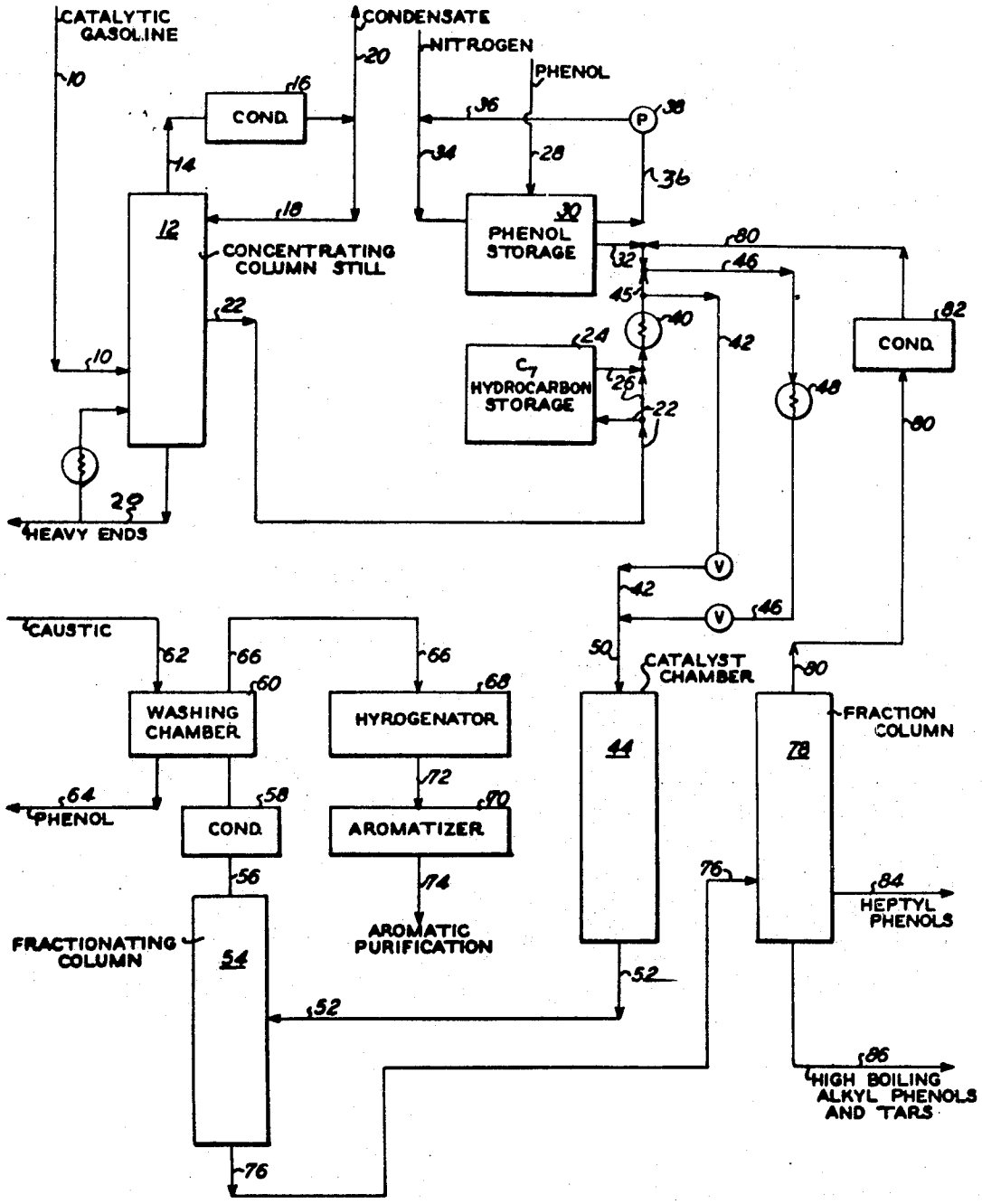
Feb. 1, 1972 R. P. BROWN ET AL 3,639,490

HEPTYL PHENOL ALKYLATION

Filed Feb. 25, 1966



United States Patent Office

3,639,490

Patented Feb. 1, 1972

3,639,490

HEPTYL PHENOL ALKYLATION

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Filed Feb. 25, 1966, Ser. No. 529,979

Int. Cl. C07c *39/06*

U.S. Cl. 260—624 4 Claims

ABSTRACT OF THE DISCLOSURE

A C_7 heart cut of catalytic gasoline containing large quantities of olefines and cycloolefines is converted to a substantially saturated dehydroaromatization feedstock composed predominantly of C_7 paraffins and cycloalkanes while simultaneously producing highly economically a mixture of alkyl phenols by using up the olefine and cycloolefine content of the unsaturated C_7 heart cut in an alkylation reaction upon phenols.

This invention relates to alkylation of phenol with a C_7-olefinic stream; to the removal of C_7 olefines from a catalytic gasoline stream by alkylation of phenol therewith; and to a mixture of heptyl phenols formed by phenol alkylation with a C_7 olefine-containing stream obtained from catalytic gasoline. Removal of C_7 olefines from said stream further produces a material suitable for subsequent processing for the recovery of aromatics.

The C_6–C_8 hydrocarbon mixture, predominantly C_7, comprising catalytic gasoline, is a wide ranging mixture of hydrocarbon types comprising substantially large quantities of olefines, paraffins and naphthenes with very minor quantities of aromatics, cycloolefines and di-olefines. Such feedstream must be hydrogenated before converting the naphthenes by dehydrogenation to aromatics, in which the most valuable product is toluene, but a large heterogeneous mixture of hydrocarbon types is simultaneously formed, many hydrocarbon components of which have little economic value, and with little or no decomposition of naphthenes. The unreacted material contains about 40 to 50% naphthenes, largely toluene precursors, and about 8 to 9% native toluene. The low recycle olefine content of this unreacted portion may be easily removed by hydrogenation or it can be diluted to useable levels by simple admixing with other feedstocks of low olefine content.

According to the present invention a full boiling C_6–C_8 catalytic gasoline stream comprising 40 to 60% olefines, and preferably a C_7 heart cut thereof, is mixed with a phenol and the mixed stream contacted with an alkylation catalyst to convert the olefins in high yield to alkyl phenols, the alkyls of which are largely a mixture corresponding to the olefinic components originally contained in the catalytic gasoline stream, whereby to produce a valuable mixed alkyl phenol product and a relatively saturated feedstream for further formation of aromatics. While the reacted hydrocarbon stream still may contain some olefines, usually about 5%, these may be easily

reduced by hydrogenation or bleeding prior to aromatizing.

The alkyl phenols formed herein are a mixture largely of branched chain alkyls and therein are improved in the typical use of these mixed iso-alkyl phenols as antioxidant. Thus, a valuable commercially-improved alkyl phenol product is produced while simultaneously improving the feedstream for processing to an aromatic product, by removing most of the olefinic components thereof, thus producing a better toluene-yielding feedstock for ultimate aromatization.

The phenolic reagent may be ordinary phenol or cresols produced synthetically or naturally available by distillation or extraction from commercial oils such as tar acids derived from coal tar distillate or natural petroleum phenolic extract. Thus, the phenols added for alkylation by the C_7 olefines hereof may be natural phenol, cresols, xylenols, guaiacols, cumenols or even synthetic higher phenols such as hydroquinone, catechol or the like.

In a typical gasoline feedstream, the C_7 fraction characteristics may be as shown in the following table:

TABLE 1

Analysis of C_7 fraction

[ASTM distillation, ° F. (corrected)]

IBP	181.4
10%	185.4
20%	187.4
30%	188.4
50%	190.4
70%	193.4
90%	197.4
FBP	209.4
Rec. (percent)	98
Gravity	0.727
Bromine No.	87.8
Maleic anhydride value	6.3
DMP/MH ratio	[1] 1
DMP/MH plus NC_7	0.6

[1] Probably 0.5.

A C_7-rich olefine heart cut comprising 10 to 14% of an original catalytic feedstock may be selected in a narrow boiling range of about 180 to 215° F., and the compositions thereof may be, typically, about 50 to 52% olefines including 0.5 to 1.5% diolefines and 6 to 9% cycloolefines and the balance, "saturated" hydrocarbon, comprising about 15% paraffins, about 24% naphthenes and the balance, about 4%, aromatics. The C_7 heart cut separated from the catalytic gasoline as fourteen cuts is analyzed as follows:

TABLE 2.—HYDROGENATED GAS CHROMATOGRAPH ANALYSIS

[Weight percent]

Component (after hydrogenation)	Cut 2	Cut 4	Cut 6	Cut 7	Cut 8	Cut 10	Cut 12	Cut 13	Cut 14	Composite
n-Butane	0.10				0.01					
Isopentane	0.29	0.17	0.10	0.08	0.08	0.04	0.06	0.08	0.11	0.01
n-Pentane	0.13	0.09	0.06	0.04	0.03	0.02	0.02	0.05	0.08	0.10
Cyclopentane	0.03	0.03		0.01	0.01	0.01	0.01	0.01	0.02	
2, 3 dimethylbenzene	2.29	1.63	0.77	0.57	0.41	0.24	0.14	0.14	0.14	0.83
2 methyl pentane	2.52	1.63	0.78	0.59	0.42	0.26	0.18	0.22	0.26	1.05
3 methyl pentane	6.32	3.78	1.76	1.70	1.00	0.46	0.34	0.32	0.35	2.00
n-Hexane	4.12	2.75	1.28	0.98	0.73	0.34	0.27	0.26	0.29	1.37
Methyl cyclopentane	15.59	12.07	6.10	5.02	3.91	1.76	1.13	1.01	0.90	6.50
3, 3 dimethyl pentane	0.63	0.72	0.42	0.44	0.34	0.19	0.13	0.10	0.05	0.48
Cyclohexane	11.35	9.06	4.86	4.03	2.94	1.54	0.95	0.78	0.65	6.58
2, 2 dimethyl pentane	1.24	0.60	0.27	0.33	0.26	0.14	0.08	0.04	0.04	0.66
2, 2, 3 trimethyl pentane		0.33	0.19	0.20				0.03	0.15	0.15
2, 4 dimethyl pentane	6.03	4.80	3.09	2.44	1.85	0.94	0.65	0.47	0.39	2.58
2, 3 dimethyl pentane			11.21					11.65		10.28
2 methyl hexane	25.10	32.84	22.50	34.21	33.88	23.55	20.10	8.07	16.75	15.65
1, 1 dimethyl cyclo-entane	0.90	0.90	0.61	0.53	0.45	0.28	0.17	0.12	0.10	0.39
1, cis 3 dimethyl cyclopentane / 3 methylhexane	15.77	21.30	32.70	34.79	32.35	40.30	35.46	32.59	27.69	29.54
1, trans 3 dimethyl cyclopentane	2.27	3.66	6.86	7.48	6.16	6.70	6.64	5.24	4.48	5.59
1, trans 2 dimethyl cyclopentane	2.94	2.65	4.07	4.42	9.55	7.85	6.64	5.53	5.14	4.12
3 ethylpentane	0.67	0.64	1.14	1.26	2.05	3.09	3.90	3.29	3.04	2.28
n-Heptane	0.32	0.19	0.91	0.95	2.69	7.21	17.42	18.78	18.02	6.18
1, cis 2 dimethyl cyclopentane	0.14	0.16	0.33	0.42	0.77	1.57	3.96	5.29	6.45	1.63
Methyl cyclohexane					0.04	0.06	1.45	4.11	10.33	
1, 1, 3 trimethyl cyclopentane								0.26	1.17	
Ethyl cyclopentane								1.36	2.53	0.35
Dimethyl hexane						3.35	1.26	0.20	0.87	
Benzene	1.24				0.17	0.10	0.04			0.47

The description of composite hydrocarbon types is further shown as follows:

TABLE 3.—A. PONA ANALYSIS

	Volume percent			
	Paraffins	Naphthenes	Aromatics [1]	Olefines [2]
Composite C_7 fraction	21	24	4	51
Composite after hydrogenation	66	29	4	1
Cut 11	26	10	1	63
Cut 13	27	8	1	64

[1] By GLC. [2] From bromine number.

B. DMP/MH Ratio:

Cut 6	0.67
Cut 13	1.52
Composite	0.89

An alkylation type catalyst, particularly acid clays or emperical dry acid substances as well as acid exchange resins may be used, many of which are commercially available, of which such commercially available types as

Dow 50 W–X8 cation exchange resin,
Amberlyst 15 cation exchange resin,
Super Filtrol Clay, and
Filtrol Grade 24 Clay

have been successfully used in the present alkylation. Other known useful alkylation catalysts such as sulfuric or phosphoric acids and Friedel-Crafts catalysts such as aluminum chloride or boron trifluoride may be used.

The resin exchange catalyst is activated by washing with concentrated sulfuric acid and then washed with methyl alcohol and dried under vacuum. The clay catalyst is then packed into a column and the stream is contacted therewith as set forth in the examples below.

The invention is further described in the single figure of drawings illustrating the steps of the process diagrammatically.

Catalytic gasoline enters the system through line **10** and is passed to a partial concentrating column still **12**. The light volatiles boiling below about 180° F. pass overhead through line **14**, are condensed in a condenser **16** and a portion of the condensate is returned as reflux through line **18** to the top of the column, and the remainder passes out of the system through line **20**. C_7-concentrate having the composition as identified above, is withdrawn as a side stream through line **22** and passes to storage chamber **24** for use in the system or enters the alkylation system directly through line **26**. A supply of phenol enters the system through line **28** to storage chamber **30** and thence through line **32**.

A dry gas blanket such as nitrogen is maintained above the storage tank **30**, entering through line **34** and exiting at vent **36** to maintain an inert, non-oxidizing atmosphere above the stored phenol in tank **30** at atmospheric pressure and 125° F.

The C_7-fraction in line **26** is preheated in an exchanger **40** to about 150° F. and a portion passed directly through lines **42** and **50** for purging the catalyst chamber **44**, particularly to flush the same free of phenol for recovery thereof prior to change of a spent catalyst bed. In normal flow of the C_7-stream, it passes through line **45** where it meets and mixes with a feedstream of phenol from line **32**, passing as an approximately equal molar-mixed stream of olefine to phenol by way of line **46**, the mixture being further heated in exchanger **48** so that the reactor effluent **52** will have a temperature of approximately 285 to 300° F. The mixture then passes downward through line **50** into the top of catalyst chamber **44** at a contact pressure of 25 to 75 p.s.i.g. to insure smooth flow through the catalyst bed. The alkylation reaction is exothermic; therefore, the temperature of the mixture entering the catalyst chamber **44** will have a lower temperature than the reactor effluent. The effluent product in line **52** is passed to an intermediate point of a fractionating column **54**. The unreacted feedstream comprising heptanes and some unreacted heptenes passing overhead in the column through line **56** is condensed to liquid in condenser **58**. The condensate is extracted with caustic in a washing chamber **60** by a stream of extracting caustic entering through line **62** and withdrawn as a weak phenol solution in line **64**. The washed spent substantially-saturated hydrocarbon stream overhead passes through line **66** to a hydrogenation chamber **68** and thence to an aromatizing unit **70** by way of line **72**. The aromatized product in line **74** is then treated such as by extraction to recover the aromatics, typically toluene. The alkyl phenols remaining as bottoms of still **54** are withdrawn through line **76** and passed to a fractionating column **78** wherein the unreacted phenol is withdrawn overhead through line **80** and cooled by condenser **82** and recycled to line **32** as unreacted phenol returned to the system. A side stream of heptyl phenols are withdrawn through line **84** to storage, high boiling alkyl phenols and tars being withdrawn through a line **86**.

The phenol is reacted in a premixed solution with the whole catalytic gasoline, or a C_7-heart cut thereof in pro-

portion to the olefin content, in proportion ranging from about 0.5 to 2 mols of phenol per mol of olefin contained in the hydrocarbon, preferably about 0.75 to 1.4 mols of phenol per mol of hydrocarbon. There is reason to believe (U.S. Pat. No. 2,732,408) that small quantities of water tend to improve catalyst action when Filtrol Clay is the catalyst. Generally, the alkylation reaction will vary from 160° through 250° F., more usually between 190° F. to 240° F., and is carried usually under sufficient pressure to maintain the system liquid, at the reaction temperature. It is preferred, moreover, to flow the reaction mixture over the catalyst at a flow rate of about 0.5 to 10 volumes of reaction mixture per volume of catalyst per hour.

The following examples illustrate the practice of this invention:

EXAMPLE I

A catalyst tower was packed with Dow 50W–X8 cation exchange resin converted to its acid form by washing with 15% concentrated sulfuric acid and then with methyl alcohol, the catalyst being finally dried under vacuum for 10 hours. A mixture of equal parts by weight of a catalytic gasoline comprising about 51% olefins, 21% paraffins, 24% naphthenes and 4% aromatics, boiling in the range of 181.4 to 209.4° F. and having the characteristics shown in Table 3 and phenol were passed through the catalyst at a rate of about 5 volumes of liquid reaction mixture per volume of catalyst per hour at a temperature maintained between 220 and 240° F. The reactor effluent had the following distillation characteristics:

ASTM distillation

	° F.
IBP	160
Percent:	
7	346
10	346
20	348
30	352
40	364
51	366
53	418
54	478

This fraction contains approximately ten percent materials boiling higher than heptyl phenols. The bromine number on the phenol-free sample indicates a yield of 85% of theory (wt. percent).

EXAMPLE II

Super Filtrol Grade Clay was dried for several days at 120° C. and packed into an experimental column as in Example I. A mixture of 945 grams of phenol and 1979 grams of C_7-fraction of catalytic gasoline was prepared as reactor charge. The charge was pumped through the column containing 66 grams of clay at the rate of 76 cc./hr. Reactor temperature during the run was 190 to 200° F. The reactor effluent had the following distillation characteristics and by bromine number was estimated to comprise a yield of 83 weight percent of theoretical.

ASTM distillation

	° F.
IBP	180
Percent:	
10	192
20	194
30	200
40	220
50	362
60	440
70	522
80	538
90	572
93	—

EXAMPLE III

A solution of equal weights of C_7-fraction (49.5% olefines) from catalytic gasoline and phenol was prepared as reactor feed for a column packed with 43.7 grams of Filtrol Grade 24 Clay which had been dried for three days at 100° C. Reactor temperature throughout the run was maintained at 280° F. to 290° F. and the flow rate was 0.568 gram of feed per gram of catalyst per hour. 94% of the available olefins were removed as alkyl phenols as indicated by a material balance performed on data obtained from an analytical distillation of 903.8 grams of reactor effluent. An analytical presentation of the distillation data is given in Table 1. It should be noted that there are no intermediate boiling fractions between the C_7-fraction and phenol, nor between phenol and the alkyl phenols.

A sample of the C_7-fraction distillate was caustic washed to remove residual phenol and then analyzed for hydrocarbon types. The following analyses reveal that the aromatics and aromatic formers were concentrated 186.9% by olefine removal.

C_7-fraction composition before alkylation, (vol. percent)

49.5 total olefines
25.0 saturated cycloparaffins
21.5 paraffins
4.0 aromatics
29% aromatics and aromatic formers

C_7-fraction composition after alkylation, (vol. percent)

5.6 total olefines
46.7 saturated cycloparaffins
40.2 paraffins
7.5 aromatics
54.2% aromatics and aromatic formers

The C_7-fraction may then be hydrogenated and passed through a platforming unit as described in U.S. Pat. No. 2,959,626, and the naphthenes dehydrogenated to aromatics.

The alkyl phenols recovered as still bottoms from the analytical distillation were subjected to an ASTM distillation with the following results:

Percent:	° F.
20	520
30	522
40	528
50	528
70	547
80	566
90	590
95	620
FBP	640

Various modifications will occur to those skilled in the art. Other alkylation catalysts may be used in rates variable with the activity of the catalyst flow, and at various usefully modified alkylation temperatures and pressures. The unreacted hydrocarbon may be hydrogenated and may be further treated to remove other select fractions of some of the products identified above before or after aromatizing. It is accordingly intended that the drawings and specific examples given be regarded as illustrative and not limiting except as defined in the claims appended hereto.

What is claimed is:

1. The method of forming heptyl phenols and a naphtha base useful for aromatization, comprising distilling a catalytic naphtha to separate a C_7 heart cut boiling in the range of 180 to 215° F., comprising 40 to 60% olefines and a substantial quantity of paraffins and naphthenes, reacting a phenol with said heart cut C_7 naphtha in proportion of about 0.5 to 2 moles of phenol per mole of olefine contained in the said naphtha at a temperature in the range of 160 to 250° F. in the presence of an alkylation catalyst selected from the group consisting of acid clays,

acid exchange resins, concentrated sulfuric acid, concentrated phosphoric acid, aluminum chloride, and boron trifluoride, to form heptyl phenols and separating said heptyl phenols from unreacted hydrocarbon and phenol.

2. The method of claim 1 wherein the phenol is selected from the group consisting of phenol, cresols, xylenols, cumenol, guaiacol, hydroquinone and catechol.

3. The method of claim 1 wherein the phenol is commercial phenol.

4. The method of claim 1 wherein the phenol is a cresylic tar acid fraction.

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U.S. Cl. X.R.

260—673.5, 671, 625; 208—133, 308