

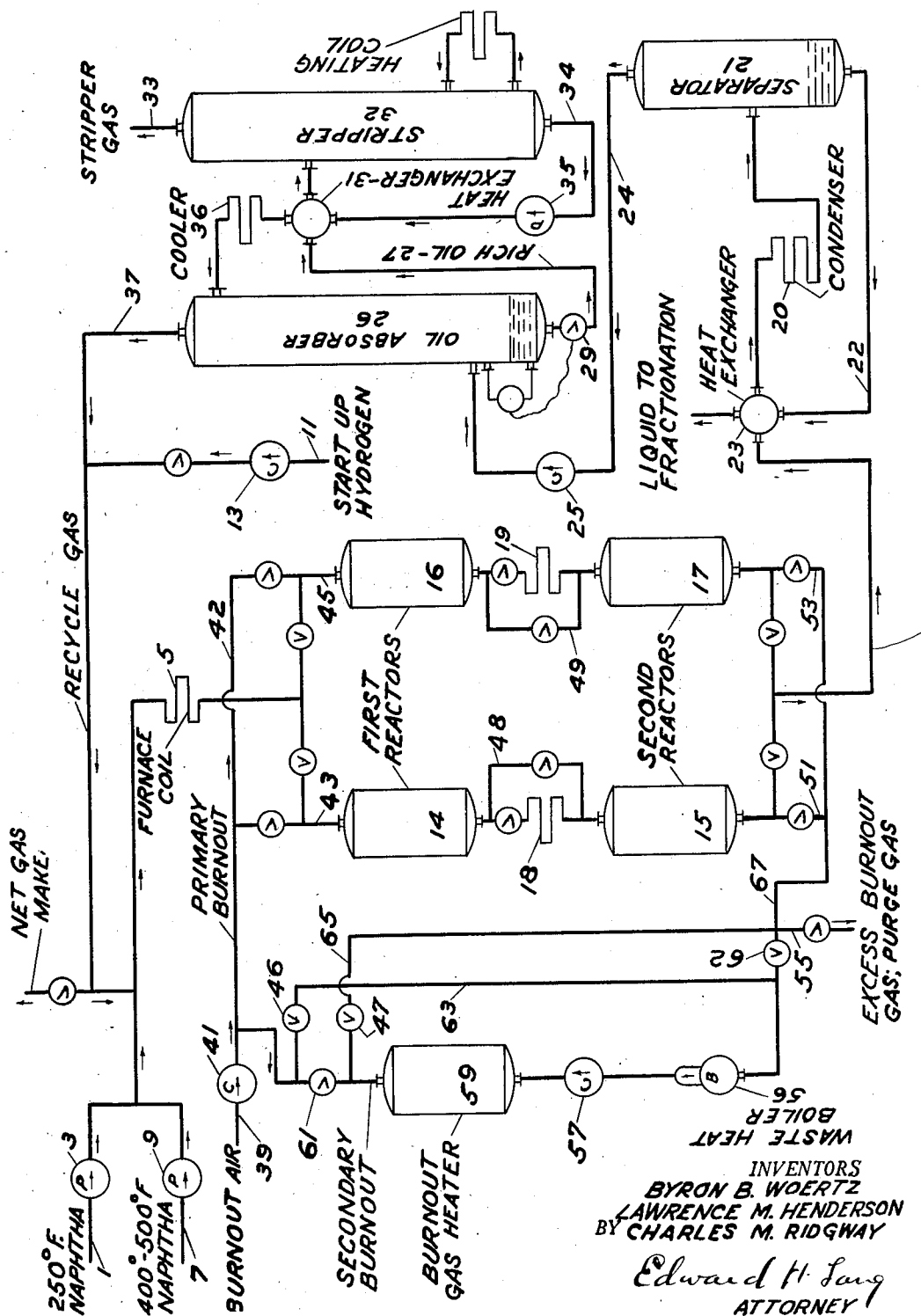
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BLENDING OF HYDROFORMER FEED STOCKS

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BLENDING OF HYDROFORMER FEED STOCKS

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1

This invention relates to a process for producing aromatic hydrocarbons from naphthenic, paraffinic and olefinic hydrocarbons and is more particularly concerned with a process for producing a high yield of alkylated benzenes.

It is well known in the art to convert naphthenic, olefinic and paraffinic hydrocarbons to aromatic hydrocarbons by contacting naphthenic, paraffinic and/or olefinic hydrocarbons with a dehydrogenation catalyst in the presence of hydrogen or hydrogen-bearing gas. This process is commonly known in the art as catalytic hydroforming and involves the contact of the charging stock with a dehydrogenation and aromatization catalyst in the presence of hydrogen or hydrogen-bearing gas at temperatures of approximately 850°-1100° F., and at pressures of approximately 100-800 pounds per square inch, and preferably between 150-300 pounds per square inch. As catalysts in the process aluminum oxide in the form of activated alumina, bauxite, aluminum hydrate or aluminum gel containing approximately 1%-20% by weight of a metal oxide or sulfide from the group of metals of the IV, V, VI and VIII group of the periodic system is generally used. The catalyst may be made by co-precipitation or by impregnating the alumina with the sulfide or oxide. Activated alumina or peptized aluminum gel containing from 1%-20% by weight of molybdenum oxide or chromium oxide has been widely used in commercial operations. Other oxides or sulfides which may be used to impregnate the aluminum oxide are those of vanadium, tungsten, and nickel.

We have discovered that if the middle fraction of the naphtha stock which is charged to a conventional hydroforming operation is eliminated from the charge, an aromatic solvent rich in alkylated benzenes can be produced without undue carbonization of the catalyst.

One of the objects of the invention is to provide an improved process for preparing aromatic hydrocarbons from non-aromatic hydrocarbons.

Another object of the invention is to provide a method for producing a high yield of aromatics without excessive coking of the catalyst.

A still further object of the invention is to provide a method for preparing a product suitable as a solvent which is rich in alkylated benzenes.

Other objects of the invention will be apparent from the following description and the accompanying drawing of which the single figure is a diagrammatic view of apparatus suitable for carrying out the invention.

Referring to the drawing, the numeral 1 indicates a line through which a low end point naphtha is charged by means of pump 3 to heat-

2

ing coil 5. The numeral 7 indicates another line through which a high boiling range naphtha is charged by means of pump 9 to heating coil 5. The low end point naphtha charged through line 1 preferably has an end point below 300° F., and preferably not above 250° F., and may have an initial boiling point ranging from approximately 150°-200° F. The high boiling naphtha fraction should have a minimum boiling point of approximately 325° F. and an end point not above approximately 550° F.; preferably it will lie within the range of 400°-500° F. It is important to charge a substantial portion of low end point naphtha in admixture with a high boiling fraction in order to prevent excessive coking of the catalyst. The amount of light naphtha which is preferably mixed with the heavy fraction ranges from 50%-95% by volume of the total charge.

It will be apparent that instead of mixing a low end point naphtha with a high boiling range naphtha, a full boiling range naphtha may be fractionated by eliminating a middle portion boiling between the limits of approximately 250°-450° F., and remaining portion of the naphtha used as charging stock for the process.

We prefer to use as charging stock a high boiling range naphtha which is rich in naphthene hydrocarbons since naphthene hydrocarbons are most readily converted to aromatics.

The charging stock is heated in heating coil 5 to a temperature of approximately 850°-1100° F., and preferably to a temperature of between 900°-1000° F. under a pressure of approximately 100-800 pounds per square inch, and preferably at a pressure of 150-300 pounds per square inch. In starting up the process it may be advisable to charge hydrogen or gas rich in hydrogen through line 11 in an amount equal to approximately 250 mol per cent of the charging stock. The gas will be charged through line 11 into heating coil 5 by means of compressor 13. The heated reaction mixture passes through either catalytic reactors 14 and 15 or 16 and 17. Reaction products are reheated in passing from first reactor 14 or 16 to second reactor 15 or 17, respectively, by means of heating coil 18 or 19, respectively. One set of reactors will be on stream while the other is undergoing regeneration. The reactors are filled with a dehydrogenation and aromatization catalyst such as those previously mentioned. We prefer to use as catalysts alumina gel, activated alumina or bauxite, each of which is impregnated or co-precipitated with approximately 9% of molybdenum oxide such as catalyst marketed by Standard Oil Co. of California. In the reactors among the reactions which occur are the conversion of naphthene hydrocarbons to aromatic hydrocarbons and the paraffin hydrocarbons to olefins and aromatic hydrocarbons. Upon leaving the catalytic reactor,

3

the reaction products are cooled in condenser 20 to a temperature of approximately 100° F., and pass to separator 21 where they are separated into gas and liquid fractions. The liquid is withdrawn through line 22 and passes through heat exchanger 23 to a fractionating tower not shown, where it is separated into various cuts including a cut boiling between approximately 325°–375° F. Residual gas is withdrawn from the top of separator 21 through line 24 and compressed by means of compressor 25 to a pressure sufficient to force recycle gas back into the reaction system. The compressed gas passes into the lower part of absorber 26 wherein it is contacted with a descending stream of absorption oil. Rich oil leaves the bottom of the absorber through line 27, controlled by float-controlled valve 29 and passes through heat exchanger 31 into stripper 32, wherein pressure is reduced to approximately atmospheric and the oil is denuded of its absorbed constituents which leave the stripper through line 33. Lean absorption oil leaves the bottom of the stripper through line 34 and is pumped by means of pump 35 through heat exchanger 31 and cooler 36 back to absorber 26. Unabsorbed gas is recycled from absorber 26 back to the system through line 37.

After operation of the process begins and gas is produced, the gas can be recirculated, and the injection of hydrogen through line 11 stopped. Because the action which takes place in the catalytic reactors 14, 15, 16 and 17 is essentially one of dehydrogenation and aromatization, the gas recycled through line 37 will be rich in hydrogen.

When the yield and character of the reaction products indicates that the catalyst is no longer effective, the operation is switched from one set of reactors to the other and the reactors taken off stream may be flushed with inert gas such as nitrogen, steam or combustion gases. After the reactors have been flushed to remove any volatile material, the catalyst is regenerated by charging thereto diluted oxygen or air through line 39 by means of compressor 41 until the carbon or coke is burned off the catalyst. The rate of injection of air or oxygen is controlled so as not to cause the temperature during regeneration to rise above 1200° F. In order to control the temperature during regeneration, the air may be diluted with inert gas such as nitrogen, carbon dioxide, steam and/or spent burnout gas so that it contains from 0.5 to 5.0% by volume of oxygen. The length of the regeneration period and the length of the reforming period will vary somewhat, but we have found that a cycle of six hours for reforming and six hours for purging and regeneration give a satisfactory operating cycle.

During the primary burning out period, the fresh burnout gas passes through line 42 and either line 43 or 45 depending upon which set of reactors is being regenerated. Valves 46 and 47 are closed. By-pass lines 48 and 49 are provided around heating coils 18 and 19, respectively, so that regeneration gases can by-pass around the heaters. Regeneration products leave the reactors through either line 51 or 53. A portion of the gas is eliminated from the system through line 55. The remainder of the gas is recycled through waste heat boiler 56 by means of compressor 57 and through heater 59 for dilution of incoming air. While not shown in the drawing, provision is ordinarily made for separately regenerating each reactor, rather than in series.

The reactors undergoing regeneration are generally subjected to a secondary burn out by revers-

4

ing the gas flow therethrough. By opening valves 46 and 47 and closing valves 61 and 62, burnout gas is caused to flow through by-pass line 63 and then forced by compressor 57 through by-pass line 65 and line 67 into the bottom of second reactor 15 or 17.

It will be apparent from the arrangement of lines and valves in the drawing that one set of reactors can be maintained on stream while the other set is being regenerated.

In order to demonstrate the invention, a series of runs were made using different charging stocks, some of which contained middle boiling range naphtha and some of which were devoid of middle range naphtha. The runs were all made in a pilot plant using Standard Oil Company of California catalyst and the conditions under which the runs were performed and the results obtained are tabulated in the following Table I:

TABLE I.

Run No.	68	73	69	70	71	72
Time on Stream (Hours)	6	6	6	6	6	6
Charge:						
Vol. Per Cent st. run Naphtha 406°–496° F.	33½	33½	33½	10	10	25
Vol. Per Cent st. run Naphtha 315°–400° F.	33½	33½	0	15	0	0
Vol. Per Cent st. run Naphtha 190°–299° F.	33½	33½	66½	75	90	75
Reaction Pressure, p. s. i.	227	235	224	233	229	233
Average Reaction Temperature, °F.	940	940	940	942	940	942
Space Velocity, V/Hr./V ₀	0.442	0.450	0.448	0.446	0.445	0.445
H ₂ in recycle gas (Volume Per Cent)	74.1	83.2	68.6	85.0	88.4	81.9
Yield—Weight Per Cent Feed (No loss basis):						
Gas	33.21	31.30	34.92	30.00	29.18	33.83
Liquid	65.39	67.86	63.05	68.91	69.91	64.92
Coke	1.40	0.84	2.03	1.09	0.91	1.25
Gravity API (calculated) of debutanized hydroformate	43.5	44.2	45.4	47.5	48.3	48.0
Yield (Weight Per Cent of feed) of 325°–375° F. fraction	8.84	9.71	4.54	5.28	3.24	3.48
Properties of 325°–375° F. product:						
A. P. I. Gravity	36.2	37.0	31.6	32.8	31.2	32.2
Bromine No.	1.0	1.5	1.2	0.9	1.0	1.4
Volume Per Cent olefins	0.9	1.4	1.1	0.8	0.9	1.3
Volume Per Cent alkylated benzenes	73	70	93	87	96	91
Mixed Aniline Point:						
°C	33.8	34.8	20.6	24.0	18.0	22.6
°F	92.8	94.6	69.1	75.2	64.4	72.7

The properties of the several fractions used as charging stock are given in the following Table II:

TABLE II

Charge stock properties of Mid-Continent straight run naphthas

Fraction	406–496° F.	315–400° F.	190–299° F.
Properties:			
API Gravity	41.8	47.6	60.3
ASTM Distillation:			
IBP, °F	406	315	190
5%	419	330	202
10%	422	334	204
30%	430	346	210
50%	441	355	218
70%	454	365	230
90%	476	380	254
95%	486	390	271
End Point	496	400	299
Percent Loss	0.5	0.8	1.1
Mixed Aniline Point, °F	143	138	143
Bromine Number		1.2	0.7
Volume Percent Olefins	0.9	1.1	0.5
Volume Percent Aromatics	14.6	15	4.5
ASTM mm. Octane			52.2

Referring to Table I, it will be seen that in runs 68 and 73, in which the charging stock had

equal parts of low end point, middle range and high boiling range naphtha, the aromatic content of the 325°-375° F. portion of the product was low, being of the order of 73% and 70% by volume, respectively. On the other hand, where the charging stock contained no middle range naphtha, such as the charge in runs 69, 71 and 72, the aromatic content of the 325°-375° F. fraction was uniformly high, being above 90% in each case. The effect of eliminating the middle range naphtha is pointed up by a comparison of runs 73 and 69, and by a comparison of run 70 with runs 71 and 72. By substituting low or high boiling range naphtha for middle boiling range naphtha, the concentration of alkylated benzenes in the 325°-375° F. fraction is very materially increased. It is notable that the 325°-375° F. fraction is very low in olefins as indicated by the bromine number. This fraction of the reaction product is composed chiefly of alkylated benzenes which may be separated into substantially pure aromatic hydrocarbons by suitable fractionation methods or which may be used as an aromatic solvent. The presence in the charging stock of benzenoid hydrocarbons boiling within the middle naphtha boiling range is not objectionable because the benzenoid hydrocarbons pass through the process without substantial alteration. Hence, recycling of hydroformed material within this range may be practiced without materially detracting from the process.

By charging a blend of a low boiling fraction with a high boiling fraction, or by eliminating a middle boiling fraction from a composite charge, the yield of alkylated benzenes over that which can be obtained from charging either a high boiling or low boiling fraction is increased, thereby obtaining an unexpected result. This increase in yield from the blend of the high boiling and low boiling fraction is demonstrated by a comparison of the results in the following Table III:

TABLE III

Run No.	69	71	72	60	64	61	62	63
Feed Composition, Volume Per cent:								
406-496° F.	33½	10	25	0	0	100	100	100
315-400° F.	0	0	0	0	0	0	0	0
190-299° F.	66½	90	75	100	100	0	0	0
Average Reaction Temp., °F.	940	940	942	941	949	943	946	943
Volume Per cent Debutanized Hydroformate on charge, No loss basis.	60.30	66.23	62.41	65.91	72.90	66.47	69.64	67.44
Alkylated Benzene Concentration in 325°-375° F., Volume Per cent	93	96	91	98	96	97	96	90
Yield on Charge, Volume Per cent:								
325°-375° F. Column Head Fraction	3.99	2.77	3.05	1.61	1.53	2.39	2.44	3.00
Alkylated Benzene in 325°-375° F. Fraction	3.71	2.66	2.78	1.58	1.47	2.32	2.34	2.70
API Gravity of 325°-375° F. Fraction	31.6	31.2	32.2	30.1	30.4	31.2	30.4	32.1

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,313,117	Becker	Mar. 9, 1943
2,328,773	Benedict	Sept. 7, 1943
2,338,573	Creefman	Jan. 4, 1944
2,375,573	Meier	May 8, 1945

Note particularly run 69 where the yield of alkylated benzenes was 3.71%, a figure considerably in excess of the yield obtained in any of the runs numbering 60-64, inclusive, in which the charge was either 100% high boiling fraction or 100% low boiling fraction.

It will be seen, therefore, that in accordance with our invention not only is it possible to obtain a high concentration of alkylated benzenes in the reaction product, but the yield of alkylated benzenes obtained is greater than can be obtained by charging either the high boiling or low boiling fraction alone.

What is claimed:

1. The method of preparing alkylated benzene hydrocarbons comprising, contacting a mixture of predominantly paraffinic and naphthenic hydrocarbons consisting substantially entirely of two fractions of virgin naphtha boiling within the ranges of 190° to 300° F. and 400° to 500° F., with a dehydrogenation catalyst in the presence of hydrogen under substantial pressures exceeding atmospheric and at temperatures of approximately 850° to 1100° F.

2. The method in accordance with claim 1 in which the catalyst is a combination of a highly porous form of alumina and molybdena.

3. The method in accordance with claim 1, in which the hydrocarbon charge is made up of fractions in the two boiling ranges of substantially equal volume.

4. The method in accordance with claim 1 in which the hydrocarbons contacted with the catalyst consist of a mixture of 10 to 33½ per cent by volume of straight-run naphtha boiling between approximately 400° to 500° F., and 90 to 66½ per cent by volume of straight-run naphtha boiling between approximately 190° to 300° F.

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Number

2,392,398

2,406,117

65 2,406,394

Name

McMillan et al. Jan. 8, 1946

Welty Aug. 20, 1946

Newton Aug. 27, 1946

Date

OTHER REFERENCES

"Conversion of Petroleum," by Sachanen, 1st edition, 1940, Reinhold Publishing Corp. New York, page 173.