

UNITED STATES PATENT OFFICE

2,223,133

TREATMENT OF PETROLEUM PRODUCTS

Alexander N. Sachanen and Rowland C. Hansford, Woodbury, N. J., assignors to Socony-Vacuum Oil Company, Incorporated, New York, N. Y., a corporation of New York

No Drawing. Application September 1, 1938,
Serial No. 227,977

10 Claims. (Cl. 260—672)

This process relates to the production of aromatic compounds from petroleum products.

The importance of benzene, toluene, benzenoid compounds in general, naphthalene, anthracene and similar aromatic compounds, all of which are usually termed coal tar products in view of the fact that coal tar has been their original, and in general their only feasible, source, is well known. The myriad of uses of these compounds, both as such and, more particularly, as starting materials in the synthesis of numerous other organic compounds is common knowledge. Moreover, of late years, the alkyl-substituted aromatic compounds of relatively low molecular weight have become of increasing importance, e. g., as solvents, and especially as gasoline additive agents because of their high anti-knock characteristics.

In view of the tremendous importance of the benzenoid derivatives and other aromatic compounds, many attempts have been made in the past to devise a commercially feasible process for producing such compounds from petroleum. While several of these processes, as is well known, have been capable of actually yielding aromatic compounds, they are subject to disadvantages which prevent their usage, except possibly in extreme cases of demands for such products.

Perhaps the best known of the prior processes is the one involving pyrolytic cracking. The formation of aromatic hydrocarbons in cracking depends largely on the temperature. At comparatively mild temperatures of cracking below 500° C. the products of cracking contain all classes of hydrocarbons—paraffins, olefins, naphthenes and aromatics. At temperatures of about 500–600° C. mostly olefins and aromatics are formed. At temperatures higher than 600° C. the formation of aromatics becomes predominant. Therefore, by carrying out the cracking at temperatures around 700° C. a considerable yield of aromatic compounds may be obtained. The main objections to the pyrolytic cracking processes for producing aromatic compounds (see Ellis, The Chemistry of Petroleum Derivatives, page 162) are the high gas waste and extensive treatment required to separate them from olefins and diolefins which are formed simultaneously with aromatics. It is also known that aromatic compounds may be produced by high temperature treatment of light hydrocarbon gases, such as methane, propane, ethylene, etc. The reactions require as high temperatures as 850–1100° C. and involve the use of very expensive metallic alloys for reaction tubes. Various catalysts have been

tested in the above processes, however, in general, without much success.

It is an object of this invention to provide a process for the preparation of valuable aromatic compounds from petroleum products.

It is a further object of this invention to provide an efficient and economical process which affords a practical means for the production of valuable aromatic compounds from petroleum products.

A more specific object of the invention is to provide a process for treating certain petroleum products, including hydrocarbon by-products of petroleum refining, whereby relatively high yields are obtained of benzene and naphthalene derivatives.

Still another specific object of the invention is to provide a process for treating certain petroleum products, including hydrocarbon by-products of petroleum refining, whereby relatively high yields are obtained of aromatic compounds boiling within the gasoline boiling range, as well as relatively high yields of alkyl naphthalenes boiling up to 300° C.

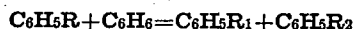
Our invention is based upon the discovery that certain petroleum products may be treated with benzene at relatively high temperatures of the nature herein disclosed alone or in the presence of suitable catalysts to produce substantial yields of valuable benzene and naphthalene derivatives.

It appears that the novel results of our invention are primarily attributable to the fact that when certain petroleum products are treated with benzene under conditions of our process, an optimum state is obtained for "destructive" reactions involving, among others, dealkylation and dehydrogenation whereby large complex molecules of the petroleum products are converted into valuable aromatic compounds of relatively low molecular weight.

A remarkable feature of the present discovery is the fact that an almost complete recovery of the benzene charged to the reaction is obtained. While in some cases a slight amount of this benzene is consumed (possibly to form alkyl aromatic compounds), in general the recovery is practically complete.

The complete or nearly complete recovery of benzene in the destructive dealkylation of solvent tar and cracking tars, as well as the other petroleum products treated is quite unexpected and raises the question as to the origin of the alkylated benzenes formed. While we do not wish to be held to any theory, a possible source of the alkylated benzenes formed might be some

high molecular weight and high boiling alkyl benzenes present in the petroleum products treated. These high molecular weight alkyl benzenes may possibly be destructively dealkylated by benzene according to the following general equation wherein R breaks down into smaller radicals R₁ and R₂:



B. P. > 400° F. B. P. < 400° F. B. P. < 400° F.

The formation of alkyl naphthalenes is due probably to the similar partial dealkylation of highly alkylated naphthalene derivatives present in the virgin product. If naphthenic hydrocarbons are present, it is quite probable that they first undergo a dehydrogenation reaction to form alkyl aromatic hydrocarbons and then the alkyl aromatic hydrocarbons thus formed undergo dealkylation reactions of the type above illustrated.

A partial dealkylation of alkyl aromatics, formed in the initial stages of the process, completely to benzene in the latter stages of the reaction may explain the total or almost total recovery of benzene. These conclusions are supported by our further experiments which show that in some cases the amount of recovered benzene exceeds that of benzene used for the reaction.

In addition to treating with benzene, we have carried out the destructive dealkylation of petroleum products by treating with other aromatic hydrocarbons instead of benzene, for example, naphthalene, alpha methyl naphthalene and alkyl naphthalenes. The yields of aromatic hydrocarbons in these experiments are much lower than with benzene. This indicates that the capacity of condensed rings such as naphthalene for alkylation is much less than that of benzene at these temperatures, which might be expected because of the relatively higher thermal stability of alkylated benzenes. The dealkylation of tars with naphthalene and its derivatives does not produce high aromaticity in the fraction 95° to 200° C., the specific gravity of which may be as low as 0.835.

As sources of petroleum material to be treated by our process, we wish to call particular attention to solvent tars which, as is well known, are the by-product from the present-day solvent-refining processes of petroleum. Accordingly, by our process we not only afford means of obtaining extremely valuable aromatic products but also afford a use for a material which is now usually considered a waste by-product of the petroleum industry. In addition to the solvent tars, it is to be clearly understood that the present process is applicable to the treatment of many other petroleum products and in fact is applicable to the treatment of any petroleum product containing substantial amounts of aromatic or naphthenic hydrocarbons. For instance, the petroleum products containing a considerable amount of aromatic or naphthenic hydrocarbons which are to be treated may include solvent and cracking tars, straight run residua and high boiling distillates (including distillates from tars). The distillates may be any distillates boiling in the range of kerosene or higher and containing substantial amounts of aromatic or naphthenic hydrocarbons. Some specific examples of petroleum materials suitable for treating, which are mentioned here merely for illustrative purposes, include Mirando, Rodessa, and East Texas furfural solvent tars from neutrals (distillates of lubricating oil fractions), Pennsylvania Chlorex solvent tar from

neutrals, dewaxed distillates, burning and power kerosene distillates, naphthenic distillate for cracking, distillate from an Ellis (coil or drum) cracked residuum and an Ellis cracked residuum.

Suitable catalytic material for our process should be capable of simultaneously promoting dealkylation and dehydrogenation reactions under the high temperature conditions of our process. There appear to be various catalysts which fulfill these capabilities as, for instance, those which are commonly designated as clay type. In addition to the various clays themselves and the various activated clays, there are other porous refractory adsorptive materials of a neutral character which may be used and come under the common designation of clay type catalysts, for example fuller's earth. Furthermore, it is to be understood that these various catalysts which have other suitable catalytic materials impregnated therein or thereon or otherwise conjoined for service may also be used.

Since the reactions involved bring about a gradual poisoning or deterioration of the catalyst by the deposit of carbon and carbonaceous impurities thereon, it is well to use a catalyst which may be regenerated in a relatively simple and economical manner. Likewise, as is obvious, the catalyst should be in a physical form which renders it capable of efficient operation. A convenient and efficient form for the catalyst is small granules, rods or cylinders. In carrying the process out in a batch operation, the relative amount of catalyst as, for instance, an activated clay, is usually about 15 to 30% by weight. When carrying the operation out in a continuous manner, the rate of charge is usually about 10 to 40 litres (measured as cold oil) of charging mixture per 20 litres of catalyst per hour.

As stated hereinbefore, our process may also be carried out in the complete absence of catalytic material. The conditions of operation in other respects, e. g., amount of benzene added, temperature, pressure, etc. may be essentially the same. We have found that under non-catalytic conditions yields of alkyl benzenes are generally somewhat lower than under catalytic conditions. For instance, in a catalytic (clay catalyst) and a non-catalytic treatment of a Mirando solvent tar, the yields of desirable alkyl naphthalenes were the same (about 20%) and the yields of alkyl benzenes from the non-catalytic treatment were about 10% as compared to 18% for the catalytic treatment.

The temperatures employed in our process should be upwards of about 800° F. and preferably between about 800° F. and 975° F. The particular temperature employed depends somewhat upon the other factors present. For instance, if the process is being carried out in a batch operation under high pressures, temperatures of about 800° F. to about 900° F. appear to be most desirable, with temperatures of about 875° F. to about 900° F. being optimum. If the process is carried out, for instance, in a continuous manner and under atmospheric or very slight pressure, temperatures of about 875° F. to about 975° F. appear to be most desirable, with temperatures of about 925° F. being optimum. However, for certain very refractory aromatic materials temperatures as high as 1100° F. may be employed to advantage in continuous non-catalytic operation. As indicated above, the present process may be operated either under low pressures or under high pressures, as for instance, pressures ranging from atmospheric to about 2,500 per square inch,

and, in general, relatively higher temperatures are used with the lower pressures. Particularly, when operating at low pressures, we prefer to carry out the operation in a continuous manner, although it is to be understood that the process is not so limited.

An important feature of the present invention, especially from the practical or commercial standpoint, is the relatively short time required for carrying out the process. For instance, when the process is carried out in a continuous manner at a temperature between about 875 and 975° F. and under a low pressure, say of the order of atmospheric to about 30 lbs. per square inch, the usual reaction time is only about one minute. Moreover, when the treatment is carried out in batch operation, for instance, at a temperature between 800° F. and 900° F. and under a rela-

zenes in comparison with the low pressure process (40% versus 25%), but this higher yield is accompanied by considerable consumption of benzene. It is probable that the increase of the yield of alkyl benzenes in the high pressure process for straight run distillates is due to the secondary reaction of alkylation of benzene with olefines formed. In the low pressure process, the conditions for the secondary reaction of alkylation are not so favorable because of the low pressure.

The following data obtained from the treatment of a Miranda solvent tar at high temperature and high pressure according to our process exemplifies the type of results that may be expected when applying our invention to the production of desirable aromatic materials from tars:

TABLE I
Destructive dealkylation of Miranda solvent tar
(from neutrals) at high pressure

Amount of benzene per 1 vol. of tar	Catalyst	Temp., °F.	Time, mins.	Light ends	Toluene in frac- tion 78°-95° C	Alkyl benzenes 95°-200° C.	Spec. grav. of alkyl benzenes
				Per cent	Per cent	Per cent	
2 volumes.....	None.....	900	39	10.8	2.3	10.8	0.883
Do.....	Fresh clay 30%.....	800	15	0.8	3.3	9.2	0.890
Do.....	Fresh clay 15%.....	850	43			19.5	0.894
Do.....	Reg. clay 15%.....	850	40	7.4	4.7	16.5	0.858
Do.....	Fresh clay 15%.....	875	40	10.0	7.7	24.9	0.867
Do.....	Reg. clay 15%.....	900	40	9.0	2.6	17.0	0.876
Do.....	Fresh clay 15%.....	900	39	13.9	6.8	17.5	0.874
1 volume.....	Do.....	900	39			25	0.875
2 volumes.....	Do.....	900	60	16.1	5.8	24.5	0.873
Do.....	Fresh clay 30%.....	900	40	10.8	5.4	24.8	0.874
1 volume.....	Fresh clay 15%.....	910	120	4.7	3.1	20.0	0.876

tively high pressure, say of the order of 1000 to 2500 lbs. per square inch, the usual reaction time is only about 30 minutes. The very short time of reaction in the continuous operation is probably explained by the fact that the continuous process takes place in the presence of a large excess of catalyst which occupies the entire reaction chamber. Therefore, in view of the simplicity of the process, the short time of reaction and the efficient yields of valuable aromatic compounds, the present invention appears to be of tremendous importance in providing a practical link between petroleum and the so-called coal-tar aromatic compounds, as well as a highly efficient source of alkyl aromatics of high anti-knock characteristics boiling in the gasoline boiling range.

As a whole, the operations at different pressures give very close results relative to the yields and properties of products, recovery of benzene, etc. For instance, the yields of alkyl benzenes and alkyl naphthalenes from Miranda tar in the low pressure process are about 18% and 25% respectively, whereas in the high pressure process, the respective yields are about 20% and 23%. The purity and aromaticity of alkyl benzenes in the high pressure process is a little higher than in the low pressure continuous process. The recovery of benzene is usually practically complete in both operations for such materials as solvent tars. High pressure dealkylation of straight run distillates produce higher yields of alkyl ben-

Fraction 78-95° C. represents the fraction containing recovered benzene. It contains usually a small amount of impurities, mostly toluene.

It is to be noted that appreciable yields were obtained in the first operation without the use of a catalyst. It is further to be noted that in the above operations up to 40 to 45% of fractions boiling in the boiling range of gasoline are produced including 25% of almost pure aromatic hydrocarbons boiling between 95 to 200° C. (toluene and higher).

The process of destructive dealkylation of Miranda furfural tar and other solvent tars and cracked products forms also comparatively high yields of alkylated naphthalenes, about 25% for Miranda tar.

Alkyl benzenes produced by destructive dealkylation of Miranda tar contain 90% pure alkylated benzenes and only 10% impurities, mostly olefins and naphthenes. Alkyl naphthalenes produced from the same tar contain 15% alkyl benzenes boiling between 200-215° C., 75% pure alkylated naphthalenes and only 10% impurities, mostly olefins and naphthenes.

By way of comparison, the following data obtained from conventional cracking of Miranda solvent tar wherein similar conditions of operation were employed to those of the present process except that no benzene was used, clearly illustrates the novel results that may be obtained by practicing our invention.

Amount of benzene per 1 vol. of tar	Catalyst	Temp., °F.	Time, mins.	Light ends	Fraction boiling 95°-200° C.	Sp. gr. of 95°-200° C. fraction
				Percent	Percent	
0.....	None.....	900	16	4.4	13.6	0.775
0.....	Fresh clay 15%.....	900	35	3.4	16.1	0.785

It can be seen from the above data that while a certain amount of material is produced which boils in the range of 95°-200° C., there is substantially no aromatic material, if any, contained therein, as all such aromatic materials have specific gravities above about 0.860. Accordingly, by the addition of benzene as a treating agent applicants have obtained entirely different results whereby they obtain valuable aromatic compounds from petroleum sources and in addition are able to recover substantially all of the benzene treating agent employed. The amount of benzene that may be used may vary considerably. From a practical standpoint we have found a ratio of benzene to stock treated of about 1/2 volume to 2 volumes of benzene to 1 volume of stock treated usually gives proper proportioning for obtaining our desired results. It is to be understood, however, that the invention is not limited to these ratios but rather contemplates the broad use of benzene in any amount sufficient to give our novel results.

The following data on low pressure treatment of Mirando tar by our process discloses that results somewhat similar to high pressure results are obtained thereby:

TABLE II
Continuous destructive dealkylation of Mirando
furfural tar at low pressure

Ratio benzol to charging stock	Catalyst	Temp., ° F.	Rate, liters per 20 l. cat./hr.	Cycle in minutes	Condensable light end to 78° C., vol. percent of stock	Alkylated benzene fraction 95°-200° C.		Alkylated naphthalenes 200-300° C.		Percent benzene recovered
						Volume percent of stock	Sp. gr.	Volume percent of stock	Sp. gr.	
2:1.....	Regen. clay	925	20/20	20	10.8	18.3	0.868	25.9	0.983	99.0
2:1.....	do	975	20+20	10	9.0	17.9	0.872	24.4	0.993	95.0
2:1.....	do	875	20-20	20	12.5	18.4	0.858	28.3	0.973	99.7
2:1.....	do	900	18/20	20	14.3	18.8	0.863	27.2	0.981	100.2
1:1.....	do	900	20-20	20	11.2	16.8	0.856	27.6	0.972	102.5
1/2:1.....	do	900	10/20	20	12.5	20.7	0.859	27.2	0.978	106.0

Representative of the results obtainable from cracked petroleum products when treated at high temperatures and pressures by our process may be seen from the following data derived from the treatment of a distillate from an Ellis cracked residuum boiling above 460° F., S. G. 0.925 and an Ellis cracked residuum, S. G. 0.983.

TABLE III
Destructive dealkylation of cracked products at
high pressures (2 vol. benzene+1 vol. cracked
product)

Product	Catalyst	Temp., ° F.	Time, mins.	Light ends	Toluene in fraction 78°-95° C.	Alkyl aromatic 95°-200° C.	Sp. gr. of alk. arom.
Distillate..	Percent	900	40	Percent	Percent	Percent	
Residuum..	15	900	40	5.8	8.0	22.0	0.870
Do.....	15	900	40	6.5	5.5	12.4	0.861
	30	900	40	6.4	3.5	16.7	0.868

The formation of coke took place to some extent in the experiment with cracked residuum. The yield of alkyl aromatics from the distillate is about the same as from Mirando tar. Cracked residuum forms a lower amount of alkyl aromatics. The recovery of benzene is 95 to 99% or 97 to 102% including toluene in recovered benzene. As straight run products Red Band Aero oil, S. G. 0.883; dewaxed distillate, S. G. 0.888; and residuum of Oklahoma City crude, S. G. 0.888; are typical of the petroleum products treated by our process at high pressure. Results obtained thereby are shown in the following table:

TABLE IV

Destructive dealkylation of straight run products at high pressures (2 vol. of benzene per 1 vol. of product, 15% clay)

Temp., °F.	Time, mins.	Ben- zene recov- erable, per- cent	Products of dealkylation			
			Light ends, per- cent	Toluene in frac- tion 78°- 95° C., percent	Alkyl arom. 95°-200° C., percent	Spec. grav. of alkyl arom.
RED BAND AERO OIL						
800 900	60 40	95 87	6.6 37.7	4.9 10.0	17.1 42.0	0.818 0.863
STRAIGHT RUN RESIDUUM OF OKLAHOMA CITY CRUDE						
845 900	60 40	99½ 83	27.7 27.3	8.8 7.3	23.1 21.8	0.816 0.861
DEWAXED DISTILLATE						
885	40	88	28.3	10.1	38.9	0.860

Under more severe conditions (885° to 900° F. and 40 minutes time) destructive dealkylation of straight run naphthenic materials produces an enormous yield of low boiling products, distilling in the boiling range of gasoline, up to 80 to 90% of the original material. The formation of these

low boiling products is accompanied by the consumption of benzene which is about 25% with respect to the original material. At the expense of this consumption of benzene, the yield of alkyl aromatics is very high (about 50%, including toluene in the recovered benzene). If recovered benzene is used for further dealkylation without separation of toluene, the consumption of benzene is only 15% with respect to the original material and the yield of alkyl aromatics is 40%. The following data is representative of the results that may be obtained in treating straight

run petroleum products at low pressure, according to our process:

Example II.—A distillate of a Cross cracked residuum is treated with benzene under the con-

TABLE V
Continuous destructive dealkylation of straight run stocks at low pressure and in the presence of a clay catalyst

Charging stock	Ratio, benzol to stock	Temp., °F.	Rate, liters per 20 l. cat. /hr.	Cycle in minutes	Condensable light ends to 78° C.		Alkylated benzene fraction 95-200° C.		Recycle stock 200-300° C.		Percent benzene recovered
					Vol. percent of stock	Sp. gr.	Vol. percent of stock	Sp. gr.	Vol. percent of stock	Sp. gr.	
Dewaxed distillate (497½ stock).....	2:1	975	20+/-20	20	35.9	0.70	19.5	0.853	11.0	0.959	94.5
Do.....	1:1	925	10+/-20	20	29.8	0.70	21.6	0.841	12.6	0.945	100.2
Naphthenic dist. (from atm. tower).....	1:1	925	10+/-20	20	22.2	0.70	23.1	0.858	34.4	0.899	95.8
Do.....	2:1	925	20+/-20	20	26.4	0.71	19.9	0.856	50.3	0.882	93.8
Recycle stock (from naphth. dist.).....	1:1	925	10+/-20	20	22.8	0.72	17.3	0.859	54.0	0.915	95.0

The following data for treatment of Miranda tar at low pressure according to our process show the influence of temperature on the yield of gas, coke and alkyl benzenes and on the properties of the alkyl benzenes, other conditions being equal (ratio of benzene to Miranda tar 2:1; rate of charge 20 per 20 per hour; cycle 20 minutes)

Temp.	Yield of gas by wt.	Yield of coke by wt.	Yield of alkyl benzenes by vol.	Sp. gr. of alkyl benzenes	Iodine No. of alkyl benzenes
	Percent	Percent	Percent		
875° F.....	3.3	7.0	18.4	0.858	25
900° F.....	5.8	8.9	18.8	0.863	19
925° F.....	11.1	11.7	18.3	0.868	16
975° F.....	17.8	16.4	17.3	0.873	12

Thus the yield of alkyl benzenes practically does not depend on the temperature when in the above range, but the aromaticity of the alkyl benzenes formed is strongly influenced by the temperature, as shown by the specific gravities and iodine numbers. The time of dealkylation has the same effect as the temperature and thus, other conditions being equal, the aromaticity of alkyl benzenes is enhanced by a greater time of processing. The ratio benzene to stock has the same effect as temperature and time, but to a much lesser extent, higher ratios being in effect the same as a lower rate of stock through the unit. The influence of temperature, rate and ratio of benzene to stock on the aromaticity of alkyl benzenes and yields is the same for all investigated products including straight run distillates.

The invention may be further illustrated by the following specific examples. However, it is to be clearly understood that nothing therein is to be construed as limiting as there may be wide variations therefrom, as indicated herein without departing from the spirit of the invention.

Example I.—A solvent tar of a Miranda lube distillate is treated with benzene at 900° F. under a pressure of 1300 pounds per square inch for 40 minutes in the presence of 15% activated clay; about 2 volumes of benzene per 1 volume of tar are used. The following products are recovered:

	Per cent
Condensable light ends (up to 80° C.).....	10
Alkylated benzenes, sp. gr. 0.87, 110-200° C.....	22
Alkylated naphthalenes, sp. gr. 0.98, 200-300° C.....	25
Residuum, sp. gr. 1.1, above 300° C.....	30

ditions of Example I. The following products are recovered:

	Per cent
Condensable light ends.....	20
Alkylated benzenes, sp. gr. 0.87, 110-200° C.....	20
Alkylated naphthalenes, sp. gr. 0.98, 200-300° C.....	26
Residuum, sp. gr. 1.1, above 300° C.....	24

Example III.—A solvent tar of a Miranda lube distillate is charged with two volumes of benzene to a convertor containing a clay catalyst maintained at a temperature of 925° F. and under a pressure of 30 pounds per square inch, the rate of charge being 20 liters per 20 liters of catalyst per hour and the cycle 20 minutes. The following products are recovered:

	Per cent
Condensable light ends.....	17.4
Alkylated benzenes, sp. gr. 0.868.....	18.3
Alkylated naphthalenes, sp. gr. 0.983.....	25.9
Residuum above 300° C., sp. gr. 1.06.....	23.4

Example IV.—Non-catalytic process: A solvent tar of a Miranda lube distillate is treated with 2 vol. of benzene at 900° F. under a pressure of 1200 pounds per sq. inch for 40 minutes without any catalyst. The following products are recovered:

	Per cent
Condensable light ends.....	10
Alkylated benzenes, sp. gr. 0.870, 110-200° C.....	9
Alkylated naphthalenes, sp. gr. 0.97, 200-300° C.....	20
Residuum, sp. gr. 1.1, above 300° C.....	46

In the specification and claims where we speak of recovering benzene (or equivalent treating agent), it is to be understood that the term "substantial recovery of benzene" (or equivalent expression), means that benzene (or the equivalent treating agent) is recoverable in any amount above 100% and recoverable below 100% in the order shown herein in the specification.

We claim:

1. The process of producing alkyl aromatic compounds boiling below 300° C. from heavy petroleum products containing substantial amount of higher boiling cyclic compounds which products are selected from the class consisting of petroleum tars and residues, which comprises heating said products in the presence of benzene at a temperature between about 800° F. and about 1100° F. for a sufficient length of time to produce the desired alkyl aromatic compounds, recovering at least substantially all the added benzene, sep-

- arating a 100°-200° C. fraction comprising essentially alkyl benzenes from the treated products and separating a 200°-300° C. fraction comprising essentially alkyl naphthalenes and other bicyclic aromatic hydrocarbons from the treated products, the ratio of benzene to petroleum products being between about ½ volume to about 2 volumes of benzene to 1 volume of petroleum products.
2. The process of producing valuable alkyl aromatic hydrocarbons boiling below about 300° C. from a petroleum product containing a high concentration of cyclic hydrocarbons other than said alkyl aromatics and which are solely of petroleum origin which comprises treating said petroleum product with an aromatic from the class consisting of low molecular weight, substantially unsubstituted benzenes and naphthalenes at a temperature between about 800° F. and about 1100° F., the ratio of said low molecular weight, substantially unsubstituted aromatic added to the petroleum product being upwards of about ½ volume of aromatic to 1 volume of petroleum product, whereby the petroleum product is dealkylated and a reaction mixture is obtained containing said valuable alkyl aromatic hydrocarbons and an amount of said low molecular weight substantially unsubstituted aromatic equal at least to substantially all of such aromatic added to the petroleum product.
3. The process of claim 2 wherein the treatment is carried out in the presence of a clay catalyst.
4. The process of producing valuable alkyl aromatic hydrocarbons boiling below about 300° C. from a petroleum product containing a high concentration of cyclic hydrocarbons other than said alkyl aromatics and which are solely of petroleum origin which comprises treating said petroleum product with benzene at a temperature between about 800° F. and about 1100° F., the ratio of benzene added to the petroleum product being upwards of about ½ volume of benzene to 1 volume of petroleum product, whereby the petroleum product is dealkylated and a reaction product is obtained containing said valuable alkyl aromatic hydrocarbons and an amount of recoverable ben-

zene equal at least to substantially all the benzene added to said petroleum product.

5. The process of claim 4 wherein the treatment is carried out in the presence of a clay catalyst.

6. The process of claim 4 wherein the treatment is carried out at a temperature between about 800° F. and about 975° F. and in the presence of an activated clay catalyst.

7. The process of producing alkyl benzenes boiling below about 200° C. and alkyl naphthalenes and other bicyclic aromatic hydrocarbons boiling below about 300° C. from a petroleum product containing a high concentration of relatively complex higher boiling cyclic hydrocarbons and which are solely of petroleum origin which comprises treating said petroleum product with benzene at a temperature between about 800° F. and about 1100° F., the ratio of benzene to petroleum product being about ½ to about 2 volumes of benzene to 1 volume of petroleum product, and recovering substantially all of said benzene from the treated product.

8. The process of claim 7 wherein the treatment is carried out at a temperature between about 800° F. and about 975° F. and in the presence of a clay catalyst.

9. The process of producing alkyl benzenes boiling below 200° C. from a heavier petroleum product selected from the class consisting of petroleum tars and residues containing a high concentration of relatively complex cyclic hydrocarbons which are solely of petroleum origin which comprises treating said petroleum product with benzene at a temperature between about 800° F. and about 1100° F., the ratio of benzene to petroleum product being upwards of about ½ volume of benzene to 1 volume of petroleum product, and recovering substantially all of said benzene from the treated product.

10. The process of claim 9 wherein the treatment is carried out at a temperature between about 800° F. and about 975° F. and in the presence of a clay catalyst.

ALEXANDER N. SACHANEN.
ROWLAND C. HANSFORD.