

[54] **CATALYTIC CRACKING OF FCC GASOLINE AND VIRGIN NAPHTHA**
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3,247,098	4/1966	Kimberlin.....	208/120
3,284,341	11/1966	Henke et al.	208/120
3,679,576	7/1972	McDonald	208/74
3,706,654	12/1972	Bryson et al.....	208/74
3,748,251	7/1973	Demmel et al.	208/74
3,758,403	9/1973	Rosinski et al.	208/120
3,758,628	9/1973	Strickland et al.....	260/683.43
3,761,391	7/1973	Conner	208/76
3,761,394	7/1973	Reynolds et al.	208/120
3,776,838	12/1973	Youngblood et al.	208/74
3,784,463	1/1974	Reynolds et al.	208/74
3,816,294	6/1974	Wilson et al.....	208/67

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[56] **References Cited**
UNITED STATES PATENTS

2,376,501	5/1945	Nelson et al.....	208/14
2,406,394	8/1946	Newton.....	208/74
2,425,555	8/1947	Nelson.....	208/70
2,426,903	9/1947	Sweeney	208/67
2,921,014	1/1960	Marshall	208/74
2,981,674	4/1961	Good	208/70

[57] **ABSTRACT**

A combination process is described for improving the quality and volatility of a refinery gasoline pool comprising the cracking of gasoline product of gas oil cracking and separate product recovery thereof, cracking of virgin naphtha and alkylating olefins formed in the combination process for blending with pool gasoline.

10 Claims, 3 Drawing Figures

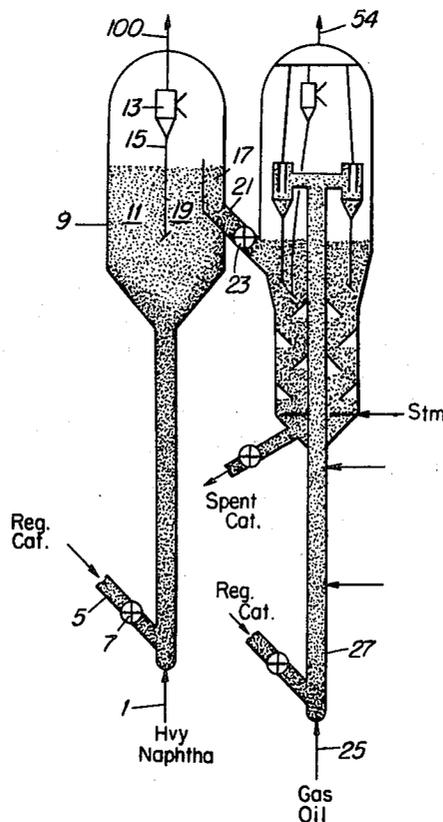
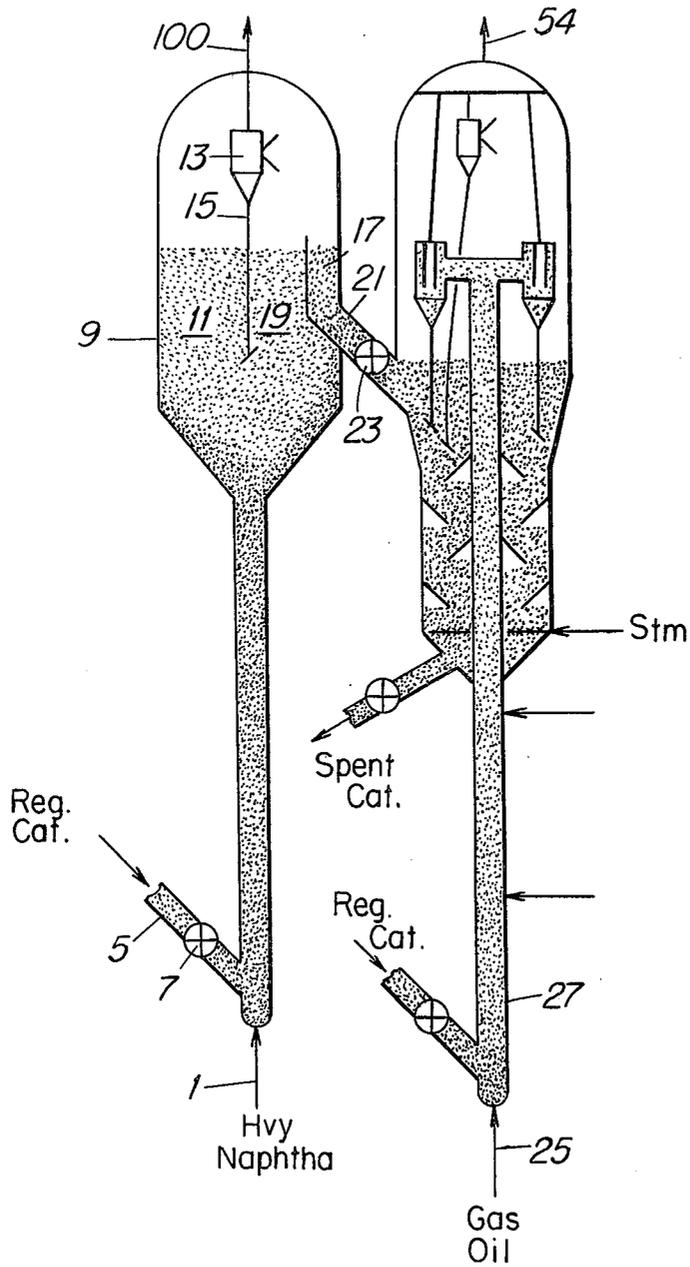


FIGURE II



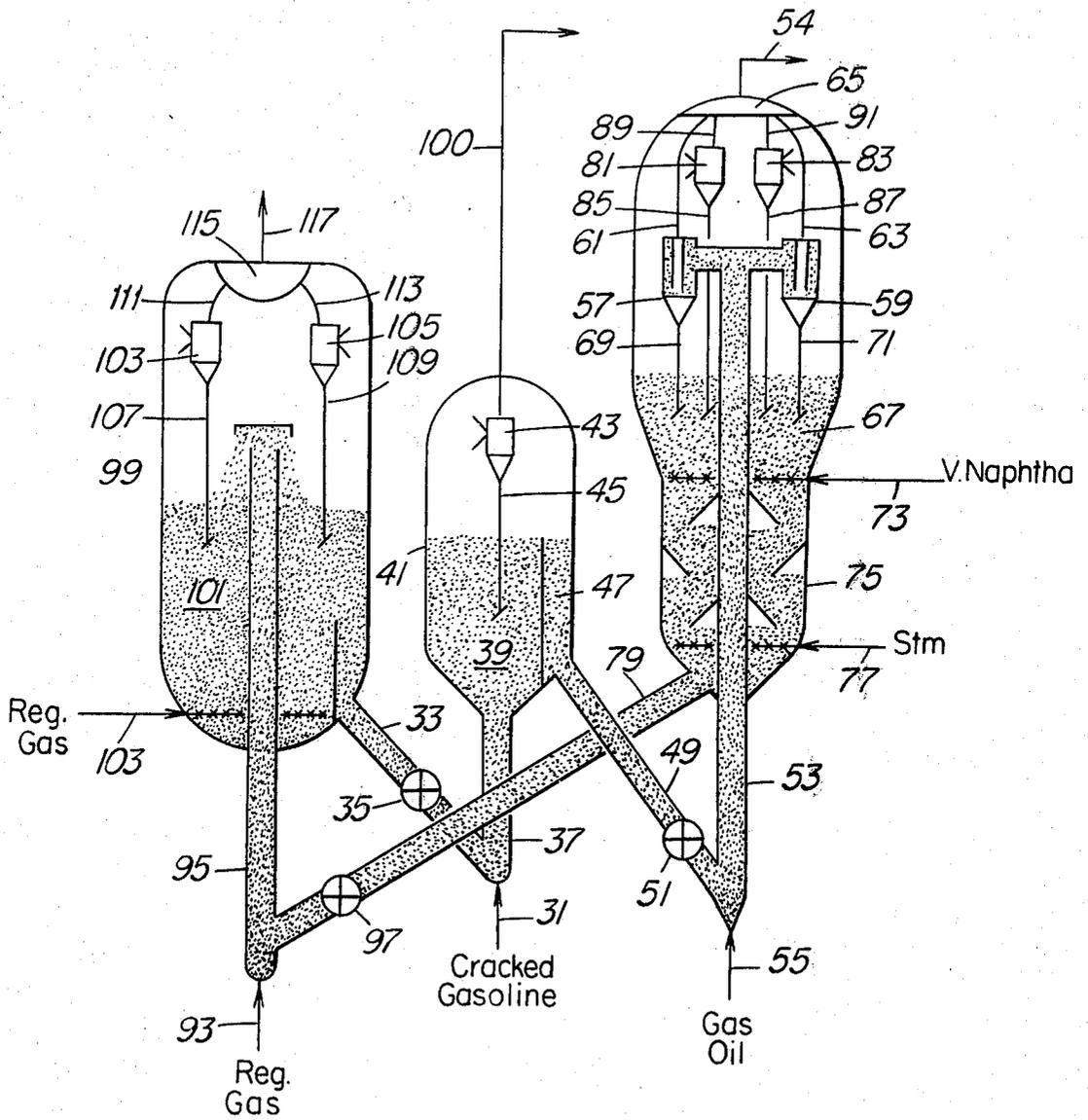


FIGURE III

CATALYTIC CRACKING OF FCC GASOLINE AND VIRGIN NAPHTHA

BACKGROUND OF THE INVENTION

The fluid catalyst system as we know it today embodies the technique of utilizing finely divided solid particulate material in a fluid or a freely moving state such that a mass of solids can be circulated much in the same way as a liquid. Thus in catalytic cracking operations, the fluid catalyst is caused to flow between and through a hydrocarbon conversion zone and a catalyst regeneration zone. The catalyst has been used in dispersed and/or dense phase condition or combinations thereof to permit contact of reactant materials therewith followed by separation of catalyst particles from products of reaction. Thus the catalyst has been used either as a dense fluid bed of catalyst in the reaction and regeneration zones or passed in a dispersed phase condition upwardly through one or both zones.

During World War II, the demands for large volumes of high octane gasoline suitable for military use prompted the re-cracking of gasoline products of thermal and catalytic gas oil cracking operations over conventional amorphous silica-alumina catalysts in order to achieve high octane materials. Throughout the history of catalytic cracking, hydrocarbon materials insufficiently cracked to produce gasoline boiling range material have been recycled and subjected to further catalytic cracking. To improve the crackability of heavy recycle fractions, they may be subjected to a prehydrogenation treatment before further cracking thereof. Some early patents directed to the techniques above expressed are: Nelson U.S. Pat. No. 2,376,501 issued May 22, 1945; Newton U.S. Pat. No. 2,406,394 issued Aug. 27, 1946; Sweeney U.S. Pat. No. 2,426,903 issued Sept. 2, 1947; Nelson U.S. Pat. No. 2,425,555 issued Aug. 12, 1947 and Marshall U.S. Pat. No. 2,921,014 issued Jan. 12, 1960.

During the last decade cracking catalyst compositions comprising crystalline aluminosilicate zeolites have been widely adopted in both fluid and moving bed cracking operations. The use of these zeolite catalysts is so widespread that they represent over 90% of catalyst used in fluid operations today. They are used in dispersed phase riser reaction zones alone or in combination with dense catalyst phase reaction zones. Most of these composite catalysts consist of a small percentage (5 to 20%) of the crystalline zeolite in a larger percentage of an amorphous cracking catalyst such as silica-alumina.

Currently the extreme difficulties encountered throughout the United States because of atmospheric pollution have imposed many requirements or potential requirements on motor fuels. Every effort is being made to reduce atmospheric pollution by products of combustion from automobiles. These efforts, in turn, result in specific detailed objectives with motor fuels. For example, reduced use of tetraethyllead is sought. This necessitates gasolines of high intrinsic octane number. Higher volatility is being considered to ensure good driveability of new engines. For instance, it has been recently proposed by General Motors to set the 50%, 90% and end boiling points of quality gasoline in the range of 190°-210°F., 280°-320°F. and 330°-380°F. respectively. California has a bromine number specification for gasoline because olefins in

gasoline contribute to pollution. Since sulfur compounds also contribute to pollution, low sulfur levels are sought.

To meet higher volatility requirements, it is necessary to reduce the boiling ranges of certain blending components of the gasoline pool such as the gasoline product of catalytic cracking and reforming.

One simple route for lowering the 50% boiling point of gasoline is by undercutting the cracked stock or by lowering the end point of a reforming charge stock. However, this is a most expensive route for producing high volatility gasoline and in times of crude oil shortage, operates to oppose the conservation of energy fuels.

SUMMARY OF THE INVENTION

It has been discovered that heavy cracked gasoline can be re-cracked over a zeolite-containing catalyst at particular operating conditions to provide an improved and modern approach to the production of gasoline satisfying stringent new quality specifications as now dictated by the need to reduce emissions from internal combustion engines.

The zeolite catalyst is able to effect a degree of octane improvement necessary for today's needs and not heretofore possible with amorphous silica-alumina catalysts. Moreover the zeolite catalyst effects significant volatility improvement and reduces olefins in the liquid cracked product to a level not practically attainable with a silica-alumina catalyst. Re-cracking removes the bulk of the sulfur from the heavy cracked gasoline. It produces high yields of propylene, butenes and isobutane which are valuable as alkylation charge stocks.

Cracking of a virgin heavy naphtha over zeolite catalyst effects large improvements in octane number and volatility, not practical over silica-alumina. It produces gaseous olefins and isobutane, valuable as alkylation feed stocks.

There are a number of ways of accomplishing these benefits. As one alternative, cracked naphtha is recycled and/or virgin naphtha is added to a riser cracking zone along with a gas oil feed. A second alternative may involve a multi-stage operation in which a cracked naphtha is re-cracked or a virgin naphtha is cracked in a separate riser reactor or a dense fluid catalyst bed reactor. As a third alternative, the choice of conditions for cracking heavy cracked gasoline and heavy virgin naphtha can be met in a combination process in which heavy cracked gasoline is re-cracked at high temperature in a dense bed, gas oil is cracked in dispersed phase in a riser, and virgin naphtha is cracked at a lower temperature in a dense fluid catalyst bed.

DISCUSSION OF SPECIFIC EMBODIMENTS

It has been found when following the concepts of this invention that the cracking of selected hydrocarbon fractions under particular operating conditions offers a greater potential in various refinery applications for producing high volatility gasoline, high octane blending stock, light olefins for alkylation reactions, aromatic concentrates for use in petrochemicals, improved isobutane production and a reduction in olefin and sulfur in the gasoline product.

Exploratory studies of the concepts of the present invention were made in laboratory bench scale equipment which involved passing a heavy gasoline charge material over 180 to 300 gms. of catalyst in fixed fluidized bed at preselected process conditions. Time on

stream for each cycle of run was 5 minutes and after each cycle the reactor was purged and the catalyst regenerated in-situ. The products were cooled and weathered at 120°F. The resulting liquid product was found to have 40–50 volume percent of the total C₅'s produced. Both liquid and gaseous products were fully analyzed. The ranges of operating conditions selected were: reactor temperature from 850° to 1100°F; catalyst to oil ratio from 2 to 10 w/w; the liquid hourly space velocity from 1 to 6 and a vapor residence time of several seconds.

In another group of examples cracked and virgin naphthas were cracked in a short-contact-time semi-commercial riser pilot unit. The riser cracking zone discharge temperature was varied from about 900° to about 1200°F. and the catalyst-to-oil ratio was varied from about 8 to 60 w/w. Oil and catalyst contact times were of the order of 4 to 7 seconds.

Most of the examples relate to one identified cracked naphtha and to one identified virgin naphtha. Properties of these naphthas are reported in Table I. The one cracked gasoline or naphtha fraction was produced by cracking over a zeolite catalyst. A few fractions of similar materials but of different boiling ranges were examined.

TABLE I

Properties	CHARGE STOCKS	
	Virgin Straight Run Naphtha, 260–380°F. Fraction	FCC Cracked Gasoline 260–380°F. Fraction
Gravity, °API	51.1	39.3
Sulfur, wt.%	<0.001	0.10
Bromine No.	<0.1	18.8
ASTM Distillation, °F		
IBT	278	280
10%	288	293
30%	296	301
50%	303	309
70%	315	322
90%	334	343
FBP	352	361
Research Octane Number, clear	40.8	93.5
PONA Analysis, vol.%		
Paraffins	44.7	12.7
Naphthenes	37.4	8.7
Olefins	0.4	13.6
Aromatics	17.5	66.0

Four catalysts have been used. Catalyst A was a commercial equilibrium fluid catalyst and consisted of about 10% REy zeolite in a silica-alumina-zirconia-clay matrix. Catalyst B was also a commercial equilibrium fluid catalyst and consisted of about 15% REY zeolite

in a similar matrix. Catalyst C was a laboratory steamed catalyst and consisted of 5% of zeolite ZSM-5 on catalyst B. Thus it contained about 15% REY and 5% ZSM-5. Catalyst D was a laboratory steamed catalyst and consisted of 10% ZSM-5 on the matrix material of catalyst A.

RECRACKING OF HEAVY FCC GASOLINE

Approximately 23 weight percent (wt.%) of the gasoline charge stock was cracked to C₄ or lighter products when a heavy (260°–380°F) FCC gasoline was contacted in a dense bed with commercial equilibrium Catalyst A at nominal gas oil cracking conditions (e.g. 1050°F. reactor temperature and 6 C/O ratio). Conversion, defined as the weight percent of charge stock converted to C₄ or lighter products and to coke increased with reactor temperature and catalyst to oil ratio (C/O). The cracking activity of Catalyst C was approximately the same as that of Catalyst A.

Conversion to C₄ and lighter, plus coke, is here defined as "conversion" because these products are generally outside of the gasoline boiling range and therefore not directly usable in motor gasoline. However, isobutane and the light olefins are convertible to alkyl-

ate and butanes can be used in the finished gasoline to give desired vapor pressure.

Tables II and III report results of Examples I to XI involving cracking of heavy FCC gasoline.

TABLE II

Example Catalyst	Cracking of 260–380 FCC Naphtha in dense bed bench unit				
	I A	II A	III A	IV C	V D
Operating Conditions					
Avg. Reactor Temp. °F.	1050	1050	950	950	1050
Cat. to Oil Ratio, wt.	2.1	6.0	6.1	6.2	6.3
WHSV	5.7	2.0	2.0	1.9	1.9
Conversion to C ₄ -, wt. % charge*	16.5	22.9	17.2	18.8	17.8
Product Yields, % Charge					
C ₅ + Liquid, vol. %	82.6	75.5	81.9	80.7	80.7
Total C ₅ 's, vol. %	5.7	6.0	7.3	7.7	3.7
Total C ₄ 's, vol. %	9.8	12.0	11.5	11.9	8.4
Total Dry Gas (wt. %)	8.4	11.5	7.1	7.9	11.3
Coke (wt. %)	1.07	3.04	2.03	2.46	0.53
Isobutane, vol. %	4.4	6.0	7.0	7.4	2.0
Butene, vol. %	4.2	4.0	2.4	2.4	5.9
Propene, vol. %	5.6	5.1	3.2	3.6	9.8
Product Properties					
Sulfur, wt. %	0.050	0.042	0.027	0.026	0.056
Research O.N. clear	99.5	102.0	100.0	101.1	>9.7
PONA analysis, C ₆ +, vol. %					

TABLE II-continued

Example Catalyst	Cracking of 260-380 FCC Naphtha in dense bed bench unit				
	I A	II A	III A	IV C	V D
Paraffins	12.8	10.4	12.4	9.5	14.1
Naphthenes	5.2	4.4	5.3	3.4	7.9
Olefins	1.8	2.3	1.9	1.1	2.8
Aromatics	80.1	82.9	80.4	85.9	75.2

*Includes conversion to coke.

TABLE III

Example Catalyst	Cracking of FCC Naphtha in Riser Pilot Plant						
	VI B	VII B	VIII B	IX B	X B	XI A	
Boiling Range	← 260-380 →					260-450	260-380
Operating Conditions							
Riser Top Temp., °F.	986	1005	1028	1173	1010	1013	
Cat. to Oil Ratio, w/w	7.7	19.6	35.3	62.9	20.4	10.1	
Oil Contact Time, sec.	5.5	5.1	4.8	5.2	5.0	5.6	
Cat. Residence Time, sec.	7.1	6.8	6.7	7.4	6.7	7.2	
Conversion to C ₄ -, wt.% charge*	15.9	24.0	32.9	55.2	25.9	13.2	
Product Yields, % charge							
C ₅ + Liquid, vol.%	84.0	75.8	66.4	42.5	74.3	86.7	
Total C ₃ 's, vol.%	8.1	9.5	9.5	4.1	9.3	6.6	
Total C ₄ 's, vol.%	11.8	15.5	18.4	14.1	15.4	10.1	
Total Dry Gas, wt.%	6.2	9.3	12.7	29.1	10.2	5.3	
Coke, wt.%	15.1	4.06	7.49	16.27	5.28	0.82	
Isobutane, vol.%	6.5	9.5	11.8	5.8	9.5	4.6	
Butene, vol.%	3.2	2.2	1.5	2.6	2.0	4.2	
Propene, vol.%	5.3	5.0	4.2	5.1	4.7	4.7	
Product Properties							
Sulfur, wt.%	0.042	0.028	0.023	0.014	0.077	0.042	
Bromine No.	5.5	3.1	2.1	1.7	3.1	8.7	
Research O.N., clear	100.7	104.3	105.4	110.6	103.9	99.8	
PONA Analysis, C ₆ +, vol.%							
Paraffins	12.6	8.7	3.2	0.5	6.5	14.3	
Naphthene	4.0	1.5	0.1	0.1	1.1	5.9	
Olefins	1.9	1.6	1.1	0.1	1.0	3.0	
Aromatics	81.6	88.2	95.6	99.3	91.3	76.7	

*Includes conversion to coke.

Gasoline octane number is of prime importance and the octane number in the absence of lead is of special importance because of problems with air pollution. Example I, Table II, illustrates the fact that re cracking heavy FCC gasoline to about 17% conversion raises the clear octane number by six units (from 93.5 to 99.5). More extensive conversion increases octane number still further and 33% conversion gives about 12 units (93.5 to 105.4, Example VIII, Table III) while 55% conversion gives about 17 units (93.5 to 110.6, Example IX). Re cracking at 33-55% conversion converted the cracked gasoline to a liquid product containing over 95% aromatics (Examples VIII and IX). Conversions of 16% up to 55% were obtained in dense bed and riser units. Conversion increased with temperature and with catalyst-to-oil ratio; and octane number (and aromatic content) increased with conversion. Catalysts A, B and C were roughly similar in performance. In the riser cracking unit, heavy FCC gasoline of 260°-450°F. boiling range cracked very much like the 260°-380°F. fraction. (Compare Examples VII and X). Similarly, cracked fractions boiling up to 500°F. are desirable charge stocks. Amorphous silica-alumina cracking catalysts are not able to produce these high conversions.

Olefin content and bromine number of liquid products thus obtained is also of interest because of the

effect of olefins on air pollution. Whereas the original heavy FCC gasoline contained 13.6% olefins, 20% conversion of this fraction by re cracking reduced olefins to about 2%; 33% conversion dropped olefins to near 1% while 55% conversion removed essentially all olefin. Similarly, 16% conversion reduced bromine number from 18.8 to about 6 and higher conversion reduced bromine number still more. With these zeolite catalysts, a degree of olefin removal is attained which is not practical with amorphous silicaalumina.

Light olefins (C₂=~C₄=) produced could be further processed to produce gasoline blending stocks or separated for certain petrochemical manufacturing. Gasoline cracking over ZSM-5 catalyst showed exceptionally high yields of light olefins as illustrated by Examples V and XIX. For instance, 70-75 wt.% of the C₄+ lighter products in these examples were light olefins. Therefore, if light olefins are desired, heavy naphtha or FCC gasoline could be processed over ZSM-5 catalyst.

Re cracking of heavy FCC gasoline improves the volatility thereof and this contributes to improved volatility of the whole gasoline pool. Table IV reports simulated distillation data obtained by gas chromatography for the products from a dense fluid catalyst bed example.

TABLE IV

THE EFFECT OF RECRACKING HEAVY FCC GASOLINE ON VOLATILITY DENSE BED UNIT						
Example	Charge	I	II	III	IV	V
Conversion	0	16.5	22.9	17.2	18.8	17.8
Simulated Distillation, °F.						
IBP	239	113	98	77	17	30
10%	273	231	221	222	227	231
30%	296	279	273	279	274	278
50%	328	300	291	296	286	292
70%	351	335	330	335	322	328
90%	382	376	375	379	354	359
95%	404	414	421	419	375	371
EP	553	606	596	613	527	494

The 10% point is reduced 40°–50°F. and the 50% point is reduced about 30°–40°F. Table IV indicates some reduction in 90% point but an increase in end-point. At the dense fluid catalyst bed conditions there are some polymerization and condensation reactions to form a small amount of heavy ends. These can be removed as a very few percent of byproduct by distillation.

Table V reports ASTM distillation data for charge and products of a riser pilot plant.

TABLE V

THE EFFECT OF RECRACKING HEAVY FCC GASOLINE ON VOLATILITY RISER PILOT PLANT							
Example	Charge	VI	VII	VIII	IX	X	XI
Conversion	0	15.9	24.0	32.9	55.2	25.9	13.2
ASTM Distillation, °F.							
IBP	280	102	88	103	135	95	102
10%	293	202	189	202	220	188	217
30%	301	283	272	265	244	274	291
50%	309	306	292	283	259	294	313
70%	322	329	318	312	286	325	335
90%	343	391	422	441	456	471	413
95%	—	499	544	—	520	574	580
E.P.	361	539	552	591	623	607	605

Again, the 10% point is reduced by a large amount. The 50% point is reduced 25° to 60° at the 33–55% conversion. The riser system produces more heavy ends and, in this case, the 90% point was increased. The 90% point of the charge is retained by removal of 9–11 vol.% of heavy ends by redistillation.

Recracking of heavy FCC gasoline has the added beneficial effect of reducing sulfur content. Examples I–IV, Table IV, indicate 50–75% sulfur removal at about 16–23% conversion. Similarly, Examples VI–IX and XI, Table V, resulted in 58–85% sulfur removal at 16–55% conversion.

Cracking of heavy FCC gasoline, unlike reforming, produces olefins which can be alkylated to increase gasoline yield. During the recracking of heavy FCC

gasoline significant yields of propene and butene are produced. Examples I to XI, Tables IV and V, indicate that the amounts produced are greater at higher cracking temperatures and are greatest at moderate conversions, decreasing at higher conversion levels. At the same time, significant amounts of isobutane are produced which can be alkylated with these olefins. The amount of isobutane produced is highest at low cracking temperatures and at high conversion levels.

In summary, the recracking of a gasoline product of

gas oil cracking experiments has demonstrated that the heavy gasoline fraction can be recracked to produce lighter, cleaner and higher octane gasoline at the expense of the gasoline volume. However, if C₃=, C₄= alkylate material is included, the loss in total recoverable liquid per octane boost is much less.

CRACKING OF HEAVY VIRGIN NAPHTHA

Heavy virgin naphtha is more easily cracked than a heavy gasoline product of catalytic cracking and the cracking reaction can be accomplished at lower temperatures. Tables VI and VII report the results of Examples XII to XXV. Heavy virgin naphtha was cracked in both a dense fluid catalyst bed test unit and in a riser pilot plant test unit.

TABLE VI

CRACKING OF 260–380° VIRGIN NAPHTHA IN DENSE BED BENCH UNIT								
Example Catalyst	XII A	XIII A	XIV A	XV A	XVI A	XVII B	XVIII C	XIX D
Operating Conditions								
Avg. Reactor Temp. °F	850	950	1050	1050	1100	1100	950	1050
Cat. to Oil Ratio, wt.	10.0	6.2	6.1	2.0	10.1	10.1	6.1	6.0
WHSV	1.2	1.9	2.0	6.0	1.2	1.2	2.0	2.0
Conversion to C ₄ –, wt.% charge*	23.7	25.7	34.4	25.2	45.7	54.2	24.1	17.6
Product Yields, % charge								
C ₅ + Liquid, vol.%	77.9	74.4	65.5	74.6	53.8	44.6	76.6	82.2
Total C ₅ 's, vol.%	13.1	11.0	10.7	7.0	9.3	7.7	13.4	3.4

TABLE VI-continued

CRACKING OF 260-380° VIRGIN NAPHTHA IN DENSE BED BENCH UNIT								
Total C ₄ 's, vol.%	21.0	20.2	22.0	14.5	20.4	21.1	19.0	7.8
Total Dry Gas, wt.%	7.0	9.6	16.0	13.7	21.3	31.9	9.0	11.1
Coke, wt.%	1.32	1.11	1.89	0.59	4.23	6.64	0.98	0.45
Isobutane, vol.%	15.2	13.4	12.8	8.3	11.3	11.6	12.2	2.0
Butene, vol.%	1.8	3.1	5.3	4.0	6.3	4.9	3.4	5.1
Propene, vol.%	2.6	4.4	7.0	5.0	9.8	9.2	4.6	8.5
Liquid Product Properties								
Research ON clear	75.1	69.6	73.2	62.7	82.4	87.8	72.5	58.6
Gravity, °API	49.6	48.2	46.1	49.3	41.5	38.8	48.8	50.7
Sulfur, wt.%	.001	.003	.001	.005	.007	.003	.001	.004
PONA Analysis, C ₆ +, vol.%								
Paraffins	38.2	41.3	37.8	42.5	30.6	24.6	39.0	42.9
Naphthenes	16.2	17.7	17.2	21.4	12.4	8.5	15.7	32.4
Olefins	1.1	1.8	2.5	2.7	2.4	2.3	1.6	2.6
Aromatics	44.3	39.1	42.5	33.4	54.6	64.4	43.8	22.1

*Includes conversion to coke

TABLE VII

CRACKING OF VIRGIN NAPHTHA IN RISER PILOT PLANT						
Example	XX	XXI	XXII	XXIII	XXIV	XXV
Catalyst	B	B	B	B	B	A
Boiling Range, charge	← 260-380 →			380-500	260-380	
Operating Conditions						
Riser Top Temp. °F.	998	995	1036	914	977	985
Cat. to Oil Ratio, w/w	13.3	17.3	26.8	37.7	15.1	9.4
Oil Contact Time, sec.	5.3	4.4	4.3	5.0	4.2	4.9
Cat Residence Time, sec.	6.9	5.8	5.8	7.1	5.6	6.3
Conversion to C ₄ -wt. % charge*	27.2	33.6	49.2	32.5	32.7	20.9
Product Yields, % charge						
C ₃ + Liquid, vol. %	75.0	68.1	51.8	69.5	72.0	79.9
Total C ₃ 's, vol. %	15.3	16.0	17.7	17.8	17.5	11.0
Total C ₄ 's, vol. %	20.8	26.1	33.8	26.1	24.6	16.6
Total Dry Gas, wt. %	10.1	11.7	18.9	9.5	11.5	7.7
Coke, wt. %	1.71	2.73	5.49	3.80	4.13	0.83
Isobutane, vol. %	12.4	16.3	21.8	17.5	14.5	8.7
Butene, vol. %	5.0	4.0	3.4	2.1	5.3	3.3
Propene, vol. %	7.8	7.4	7.7	4.3	8.5	6.9
Product Properties						
Research						
ON clear	79.6	87.7	97.2	90.0	90.6	77.0
Gravity, °API	52.0	53.0	46.6	51.4	50.2	53.7
Sulfur, wt. %	.004	.003	.006	.003	.12	<.001
PONA Analysis, C ₆ +, vol. %						
Paraffins	37.7	30.5	16.8	28.4	27.0	40.6
Naphthene	13.2	6.9	1.9	5.7	6.7	17.5
Olefins	2.4	1.9	1.3	1.1	2.3	3.5
Aromatics	46.8	60.8	80.1	64.0	64.1	38.4

*Includes conversion to coke

Conversion increases with temperature and with catalyst-to-oil ration as shown by the above tables. Catalyst B was more active than catalyst A. Catalyst C had an activity much like that of Catalyst A.

Octane improvements are greater on cracking virgin

naphtha than on re cracking gasoline product of gas oil cracking, but octane numbers reached are not as high. At conversion levels of 25 to 55%, the clear octane number was raised from 41 for the change to products in the 70 to 90 octane number range.

TABLE VIII

THE EFFECT OF CRACKING HEAVY VIRGIN NAPHTHA ON VOLATILITY DENSE BED UNIT									
Example	Charge	XII	XIII	XIV	XV	XVI	XVII	XVIII	XIV
Conversion	0	23.7	25.7	34.4	25.2	45.7	54.2	24.1	17.6
Simulated Distillation, °F									
IBP	239	—	52	78	77	—	—	20	21
10%	264	—	175	213	229	—	—	163	232
30%	295	—	257	258	267	—	—	253	275
50%	317	—	286	288	293	—	—	281	298
70%	391	—	319	317	322	—	—	308	323
90%	367	—	354	353	354	—	—	338	351
95%	384	—	392	393	383	—	—	353	364
E.P.	485	—	597	599	577	—	—	492	516

TABLE IX

THE EFFECT OF CRACKING HEAVY VIRGIN NAPHTHA IN VOLATILITY RISER PILOT PLANT							
Example	Charge	XX	XXI	XXII	XIII	XXIV	XXV
Conversion ASTM	0	27.2	33.6	49.2	32.5	32.7	20.9
Distillation, °F.							
IBP	278	88	83	83	89	86	87
10%	288	149	128	130	133	122	156
30%	296	249	217	224	219	187	267
50%	303	284	281	273	277	276	288
70%	315	309	309	301	306	366	310
90%	334	363	421	499	369	553	351
95%	—	508	—	—	—	—	—
E.P.	352	522	528	576	522	640	455

Cracking virgin naphtha improves volatility. The 50% point is lowered 20° to 40°F. at conversions of 25 to 50%. The 90% point is reduced in the dense fluid catalyst bed examples (Table VIII). In the riser pilot plant test unit (Table IX) there was some formation of heavy ends and redistillation to remove about 5 to 8 weight percent of heavy ends is needed to maintain the 90% point and the end point. There is a very minor formation of heavy ends in the dense fluid catalyst bed examples which raised the endpoint.

As obtained in re cracking of cracked gasoline, liquid cracked products from virgin naphtha have a very low olefin content.

Cracking of virgin naphtha produces very large yields of isobutane, butene and propene, all valuable alkylation charge stocks. Cracking is especially selective to isobutane over these zeolite catalysts at low temperatures. At 850°F. and 10 catalyst-to-oil ratio there is a yield of 15% isobutane at 24% conversion. Lower temperatures, such as 800°F., and higher catalyst-to-oil ratios, such as 20, will increase isobutane yield.

As for (FCC) fluid catalytic cracking gasoline re cracking, ZSM-5 catalysts produce very large yields of light olefins ($C_2 \sim C_4$). These light olefins could be alkylated for blending into gasoline pool or separated for petrochemical manufacturing.

The amounts of potential alkylate produced are so large that, at moderate conversions, combined yields of re cracked gasoline and alkylate, adjusted to gasoline vapor pressure, approach 100% of the volume of the charge. Table X reports the combined yields of re cracked gasoline plus alkylate.

TABLE X

RECOVERY OF TOTAL LIQUID PRODUCT FROM HEAVY FCC GASOLINE				
	C_3 + Liquid Vol.% of Chg.	Potential Alkylate Vol.% of Chg.	Outside $i-C_4$ to be purchased Vol.% of Chg.	Total Liq. Recovery Vol.% of Chg.
Ex. I	82.6	17.2	7.5	99.8
II	75.5	16.1	5.0	91.6
III	81.9	9.9	-2	91.8
IV	80.7	10.6	-1	91.3
V	80.7	27.5	17.1	108.2
VI	84.0	15.1	3.8	99.1
VII	75.8	12.8	-6	88.6
VIII	66.4	10.2	-4.7	76.6
IX	42.5	13.7	3.6	56.2
X	74.3	12.0	-1.3	86.3
XI	86.7	15.7	6.1	102.4

In summary, it has been demonstrated that a significant benefit can be achieved by cracking heavy virgin naphtha over fluid catalytic cracking catalysts since a relatively high octane gasoline product was obtained

which can be blended in a gasoline pool and high yields of isobutane are obtained which can be alkylated to produce a high octane blending stock.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. I is a diagrammatic sketch in elevation of one arrangement of apparatus and system for practicing the separate riser re cracking of gasoline product of gas oil cracking in another separate riser reactor with related product recovery equipment.

FIG. II is a diagrammatic sketch in elevation of another arrangement for practicing the concepts identified with FIG. I except a dense fluid bed of catalyst is relied upon to carry out the re cracking of gasoline product of gas oil cracking alone or along with a virgin naphtha fraction.

FIG. III is a diagrammatic sketch of a further embodiment and arrangement of reactor systems sequentially connected for practicing the concepts of the invention wherein gasoline product of gas oil cracking is re cracked in a dense fluid catalyst bed reaction zone with freshly regenerated catalyst, the catalyst used for gasoline re cracking is then used for gas oil cracking in a riser cracking zone and catalyst separated from the riser cracking operation is relied upon for effecting cracking of virgin naphtha.

Referring now to FIG. I there is shown a gas oil riser cracking reactor with a product fractionation step in combination with a separate heavy naphtha or gasoline product of gas oil cracking operation in a separate riser reactor with its own independent product recovery system. The re cracking operation recovery system is

related to the primary fractionation system in a manner to recover a common gasoline product stream of improved octane rating and a common light cycle oil stream. However, it is also contemplated using a single

riser reactor system wherein the gasoline or naphtha to be subjected to re cracking initially contacts the hot freshly regenerated catalyst introduced to the riser and the gas oil charge is then introduced to a downstream portion of the riser reactor for cracking thereof to gasoline boiling product. In the arrangement of FIG. I, a regenerator 2 is shown containing a bed of catalyst 4 which is contacted with oxygen-containing regeneration gas such as air introduced by conduit 6 to an air distributor grid 8. Cyclone separators 10 provided with diplegs 12 are located in the upper portion of the regenerator for separating flue gases from entrained catalyst particles. The separated catalyst particles are returned by the diplegs 12 to the catalyst bed 4 and flue gases are removed as by conduit 14. Regenerated catalyst is removed from bed 4 as by withdrawal well 16 and conveyed to conduit 18 communicating with the lower end of riser 20. A catalyst flow control valve 22 is provided in conduit 18. Regenerated catalyst is also conveyed from well 16 by conduit 24 to the bottom portion of riser 26. Catalyst flow control valve 28 is provided in conduit 24. A gas oil feed boiling in the range of 650°F. to about 1000°F. is introduced by conduit 30 to the bottom portion of riser 26 for admixture with hot regenerated catalyst introduced by conduit 24. A catalyst-oil suspension is thus formed providing a temperature of at least about 950°F. and more usually in the range of 1000°F. up to about 1100°F. which is then passed upwardly through the riser reactor 26 at a velocity to provide a hydrocarbon residence time therein within the range of about 1 second up to about 10 seconds. During passage of the suspension through the riser conversion of the gas oil feed to lower and higher boiling products occurs. These products are separated after removal of catalyst therefrom in a product fractionator as discussed below. The catalyst-hydrocarbon suspension after traversing the riser reactor is caused to flow directly into a plurality of cyclonic separators 32 attached to the end of the riser through a T-connection. Diplegs 34 attached to separators 32 pass separated catalyst to an annular stripping zone 36 provided with baffles 38. Stripping gas such as steam is introduced to the lower portion of the stripping zone by conduit 40. Stripped catalyst is removed from the lower portion of the stripping zone by conduit 42 and conveyed to the bed of catalyst 4 in the regeneration zone. A flow control valve 44 is provided in conduit 42.

Stripping gas and stripped hydrocarbon material are removed from the bed of catalyst in the stripping zone and enters cyclone separator 46 wherein entrained catalyst particles are separated from the stripping gas. Separated catalyst particles are returned to the catalyst bed by dipleg 48. Stripping gas and hydrocarbon material are then passed from separator 46 by a connecting conduit to a plenum chamber 52. Hydrocarbon material separated from the riser reactor 26 by separators 32 pass by connecting conduit 50 to plenum chamber 52. Hydrocarbon material and stripping gas are passed from chamber 52 by conduit 54 to a fractionator 56.

For the purpose of this discussion, fractionator 56 is relied upon to separate a heavy cycle oil (HCO) withdrawn by conduit 58; a light cycle oil (LCO) withdrawn by conduit 60; a heavy naphtha withdrawn by conduit 62; material boiling below the heavy naphtha withdrawn by conduit 64 and a bottoms fraction withdrawn by conduit 66. All or a portion of the bottoms fraction may be passed through heater 66 and returned to the bottom of the tower 56 by conduit 68. Generally the

temperature of the bottom of the tower will be about 690°F. The material boiling below the heavy naphtha fraction and withdrawn from the fractionator by conduit 64 is passed through cooler 70 and thence by conduit 72 to drum 74 maintained at a temperature of about 100°F. In drum 74 a liquid condensate is recovered and recycled by conduit 76 to the upper portion of the fractionator 56 as reflux. Uncondensed product is withdrawn from drum 74 by conduit 78 and passed to cooler 80 and conduit 82 to drum 84 maintained at a temperature of about 100°F.

The heavy naphtha separated in fractionator 56 and withdrawn by conduit may be passed all or in part by conduit 86 to the inlet of riser reactor 20 where it is combined with hot regenerated catalyst introduced by conduit 18 to form a suspension at a temperature within the range of 950°F. to about 1250°F. When virgin naphtha is used as the hydrocarbon feed to riser 20 instead of the heavy naphtha fraction it may be introduced by conduit 88. The suspension formed in the bottom of the riser 20 is passed upwardly there-through under conditions to provide a hydrocarbon residence time in the range of 1 to about 10 seconds before separating the suspension into a catalyst phase and a hydrocarbon phase in cyclone separator 90. The catalyst phase separated in cyclone 90 is passed by dipleg 92 to the bed of catalyst in the stripping zone as above discussed. To complete the separation of catalyst particles from hydrocarbon products of cracking the hydrocarbon phase is removed from separator 90 by conduit 94 and passed to a second separator 96. Catalyst separated in separator 96 is passed by dipleg 98 and 92 to the catalyst bed being stripped. Hydrocarbon vapors are recovered from separator 96 and conveyed by conduit 100 to cooler 102 wherein the vapors may or may not be cooled. The vapors then pass by conduit 104 to tower 106 maintained at a bottom temperature of about 550°F. and a top temperature of about 350°F. A bottoms product boiling in the light cycle oil boiling range is withdrawn from the bottom of the tower by conduit 108 and combined with light cycle oil in conduit 60 withdrawn from fractionator 56. An overhead hydrocarbon portion is withdrawn from tower 106 by conduit 110 and combined with hydrocarbon material in conduit 78. Condensate material comprising gasoline boiling range material is withdrawn from drum 84 by conduit 112 and recycled in part by conduit 114 to tower 106 as reflux. The remaining gasoline boiling condensate material is recovered by conduit 116. Uncondensed vaporous material is withdrawn from drum 84 by conduit 118 and sent to, for example, the refinery gas plant.

The processing arrangement of the present invention contemplates injecting the heavy naphtha to be re-cracked at the base of riser reactor 26 and introducing gas oil to be cracked to a downstream portion of the riser by either or both of inlet conduits 120 or 122. In such an arrangement it is contemplated cracking a virgin naphtha in riser 20 in combination with cracking gas oil alone or in combination with heavy naphtha cracking in riser 26.

Referring now to FIG. II, there is shown diagrammatically in elevation an embodiment of the reactor arrangement of FIG. I in which the heavy naphtha fraction is re cracked in a riser discharging into the bottom of a dense fluid bed of catalyst and deactivated catalyst separated from the dense fluid bed cracking step is combined with catalyst separated from the gas oil

cracking operation and passed through the catalyst stripping zone. In the arrangement of FIG. II, a heavy naphtha fraction separated from the product of gas oil cracking as shown in FIG. I is introduced by conduit 1 to the bottom of riser 3 for admixture with freshly regenerated catalyst introduced by conduit 5 containing catalyst flow control valve 7. A suspension is formed in the lower portion of riser 3 at an elevated cracking temperature. The suspension passes upwardly through riser 3 and is discharged into the bottom of an enlarged zone 9 containing a dense fluid bed of catalyst 11. Cracking of the gasoline fraction is accomplished in the dense fluid catalyst bed 11. Hydrocarbon vapors comprising the re-cracked gasoline vapors are passed through one or more cyclone separators 13 provided with catalyst dipleg 15. The cracked gasoline vapors are withdrawn by conduit 100 and passed to product separation as defined with respect to FIG. I.

In the arrangement of FIG. II, catalyst is withdrawn from the upper surface of fluid bed 11 into a well 17 defined by baffle 19. The catalyst is withdrawn from well 17 by conduit 21 provided with a flow central valve 23. The riser reactor 27 provided for converting a gas oil feed introduced by conduit 25 is intended to be operated in the same manner as described with respect to FIG. I for riser 26. Thus in the arrangement of FIG. II, the hydrocarbon product of gas oil cracking and stripping gas are withdrawn from the top of the vessel by conduit 54 for separation in a manner similar to that described with respect to FIG. I.

FIG. III departs from the arrangements of either FIG. I or II by the combination of cascading regenerated catalyst first through a dense fluid catalyst bed gasoline re-cracking zone, then a gas oil riser cracking zone and the catalyst separated from the gas oil cracking operation and collected as a dense fluid bed of catalyst is then relied upon to crack virgin naphtha prior to the catalyst passing to a stripping zone. The stripped catalyst is then passed to a catalyst regeneration operation. The hydrocarbon products of the gasoline re-cracking step and the separate gas oil cracking step are recovered in a manner similar to that described with respect to FIG. I. Products of virgin naphtha cracking are recovered in the gas oil separation system. In the arrangement of FIG. III, a heavy cracked gasoline fraction is introduced by conduit 31 for admixture with hot regenerated catalyst withdrawn from a catalyst regeneration zone by conduit 33 provided with a catalyst flow control valve 35. A suspension is formed at an elevated temperature of at least 1000°F. which is conveyed by inlet conduit 37 into the bottom portion of a dense fluid bed of catalyst 39 confined in a cracking zone 41. Hydrocarbon product of gasoline cracking is passed through cyclonic separation means 43 provided with separated catalyst dipleg 45. Hydrocarbon vapors are withdrawn by conduit 100 and passed to product separation similar to that described in FIG. I. Catalyst is withdrawn into a well 47 from an upper portion of bed 39 and conveyed therefrom by conduit 49 provided with valve 51 to the bottom portion of gas oil cracking riser 53 to which a gas oil feed is introduced by conduit 55. A suspension at an elevated gas oil cracking temperature is formed in the lower portion of riser 53 and passes upwardly therethrough for discharge into cyclonic separation zones 57 and 59. Hydrocarbon vapors separated in zones 57 and 59 are withdrawn by conduits 61 and 63 communicating with chamber 65 and withdrawal conduit 54. Catalyst particles separated

by cyclonic means 57 and 59 are conveyed to a dense fluid bed of catalyst 67 by diplegs 69 and 71. A virgin naphtha fraction is introduced to the collected bed of catalyst discharged from riser 53 by conduit 73 for conversion thereof to higher octane product and olefin constituents as described above. Catalyst bed 67 is a continuous downwardly moving bed of catalyst which passes into a stripping zone beneath the virgin naphtha inlet distributor grid. The catalyst thus sequentially used as above identified passes downwardly through a stripping zone 75 provided with stripping gas introduced by conduit 77. Stripped catalyst is then withdrawn by conduit 79 for transfer to a catalyst regeneration operation. Hydrocarbon vapor product of virgin naphtha cracking and stripping gas pass through cyclonic separation zones 81 and 83 wherein entrained catalyst is separated and returned to the catalyst bed 67 by diplegs 85 and 87. Hydrocarbon vapors and stripping gas then pass by conduit 89 and 91 to chamber 65. Vaporous material withdrawn by conduit 54 is then separated in the manner described with respect to FIG. I.

Catalyst withdrawn from the stripping zone by conduit 79 provided with valve 97 is combined with regeneration gas 93 in the lower portion of a riser regenerator 95. The suspension thus formed passes upwardly through the riser regeneration zone and is discharged into an enlarged separation-regeneration zone 99 and above a dense fluid bed of catalyst 101 in the lower portion thereof. Additional regeneration gas is introduced to a lower portion of the regeneration zone by conduit 103. In the riser and dense catalyst phase regeneration zones, carbonaceous material deposited during hydrocarbon conversion is removed by burning with the introduced oxygen containing regeneration gas. Gaseous products of combustion pass through separators 103 and 105 wherein entrained catalyst fines are removed from the flue gases. Separated catalyst fines are returned to the catalyst bed 101 by diplegs 107 and 109. Flue gases then pass by conduits 111 and 113 into chamber 115 from which they are withdrawn by conduit 117.

In the arrangement of FIG. III, it is preferred that the catalyst employed be a mixture of crystalline zeolite conversion catalyst of small and large pore diameter crystalline materials and that the small pore crystalline material be of the ZSM-5 type. The large pore crystalline zeolite may be either of the X or Y type of crystalline zeolite.

Having thus provided a general discussion of this invention and provided specific embodiments going to the very essence thereof, it is to be understood that no undue restrictions are to be imposed by reason thereof except as defined by the following claims.

We claim:

1. A method for upgrading hydrocarbons which comprises
 - cracking a gas oil boiling range feed in a first cracking zone in the presence of a crystalline zeolite cracking catalyst at an elevated temperature of at least 850°F to obtain conversion of the gas oil feed to materials including a heavy cycle oil, a light cycle oil, a heavy naphtha fraction and materials lower boiling than said heavy naphtha fraction,
 - cracking the heavy naphtha fraction above obtained in a second cracking zone in the presence of freshly regenerated crystalline zeolite cracking catalyst at an elevated temperature within the range of 850°F

to about 1000°F, separating the product of said heavy naphtha fraction cracking operation in a zone separate from the gas oil product separation under conditions to recover gasoline boiling range material rich in aromatics and lighter hydrocarbon material from a light cycle oil product material, combining said light cycle oil recovered products, combining materials lower boiling than said heavy naphtha product of gas oil cracking with said gasoline boiling and lighter materials separated from the product of said heavy naphtha cracking operation and

separating the combined materials lower boiling than light cycle oil into a gasoline boiling range product fraction and a lower boiling uncondensed vaporous product fraction.

2. The method of claim 1 wherein a freshly regenerated crystalline aluminosilicate containing cracking catalyst is sequentially passed through said heavy naphtha cracking step, said gas oil cracking step and a virgin naphtha cracking step before stripping of the catalyst and passing stripped catalyst to catalyst regeneration.

3. The method of claim 2 wherein the cracking catalyst comprises a faujasite type of crystalline zeolite in combination with a crystalline aluminosilicate of the ZSM-5 type.

4. The method of claim 1 wherein freshly regenerated catalyst is used for re-cracking the heavy cracked

naphtha material and the gas oil feed and catalyst used in each cracking operation is passed to a common catalyst stripping operation before being regenerated.

5. The method of claim 1 wherein re-cracking of said heavy naphtha fraction is accomplished in a high temperature riser cracking zone at a temperature of at least 950°F.

6. The method of claim 1 wherein the re-cracking of said heavy naphtha fraction is accomplished in a riser cracking zone.

7. The method of claim 1 wherein re-cracking of said heavy naphtha fraction is accomplished in a high temperature riser cracking zone terminating in a dense fluid bed cracking zone.

8. The method of claim 1 wherein catalyst separated from said gas oil riser cracking step is used to convert a virgin naphtha at an elevated cracking temperature to improve its octane rating and the products of said virgin naphtha cracking step are separated with products of said gas oil cracking step.

9. The method of claim 1 wherein the heavy naphtha fraction subjected to re-cracking contains hydrocarbon components boiling up to about 500°F.

10. The method of claim 1 wherein a virgin naphtha is cracked in the presence of said heavy cracked naphtha.

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