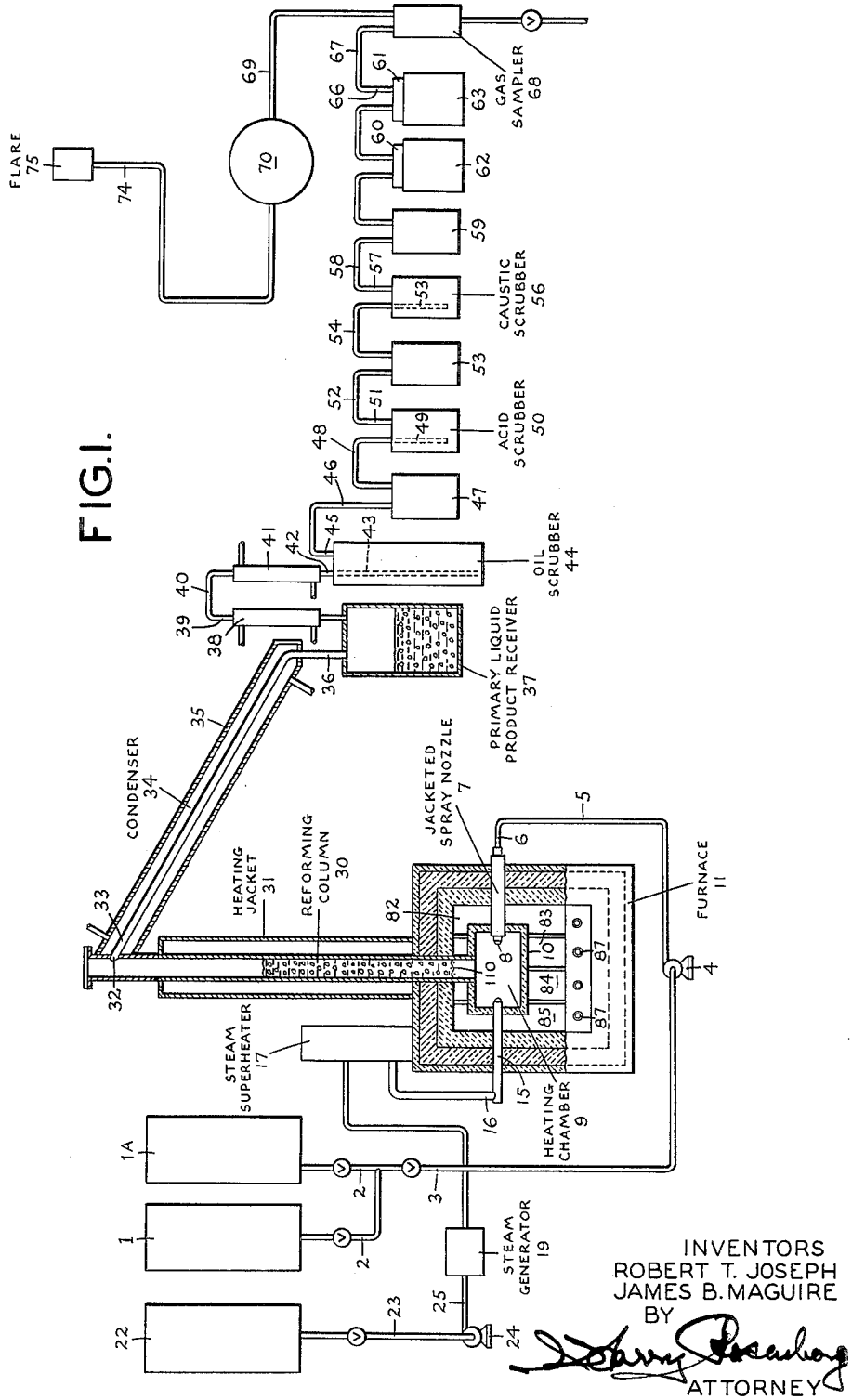
March 28, 1961 R. T. JOSEPH ET AL 2,977,299

PRODUCTION OF CHEMICAL PRODUCTS FROM COAL PRODUCTS

Filed Oct. 15, 1957 2 Sheets-Sheet 1

FIG. 1.



INVENTORS
ROBERT T. JOSEPH
JAMES B. MAGUIRE
BY

ATTORNEY

March 28, 1961 R. T. JOSEPH ET AL 2,977,299

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Filed Oct. 15, 1957 2 Sheets-Sheet 2

FIG.4.

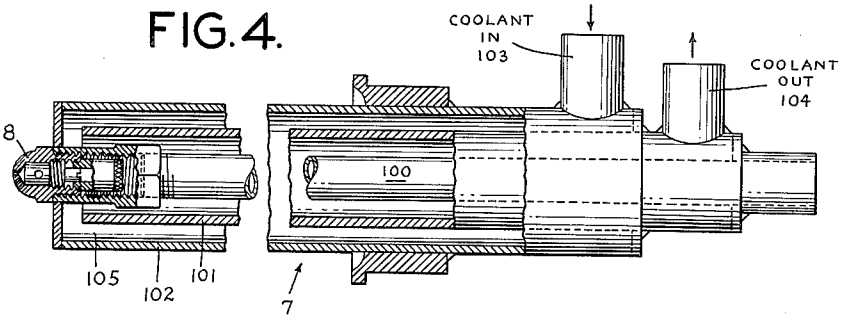


FIG.2.

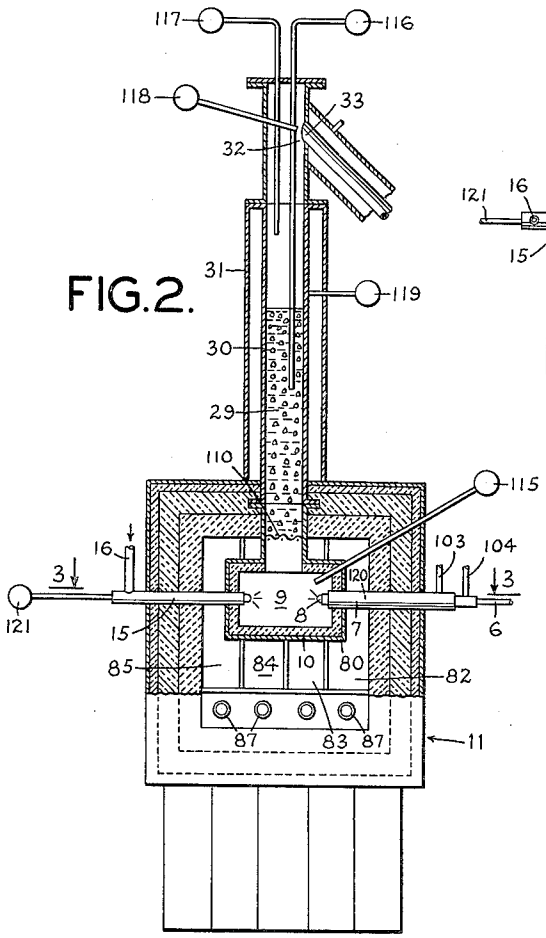
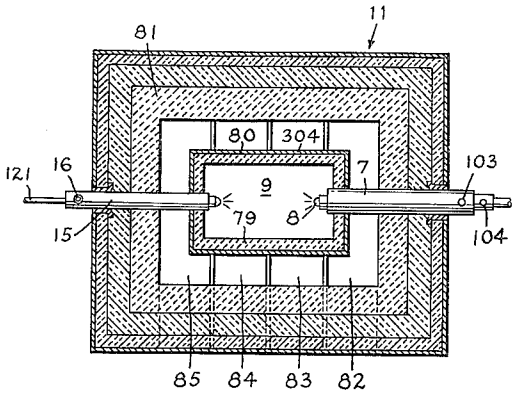


FIG.3



INVENTORS
ROBERT T. JOSEPH
JAMES B. MAGUIRE
BY
Harry Rosenberg
ATTORNEY

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PRODUCTION OF CHEMICAL PRODUCTS FROM COAL PRODUCTS

Robert T. Joseph, Northampton Township, and James B. Maguire, Elkins Park, Pa., assignors to Allied Chemical Corporation, a corporation of New York

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13 Claims. (Cl. 208—8)

This invention relates to a method for the production of valuable chemical products from coal products; that is, from coal and related carbonaceous materials such as lignite and peat, as well as tars derived therefrom, especially by low temperature carbonization processes, and fractions, especially residues, obtained in the recovery of valuable products from coal tars of various types. Thus it includes processes for the production of (1) gaseous products valuable for their heat content and chemical composition, and (2) a light oil-tar product containing valuable aromatic chemicals in quantity and quality similar to those present in tars produced by high temperature carbonization of bituminous coal, from such raw materials as coals, lignites, peats, and products derived from the high and low temperature carbonization of these substances, including low temperature tars, middle oils from high temperature tars, residual oils, pitches, and the like. It relates especially to the production of valuable gases and organic aromatic chemical compounds from tars and oils obtained in the low temperature carbonization of bituminous coals and in the low temperature carbonization of lignites, from oils, pitches and residues obtained in the distillation of high temperature coal tar, and from residues from the refining of tar acids and tar bases.

The major source of organic chemicals of the aromatic class is coal tar obtained in the high temperature carbonization of bituminous coal, despite the fact that certain aromatic chemicals are obtained, to some extent, by the synthesis from petroleum products. For the most part, the coal tar is a by-product containing approximately 15% of aromatic chemicals which are recovered by fractional distillation of the coal tar, leaving a residue of about 85% having only low economic value and used for such purposes as wood preserving, weatherproofing, and burning as a source of carbon or as a fuel.

The coking of bituminous coal is normally carried out for the purpose of producing metallurgical coke. With advances in the coking procedure, the supply of by-product tar is reduced. Some tar is also formed in the manufacture of carburated water-gas, but here also the supply is limited.

The coking of coals of types selected for the production of a particular type of coke desired for use in metallurgy is generally carried out as a batch operation, at a high temperature—for example, about 1200° C.—in large retorts or ovens from which by-products are collected by drawing off the gases and vapors produced in the coking, and cooling and washing them. The tar fraction of the by-products, which is recovered in the so-called hydraulic main, consists of a dark oily liquid mainly composed of aromatic products, such as, benzene, toluenes, xylenes, phenols, cresols, xylenols and other so-called tar acids, naphthalene, anthracene, creosote oils, pyridine, quinoline and other tar bases, and higher boiling substances. A characteristic feature of such high temperature coal tars is their low content of paraffinic compounds.

For the recovery of the individual products, the tar is subjected to fractional distillation, and individual cuts are taken, depending upon the degree of refinement desired and the extent of separation of the individual components desired.

In the distillation of coal tar (high temperature tar), a pitch residue is left which may vary in nature from a fluid to a viscous solid, depending upon the conditions of distillation, and which is of low economic value as compared with the higher priced products of the distillation, such as the aromatic hydrocarbon fractions, tar acids and tar bases.

The coking of coal for the production of metallurgical coke requires coal of particular characteristics which are not possessed by a number of varieties of coal nor by lignite nor peat. In addition, the coking process, as pointed out above, is generally operated as a batch process and requires from 16 to 24 hours for the coking of a single batch.

Extensive research has been carried out directed to the utilization of coals, lignite and the like, not suitable for the production of metallurgical coke, with a view to increasing their value as fuels. Thus, processes have been developed which involve a heat treatment of the coal, lignite and the like, at relatively low temperatures (for example, 600°–800° C.), or at medium temperatures (for example, 800°–1000° C.), by continuous procedures with formation of a main product consisting of an improved fuel. These processes carry out the heating for a considerable period of time.

As in the high temperature coking of coal, the low temperatures and medium temperature processes produce gaseous and vaporous products which, when subjected to condensation, result in a tarry product; but such tars are of an entirely different nature from ordinary coal tar (high temperature tar). Thus, they do not contain any low boiling aromatic constituents, and the middle boiling and high boiling constituents are paraffinic and naphthenic in nature (they are low in content of unsaturated compounds). About 20% of the tar is extractable with caustic alkali, yielding high boiling tar acids which are probably long-chain alkyl-substituted aromatic compounds. Their content of nitrogen is higher than that of high temperature tar and is mostly in the form of nitriles rather than tar bases (pyridine, quinoline, etc.)

Various attempts have been made to utilize the low temperature and medium temperature tars; but, for the most part, they are burned as a fuel oil substitute.

The principal object of the present invention is to produce aromatic chemicals from coal products from which they are not at present obtained, such as those referred to above.

An additional object of the present invention is to provide a method for obtaining a gaseous product, useful as a source of gaseous chemicals and as a fuel, from coal products of the type referred to above.

Other objects of the present invention are to provide a method of utilizing low temperature and medium temperature tars as a source of aromatic chemicals and pitches normally derived from the refining of high temperature coal tar, and to provide a method whereby low temperature and medium temperature tars can be converted to more valuable products.

Further objects of the present invention are to provide a method for utilizing lignite tar as a source of aromatic chemicals and pitches normally derived from the refining of coal tar produced by high temperature carbonization of bituminous coal, and to provide a method whereby lignite tar can be converted to products of greater commercial value.

Additional objects in part will be obvious and in part will appear hereinafter.

The present invention is based upon the discovery that low temperature coal tars, lignite tars, coal tar distillates and residues, and other coal products, including coal itself, can be converted to products similar to those obtained in the high temperature coking of coal by subjecting the low temperature coal tar, lignite tar, or other coal products to extremely rapid pyrolysis at temperatures above 600° C. and especially at 800°–1000° C., preferably in the presence of steam, followed by rapid passage of the resulting pyrolysis products through a heated reforming chamber maintained at a temperature above 600° C., and preferably containing coke, followed by cooling of the resulting reformed products, preferably below 100° C. When coke is employed, the preferred size is such that the coke is maintained in a fluidized state by the passage of the products therethrough.

While we do not wish to be limited to any theoretical explanation, we believe the process involves a cracking of the tar or other coal products into active chemical products containing carbon and hydrogen, which recombine during the reforming and cooling operations to form the desired products, including liquid aromatic compounds, and gaseous products. The presence of the steam appears to prevent the formation of substantial quantities of carbon and to lead to the formation of oxygen-containing products by combining with the active chemical groups formed in the pyrolysis and/or by reacting with the constituents during the pyrolysis.

Thus, we have discovered that a tar resulting from the low temperature carbonization of lignite and having the composition set out below in Example 1 can be converted to a tar product containing aromatic solvents and resin monomers of the indene type boiling below 200° C., as well as coal tar pitches, while at the same time producing a considerable amount of gas containing mainly methane, ethylene and propylene, by atomizing the lignite tar into a pyrolysis chamber maintained at 950° C., wherein the lignite tar is raised to said temperature in a fraction of a second, while passing in an equal amount of superheated steam, passing the resulting pyrolysis products through an elongated reforming chamber containing coke maintained at a temperature of about 850° C., the time of passage through said reforming chamber preferably being a fraction of a second, followed by cooling the resulting gas and vapor mixture below 100° C., and collecting the resulting gaseous and liquid products.

The lignite tar is converted to approximately 40 weight percent of gas, 54 weight percent of high-temperature tar and 6 weight percent of coke.

The gas stream analyzes 21% ethylene, 20% methane, 6% propylene, 1.4% butadiene, about 0.5% acetylene and 4% benzene as the major components of value.

The pitches produced from the tar are of the type used in the building and waterproofing fields.

Of the nitrogen compounds in the lignite tar, 7.4% of the feed stock is reformed to tar bases, 90% of which boil in the pyridine and quinoline ranges.

It is a feature of the present invention that such coal products as low temperature tars, medium temperature tars, lignite tars, coal tar distillation residues, and even coal, lignite, peat and similar coal products of low economic value, can be converted to products similar to high temperature coal tars and components thereof of a high economic value, by a continuous procedure which is simple to operate and easy to control.

The invention accordingly comprises the several steps and the relation of one or more of such steps with respect to others thereof, and the apparatus embodying features of construction, combinations of elements and arrangement of parts which are adapted to effect such steps, all as exemplified in the following detailed disclosure. The scope of the invention will be indicated in the claims.

In the practice of the present invention, a coal tar product, such as one of those referred to above, is subjected to substantially instantaneous pyrolysis at a temperature above 600° C., the resulting pyrolysis mixture is then held for a short period of time at a temperature of 600° to 850° C., and the resulting mixture is cooled. The products thereby formed are collected.

The pyrolysis is preferably carried out in the presence of steam, thereby reducing the formation of coke and carbon in the pyrolysis chamber and leading to the formation of aromatic compounds and oxygen-containing products, such as tar acids, as well as tar bases.

The coal product is supplied to be pyrolysis chamber in the form of a fine dispersion. Thus, in the case of oils or other coal products which are liquid at normal or slightly elevated temperatures (e.g., up to 150° C.), the liquid is sprayed into the hot pyrolysis chamber in the form of a fine spray. In order to prevent the high heat of the pyrolysis chamber from causing overheating of the feed before it is introduced into the pyrolysis chamber and thereby causing decomposition and choking of the spray system, the feed is introduced into the pyrolysis chamber through a jacketed nozzle, through the jacket of which water, steam, oil or other suitable temperature-regulating medium is circulated. Thus, in the operation on liquid feeds, the oils or tars are heated only to a temperature which will insure even flow characteristics without excessive pressure across the pumping system, and the resulting liquid feed is conducted from heated reservoirs through jacketed lines to a feed pump and spray jet complex. The feed pump is a standard fuel oil burner pump which can maintain pressures from 20 pounds to 120 pounds against a calibrated fuel oil burner jet of standard type. To accomplish the instantaneous heating effect, the feed oils are led from the pump under suitable selected pressures to the jet in a jacketed spray nozzle which extends through the furnace wall to the interior of the heating chamber. The feed stock is maintained at the desired temperature by circulating the temperature regulating fluid through the jacket.

Steam is preferably introduced into the pyrolysis chamber simultaneously with the coal product feed, preferably in an amount ranging from 1 to 4 times the weight of the coal product feed, and preferably in the form of superheated steam under a slight pressure (e.g., 1 to 2 lbs. above the pressure in the heating chamber), so as to cause thorough commingling of the steam with the spray of coal product and cracking products formed in the pyrolysis chamber.

When solid coal products are employed as the feed, such as bituminous coal, the solid is preferably employed in the form of a finely divided powder and is fed into the pyrolysis chamber through a similarly cooled feed, for example, by a worm or screw feed. In that case, the steam is employed as a jet to disperse the incoming powdered solid feed. The powdered feed may also be dispersed by feeding it into the pyrolysis chamber in the form of a jet propelled by nitrogen or other suitable gas.

It is a feature of the present invention that the rapid dispersion of the finely divided coal product feed into the pyrolysis chamber which is at high temperature causes substantially instantaneous pyrolysis of the feed. Thus, the feed is cracked and gasified in a fraction of a second after its entry into the chamber. Preferably the feed is so regulated as to secure pyrolysis in less than $\frac{1}{10}$ second.

The gas and vapor mixture produced in the heating chamber is then passed through a reforming chamber where the pyrolysis products and steam reaction products are subjected to a heat treatment for a short period of time— considerably less than 10 seconds, and preferably not more than 1 second—preferably in the presence of a reforming catalyst and especially high temperature coke.

The gases and vapors leaving the reforming chamber are then rapidly cooled, preferably below 100° C. in

suitable condensing apparatus wherein unreacted steam and tar are condensed as liquid and separated from gaseous and liquid products of high vapor pressure, such as benzene and toluene. The resulting products are then subjected to usual separation treatments for the recovery of individual components in the manner conventional in the gas separation, benzol recovery, and tar distillation arts.

In the drawings, there are disclosed partly in diagrammatic form and partly in section apparatus suitable for carrying out the process of the present invention. Figure 1 represents one form of the combined apparatus. Figure 2 represents a specific form of heating chamber and reforming column for effecting the heating and reforming operations in connection with the pyrolysis of liquid feed stocks. Figure 3 is a horizontal section of the heating chamber taken on the line 3—3 of Figure 2. Figure 4 represents a specific form of cooled nozzle for spraying liquid feed stocks into the heating chamber.

Referring to Figure 1 of the drawing, the numerals 1 and 1A represents storage tanks for the feed stock, which are suitably provided wit hthe heating jackets to maintain their contents in fluid form, and which are adapted to be alternately connected to the feed line 3 by suitable valved connections 2. The line 3 is connected to the inlet of a pump 4 for the feed stock, which in turn is connected by a suitable conduit 5 to the inlet 6 of the jacketed spray nozzle 7 which is mounted with its spray tip 8 within a heating chamber 9.

The heating chamber 9 is adapted to be heated to temperatures above 600° C. by external heat such as hot flue gases, gas flame, or the like, contacting the outer walls 10 of the chamber within a suitable furnace 11. The heating chamber is formed of suitable material to withstand the temperature, such as steel, the inner surface of which is lined with a thin lining of refractory material such as alumina or an alumina-silica fire clay, which function as cracking catalysts.

Heating chamber 9 is also supplied with an inlet for superheated steam 15 which is supplied through conduit 16 from a steam superheater 17 adapted to superheat by indirect contact with a suitable source of heat, such as flue gases, electrical resistance heating and the like, steam supplied to the superheater by a conduit 18 from a steam generator 19. Water for generation of the steam is supplied from a suitable reservoir 22 thru valved connection 23 by a pump 24 and a conduit 25.

The heating chamber 9 communicates directly with an elongated reforming column 30 which is suitably heated to temperatures above 600° C. by indirect heat, as for example, by furnace gases, flue gases, electrical resistance heating or the like, within a heating jacket 31. The chamber 30 is formed of suitable material capable of withstanding the elevated temperatures, such as stainless steel containing iron, chromium and nickel, e.g., stainless steel No. 304.

The outlet 32 of column 30 is connected to the inlet 33 of a condenser 34 adapted to be cooled by a suitable fluid flowing through a jacket 35, such as water, steam or oil. The outlet 36 of the condenser is connected to a primary liquid product receiver 37 which leads to a reflux condenser 38. The vapor outlet 39 of the reflux condenser is connected by a conduit 40 to a condenser 41, the outlet 42 of which is connected by a dip pipe 43 which leads into oil scrubber 44 which is partially filled with mineral oil adapted to scrub the gases and vapors passing through it. The mineral oil is of the type normally employed in the benzol scrubber of the usual coal gas by-product recovery processes. The outlet 45 of the scrubber is connected by a conduit 46 to an empty overflow chamber 47 which, in turn, is connected by conduit 48 with a dip pipe 49 which leads into a scrubber 50 partially filled with a suitable mineral acid adapted to remove ammonia and organic bases present in the gas and vapor mixture passing through it, for example, 20% aqueous hydrochloric acid. The outlet 51 of the scrubber 50 is connected by a conduit 52 with an overflow chamber 53 which, in turn, is connected through conduit 54 with a dip pipe 55 which leads into a scrubber 56 partially filled with dilute aqueous caustic alkali or other scrubbing liquid adapted to remove sulfur present as H_2S from the gases or vapors passing through it, for example, 20% aqueous sodium hydroxide. The outlet 57 of the caustic scrubber 56 is connected by a conduit 58 to an overflow chamber 59 which, in turn, is connected in series with two vessels 60 and 61 which are surrounded by solid carbon dioxide ("Dry Ice") jackets 62 and 63 to reduce the temperature of said chambers to that of solid carbon dioxide. The outlet 66 of the chamber 61 is connected by a conduit 67 with a gas sampler 68 which, in turn, is connected by a conduit 69 to a wet test meter 70, the outlet of which is connected to a flare 75 by a conduit 74.

Referring to Figures 2 and 3 of the drawing, the heating chamber 9 consists of a shell 80 formed of suitable material, such as stainless steel 304, mounted in spaced relation within a furnace 81 and surrounded by flues 82, 83, 84 and 85 carrying burner gases from gas burners 87. The exits from the flues are connected to a stack (not shown). The inner surface of the heater 9 is coated with a thin layer of alumina-silica fire clay 79. The heater 9 is provided with a jacketed spray nozzle 7 which is mounted centrally of one wall of the chamber 9 so as to project a fine dispersion of the liquid fed into the chamber onto the hot inner walls of the chamber.

As shown in Figure 4, the jacketed spray nozzle 7 consists of a tube 100 surrounded by two progressively larger tubes 101 and 102 mounted in spaced relation to provide a narrow passage 105 between them and between tubes 100 and 101 for the flow of temperature-regulating fluid, such as water, steam, oil, etc., depending on the temperature to be maintained. Tubes 101 and 102 are provided with couplings 103 and 104 for the entrance and exit of the temperature-regulating fluid. The inner end of the tube 100 is provided with a spray tip 8 which is of the type normally employed for dispersing oil in the form of a cone into an oil burner of the conventional type, e.g., an oil burner of the type employed for steam generation—as, for example, a Monarch oil burner nozzle. Such nozzles are rated according to the number of gallons per hour of No. 2 fuel oil which they are adapted to deliver as spray under a head of 100 p.s.i.

The heater 9 is also provided with an inlet 15 for superheated steam which is mounted within the heater on the opposite wall from the spray nozzle 7 so as to deliver superheated steam into the interior of the chamber 9 in intimate contact with the spray of feed stock from nozzle 7.

The reforming column 30 is mounted on the heating chamber 9 in direct communication with the interior thereof, and is surrounded by heating jacket 31. It is provided with a screen 110, for example, a 16 mesh stainless steel screen, mounted near the bottom thereof and adapted to retain a column of reforming catalyst 29 within the column 30. When coke is used as the reforming catalyst, a layer of "Alundum" spheres is placed over the screen to support the coke particles.

The apparatus is provided with suitable temperature-recording mechanism connected to thermocouples at the following points: 115 within the interior of the heater 9; 116 in the interior of the heating column 30; 117 in the interior of the heating column 30 near the top thereof; 118 in the outlet 32 of the column 30; 119 at the outer wall of the column 30; 120 in the interior of the jacketed nozzle 7; and 121 in the interior of the steam inlet 15.

The apparatus is further provided with means for recording pressures (not shown) at suitable points within the apparatus, such as the interior of the heating chamber

9, the top of the column 30, the steam superheater 17, and the conduit 5 of the spray nozzle inlet 6. Suitable heating jackets (not shown) are also provided for the lines and other parts carrying fluids at temperatures above atmospheric temperature.

In the operation of the apparatus referred to above, the heating chamber 9 and reforming column 30 are first brought to temperature by suitable passage of burner gases through the furnace 11 and heating jacket 31. Water is then introduced into the steam generator 19 and heat is supplied to the steam superheater 17, and superheated steam is pumped into the heating chamber 9. If coke is employed in the reforming column 30, which constitutes the preferred practice of the present invention, some water-gas is formed in the reforming column and passes through the system and is burned at the flare 75. Operation is continued until the system has been cleared of air. If no coke is employed in the reforming column, the system is cleared of air by the passage of steam, evidenced by condensation of water in the condenser 34 and primary liquid product receiver 37.

Pump 4, supplying the particular liquid feed to be pyrolyzed, is then placed in operation and the temperature-regulating fluid is passed through the tubes 101 and 102 to regulate the temperature of the feed and maintain it at the desired temperature. To prevent the starting material from undergoing undesirable preliminary decomposition, with resultant plugging of the spray nozzle, the feed to the pyrolyzer is preferably maintained at a temperature below 150° C., and usually at a temperature merely sufficient to insure adequate fluidity for spraying through the spray nozzle. Ordinarily the feed is adequately fluid at temperatures lower than 110° C.

Adequate pressure is exerted by pump 4 to secure a fine dispersion of the feed within the heating chamber 9, depending upon the rate of feed desired and the size of the spray tip 8. The rate of feed of superheated steam through inlet 15 is then adjusted to the desired ratio with respect to the feed of stock thru the spray tip 8.

Operation is then continued with adjustment of the heat supplied to the heating chamber 9 and reforming column jacket 31; since with continued operation the supply of heat required to maintain operating temperature decreases, presumably by reason of the fact that exothermic as well as endothermic reactions occur in the heating chamber and reforming column.

Tars produced by the process are condensed and collected in the receiver 37 together with unreacted steam which condenses as water. Light oil fractions are absorbed and removed in the mineral oil scrubber 44. Organic bases and ammonia are removed in the acid scrubber 50. Hydrogen sulfide is removed in the alkaline scrubber 56.

The tars do not always form completely in receiver 37, but sometimes tars also are formed farther along in the recovery system. Thus tar has been found to collect in the oil scrubber 44, and in some cases a crystalline material was formed in vessels 60 and 61 which, when warmed to room temperature, formed a tar.

In order to determine the composition of the collected tar, it is subjected to the standard coal tar fractional distillation in a 1" x 36" Stedman packed column operated at maximum efficiency, 1% readings being taken and the cut points being selected to correspond to standard cut points for the following fractions: pre-benzol, crude benzol, toluene, solvent naphtha, high flash solvent, naphthalene, quinoline, quinoline residues, heavy and light creosote oils, and pitches. Tar base and tar acid contents are determined by the contraction test method contained in "Methods of Testing Coal Tar Products," Barrett Division, Allied Chemical & Dye Corporation, copyright 1950, Tests Nos. G7, page 96, and G12, page 108.

The invention will be illustrated by the following specific examples, but it is to be understood that it is not limited to the details thereof and that changes may be made without departing from the scope of the invention. The temperatures are in degrees centigrade and the parts and percentages are by weight, unless designated as parts by volume. Where parts are by volume, the amount signifies the volume occupied by the same number of parts by weight of water at 4° C.

Example 1

The starting material employed in this example was lignite tar produced from Texas lignite at the Rockdale plant of the Texas Power and Light Company by low temperature carbonization of lignite. After filtration to remove 1–1.5% finely divided solids, it was a viscous, sticky mass at 25° having the following characteristics:

Specific gravity at 15.5°	1.025
Water content—percent	0.2
Matter insoluble in benzene—do	0.9

At 100° it had the consistency of a thin oil. When subjected to the usual tar analysis by distillation in a 1" x 36" Stedman fractionation apparatus at 760 mm. mercury pressure and a 2" water pressure drop, the following percentages of the tar were obtained as distillates:

	Percent
Up to 80°	0.00
80 to 100°	1.20
100 to 125°	0.00
125 to 150°	0.00
150 to 200°	8.80
200 to 230° (no naphthalene)	12.00
230 to 250°	4.00

On further distillation of the residue according to ASTM Standard Method D20–56, the following percentages of tar were obtained as distillates:

	Percent
250 to 270°	6.70
270 to 300°	10.20
300 to 325°	22.90

The residue, which amounted to 33% of the tar, consisted of coke and carbon.

The filtered tar was subjected to pyrolysis and reforming in the presence of steam in accordance with the present invention, in the following manner:

The cracking chamber 9 shown in Fig. 2 was heated to a temperature of 925° and superheated steam was introduced into the chamber. The column 30 was filled about one-half with coke particles 1 inch in size and was heated to 850°. The oil burner nozzle 8 was rated at one gallon per hour at 100 lbs. pressure. The feeds of filtered lignite tar and superheated steam were then adjusted to introduce equal parts by weight of superheated steam and lignite tar into the cracking chamber. The pressure on the steam jet was 2 p.s.i.g. and in chamber 9 was 1 p.s.i.g. The pressure on the tar feed was 50 pounds.

After preliminary operation as set out above, to establish the desired conditions, the tar was pyrolyzed continuously at a rate giving a residence time in the pyrolyzer and reformer of about 0.1 second.

The products consisted of gas, a tar and some coke. The analysis of the principal components of the product were as follows, in terms of percent by weight, based on the lignite tar charged:

	Yield percent
Total gas product	41.7
Principal components of gas product:	
Hydrogen	1.65
Methane	9.79
Nitrogen	10.42
Ethylene	8.73
Ethane	1.16
Propylene	2.70
Carbon dioxide	4.23
Benzene	1.60

The tar separated from receiver 37, after removal of water condensed from unreacted steam, was a viscous fluid of which 11% was insoluble in benzene.

	Yield percent
Total tar product	54
Tar analysis by distillation (1" x 36", Stedman fractionation as above):	
Up to 80°	0.0
80 to 100°	5.0
100 to 125°	1.8
125 to 150°	0.0
150 to 200°	2.7
200 to 230°	7.0
230 to 250°	2.0

The residue had a softening point (shouldered ring and ball) of 60°, and 28.5 percent was insoluble in benzene.

	Yield percent
Distillation of residue (ASTM D20–56):	
250 to 270°	0.0
270 to 300°	0.09
300 to 325°	2.1
325 to 360°	6.1
Residue	33.1

The residue had a softening point (shouldered ring and ball) of 188°, and 54.8 percent was insoluble in benzene.

The fraction boiling below 200° contained benzene, toluene, higher solvents and resin monomers.

Examples 2, 3 and 4

The starting material employed in these examples was so-called "Disco" tar, a tar produced by a low temperature carbonization of coal and containing 35 percent of fine particles of coal which could be separated by suction filtration. The characteristics of the crude low temperature tar and the filtered tar were as follows:

	Crude Tar	Filtered Tar
Specific Gravity at 15.5°	1.180	1.095
Carbon Insol. in CS_2 (Cold)—Percent	28.5	13.2
Carbon Insol. in Quinoline (Hot)—do	19.5	0.6
Ash—do	5.2	0.02

ULTIMATE ANALYSIS

	Crude Tar, Percent	Filtered Tar, Percent
Hydrogen	6.36	7.67
Carbon	80.53	82.00
Nitrogen	1.07	1.42
Sulfur	0.88	0.95
Oxygen	11.61	8.42

The tar distillation analyses of the unfiltered and filtered low temperature tar are included below in Table 1, giving the analyses of the tar products. From 50 to 60% of the tars are oils of paraffinic nature.

The filtered low temperature tar (Examples 2 and 3) and the crude tar (Example 4) were subjected to pyrolysis in the above manner in equipment of the type employed in Example 1 under the following conditions, employing coke particles of 30 mesh size about half filling the reforming column 30 when in quiet state:

	Example 2	Example 3	Example 4
Temp. in Cracking Chamber 9—degrees	750	600	780
Temp. in Reformer 30—do	650	525	750
Ratio of Steam Feed to Tar Feed (by wt.)	1:1	1:1	1:1
Residence time in Pyrolyzer and Reformer—sec.	<0.1	<0.1	<0.1

The products consisted of a gas product rich in methane, carbon monoxide, hydrogen, and ethylene, the percentages by weight of which based on the tar feed are included in Table 1 below, and a tar having the analysis in percent by weight of the tar feed included in Table 1 below.

TABLE 1

	Crude Tar	Filtered Tar	Example 2	Example 3	Example 4
Gas (Up to 75°)	0	0	26.6	7.18	19.25
Total from 90 to 125°	0.27	1.00	2.00	1.83	1.37
Tar Acids	0.09	0.77	0.58	0.26	0.14
Tar Bases	0.02	0.00	0.00	0.31	0.14
Unsaturated Hydrocarbons	0.04	0.06	0.00	0.10	0.00
Paraffins	0.12	0.17	1.42	1.16	1.09
Total from 125 to 150°	6.83	0.56	2.00	1.83	0.84
Tar Acids	2.25	0.43	0.58	0.26	0.05
Tar Bases	0.50	0.00	0.00	0.31	0.05
Unsaturated Hydrocarbons	1.40	0.03	1.42	1.16	0.74
Paraffins	2.68	0.10	0.00	0.10	0.00
Total from 150 to 200°	3.53	5.44	5.50	3.00	4.33
Tar Acids	2.20	4.29	2.90	2.10	2.38
Tar Bases	0.13	0.00	0.00	0.33	0.37
Unsaturated Hydrocarbons	0.28	0.14	2.59	0.39	1.38
Paraffins	0.92	1.01	0.01	0.18	0.20
Total from 200 to 230°	6.64	15.30	3.80	7.39	5.99
Tar Acids	3.22	10.90	1.26	5.60	3.36
Tar Bases	0.30	0.00	0.00	0.37	0.57
Unsaturated Hydrocarbons (Other than Naphthalene)	0.82	1.56	1.06	1.35	2.06
Paraffins	2.30	2.84	0.04	0.07	0.00
Naphthalene	0.00	0.00	1.44	0.00	0.00
Total from 230 to 250°		7.30	2.50	4.30	2.91
Tar Acids		3.20	0.13	3.44	0.55
Tar Bases		0.00	0.00	0.49	0.38
Unsaturated Hydrocarbons		2.41	2.37	0.18	0.09
Paraffins		1.69	0.00	0.19	1.89
Total from 250 to 270°					1.60
Tar Acids					0.23
Tar Bases					0.34
Unsaturated Hydrocarbons					1.03
Saturated Hydrocarbons					0.00
Residue above 270°	82.23	68.30	31.40	42.60	39.22

An outstanding characteristic of the product of Example 2 is the nature of the pitch residue obtained on distillation of the tar product. Thus, whereas the original tar gave a pitch residue which contained a large amount of material insoluble in carbon bisulfide and which was dull and brittle, the pitch from Example 2 was ductile, bright shiny black, and a much smaller amount was insoluble in carbon bisulfide.

The present invention is not limited to the conversion of tars obtained by the low temperature carbonization of lignite and the low temperature carbonization of coal, but includes the pyrolysis and reforming of various fractions thereof. Moreover, the process of the present invention may be employed for the upgrading of tar fractions, including oil and pitch residues, from the high temperature carbonization of coal. All of such materials are included in the term "coal tar oil" as employed herein. Thus, the process of the present invention may be employed for the upgrading of creosote oils, topped tars (tars and pitches from which lower boiling constituents have been removed), limpid tar oils, quinoline distillation residues, and similar oils and pitches obtained from high temperature coal tars.

The following specific Examples 5, 6, 7, 8 and 9 are illustrative of products obtained from such starting materials.

Examples 5, 6, 7 and 8

The starting material employed in these examples was a creosote oil, obtained by removing the upper carbolic oil fraction from high temperature tar, and having the following characteristics:

Specific gravity at 15.5°	1,108
Water content—percent	0.01
Matter insoluble in benzene—do	0.01

When subjected to the usual tar analysis by distillation in a 1" x 36" Stedman fractionation apparatus at 760 mm. mercury pressure and a 1" to 1½" water pressure

drop, the following percentages of oil were obtained as distillates:

	Percent
Up to 79°	0.00
79 to 100°	0.00
100 to 125°	0.00
125 to 150°	0.00
150 to 200°	1.43
200 to 230°	11.14
230 to 250°	9.26

On further distillation to the residue according to ASTM Standard Method D20–56, the following percentages of tar were obtained as distillates:

	Percent
250 to 270°	7.55
270 to 300°	16.93
300 to 325°	10.61
325 to 360°	29.38

The residue amounted to 13.7%.

The creosote oil was subjected to pyrolysis and reforming in accordance with the present invention, in the following manner:

The cracking chamber 9 shown in Fig. 2 was heated to the temperature shown in Table 2 below, and superheated steam was introduced into the chamber, except in Example 6. Except in Examples 6 and 7 wherein no reforming catalyst was used, the column 30 was filled about one-half with coke particles of the size and heated to the temperature set out in Table 2. The operation was otherwise similar to that of the above examples.

TABLE 2

	Examples			
	5	6	7	8
Temperature of Heating Chamber 9	900	900	900	750.
Temperature of Reformer 30	750	750	750	650.
Steam Feed Ratio	1:1	0	1:1	3.8:1.
Coke in Reformer	about half full.	0	0	about half full.
Size of Coke in Reformer	1 inch	0	0	30 mesh.
Pressure on oil feed, p.s.i.g.	70	75	80	60.

After preliminary operation as set out above, to establish the desired conditions, the oil was pyrolyzed continuously at a rate giving the residence time in the pyrolyzer and reformer of not more than 0.1 second.

The products consisted of gas, a tar and some coke. The yields of the various products, in terms of percent by weight of the creosote oil charged were as follows:

	Yield Percent			
	Example 5	Example 6	Example 7	Example 8
Gas	7.95	9.63	20.81	1.13
Liquid Tar Fractions (as above):				
Up to 79°	0.00	0.00	0.00	0.00
79 to 100°	0.34	2.05	1.49	1.00
100 to 125°	0.11	1.16	0.00	0.00
125 to 150°	0.18	0.53	0.00	0.00
150 to 200°	1.08	3.18	0.49	1.18
200 to 230°	18.41	8.20	14.08	15.11
230 to 250°	5.94	0.68	9.64	9.35
Fractions of Residue (as above):				
250 to 270°	8.32	0.00	0.73	72.76
270 to 300°	17.12	0.98	2.74	------
300 to 325°	17.79	0.25	14.94	------
325 to 360°	22.78	5.55	40.57	------
Residue above 360°	18.29	12.69	24.37	------
Coke and Carbon	2.64	43.01	0.53	0.22
Softening Point of Residue (Ring and Ball), degrees	95	66	69	------
Carbon Insoluble in Benzene, percent	14.4	18.9	2.5	------

The principal components of the gas product were as follows:

	Percent by Weight of Gas Product			
	Example 5	Example 6	Example 7	Example 8
Hydrogen	13.09	14.24	2.95	13.2
Methane	18.01	55.18	17.17	26.4
Carbon Monoxide	31.61	19.44	36.36	21.35
Ethylene	7.49	5.93	8.50	10.51
Propylene	3.49	0.34	2.59	7.52
Carbon Dioxide	23.09	0.00	29.54	12.07
Benzene and Toluene	0.82	3.44	0.56	0.00

Example 9

The starting material employed in this example was a residue obtained from the distillation of the quinoline fraction of high temperature tar. The characteristics of the starting material are set out in the following Table 3.

The quinoline still residue was subjected to pyrolysis and reforming in accordance with the present invention, in the following manner:

The cracking chamber 9 was heated to 800° and superheated steam was introduced into the chamber in an amount equal to the oil feed. The column 30 was filled about one-third with coke particles of 30 mesh size and heated to 750°. The operation was otherwise similar to that of the above examples.

After preliminary operation as set out above, to establish the desired conditions, the oil was pyrolyzed continuously at a rate giving a residence time in the pyrolyzer and reformer of not more than 0.1 second.

The products consisted of gas and a tar. The yields of the various products, in terms of percent by weight of the oil charged, are set out in the following Table 3.

TABLE 3

	Starting Material	Yield Percent
Gas	None	3.98
Liquid Tar Fractions (as above):		
75 to 90°	None	0.13
90 to 125°	None	5.77
125 to 150°	None	None
150 to 200°	None	0.43
200 to 230°	2.33	1.16
230 to 240°	3.67	6.12
Fractions of Residue (as above):		
240 to 250°	90.00	39.27
250 to 270°	3.00	11.10
270 to 300°	None	9.52
300 to 330°	None	6.01
Residue above 330:		
Pitch	0.05	10.98
Oil	0.05	None
Carbon Formed	----------	2.66
Softening Point of Pitch Residue (Ring and Ball), degrees	None	153
Pitch Carbon Insoluble in Carbon Bisulfide, degrees	None	56.0

Of the 90% of starting material in the 240–250° boiling range, 84.6% were tar bases. Of the products formed, 7.55% yield were solvents distilling in the range 240–300° and 57.52% yield were tar bases distilling in the range 240–330°.

The process of the present invention also may be employed for the conversion of coal itself to valuable products.

Thus, besides mixtures of tar and coal, illustrated in above Example 4, finely divided bituminous coal of medium volatility, ground to a size passing through a 200 mesh screen, can be subjected to pyrolysis and reforming preferably in the presence of superheated steam, at a temperature above 600° C. by dispersing the finely divided coal into a pyrolysis chamber maintained above 600° C., and preferably above 800° C., wherein the coal is pyrolyzed extremely rapidly, followed by passage of the pyrolysis products through a reforming chamber main-

tained at a temperature of 650 to 750° C., and preferably about 700° C..

The following Example 10 illustrates such a process.

Example 10

Bituminous coal of medium volatility (Pond Creek) was pulverized to pass about 80% through a 200 mesh screen (i.e., 80% to pass 200 mesh, 100% to pass 150 mesh). The finely divided coal was charged to a hopper from which it flowed onto a jacketed worm. In order to prevent condensation of steam on the worm, the coal was kept at a temperature of 120° and the worm feed jacket was cooled with steam. The worm feed entered the chamber **9** in approximately the same position as the spray nozzle **7** indicated in Figure 2 of the drawings. In one case the powdered coal was dispersed into the chamber by a jet where the reaction steam was introduced. In this manner the coal was conveyed and sprayed onto the walls of the chamber by the reaction steam. In another case the carrier gas used was nitrogen. By dispersing the coal with a gas stream, instantaneous pyrolysis was achieved and the temperature gradient was from ambient to operating in less than one-tenth second. The finely divided solids offered no appreciable insulation to the flow of heat with respect to time. The cracked gases mixed with the steam in the chamber **9** and moved out through the reformer **30** to the condensing and collection systems.

Using steam as the atomizing means, the cracking chamber **9** was heated to 825° and superheated steam was introduced into the chamber in the ratio of 3:4 based on the coal feed. The column **30** was filled about one-half with coke particles of 30 mesh size and heated to 750°. The operation was otherwise similar to that of the above examples.

After preliminary operation as set out above, to establish the desired conditions, the coal was pyrolyzed continuously at a rate giving a residence time in the pyrolyzer and reformer of not exceeding 0.1 second.

The products consisted of gas, light oil and a tar. No coke was formed. From 639 parts of starting material, 270 parts of non-condensible gas, 35 parts of tar, 10 parts of condensible gas, and 4 parts of light oils were recovered.

It will be evident that the invention is not limited to the details of the foregoing illustrative examples and that changes can be made without departing from the scope of the invention.

While, in the preferred practice of the process of the present invention, the pyrolysis of the coal product takes place in the presence of steam, the invention is not limited in its broader scope to the use of steam. Thus, as shown in above Example 6, the process may be carried out in the absence of steam.

Moreover, other suitable reactive gases may be employed instead of steam; as, for example, ammonia or nitrogen, especially at the more elevated temperatures—for example 900°–1100° C.—in which cases a higher proportion of tar bases is formed rather than tar acids.

Furthermore, halogens such as chlorine, may be employed, leading to halogenated products.

In the preferred practice of the present invention, the products formed by the extremely rapid pyrolysis are passed in contact with coke in a reforming chamber. The invention in its broader scope is not limited to the use of coke, however; since, as illustrated in above Examples 6 and 7, the reforming chamber may be empty, the reforming being effected by the heat imparted to the molecules by contact with the walls of the reforming chamber and by radiation from the walls of the reforming chamber. If desired, other reforming catalysts may be employed instead of coke; as for example, platinum or vanadium pentoxide.

As employed herein, including the claims, the term "tar oil" includes tars, tar residues and pitches; and the term "coal tar fraction" includes various fractions obtained in the distillation of coal tar, including residues and pitches.

We claim:

1. A method of producing products of greater value from a coal tar oil obtained from the low temperature carbonization of a coal solid which comprises subjecting said coal tar oil to rapid pyrolysis by dispersing the coal tar oil in finely divided form into a heated pyrolysis chamber maintained above 600° C., promptly passing the resulting gas and vapor mixture through a reforming chamber wherein said mixture is maintained at a temperature between 600° and 1000° C. for a period of time not exceeding 1 second while in contact with a reforming catalyst, and cooling and recovering resulting products.

2. A method of producing products of greater value from a coal tar oil obtained from the low temperature carbonization of a coal solid which comprises subjecting said coal tar oil to rapid pyrolysis in the presence of steam by spraying the coal tar oil at a temperature not exceeding 150° C. into a heated pyrolysis chamber maintained above 600° C. while introducing steam into said chamber in an amount by weight ranging from 1 to 4 times the weight of the coal tar oil, promptly passing the resulting gas and vapor mixture through a reforming chamber wherein said mixture is maintained at a temperature between 600° and 1000° C. for a period of time not exceeding 1 second while in contact with a reforming catalyst, cooling the resulting products below 100° C., and recovering resulting products.

3. A method of producing products of greater value from a coal tar oil obtained from the low temperature carbonization of a coal solid which comprises subjecting said coal tar oil to rapid pyrolysis in the presence of steam by spraying the coal tar oil at a temperature not exceeding 150° C. into a heated pyrolysis chamber maintained above 600° C. and having its inner surface formed of a refractory material selected from the group consisting of alumina and alumina-silica fire clay, whereby the coal tar oil contacts the hot refractory surface and is substantially instantaneously pyrolyzed, introducing steam into the pyrolysis chamber in an amount by weight ranging from 1 to 4 times the weight of the coal tar oil, promply withdrawing the resulting gas and vapor mixture and passing it through a reforming chamber wherein said mixture is maintained at a temperature between 600° and 1000° C. for an additional period of time not exceeding 1 second while in contact with coke particles, and cooling and recovering resulting products.

4. A method of producing products of greater value from a coal tar oil obtained from the low temperature carbonization of a coal solid which comprises subjecting the coal tar oil to rapid pyrolysis in the presence of steam by spraying the coal tar oil at a temperature not exceeding 110° C. into a heated pyrolysis chamber maintained between 600° and 1000° C. and having its inner surface formed of a refractory material selected from the group consisting of alumina and alumina-silica fire clay, whereby the coal tar oil contacts the hot refractory surface and is substantially instantaneously pyrolyzed, while introducing steam into the pyrolysis chamber in an amount by weight ranging from 1 to 4 times the weight of the coal tar oil, promptly withdrawing the resulting gas and vapor mixture and passing it through a reforming chamber wherein said mixture is maintained at a temperature between 800° and 1000° C. for an additional period of time not exceeding 1 second while in contact with coke particles of a size ranging from 30 mesh to 1 inch, cooling the resulting products below 100° C., and collecting the resulting products.

5. A method of converting a coal tar fraction into other products which comprises subjecting the coal tar fraction to rapid pyrolysis in the presense of steam by spraying it at a temperature not exceeding 150° C. into a heated pyrolysis chamber maintained above 600° C. while in-

troducing steam into said chamber in an amount by weight ranging from 1 to 4 times the weight of the coal tar fraction, promptly withdrawing the resulting gas and vapor mixture and passing it through a reforming chamber wherein said mixture is maintained at a temperature between 600° and 1000° C. for a period of time not exceeding 1 second while in contact with a reforming catalyst, cooling the resulting mixture below 100° C., and recovering resulting products.

6. A method of producing products of greater value from a coal tar fraction which comprises subjecting the coal tar fraction to rapid pyrolysis in the presence of steam by spraying it at a temperature not exceeding 150° C. into a heated pyrolysis chamber maintained above 600° C. and having its inner surface formed of a refractory material selected from the group consisting of alumina and alumina-silica fire clay, whereby the coal tar fraction contacts the hot refractory surface and is substantially instantaneously pyrolyzed, while introducing steam into the pyrolysis chamber in an amount by weight ranging from 1 to 4 times the weight of the coal tar fraction, promptly withdrawing the resulting gas and vapor mixture and passing it through a reforming chamber wherein said mixture is maintained at a temperature between 600° and 1000° C. for an additional period of time not exceeding 1 second while in contact with coke particles of a size ranging from 30 mesh to 1 inch, cooling the resulting mixture below 100° C., and collecting the resulting products.

7. A method of producing products of greater value from a residue from the distillation of coal tar which comprises subjecting a coal tar distillation residue which is liquid at a temperature below 150° C. to rapid pyrolysis in the presence of steam by spraying it at a temperature not exceeding 150° C. into a heated pyrolysis chamber maintained above 600° C. while introducing steam into the pyrolysis chamber in an amount by weight ranging from 1 to 4 times the weight of the coal tar residue, promptly withdrawing the resulting gas and vapor mixture and passing it through a reforming chamber wherein said mixture is maintained at a temperature between 600° and 1000° C. for a period of time not exceeding 1 second while in contact with coke, cooling the resulting mixture below 100° C., and recovering resulting products.

8. A method of producing products of greater value from a residue from the distillation of coal tar which comprises subjecting a coal tar distillation residue which is liquid at a temperature below 150° C. to rapid pyrolysis in the presence of steam by spraying it at a temperature not exceeding 150° C. into a heated pyrolysis chamber maintained above 600° C. and having its inner surface formed of a refractory material selected from the group consisting of alumina and alumina-silica fire clay, whereby the coal tar fraction contacts the hot refractory surface and is substantially instantaneously pyrolyzed, while introducing steam into the pyrolysis chamber in an amount by weight ranging from 1 to 4 times the weight of the coal tar residue, promptly withdrawing the resulting gas and vapor mixture and passing it through a reforming chamber wherein said mixture is maintained at a temperature between 600° and 1000° C. for an additional period of time not exceeding 1 second while in contact with coke particles of a size ranging from 30 mesh to 1 inch, cooling the resulting mixture below 100° C., and collecting the resulting products.

9. A method of converting a coal product into other product which comprises subjecting the coal product to rapid pyrolysis by dispersing it in finely divided form into a heated pyrolysis chamber maintained above 600° C., promptly passing the resulting gas and vapor mixture through a reforming chamber wherein said mixture is maintained at a temperature between 600° and 1200° C. for a period of time not exceeding 1 second while in contact with coke, cooling the resulting mixture, and recovering resulting products.

10. A method of converting a coal product into other products which comprises subjecting the coal product to rapid pyrolysis in the presence of a member selected from the group consisting of steam, ammonia, nitrogen and halogens, by spraying it at a temperature not exceeding 150° C. into a heated pyrolysis chamber maintained above 600° C. while introducing said member into the pyrolysis chamber in an amount by weight ranging from 1 to 4 times the weight of the coal product, promptly passing the resulting gas and vapor mixture through a reforming chamber wherein said mixture is maintained at a temperature between 600° and 1200° C. for a period of time not exceeding 1 second, cooling the resulting mixture, and recovering resulting products.

11. A method of producing products of greater value from a coal product which comprises subjecting the coal product to rapid pyrolysis in the presence of steam by spraying it at a temperature not exceeding 150° C. into a heated pyrolysis chamber maintained above 600° C. and having its inner surface formed of a refractory material selected from the group consisting of alumina and alumina-silica fire clay, whereby the coal product contacts the hot refractory surface and is substantially instantaneously pyrolyzed, introducing steam into the pyrolysis chamber in an amount by weight ranging from 1 to 4 times the weight of the coal product, promptly withdrawing the resulting gas and vapor mixture and passing it through a reforming chamber wherein said mixture is maintained at a temperature between 600° and 1000° C. for an additional period of time not exceeding 1 second while in contact with coke particles of a size ranging from 30 mesh to 1 inch, cooling the resulting mixture below 100° C., and collecting the resulting products.

12. A method of producing products of greater value from a coal solid which comprises subjecting the coal solid to rapid pyrolysis in the presence of steam by spraying it in finely divided form at a temperature not exceeding 150° C. into a heated pyrolysis chamber maintained above 600° C. while introducing steam into said chamber in an amount by weight ranging from 1 to 4 times the weight of the coal solid, promptly withdrawing the resulting gas and vapor mixture and passing it through a reforming chamber wherein said mixture is maintained at a temperature between 600° and 1000° C. for a period of time not exceeding 1 second while in contact with coke, cooling the resulting mixture below 100° C., and recovering resulting products.

13. A method of producing products of greater value from a coal tar oil obtained from the low temperature carbonization of a coal solid which comprises subjecting said coal tar oil to rapid pyrolysis in the presence of a member selected from the group consisting of steam, ammonia, nitrogen and halogens, by spraying the coal tar oil at a temperature not exceeding 150° C. into a heated pyrolysis chamber maintained above 600° C. while introducing said member into the pyrolysis chamber in an amount by weight ranging from 1 to 4 times the weight of the coal tar oil, promptly withdrawing the resulting gas and vapor mixture and passing it through a reforming chamber wherein said mixture is maintained at a temperature between 600° and 1000° C. for a period of time not exceeding 1 second while in contact with coke, cooling the resulting mixture below 100° C. and recovering resulting products.

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UNITED STATES PATENT OFFICE

CERTIFICATION OF CORRECTION

Patent No. 2,977,299 March 28, 1961

Robert T. Joseph et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, line 11, for "be" read -- the --; column 5, line 22, for "wit hthe" read -- with --; column 10, line 69, for "1,108" read -- 1.108 --; column 11, line 11, for "to", first occurrence, read -- of --; column 15, line 67, for "product", first occurrence, read -- products --.

Signed and sealed this 5th day of September 1961.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents