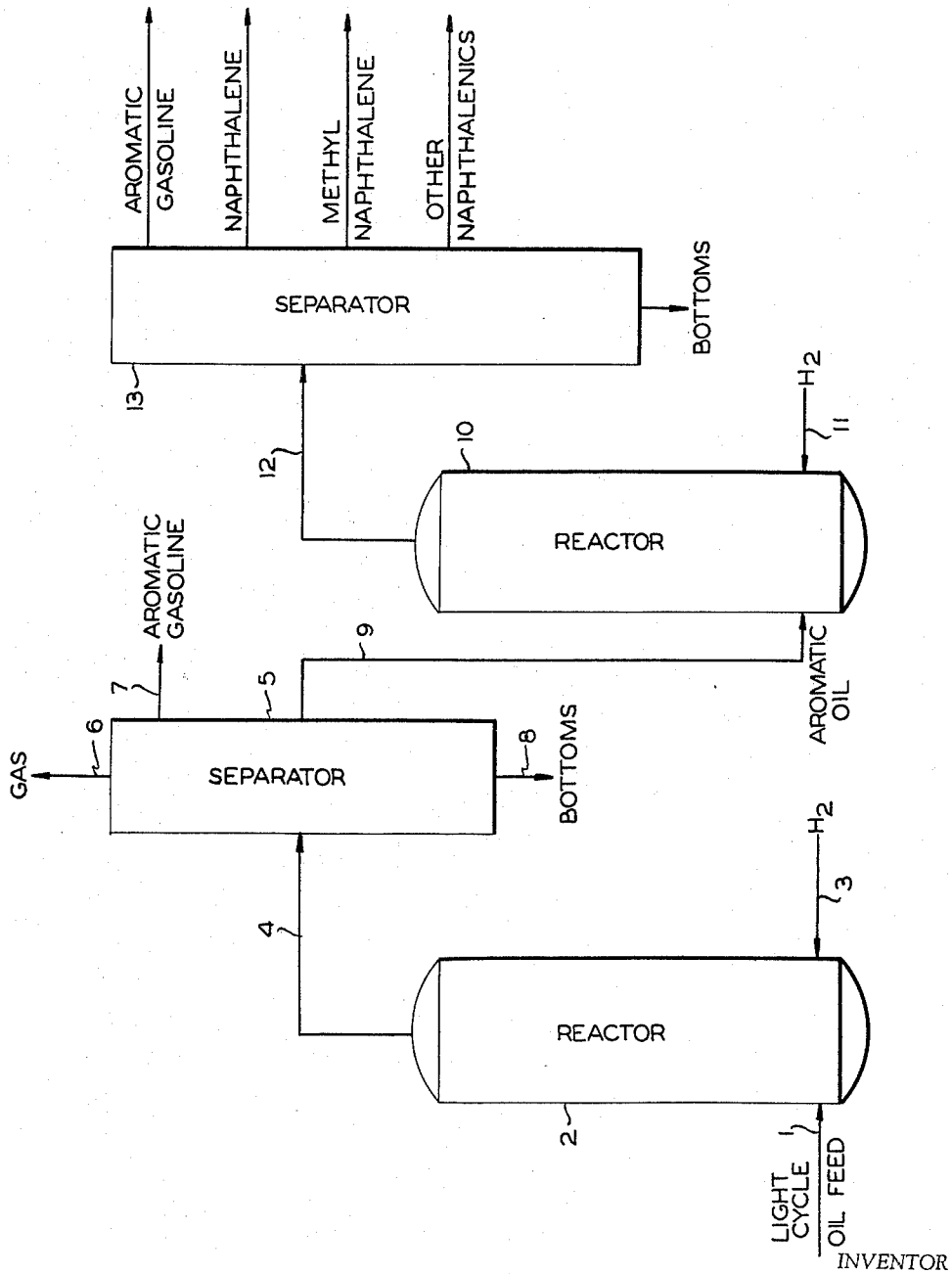
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TWO-STAGE CATALYTIC CONVERSION PROCESS FOR PRODUCING NAPHTHALENE AND AN AROMATIC GASOLINE FROM CYCLE OILS

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TWO-STAGE CATALYTIC CONVERSION PROCESS FOR PRODUCING NAPHTHALENE AND AN AROMATIC GASOLINE FROM CYCLE OILS

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This invention relates to the production of commercial grade naphthalene and, more specifically, to the production of commercial grade naphthalene and high octane aromatic gasoline. The present invention is particularly concerned with a two-stage hydroconversion process in which a light cycle oil derived from petroleum is converted to naphthalene, alkylated naphthalenes and high octane number aromatic gasoline through the utilization of certain hydroforming catalysts in the presence of hydrogen. This application is a continuation-in-part of my copending application Serial No. 434,059, filed June 2, 1954, now abandoned.

High octane gasoline and naphthalenes are highly desirable products which can be derived from petroleum hydrocarbons, and many refiners are in search of new methods of producing these materials from inexpensive charge stocks. The present invention is concerned with a two-stage process for manufacturing these products through catalytic conversion of light cycle oil stocks which are usually considered too refractory to be employed as feeds in conventional catalytic cracking procedures since the amount of coke formed on the catalysts at the conditions necessary for cracking is prohibitive.

I am aware that the production of naphthalene from cycle oils has been proposed, for instance, through utilization of the water gas reaction or hydropyrolysis. Although such processes may give desirable amounts of naphthalene, other valuable constituents of the charge stock are converted to less valuable products such as gas due to the severe conditions needed to effect the dealkylation of the alkyl naphthalenes in the cycle oils. In the present invention, I have devised a method which affords good yields of naphthalene from light cycle oils and at the same time transforms non-naphthalenic constituents to valuable high octane number aromatic gasoline.

Although my process will be defined below as a two-stage hydroconversion of light cycle oil in the presence of non-carbon based hydroforming catalysts at certain reaction conditions, these conditions can be selected or varied within the ranges disclosed to emphasize particular chemical reactions. In the first stage (Stage I) of the present process the reaction conditions can be maintained to convert the major portion of the non-naphthalenic constituents of the feed stock to aromatic and non-aromatic gasoline with a minor amount or substantially none of these constituents being aromatized to the C_{10} to C_{16} range. The gasoline is then separated and the remaining aromatic-rich oil containing naphthalenic derivatives is charged to the second or more severe reaction (Stage II) of the process to produce good yields of commercial grade naphthalene, alkylated naphthalenes and additional amounts of aromatic gasoline.

Alternatively, the Stage I conditions can be selected to effect wholly or predominantly an aromatization reaction with little or no aromatic and non-aromatic gasoline being produced. Although it is possible to produce no substantial amount of gasoline in the first stage which would obviate the desirability of a gasoline removal

operation, this stage will in most instances, produce at least a small amount of gasoline which should be removed from the higher boiling aromatic concentrate before it is subjected to the second stage reaction. In this variation of the system among the products from the second stage are again naphthalene, alkylated naphthalenes and high octane aromatic gasoline. In commercial practice, an operator can vary the first stage reaction conditions within the prescribed limits as he chooses; however, in each instance the ultimate products are essentially the same. It may even be desirable to select the conditions for the first stage reaction so that a substantial amount of gasoline is made; yet non-naphthalenes in the feed stock could also be converted in substantial amounts to C_{10} to C_{16} aromatics.

In the initial stage the reaction is regulated in severity so that valuable non-naphthalenic constituents of the feed are converted to gasoline with a minimum loss through production of less valuable gas. In general, the reaction temperature can vary from about 900 to 1200° F., while the pressure is maintained at least about atmospheric, for instance atmospheric to 1000 p.s.i.g. or higher, preferably less than 1000 p.s.i.g. The preferred reaction temperature is from about 900 to 1050° F. which affords especially high octane gasoline as a product. The space velocity, that is the volume of liquid hydrocarbon per hour per volume of catalyst (LHSV), can vary from about 0.1 to 20 LHSV; however, it must be correlated with temperature in order that neither too little nor too much conversion is effected in the first stage reaction zone. The severity of the first stage reaction is controlled so that the aromatic oil (product boiling above 400° F.) contains at least about 40 weight percent, preferably at least about 60 weight percent, of naphthalenic aromatics and not more than about 30 weight percent, preferably not more than about 20 weight percent of non-aromatic components. Should insufficient naphthalenic aromatics be present in the aromatic oil derived by a single pass through the first stage reaction zone, this oil could be recycled to Stage I for further conversion. In this stage the severity is not increased materially beyond the point where more than about 10 weight percent of naphthalene is in the aromatic oil. Also it is preferred to operate the first stage reaction so that the yield of liquid product is over 70 weight percent of the feed. The space velocity will usually be from about 0.5 to 8 LHSV, preferably about 1 to 3 LHSV. A space velocity of about 2.0 LHSV is particularly preferred in producing high octane gasoline. The temperature and space velocity employed will be affected by the extent of conversion desired in the first stage which in turn is a function of the choice of catalyst, the hydrogen partial pressure and to some extent the total pressure and the degree of catalyst deactivation or the amount of coke deposited on the catalyst at a given time in the processing cycle.

Sufficient hydrogen must be present in the first stage reaction zone to effect the reaction and maintain the activity of the catalyst through decreasing the amount of coke lay-down. In the first stage of the process the use of about 3 to 10 or 20 mols of hydrogen for each mol of feed stock produces satisfactory results. The use of about 5 to 6 mols of hydrogen per mol of feed is preferred, and the benefits derived by using more than about 10 mols of hydrogen usually do not justify the increased expense. Of course, the specific amount of hydrogen employed will vary with the feed stock charged and the reaction conditions observed. Under certain select conditions of temperature and pressure, e.g. 1000° F. and 50 p.s.i.g., operating with recycled tail gas, the net consumption of hydrogen may be reduced so that an extraneous source of hydrogen is not required. Also,

when operating with recycled tail gas, hydrogen sulfide is preferably removed from such gases.

The catalysts which can be used in both stages of the present process are non-carbon based hydroforming catalysts which can contain chromium, molybdenum, tungsten, cobalt, or vanadium (or mixtures of these) preferably deposited as oxides on non-combustible carriers such as alumina, titania, thoria, zirconia, silica, silica-alumina, silica-magnesia, or silica-zirconia. Platinum, palladium, rhodium, and other rare metals may be employed preferably in the metallic state supported on the same non-combustible type of carriers. In operating my process on a cyclic or continuous basis, the catalyst can be regenerated at intervals by treatment with air or oxygen at temperatures above 900° F.

The preferred catalyst is chromia-alumina since it affords an exceptionally selective action leading to the formation in good yields of the high octane aromatic gasoline and the aromatic-rich oil. Molybdena-alumina catalysts are, for example, not as desirable as chromia-alumina, since the former may produce more carbon and sulfur on the catalyst in both Stage I and Stage II of the process. Chromia-alumina catalysts which are generally known in the petroleum processing field can be utilized; and these catalysts usually contain from about 1.0% to about 25% or more by weight of chromia. The activity of the chromia-alumina system can be appreciably enhanced by the use of promoters which can include for instance silica, berryllium, boron, potassium and cerium. A specific catalyst found effective contains about 12% chromia, 86% alumina, and about 2% magnesium oxide as a promoter.

The feed stocks which can be employed in the initial reaction are petroleum light cycle oils boiling generally in the range from about 400 to 650° F. Also, aromatic extracts of these stocks can be used. The light cycle oils usually are composed of at least about 40 weight percent of non-aromatics and these may comprise about 50 to 65% or more of the oil. The feed stock can be desulfurized but this is not considered essential as a desulfurization reaction is effected in each stage of the present process and most of the sulfur present in the feed is removed through conversion to hydrogen sulfide in the case of chromia catalysts, or in part deposited on the catalyst as metallic sulfide, in the case of molybdenum catalysts.

In the second stage of the present process the aromatic oil from the initial reaction is treated under more severe conditions to insure the production of (*a*) sufficient yield of naphthalene in high concentration in its boiling range, (*b*) conversion of benzenoid aromatics and non-aromatic hydrocarbons to highly aromatic gasoline, and (*c*) to effect removal of nitrogen- and sulfur-containing impurities from the desired products. The temperature in the second stage reaction can vary from about 900 to 1200° F. while the space velocity will generally be from about 0.1 to 3 LHSV. The reaction pressure and amount of hydrogen supplied can be of the same range as specified for the initial stage of the process providing that one or more of the operating conditions is considerably more severe than employed in Stage I. Compared with Stage I the desired severity of the Stage II reaction may be effected by raising the temperature by at least about 125° F., preferably 150–200° F., or by increasing the hydrogen partial pressure at least about 500 p.s.i.g, preferably 500–1000 p.s.i.g.; or by reducing the liquid space velocity to at least about 0.3, preferably about 0.1 to 0.3, of that in Stage I. The severity in the second stage could then be defined, for example, as being equivalent to a rise of at least about 125° in temperature compared with that of the first stage, when the other reaction conditions are not changed. Of course, the required severity may be obtained by a partial change of more than one of these variables in the indicated directions. It is preferred to operate the second stage of my process so that the liquid product yield is over about 70 weight percent of the total feed to this stage and the product fraction boiling between 400 to 460° F. contains at least about 40 weight percent naphthalene and at least about 50 weight percent total aromatics.

The products of the second stage reaction include aromatic gasoline, naphthalene, beta-methylnaphthalene and other alkyl-naphthalenes. These products can be separated by fractional distillation. The naphthalene and beta-methyl-naphthalene are of high purity, substantially free from sulfur- and nitrogen-containing impurities, and are practically completely aromatic. Beta-methylnaphthalene and the other alkylnaphthalenes can be converted to naphthalene as for instance by recycling to the second stage of my process the aromatic oil boiling above about 400° F. from which the naphthalene has been separated. 2,6-dimethylnaphthalene may be isolated by cooling, filtering, and recrystallization from the dimethylnaphthalene fraction either from the first or second stage products. Also, when beta-methylnaphthalene and/or 2,6-dimethylnaphthalene as well as naphthalene are separated from the reaction product of the second stage, the remaining oil boiling above about 400° F. can be recycled to the second stage reaction.

When utilizing a chromia-alumina catalyst in the reaction of Stage I of this invention, I prefer the severity in operating conditions in the first stage to be equivalent to or defined by 1000 to 1100° F., 2 LHSV and 200 to 500 p.s.i.g. hydrogen partial pressure. In the second stage when employing this catalyst the preferred severity is equivalent to or defined by 1050 to 1150° F., 0.5 LHSV and 200 to 500 p.s.i.g. hydrogen partial pressure. Different catalysts do, of course, require different operating conditions to produce the best results. Thus, if a molybdena-alumina catalyst be employed the preferred severities in the separate stages are, respectively, equivalent to or defined by 900 to 1000° F., 2 LHSV, 50 to 400 p.s.i.g. hydrogen partial pressure and 900 to 1000° F., 1.0 LHSV, 200 to 500 p.s.i.g. hydrogen partial pressure.

The process of the present invention can be effected, for instance, in a single reactor system or in a system including two reactors. In the single reactor system the initial stage will be effected and the products separated as by fractionation. The aromatic-rich oil is collected and then converted in a blocked-out operation to naphthalene and additional amounts of aromatic gasoline in the reactor after the desired amount of light cycle oil has been processed. In a two-reactor system the separate stages of the process can be conducted in the separate reactors. Also, in any reaction system provision can be made for regenerating the catalyst. Also, both stages may be conducted with fluidized or moving bed type of catalytic reactors.

It is not possible to obtain satisfactory yields of gasoline and naphthalene by operating with one reactor continually recycling the 400° F. plus product from which naphthalene has been recovered. In the first place, operating conditions severe enough to effect demethylation of methylated naphthalenes are much too severe for converting the non-aromatics to gasoline, and will produce more dry gas than the economics will permit. Conversely when the conditions are optimum for gasoline production, they are not severe enough to demethylate the methylated naphthalene, whereupon the yield of naphthalene will be impracticably low and/or the concentration of naphthalene in the naphthalene cut will be too low, especially for feasible separation by fractional crystallization or distillation.

There is usually a net consumption of hydrogen in the hydroconversion reactions. This hydrogen may be supplied from a separate source, or naphtha may be charged concurrently with the cycle oil directly to the initial stage reactor to produce the needed hydrogen while being reformed.

One method of operation in the present invention consists in using the catalyst successively for reforming and the first and second stage reactions. Thus naphtha is passed over the freshly regenerated catalyst under hydroforming conditions, e.g., 0.5 LHSV, 950° F., 200 p.s.i.g. H_2, recycling 4 to 6 mols of H_2. At the end of one-half to two hours, when the reforming activity has diminished because of mild coke lay-down, the naphtha feed is cut out and replaced with cycle stock (first stage). The temperature may be raised to effect the desired reactions. Finally, after one to three hours on the first stage the reactor is switched to the second stage by feeding aromatic oil from the first stage. At the end of this operation the catalyst is regenerated and readied for the hydroforming step.

In the initial stage of my process as the operating temperature is raised, the dry gas, carbon make and conversion to gasoline increase. Also the yield of recycle oil decreases but its aromaticity increases. As shown by the following tabulation the initial stage affords advantages over the thermal cracking of the light cycle stocks conventionally effected. The gasoline produced in the reaction is higher in octane number (e.g. 86 to 95 vs. 73) and the by-product liquid is more valuable because of its low boiling range and viscosity and its utilization as a feed stock for naphthalene production.

Table I

Feed (Light Cycle Oil):			
API gravity, 60° F	21.6	21.8	21.8
Percent S	1.96	2.38	2.38
Percent Aromatics	47.9	51.2	51.2
I-BP, °F	444	422	422
50%	538	490	490
End-point	637	568	568
Operating Conditions:			
Temp., °F	899	1,000	1,050
Pressure, p.s.i.g	560	400	400
LHSV		2	2
H_2 mol ratio		5/1	5/1
Catalyst	Thermal	Cr_2O_3/Al_2O_3	Cr_2O_3/Al_2O_3
Products (Wt. percent):			
Dry gas	6.4	6.6	13.6
Coke		0.6	1.3
Gasoline (C_4–400° F.)	29.1	29.3	33.1
Research method octane no. neat (approx. 5 lbs. Reid)	73	86	95
Aromatic oil (400–600° F.)		57.7	45.6
API gravity at 60° F		(17.8)	(13.7)
Tar	64.5	3.5	2.9
API gravity at 60° F	(4.1)		
	100.0	97.7	96.5

One form of the present invention can be described with reference to the drawing which is a diagrammatic, simplified flow sheet of a system comprising separate reactors for the first and second stages, respectively, of my process.

In the drawing, light cycle oil feed enters by way of line **1** into reactor **2**, which contains the hydroforming type catalyst. A hydrogen-rich gas can enter reactor **2** by way of line **3** and the reaction product is conveyed in line **4** to separator **5**. Gas is withdrawn from separator **5** through line **6**. Aromatic gasoline is taken by way of line **7** and the bottoms are removed in line **8**. An aromatic-rich oil is drawn from separator **5** by way of line **9** and passed to the second stage reactor **10** containing hydroforming catalyst. A hydrogen-rich gas enters reactor **10** by way of line **11** and the reaction product passes through line **12** to separator **13**. Products withdrawn from separator **13** include aromatic gasoline, naphthalene, methyl naphthalene, other naphthalenics, and bottoms.

The following specific examples will serve to illustrate the present invention but they are not to be considered limiting.

EXAMPLE I

A regenerated chromia-alumina catalyst (12% Cr_2O_3, 2% MgO) was charged to a reactor and brought to a temperature of about 1050° F. A catalytic light cycle oil of the following analysis was charged to the reactor at a rate of about 2 liquid volumes per hour per volume of catalyst:

API/60° F.		21.8
Percent S	wt. percent	2.38
Olefins	wt. percent	26.8
Aromatics	wt. percent	51.2
Br No.		20.9
N_D^{25}		1.5251
B.P.		
Initial	° F	422
50%	° F	490
End-point	° F	568

Hydrogen was supplied to the reactor at the rate of 5.5 mols per mol of feed, under a pressure of 400 p.s.i.g. At the end of four one-hour runs, the products were separated and analyzed on an average basis as follows:

Product	Wt. percent of Feed
Liquid	79.4
C_4 in gas	5.9
Dry gas	13.6
Carbon on Catalyst	1.7
Sulfur on Catalyst	0.0
	100.6

The liquid product was subjected to fractional distillation and produced the following:

Product:	
Gasoline (C_4 to 400° F.)	33.4 wt. percent of Feed [1] (0.03% sulfur, 58.1% aromatics, 9.7% olefins).
Aromatic oil (400–600° F.):	
Wt. percent of feed	49.8.
API/60° F	12.5.
Wt. percent olefins	13.6.
Wt. percent aromatics	84.9.
N_D^{25}	1.575.
Specific dispersion	269.
Bottoms:	
Wt. percent of feed	1.8.

[1] Research method octane number of C_5 to 400° F. gasoline was 95.8. This yield includes C_4 from gas.

	Wt. Percent of Feed	Wt. Percent in 400–600° F. Product
Naphthalene	3.4	6.8
Alkylnaphthalenes	27.5	55.0
2,6-dimethylnaphthalene	1.86	3.7

An aromatic-rich oil stock produced according to the specific procedure noted above but analyzing:

Boiling point	° F	400–600
API/60° F.		12.7
Specific dispersion		270
N_D^{25}		1.5740
Wt. percent aromatics		81.3
Wt. percent olefins		13.2

was charged at a space velocity of 0.55 volumes per hour per volume of catalyst to a reactor containing a chromia-alumina catalyst (12% Cr_2O_3, 2% MgO). The catalyst was maintained at a temperature of about 1109° F. and a pressure of 400 p.s.i.g., and hydrogen was supplied to the reactor at a ratio of 5.7 mols per mol of feed. The reaction continued for 2 hours and the following products were obtained.

Product	Wt. Percent of Aromatic Oil Feed
Liquid	77.8
C_4+ in gas	0.6
Dry gas	19.3
Carbon on catalyst	4.34
Sulfur on catalyst	
Total	102.04

The liquid product was distilled and the following products were separated:

Product	Wt. Percent of Aromatic Oil Feed
Gasoline (C_4 to 400° F.)	[a] 21.0
Naphthalene	[b] 25.9
β-methylnaphthalene	[c] 16.6
Balance of naphthalenic product	8.2
Bottoms	6.3

[a] Research method octane number of C_5 to 400° F. gasoline was equivalent to iso-octane +0.54 ml. tetraethyl lead.
[b] 0.0% nitrogen; 0.017% sulfur.
[c] 98% beta, 2% alpha.

The results of the two-stage process are summarized below:

	Stage I	Stage II	Combined Yields [1]
Run No.	14	20	
Temp. °F. (400 lbs. p.s.i.g. H_2)	1,050	1,109	
LHSV, approx.	2	0.55	
Products (Wt. percent feed to step):			
Gasoline, C_4 to 400° F. (Vol. percent)	33.4 (40.7)	21.0	46.9 (54.3)
Percent Arom. (C_5 to 400)	58.1	100	
Percent S (C_5 to 400)	0.03		
R.M.O.N. (C_5 to 400)	95.8	106.5	98.7
M.M.O.N. (C_5 to 400)	84	106.5	90.4
Heavier liquids:			
Aromatic oil	49.8	8.2	
Naphthalene		25.9	19.2
Methylnaphthalene		16.6	
Heavier oil	1.8	6.3	5.4
Carbon on catalyst	1.7	4.3	4.4
Dry gas	13.6	19.3	25.6

[1] Ultimate yields based on original light cycle oil feed and recycling alkylnaphthalenes to extinction in Stage II to produce maximum amount of naphthalene. All percentages noted above are calculated on a weight basis unless otherwise specified.

EXAMPLE II

A regenerated molybdena-alumina catalyst (10.14% MoO_3 on Al_2O_3-5% SiO_2) was charged to a reactor and brought to a temperature of about 950° F. The same feed employed in Example I was charged to the reactor at a rate of about 2 liquid volumes per hour per volume of catalyst. Hydrogen was supplied to the reactor at the rate of 4.92 mols per mole of feed, under a pressure of 400 p.s.i.g. At the end of 3 1-hour runs, the products were separated and analyzed on an average basis as follows:

Product	Wt. percent of Feed
Liquid	80.4
C_4 in gas	3.8
Dry gas	11.5
Carbon on catalyst	4.7
Sulfur on catalyst	1.0
	101.4

The liquid product was subjected to fractional distillation and produced the following:

Product:	
Gasoline (C_4 to 400° F.)	31.7 Wt. percent of Feed [1] (64.1% aromatics, 2.4% olefins).
Aromatic Oil (400-600° F.):	
Wt. percent of Feed	49.
API/60° F	16.
Wt. percent olefins	5.3.
Wt. percent aromatics	83.7.
N_D^{25}	1.5620.
Specific dispersion	258.
Bottoms:	
Wt. percent of Feed	2.1.

[1] Research method octane number of C_5 to 400° F. gasoline was 93.8. This yield includes C_4 from gas.

	Wt. Percent of Feed	Wt. Percent of 400-600° F. Product
Naphthalene	3.05	6.1
Alkylnaphthalenes	23.2	47.3

The aromatic-rich oil stock boiling 400–600° F. was charged at a space velocity of about 1.0 volume per hour per volume of catalyst to a reactor containing a molybdena-alumina catalyst (10.14% MoO_3·5% SiO_2). The catalyst was maintained at about 985° F. and a pressure of 400 p.s.i.g. of hydrogen, and hydrogen was supplied to the reactor at a ratio of 5.9 mols per mol of feed. The reaction was continued for one hour and the following products were obtained:

Product	Wt. Percent of Aromatic Oil Feed
Liquid	73.4
C_4+ in gas	1.8
Dry gas	14.0
Carbon on catalyst	10.9
Sulfur on catalyst	0.2
	100.3

The liquid product was distilled and the following products were separated:

Product	Wt. Percent of Aromatic Oil Feed
Gasoline (C_4 to 400° F.)	19.5
Naphthalene	22.7
β-methylnaphthalene	15.7
Balance of naphthalenic product	9.7
Bottoms	5.8
	73.4

EXAMPLE III

As an example of severity control in Stages I and II of my process a number of operations were conducted using the catalyst of Example I at a variety of temperatures and space velocities. The light cycle oil feed approximated that of Example I and the hydrogen was supplied to the reactor at the rate of 7 mols per mol of feed and the total pressure was 700 p.s.i.g. In these tests it was determined that at the reaction conditions given the following temperatures and space velocities could be employed; however, when using these conditions they should be selected so that the Stage II reaction is more severe than that of Stage I as noted above.

Temperature, °F.	Stage I, Approximate Range of Space Velocity, LHSV	Stage II,[1] Approximate Maximum Space Velocity, LHSV
900	0.1 to 0.25	
950	0.2 to 0.5	0.1
1,000	0.25 to 1.0	0.2
1,050	0.5 to 2.0	0.35
1,100	0.9 to 4.5	0.7
1,150	1.7 to 9.5	1.2
1,200	3 to 20	2.5

[1] The minimum space velocity in Stage II could be about 0.1 LHSV at each temperature as a slower rate of feed would not be commercially easible.

I claim:

1. The method of producing naphthalene and high octane aromatic gasoline which comprises contacting in a first stage in the presence of hydrogen a petroleum light cycle oil consisting essentially of aromatics and about 40 to 65 percent of non-aromatic components with a hydroforming catalyst having a non-combustible base at a temperature of about 900 to 1200° F., a space velocity of about 0.1 to 20 LHSV and a pressure of at least about atmospheric while effecting conversion to an aromatic oil boiling above 400° F. and containing at least about 40 weight percent of naphthalenic aromatics and not more than about 30 weight percent of non-aromatics, said aromatic oil containing not more than about 10 weight percent of naphthalene, contacting in a second stage under more severe reaction conditions the aromatic oil with a hydroforming catalyst having a non-combustible base, in the presence of hydrogen and at a temperature of about 900 to 1200° F., a space velocity of about 0.1 to 3 LHSV and a pressure of at least about atmospheric to form naphthalene and aromatic gasoline, and separating the gasoline and naphthalene.

2. The method of claim 1 in which the aromatic oil contains at least about 60 weight percent of naphthalenic aromatics and not more than about 20 weight percent of non-aromatics and the catalyst is chromia-alumina.

3. The method of producing naphthalene and high octane aromatic gasoline which comprises contacting in a first stage in the presence of hydrogen a petroleum light cycle oil consisting essentially of aromatics and about 40 to 65 percent of non-aromatic components with a hydroforming catalyst having a non-combustible base at a temperature of about 900 to 1200° F., a space velocity of about 0.1 to 20 LHSV and a pressure of at least about atmospheric while effecting conversion to high octane aromatic gasoline and an aromatic oil boiling above 400° F. and containing at least about 40 weight percent of naphthalenic aromatics and not more than about 30 weight percent of non-aromatics, said aromatic oil containing not more than about 10 weight percent of naphthalene, separating the high octane aromatic gasoline from the aromatic oil, contacting in a second stage under more severe reaction conditions the aromatic oil with a hydroforming catalyst having a non-combustible base, in the presence of hydrogen and at a temperature of about 900 to 1200° F., a space velocity of about 0.1 to 3 LHSV and a pressure of at least about atmospheric to form naphthalene and an additional quantity of aromatic gasoline, and separating the gasoline and naphthalene.

4. The method of claim 3 in which the aromatic oil contains at least about 60 weight percent of naphthalenic aromatics and not more than about 20 weight percent of non-aromatics and the catalyst is chromia-alumina.

5. The method of claim 3 in which the catalyst employed in both reaction stages is chromia-alumina in which the severity in operating conditions for the first stage is defined by 1000 to 1100° F., 2 LHSV and 200 to 500 p.s.i.g. hydrogen partial pressure and in which the severity in operating conditions in the second stage is defined by 1050 to 1150° F., 0.5 LHSV and 200 to 500 p.s.i.g. hydrogen partial pressure.

6. The method of claim 3 in which the catalyst employed in both reaction stages is molybdena-alumina, in which the severity in operating conditions for the first stage is defined by 900 to 1000° F., 2 LHSV, and 50 to 400 p.s.i.g. hydrogen partial pressure and in which the severity in operating conditions in the second stage is defined by 900 to 1000° F., 1.0 LHSV and 200 to 500 p.s.i.g. hydrogen partial pressure.

7. The method of claim 3 in which beta-methylnaphthalene is also separated from the product of the second stage and the remaining oil boiling above about 400° F. is recycled to the second stage reaction.

8. The method of claim 3 in which 2,6-dimethyl-naphthalene is also separated from the product of the second stage, and the remaining oil boiling above about 400° F. is recycled to the second stage reaction.

9. The method of claim 3 in which the product of the second stage boiling above about 400° F. from which the naphthalene has been recovered, is recycled to the second stage reaction.

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