of Gasoline Fraction of Product	1.4450		

for a time of 3 hours. The results show that a considerable amount of gasoline boiling range material was produced in addition to the methylcyclohexane which was not reacted. Run No. E shows that gasoline formation can be suppressed by operating at lower temperature for a longer time. Run No. F shows that some improvement can be obtained by reacting solvent extract from a catalytic gas oil with methylcyclohexane.

RUN NO. G

In this run, one batch of liquid HF—BF₃ catalyst was used to treat successively 36 batches of heavy catalytic cycle oil with methylcyclohexane as the isoparaffin. Each batch of hydrocarbon feed was treated for 3 hours at 60° C. The raffinate or hydrocarbon phase was then decanted away from the acid phase and another batch of fresh hydrocarbon feed introduced into the reactor. After 36 batches, the hydrocarbon phases were intermingled to form a single product mixture. The acid phase was decomposed with cold water and the dissolved hydrocarbons separated from the aqueous layer. The extract was analyzed for sulfur content and also fractionated into 3 fractions. A complete description of the operation is set out below. By the use of the technique of this run, it is possible to produce a material which is of fair quality for catalytic cracking charge with only a small consumption of methylcyclohexane.

Catalyst: HF, 400 g., BF₃ 39 g.

Operation: 36 batches hydrocarbon, 200 g. each. Each batch treated for 3 hours at 60° C. Raffinate was then removed and another batch added.

Product Balance	Wt. g.		
	Feed	Raff.	Ext.
MCH	3,637	3,422	
HCCO	3,516	3,007	647
	7,153	6,429	647

HCCO Loss to Ext. Layer=13.5%.
MCH Consumption=5%.

Sulfur balance:	Wt. percent, S
Feed	1.22
Raff.	0.77 (0.2 to 1.2)
Ext.	3.42
Percent S recovery	97
Refractive index change:	n _D ²⁰
Feed	1.5165
Raff.	1.4920 (1.450 to 1.503)

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BOILING RANGE OF RAFFINATE SAME AS FEED (250-380° C.)

[Composition of extract.]

Cut No.	Wt. Percent	B.P., ° C.	n_D^{20}
1-----	9	215-305	1.5914
2-----	13	305-330	1.6250
3-----	15	330-350	1.6485
4-----	16	350-365	1.6635
5-----	13	365-440	Resin
6-----	13	440-485	Resin
7-----	9	485-520	Resin
Btms-----	12	520	Coke

Thus having described the invention, what is claimed is:

1. A process which comprises contacting, under substantially anhydrous conditions, a hydrocarbon feed containing an aromatic hydrocarbon having at least two fused benzenoid rings and a methylcyclohexane, in a molar ratio of said cyclohexane to said aromatic hydrocarbon of at least about 2, with a catalyst consisting essentially of liquid HF, in an amount between about 50 and 500

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volume percent based on said aromatic hydrocarbon, and BF_3 , in an amount from about 1 to 5 moles per mole of said aromatic hydrocarbon, at a temperature between about 15° C. and 100° C. for a time between about 5 minutes and 3 hours, the longer times corresponding to the lower temperatures, separating an acid phase from a hydrocarbon phase, and separating unreacted methylcyclohexane from hydrocarbon product, which product is characterized by a hydrogen content higher than said feed.

2. The process of claim 1 wherein said feed is a catalytically cracked gas oil.

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