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NON-CATALYTIC PROCESS FOR THE RECOVERY OF ALKYLNAPHTHALENES IN THE PRESENCE OF HYDROGEN

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This invention relates to a process for recovering alkylnaphthalenes of high purity and particularly pertains to a thermal process conducted in the presence of hydrogen for recovering alkylnaphthalenes of high purity from petroleum hydrocarbon materials containing these and other components. Alkylnaphthalenes are valuable intermediates for the production of organic chemicals since, for instance, they can be oxidized, sulfonated or dealkylated.

It has been recognized for some time that naphthalene could be produced by catalytic processing of alkylnaphthalene containing petroleum hydrocarbon materials in the presence of hydrogen. The recovery of alkylnaphthalenes from the products of these reactions has been suggested. In these processes, the feedstocks usually include naphthalene, alkylnaphthalenes and other materials boiling in the alkylnaphthalene boiling range. Although naphthalene and alkylnaphthalenes can be separated using, for instance, distillation means, the other materials boiling in the alkylnaphthalene boiling range are difficult to remove without converting some of the alkylnaphthalenes to naphthalene. This "converting," obviously, will result in lower yields of alkylnaphthalenes. However, when following our thermal process which is conducted in the presence of hydrogen, petroleum hydrocarbon materials containing alkylnaphthalenes, naphthalene, and other materials boiling in the alkylnaphthalene boiling range are converted to fractions rich in alkylnaphthalenes without excessive conversion to naphthalene.

In the process of the present invention, alkylnaphthalenes of high purity are recovered from petroleum hydrocarbon materials under conditions including temperatures generally from about 1100° to 1350° F. and, preferably from about 1140° to 1220° F.; a hydrocarbon feed partial pressure generally from about 20 to 200 p.s.i.a and preferably from about 60 to 125 p.s.i.a.; and a hydrogen partial pressure generally greater than 200 p.s.i.a. and preferably greater than 500 p.s.i.a. and up to about 1000 p.s.i.a. The contact time is generally from about 0.5 to 200 and preferably from about 3 to 60 seconds. These conditions are employed in a relationship according to the formula

$$X=\frac{tP_{H_2}}{33.4\,P_{H'C}{}^{0.640}\left[e^{\left(\frac{42{,}640}{^\circ R}-26.00\right)}\right]}$$

t=contact time in seconds
P_{H_2}=partial pressure of hydrogen in p.s.i.
$P_{H'C}$=partial pressure of hydrocarbon feed in p.s.i.
e=the base of natural logarithms (=2.718 . . .)
$^\circ R$=temperature in degrees Rankine
X, hereinafter referred to as "X value," must be between about 1–100, preferably between 2–50.

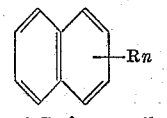
Various types of thermal conversion systems can be used such as, for instance, coil-type heaters, void reactors, or reactors packed with inert material, either fixed or moving. Reaction systems in which any part of the products are recycled for further conversion may be used.

The petroleum hydrocarbon feed materials employed in our process boil primarily in a temperature range from about 300 to 800° F., preferably in a temperature range from about 450 to 600° F., and include petroleum materials such as cracked petroleum fractions and straight run materials containing naphthenes, paraffins, aromatics and olefins in the same boiling range, as well as alkyl naphthalenes. Generally the hydrocarbon feed material includes at least about 20 weight percent and preferably about 35 to 80 weight percent of alkyl naphthalenes.

In addition the feed preferably should contain only minor amounts of biphenyl and alkylbiphenyls, fluorine and alkylfluorenes. These compounds appear to react only slowly under conditions of this process and, therefore, would have to be separated by other methods.

In some operations it may be desirable to fractionate the feedstock to maximize alkylnaphthalenes of a particular molecular weight range. In a second type of operation severity could be adjusted to maximize alkylnaphthalenes of a particular molecular weight by fractionating the products to separate the desired boiling range and recycling higher boiling material.

The alkylnaphthalenes susceptible of recovery in the above-described hydrocarbon materials correspond to the following general formula:



where n is 1 to 8 and R is an alkyl radical containing generally from about 1 to 13 and preferably from about 1 to 5 carbon atoms. The total number of carbon atoms in alkyl groups attached to the naphthalene nucleus is generally from about 1 to 13 and preferably from about 1 to 5.

The present invention will be more clearly illustrated with the following example.

EXAMPLE I

(A)

Analysis of feedstock:

API	20.2
Bromine No.	13.0
M.W.	174
Percent S	0.11
n_D^{20}	1.5365
Specific disperson	215.8
Percent aromatics:	
F.I.A.	63.5
ES45A [1]	48.8
Percent olefins:	
F.I.A.	5.8
ES45A [1]	16.7
Percent naphthalene	0.58
Percent α-methylnaphthalene	2.13
Percent β-methylnaphthalene	1.98
Percent alkylnaphthalenes, M.W. 156	17.2
Percent alkylnaphthalenes, M.W. 170	12.2
Percent alkylnaphthalenes, M.W. 184	5.0

[1] ASTM–D878

(B)

Samples of the feedstock analyzed in (A) above, were hydrothermally treated in runs 1 to 5 using a thermal reactor. The conditions as well as the results for each of these runs are presented below in Table I.

Table I

Run No.	Feed	1	2	3	4	5
Conditions:						
Temperature, ° F.		1,200	1,160	1,180	1,180	1,100
Contact Time, Sec.		25	90	4	4	35
Hydrocarbon Partial Pressure, p.s.i.a.		87	87	89	89	89
Hydrogen Partial Pressure, p.s.i.a.		628	628	310	801	626
Concentration of Naphthalenes in Fractions, Wt. percent of Fraction:						
450–475° F. Fraction (Naphthalene and Methylnaphthalenes)	20.2	100.0	100.0	72.6	78.9	80.7
475–520° F. Fraction (Alkylnaphthalenes, M.W. 156)	46.9	96.1	93.5	78.8	86.8	82.5
520–560° F. Fraction (Alkylnaphthalenes, M.W. 170)	54.6	87.1	74.0	81.7	85.9	100.0
560–600° F. Fraction (Alkylnaphthalenes, M.W. 184)	50.7	58.2	39.0	71.7	62.5	84.3
Total Alkylnaphthalenes, Wt. percent Feed	38.5	33.6	25.4	41.2	41.7	38.8
Naphthalene Yield, Wt. percent Feed	0.6	10.5	16.2	2.1	3.3	3.3
Alkylnaphthalenes Recovered, Wt. percent of Alkylnaphthalenes in Feed		87.3	65.8	107.0	108.3	100.7
X Values		35.4	67.7	2.02	5.21	9.39

It is claimed:

1. A process for the recovery of alkylnaphthalenes from petroleum hydrocarbon materials boiling in the temperature range from about 300 to 800° F., said hydrocarbon materials including about 20 to 80 weight percent of alkylnaphthalenes, the step comprising treating said hydrocarbon materials in the presence of hydrogen, in the absence of a catalyst and under thermal conditions including a temperature from about 1100° to 1350° F., a hydrocarbon partial pressure from about 20 to 200 p.s.i.a., a hydrogen partial pressure from about 200 to 1000 p.s.i.a., and a contact time from about 0.5 to 200 seconds; said thermal conditions being employed in a relationship according to the following formula

$$X=\frac{tP_{H_2}}{33.4\,P_{H'C}{}^{0.649}\left[e^{\left(\frac{42,640}{^\circ R}-26.00\right)}\right]}$$

where t is the contact time in seconds, P_{H_2} is the partial pressure of hydrogen in p.s.i, $P_{H'C}$ is the partial pressure of hydrocarbon feed in p.s.i., e is the base of natural logarithms, ° R is the temperature in degrees Rankine, and X is between about 1 and 100.

2. The process of claim 1 wherein X is between about 2 and 50.

3. A process for the recovery of alkylnaphthalenes from petroleum hydrocarbon materials boiling in the temperature range from about 300 to 800° F., said hydrocarbon materials including aromatics, olefins and about 20 to 80 weight percent of alkylnaphthalenes, the step comprising treating said hydrocarbon materials in the presence of hydrogen, in the absence of a catalyst and under thermal conditions including a temperature from about 1100° to 1350° F., a hydrocarbon partial pressure from about 20 to 200 p.s.i.a., a hydrogen partial pressure from about 200 to 1000 p.s.i.a., and a contact time from about 0.5 to 200 seconds; said thermal conditions being employed in a relationship according to the following formula:

$$X=\frac{tP_{H_2}}{33.4\,P_{H'C}{}^{0.649}\left[e^{\left(\frac{42,640}{^\circ R}-26.00\right)}\right]}$$

where t is the contact time in seconds, P_{H_2} is the partial pressure of hydrogen in p.s.i., $P_{H'C}$ is the partial pressure of hydrocarbon feed in p.s.i., e is the base of natural logarithms, ° R is the temperature in degrees Rankine, and X is between about 1 and 100.

4. The process of claim 3 wherein X is between about 2 and 50.

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