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AROMATIZATION OF OIL PRODUCED IN LOW TEMPERATURE CARBONIZATION OF COAL

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9 Claims. (Cl. 260—668)

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This invention, which is a continuation-in-part of application No. 363,381, filed on October 29, 1940, relates to the utilisation of a liquid product obtained in the carbonisation of coal. The method of carbonising coal being dealt with is the low temperature carbonisation process to obtain smokeless coke which is normally carried out at about 600–650° C. in retorts of the coke-oven type, which work on the batch or discontinuous principle. The products of this method of carbonisation include a liquid usually called "coal-oil."

The invention deals with a particular fraction of this coal-oil, namely, the fraction which consists of products having boiling points of from 100° C. to 280° C., the preferred part of this range being from 100° C. to 180° C.

Further, from this fraction for its use for the purpose of the present invention, the acidic and basic constituents are removed either before or after preparation of the fraction. In addition, any olefine constituents or part thereof may be removed leaving chemically saturated constituents thereof.

The object of the present invention is a process for the utilisation of the coal-oil fraction referred to above that is free from acidic and basic constituents by treating it to yield a mixture composed substantially of aromatic hydrocarbons, for example, benzene and toluene.

This object I find can be secured by a process according to the succeeding paragraph, in which all the features mentioned therein are essential to success, particular stress being laid on (*a*) the starting material; (*b*) the form in which the starting material is used; (*c*) the particular catalysts and (*d*) the particular temperature range. This is in contrast to processes in the prior art which have one or more of the features mentioned, but not all of them in combination, as a result of which the product obtained by the prior processes, differs from those according to the present application.

This can be seen for example with reference to Austrian patent Serial No. 101,681.

The Austrian process gives aromatics which are of the same molecular size only as the starting material. A charging stock consisting of C_6 hydrocarbons gives benzene only, for example, while a C_7 charging stock gives toluene only. In

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contrast, applicant obtains a series of aromatics from any fraction, ranging from benzene to ethylbenzene and xylene. This is probably due to the fact that under applicant's conditions the charge is completely broken down to small unsaturated molecules and that then re-synthesis takes place. At least the fact remains that applicant obtains a different result.

The difference between these two processes is not a difference due to the range of boiling cuts used in the starting materials. In applicant's case, the composition of the end product does not depend on that of the charging stock.

The invention consists in a process for the preparation of a mixture comprised substantially of aromatic hydrocarbons from a fraction having boiling points between 100 and 280° C. of the coal-oil produced in the low temperature carbonisation process to obtain smokeless coke and from which fraction the acidic and basic constituents have been removed, which process comprises submitting the aforesaid starting material in the form of its vapour to the action of a metallic catalyst of the kind known as hydrogenation-dehydrogenation catalysts at a temperature within the range 600 to 700° C., preferably at atmospheric pressure, and preferably at a space velocity of 0.1 to 0.5 litre of oil per hour, per litre active catalyst volume.

The invention also consists in a process in accordance with the preceding paragraph in which the starting material employed is the coal-oil fraction aforesaid but limited to the boiling range of 100 to 180° C.

The invention also consists in a process in accordance with either of the preceding two paragraphs in which the catalyst is employed in a form presenting to the vapours a large and active surface.

The invention also consists in a process in accordance with any of the preceding three paragraphs in which the product formed is separated into its gaseous and liquid constituents, for instance, by cooling or by adsorption or absorption in a selective solvent or by a combination of such methods.

The invention also consists in a process in accordance with any of the preceding four paragraphs in which process the liquid resulting from the process is fractionated into practically pure

benzene (boiling point 80–81° C.), practically pure toluene (boiling point 111–112° C.) and an ethyl-benzene fraction (boiling point 135–146° C.) which consists chiefly of ethylbenzene and styrene, but may also contain some xylene and into a higher boiling part which may be either totally or partly re-cycled over the catalyst.

The invention also consists in a process in accordance with any of the preceding five paragraphs, in which process the gaseous constituent is utilised as starting material for chemical syntheses or as fuel for an evaporation unit and the catalyst furnace itself or as both a starting material and a fuel.

The invention also consists in a process in accordance with any of the preceding six paragraphs, specifically directed to the case in which any olefine constituents or part of them have been removed from the starting material.

The invention also consists in a process in accordance with any of the preceding seven paragraphs, in which aromatised products thereby produced are returned into the process for a re-cycling treatment.

The invention also consists in a process in accordance with the preceding paragraph in which the products boiling between 145° C. and 195° C. are re-cycled to the reaction.

The invention also consists in processes in accordance with any of the preceding nine paragraphs, carried out as described in any of the examples given below.

The invention also consists in aromatic hydrocarbons when prepared or produced by the methods or processes of manufacture particularly described and ascertained herein.

The invention also consists in an internal combustion engine fuel when produced in accordance with any of the preceding ten paragraphs.

Several ways of carrying this invention into effect will now be described by way of example.

Example I

This is an example of a process for the treatment of coal-oil under nickel catalyst conditions

A stainless steel tube of 30 cm. length and 3 cm. diameter was filled with 400 gms. nickel pellets of pea size and heated electrically to a temperature of 700°. Then a coal-oil fraction boiling in the range 100–180° was passed through this reaction tube at a speed of 80 gms. per hour. The coal-oil fraction, before entering the reaction tube, passed through a preheater, in which it was subjected to a temperature of 220°, so that a substantial part of it was vaporised. The reaction products were cooled in an efficient condenser to room temperature so that only their gaseous constituents were allowed to escape. The liquid condensate was fractionated and the fraction boiling above 140° subjected again to the above treatment. The total liquid obtained in the two treatments, which boiled up to 140°, amounted to 53.1% of the original oil; of the products 16.8% were benzene, 16.1% toluene and 10% ethyl-benzene fraction. The remainder, boiling above 140° consisted of higher aromatic hydrocarbons, including, e. g., naphthalene. The space velocity employed in the above examples lies within 0.1 and 0.5 litre of oil per hour per litre active catalyst volume.

Example II

This is an example of the treatment of coal-oil under copper catalyst conditions

The catalyst consisted of copper needles, prepared by reduction of copper oxide needles at 225°. 300 gms. of the needles were placed in and filled the reaction tube described in Example I. The conditions of the reaction were the same as above. The total liquid obtained amounted to 54% of the original oil; 13.6% of this liquid obtained was benzene, 14.2% toluene and 14.8% ethylbenzene fraction.

Example III

This is an example of the treatment of coal-oil under the conditions of a mixed iron and copper catalyst

Under the same conditions as obtained in Examples I and II above but using an intimate mixture of iron and copper filings as the catalyst, 54.0% liquid products calculated on the charging stock of liquid were obtained of which 14.2% was benzene, 18.2% toluene and about 13.0% ethylbenzene fraction.

Example IV

This is a further example of the treatment of coal-oil under copper catalyst conditions

In this example catalyst consisting of activated copper was heated at a temperature of 690°. The total catalyst volume was 180 litres. With a speed of 25.3 litres per hour, i. e., 20.8 kg. per hour, coal-oil of a boiling range 110° to 230° was passed over the catalyst. The space velocity therefore was 0.1 litre per litre catalyst space and hour. The products formed were condensed continuously as far as possible and the escaping gases passed through a tower in which they were brought into intimate contact with an absorbing spindle oil. Per hour 15.3 litres=14.0 kg liquid product which was aromatic apart from a small head fraction, was condensed, and in the scrubbing installation 0.4 litre=0.3 kg. per hour was isolated in addition. The gas amounted to 6.9 cbm. per hour (calculated for normal temperature and pressure). As the density of the gas was 0.97 gm. per litre, its weight was 6.9 kg. Expressed in weight 69% of the charging stock were recovered in liquid form, 31% in gaseous form. An inspection of the catalyst after the experiment which was continued for twelve hours showed that substantially no carbon deposition had taken place.

Fractionation of the liquid product yielded the following components, the quantities being calculated as per cent of the charging stock:

	Per cent
Head fraction (below 80°)	0.5
Benzene	7.3
Toluene	14.7
Ethylbenzene fraction	13.7
Fraction 145–180°	13.2
Higher boiling aromatics	19.8

The fraction 145°–180° was subjected to fractionation and from it was obtained the following principal constituents:

Boiling-point:	Degrees
Isopropyl-benzene	151
1.3.5-trimethyl-benzene (mesitylene)	162
Tert. butyl-benzene	168
1.2.4-trimethyl-benzene	170
Sec. butyl-benzene	174
1.2.3-trimethyl-benzene	179
Indene	181

The mixture of these substances can be used as such as ingredient for high-grade motor-fuel in view of its fairly high octane number, but it can

also be degraded by re-cycling to substantial amounts of the low boiling aromatics as described below.

A similar fractionation of the part of the product boiling under atmospheric pressure above 180° and suitable purification by conventional methods yielded led to the following substances:

Substance	Boiling range	Per cent of total high fraction	Remarks
Tetrahydronaphthalene	205–210°	5.0	
Naphthalene	210–225°	11.3	
α methyl-naphthalene	240–247°	4.2	Picrate M. P. 140°.
β-methyl-naphthalene	240–247°	5.0	Picrate M. P. 116°.
1.2-dimethylnaphthalene	265–275°	4.2	Picrate M. P. 122–123°.
1.2.5-tri-methyl-naphthalene (probably).	195° in vacuo	2.1	Orange red picrate M. P. 134°.
Anthracene	240–260° in vacuo	3.0	
2-methylanthracene	260–270° in vacuo	4.0	
Dihydropyrene	345–347° in vacuo	7.3	Dark-red picrate M. P. 196–198°.
Dibenzochrysene	350–410° in vacuo	1.0	M. P. 288°.
Pitch	above 410° in vacuo	25	

Substantial quantities of anthracene and especially chrysene may be isolated from the pitch.

The above last two lists contain only the substances which have been isolated in substantial quantities; they do not indicate that the tabulated compounds are the only products formed.

EXAMPLE V

This is an example dealing with the re-cycling of the aromatised fraction boiling between 145–195°

The aromatised fraction boiling between 145–195° was passed over a catalyst consisting of activated copper at a temperature of 600°. The total catalyst volume was 640 cc., of which 440 cc. were at the above indicated temperature, while the temperature decreased by about 15° towards the ends of the furnace. As the rate of throughput was 70 cc. per hour, the space velocity was 0.16 litre per litre catalyst space and hour. 96% liquid products were recovered, while 4% of the charging stock was converted into gaseous products. Of the liquid product 15% boiled up to a temperature of 145°, 10% above 195°, whilst 75% retained the original boiling range. Fractionation of this part showed that the proportion of trimethylbenzenes had increased; fractionation of the product boiling below 145° showed that it consisted of the following components expressed in % of the total charge:

Below benzene	1.3
Benzene	1.5
Toluene	1.5
Ethylbenzene fraction	12.0

EXAMPLE VI

This is a modification of the preceding example, the temperature of treatment being higher

This example was carried out in a manner similar to Example V except that the temperature employed was not 600° but 680° and the total catalyst volume was 550 cc. of which 240 cc. had the stated temperature.

The space velocity was 0.19 litre per litre catalyst space and hour and the rate of throughput was fixed at 45 cc. per hour. The total weight of the charge was recovered, of this 73% in liquid and 27% in gaseous form. Of the liquid, 48% boiled below 145°, 18% boiled between 145–190°, and 34% boiled above 190°.

Fractionation of the low fraction showed that it consisted of:

	Per cent
Head fraction	0.7
Benzene	3.5
Toluene	8.0
Ethylbenzene fraction	16.5

The total amount of low boiling aromatics is therefore higher than at 600° and the increase in toluene is especially marked. In both cases, however, the xylene fraction is the principal constituent.

In the fraction boiling between 145–195°, 55% are mesitylene.

From the highest fraction inter alia naphthalene and anthracene were easily isolated; about 50% of this fraction consisted of chrysene.

EXAMPLE VII

This is an example applied to the saturated constituents of coal-oil

The unsaturated constituents of coal-oil, which form usually 40 to 50% of it, may be used for other industrial purposes, such as the production of alcohols, bromides and the like. It is therefore important that the saturated constituents, after removal of the total quantity or of part of the olefines, can also be processed by the method described in this application. The charging stock for the following process was obtained by successive treatment of the coal-oil (boiling range 100–180°) with sulphuric acid of increasing strength. The greater part of the olefines were thereby converted into alkyl hydrogen sulphates which were extracted with water. The residue was distilled and the part thereof boiling up to 180°, selected for the cracking process. 5% of the aforesaid residue boiled up to 123°, 95% up to 173°, its specific gravity was 0.807, its bromine number 19.5 g./100 g., indicating an approximate olefine content of 17%. The aforesaid part was cracked in the manner described in presence of activated copper at 680°; the space velocity was 0.11 litre per litre catalyst space and hour. The liquid product was practically completely aromatic, as its high density 0.890 indicates; the yield of liquid product amounted to 64% of the charging stock, while 36% of it were received in gaseous form. 85% of this liquid product boiled up to a temperature of 180°, and its fractionation gave the following figures (which are all expressed as % of the charging stock):

	Per cent
Light fraction (below benzene)	1.6
Benzene	3.8
Toluene	13.5
Ethylbenzene fraction	20.0
Alkylbenzenes, boiling between 145°–180°	12.5
Heavy aromatics, boiling above 180°	9.6

GENERAL

In general the reaction conditions involve a space velocity of 0.1–0.5 litre of oil per hour per litre active catalyst volume. By "active catalyst volume" is meant the volume of the catalyst which is at the correct operating temperature.

The catalytic metals for use according to the present invention are such as catalyse hydrogenation and dehydrogenation reactions, e. g., iron, copper, nickel, cobalt, silver, chromium, molybdenum, tungsten or manganese. The catalyst need not consist of a single metal; mechanical mixtures or alloys of two or more metals may be used instead with equally favourable results. The metal catalyst may also be used in the form of a deposit on a suitable carrier such as pumice. The catalyst is conveniently contained in a tube made of metal or ceramic material.

The usual catalyst poisons, contained in the coal oil, are destroyed in the course of the aromatisation reaction. If, however, the activity of the catalyst decreases, it can easily be restored by successive treatment with air or pure oxygen and hydrogen. For the reactivation process, the cracking gases, which contain a certain percentage of hydrogen, may be used advantageously.

The pressure at which the conversion is carried out should preferably be near atmospheric, although this is not essential.

As regards the starting material the coal-oil may contain a percentage of aromatic compounds the amount depending upon the temperature at which each batch of coal-oil was produced. In general the lower the temperature of production the lower the content of aromatic compounds.

The present application is, however, independent of the actual composition of the coal-oil as regards these products.

A fuel for an internal combustion engine may be provided by the products of the processes described above.

Although the end products may have boiling points not far separated there is no technical difficulty in isolating two products which have boiling points lying 5% or more apart. With ranges where the top boiling point of a lower range and the lower boiling point of an upper range are identical some substance may be common to both fractions but it is customary for all fractions to be submitted to a simple refractionation process and by this means individual components can be isolated as far as may be desired.

I claim:

1. A process for the preparation of a mixture composed substantially of aromatic hydrocarbons from a fraction having boiling points between 100 and 280° C. of the coal-oil produced in the low temperature carbonisation process to obtain smokeless coke and from which fraction the acidic and basic constituents have been removed, which process comprises passing the aforesaid starting material in the form of its vapour and at a space velocity ranging from about 0.1 to 0.5 liter of oil per hour per liter of active catalyst volume, in contact with a metallic catalyst of the kind known as hydrogenation-dehydrogenation catalysts, selected from a group consisting of iron, copper, nickel, cobalt, silver, chromium, molybdenum, tungsten, manganese and alloys and mixtures of these metals, at a temperature within the range 600 to 700° C.

2. A process as claimed in claim 1, in which the starting material employed is the coal-oil fraction aforesaid but limited to the boiling range of 100 to 180° C.

3. A process as claimed in claim 1, in which the catalyst is employed in a form presenting to the vapours a large and active surface.

4. A process as claimed in claim 1 in which the product formed is separated into its gaseous and liquid constituents by cooling.

5. A process as claimed in claim 1 in which process the liquid resulting from the process is fractionated into practically pure benzene (boiling point 80–81° C.), practically pure toluene (boiling point 111–112° C.) and an ethyl-benzene fraction (boiling point 135–146° C.) which consists chiefly of ethylbenzene and styrene, but may also contain some xylene, and into a higher boiling part which is suitable for recycling over the catalyst.

6. A process as claimed in claim 1 specifically directed to the case in which olefine constituents have been removed from the starting material.

7. A process as claimed in claim 1 in which aromatised products produced in the process are returned to the process for a re-cycling treatment.

8. A process as claimed in claim 1, in which the products boiling between 145° C. and 195° C. are re-cycled to the reaction zone.

9. In the production of aromatics, the process which comprises removing acidic and basic constituents from a coal-oil fraction, produced in the low temperature carbonization of coal to obtain smokeless coke and having a boiling point range of from about 100° to 280° C., vaporizing said fraction, passing the vapors in contact with a finely-divided metallic hydrogenation-dehydrogenation catalyst selected from a group consisting of iron, copper, nickel, cobalt, silver, chromium, molybdenum, tungsten, manganese and alloys and mixtures of these metals, at a space velocity within the range of 0.1 to 0.5 liter per hour per liter of active catalyst volume and at a temperature within the range of 600° to 700° C., separating the resulting products into a liquid fraction and gases, distilling the liquid fraction to remove products boiling below about 145° C. and recycling the higher boiling fraction in contact with said catalyst.

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