

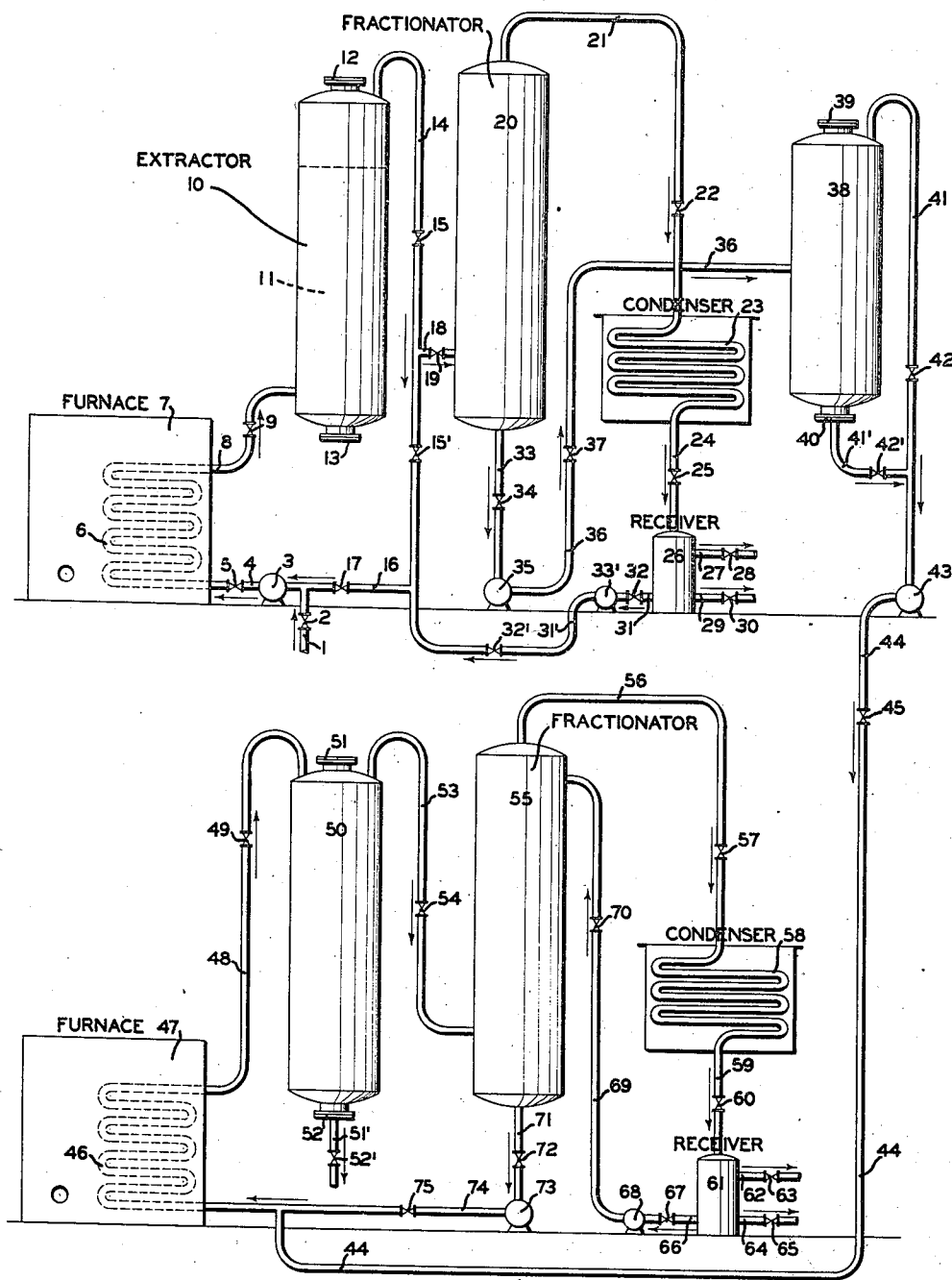
July 28, 1936.

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2,049,013

TREATMENT OF HYDROCARBON OILS

Filed Aug. 7, 1931



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UNITED STATES PATENT OFFICE

2,049,013

TREATMENT OF HYDROCARBON OILS

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Application August 7, 1931, Serial No. 555,776

3 Claims. (Cl. 196—14)

This invention relates to the treatment of hydrocarbons, and refers more particularly to the treatment of heavy hydrocarbons at elevated temperatures and pressures to convert them into lower boiling and more valuable products.

In a more specific sense the invention is concerned with the production of low boiling hydrocarbons from coal, a process being disclosed which has as its main object the production of such low boiling fractions in an improved and economic manner.

The nature of the volatile products obtained from various coals by simple heat treatment and distillation is modified to a great extent by the temperatures and pressures employed in distillation. In the distillation of bituminous coal for the production of coke for use as industrial or domestic fuel or for metallurgical operations or gas manufacture, temperatures are usually high and operations are conducted without particular regard to the amount of liquid products recovered. In the old "bee-hive" ovens which are rapidly being supplanted by more efficient apparatus, coke was produced by partial internal combustion of coals in which operations the recovery of liquid products was negligible. Later low temperature carbonization processes have increased the yield of liquid products and furnished large amounts of tars containing base materials for many chemical industries. The present invention is concerned with the production from coal of maximum yields of low boiling hydrocarbon fractions utilizable as motor fuel, the descriptive material following showing the general method of operation and the other objects and advantages of the process.

In one specific embodiment the invention comprises extracting bituminous coal with solvents to remove hydrocarbon material, distilling off, condensing and collecting the solvent for further use, separating solid materials from the coal extract, subjecting the liquid portions of the extract to conversion conditions of temperature and pressure, fractionating the products to produce low boiling fractions which are cooled, condensed and collected and insufficiently converted intermediate refluxes which are returned to the conversion zone for further treatment.

In another embodiment the invention may comprise the conversion of the total extract containing solids in suspension.

The process of the invention may be conducted in a large number of arrangements of equipment without departing from the scope thereof, but it will be of assistance in describing a character-

istic operation to refer to the attached drawing which shows diagrammatically in side elevation an arrangement of elements or parts which may be employed.

Referring to the drawing it will be seen that the layout consists generally of a primary unit for the extraction of soluble materials from coal and a secondary unit for the cracking of a portion or all of the extract. A solvent may be introduced into the system from a source of supply (not shown) through a line 1, containing a control valve 2, and leading to a pump 3 which may be employed to pump whatever solvent may be chosen through a line 4 and a regulating valve 5 through a heating element 6 suitably disposed in a furnace setting 7, the solvent being brought to a temperature best suited for extraction of the coal in a succeeding chamber. The heated solvent may be discharged through a line 8, containing a valve 9, and enter a point near the bottom of an extractor 10, containing a bed of coal 11. The extractor may have removable manheads 12 and 13 to enable the admission of fresh and the removal of treated coal. During the passage of the solvent upwardly through the coal bed the soluble matter is extracted to a degree dependent upon a number of factors such as the particular solvent employed and the temperature, which is in turn dependent upon the pressure employed if the solvent has appreciable volatility.

The solvent laden with a certain amount of soluble hydrocarbon material may pass from the top of the extractor through a line 14, containing control valves 15 and 15', and either be returned through line 16 containing a control valve 17 to the solvent circulating pump 3 in case it still possesses some solvent power or may be diverted through a line 18, containing control valve 19, to a fractionator 20 which is of a design and capacity capable of substantially separating the solution into vapors of solvent and coal extract upon release of pressure through valve 19. If the heat contained in the solution as it enters the fractionator is not sufficient to remove necessary amounts of solvent prior to the cracking of the extract in the succeeding unit, additional heat may be supplied either by passing the solution through an auxiliary tubular heating element prior to its admission to the tower or by means of a suitable reboiler placed in the bottom thereof.

The vapors from fractionator 20 may pass through a vapor line 21, containing control valve 22, and be liquefied by a condenser 23 and pass through a line 24, containing a control valve 25, 55

to an intermediate solvent accumulator 26. Since the solvent vapors may be contaminated at times by minor amounts of gaseous decomposition products, a gas release line 27, containing a regulating valve 28, may be provided on receiver 26 for the release of such gases to prevent undue rise of pressure. To provide for the withdrawal of solvent from the accumulator a line 29, containing a valve 30, is also provided. The recovered solvent may be returned for use in the extracting zone by means of a pump 33' which takes suction on the solvent receiver 26 through a line 31, containing a valve 32, and discharges the solvent through a line 31', containing a valve 32', leading to suction line 16 of pump 3.

Hydrocarbon materials may be extracted from coals by solvents of very diverse character, among which may be mentioned liquid sulfur dioxide, acetone, anthracene oil, amyl alcohol, naphthalene, tetrahydronaphthalene, nitrobenzene, cresols, aniline, quinoline, selenium, oxychloride, pyridine, piperidine, phenol, ethylene glycol derivatives, benzaldehyde, furfural, mesityl oxide, guaiacol, benzyl alcohol, amyl acetate, benzol and many others. In general, the best type of solvent for extraction processes similar to that employed in the present invention will be one which has a high solvent action and is readily recoverable without decomposition so that the extracting process may be substantially cyclic in respect to the solvent. It has been found by different investigators that certain solvents, particularly benzol, and certain aromatic hydrocarbon mixtures exert an increased solvent action upon coal at elevated temperatures and pressures, whereas their action is only moderate at temperatures corresponding to their boiling point at atmospheric pressure. It is intended to utilize this fact as a feature of the present invention, the extraction being carried on at sufficient pressure to enable the most efficient use of the particular solvent chosen. For example, if benzol is used pressures as high as 1000 pounds per square inch, corresponding to a temperature of approximately 300° C., may be employed, the solvent being circulated under these conditions until the desired extraction is accomplished.

When solvents of the type of furfural are employed which have a tendency to decompose during extraction and subsequent recovery by distillation slightly lower temperatures of extraction may be employed and if necessary the recovery may be effected under subatmospheric pressures.

Referring again to the drawing the extracted material from coal, relieved to a certain extent of the solvent, may leave the bottom of the fractionator through a line 33, containing control valve 34, to pass to a pump 35 which discharges the entering material through a line 36, containing control valve 37 to a settling chamber 38, which is preferably of sufficient capacity to provide time for the sedimentation of solid particles as it has been found that the extracted material from coal may be divided roughly into two groups of substances, the first being essentially of a liquid hydrocarbon character and the other of a more or less solid character consisting of oxygen and nitrogen derivatives of hydrocarbons. Settling chamber 38 typifies any arrangement of chambers which may be employed in parallel to permit the use of some for settling while others are being cleaned, such

chambers being provided with manheads 39 and 40 to permit entry for cleaning purposes.

Liquid extract substantially free from suspended solids may be taken by a pump 43 through a line 41, containing a regulating valve 42, and discharged through a line 44, containing a valve 45, to furnish raw material for the second stage of the process which consists in general in cracking the extract to produce motor fuel fractions, gases and residual products characteristic of cracking operations conducted upon analogous materials produced from the cracking of petroleum fractions. As previously intimated, the total extract may be cracked in the succeeding unit if desired in which case the materials entering settling chamber 38 may be totally discharged from the bottom thereof through a line 41', containing a valve 42', the suspension being then transferred to the cracking unit.

The primary element of the cracking unit may be a tubular heating element 46 of the type commonly employed in cracking processes consisting of successive end connected pipe lengths to form a continuous coil which is suspended in a suitable furnace 47.

The temperatures maintained at the exit of the heating element will necessarily vary with the type of charging stock derived from the coal processed in the preceding unit and the cracking effect desired, being usually comprised within the moderately low range of 800 to 900° F. on account of the marked tendency of coal extracts to deposit carbon during cracking. However, since it is within the scope of the invention to retain a definite amount of solvent in admixture with the extract during the cracking step still higher temperatures may be employed without serious consequences arising from coke deposits in the heating coil if suitably high velocities are maintained. Pressures employed may be those commonly utilized in cracking petroleum fractions such as, for example, 100 to 500 pounds per square inch, more or less, though good results may be obtained by the use of moderate pressures between 200 and 300 pounds per square inch.

The heated products may pass through a transfer line 48, containing a control valve 49, and enter an enlarged vaporizing and reaction zone 50 which is provided to permit time for the continuance of conversion reactions to a desired point, the reactions proceeding as desired to a point corresponding to the deposition of solid coke or being stopped while the non-vaporized materials are still liquid. The reaction chamber may have removable manheads 51 and 52 to permit entry for cleaning and inspection and a line 51', containing a control valve 52', may be provided to permit the intermittent or continuous removal of liquids to storage or to use as fuel. The chamber may be suitably lagged to conserve heat necessary for decomposition reactions, which are of an endothermic nature.

The vapors from the reaction chamber may pass through a line 53 containing a regulating valve 54, and enter a fractionator 55 which represents any arrangement of equipment which may be utilized for the production of overhead products of motor fuel boiling point range as well as side cuts if desired through exit lines for these intermediate fractions are not indicated in the drawing. The overhead vapors may pass through a vapor line 56 provided with a valve 57 and pass through a condenser 58 in which liquefiable vapors are condensed and pass along with fixed gases through a line 59, containing a valve 60, to receiver 61.

The fixed gases may be released at a rate dependent upon desired pressure conditions through a line 62, containing control valve 63, and liquids of desired boiling point range may be withdrawn to chemical treatment or storage through a line 64, containing control valve 65. To assist in maintaining a definite boiling point range in the overhead vapors from the tower a portion of the condensed liquids may be returned through line 66, containing valve 67, pump 68 and recirculating line 69, containing control valve 70.

Insufficiently converted intermediate refluxes may be returned from the bottom of the fractionator to the heating element through a line 71, containing a control valve 72, a pump 73 and a discharge line 74, containing control valve 75.

It will be appreciated that the process of the invention is applicable to any coal containing sufficient extractable matter to warrant its treatment from an economic standpoint. As an example of results obtainable, the case of a West Virginia bituminous coal may be considered, this coal being extracted by approximately four parts by weight of benzol at a pressure of 900 pounds per square inch and a temperature of 600° F. After distilling off substantially all of the solvent for use on further amounts of coal the total extract comprising approximately 30 gallons of tar per ton of coal may be cracked at a pressure of 200 pounds per square inch and a temperature of 875° F. to produce a yield of 30% of motor fuel containing 20% of tar acids removable by caustic treatment, thus making an overall yield per ton of coal of 7.2 gallons of highly aromatic and non-detonating motor fuel, the latter property being evidenced by the fact that the octane number may be as high as 90.

Approximately similar results may be obtained by using furfural as a solvent though the temperature of extraction need not be as high as that employed with benzol, being only in the neighborhood of 500° F. with the corresponding lower pressure of 500 pounds per square inch due to the lower volatility of the solvent, its boiling point being approximately 320° F. As already mentioned, the recovery of the furfural may be accomplished under reduced pressure to prevent any material amount of decomposition, though in general some slight decomposition may occur during the coal extracting stage.

The process of the present invention is one of

wide applicability and results in greatly increased economy in the utilization of coals and similar materials for the production of low boiling hydrocarbon mixtures of a boiling point range adapted to use in explosion motors, the descriptive material and examples having been given to clearly define the invention, but it is to be understood that it is not to be limited to the specific details disclosed.

I claim as my invention:

1. A process which comprises treating coal with a solvent at elevated temperature in an extracting zone maintained under substantial superatmospheric pressure to dissolve hydrocarbon material from the coal, removing the resultant solution of hydrocarbon extract from the extracting zone and introducing the same, prior to any substantial cooling thereof, into a distilling zone maintained under a sufficiently lower pressure than the extracting zone to vaporize a substantial quantity of the solvent by latent heat distillation, condensing the vapors of the solvent evolved in the distilling zone and recycling the resultant condensate to the extracting zone for re-use as a solvent therein, and maintaining elevated temperature in the extracting zone by heating the recycled condensate prior to its introduction to the extracting zone.

2. A process which comprises extracting hydrocarbon material from coal by treating the latter with a solvent, separating a portion of the solvent for re-use in the extraction step from the resultant solution of hydrocarbon extract while retaining the remainder of the solvent in the solution, and then cracking the hydrocarbon extract in the presence of said remainder of the solvent.

3. A process which comprises extracting hydrocarbon material from coal by treating the latter with a solvent at elevated temperature under substantial superatmospheric pressure, removing the resultant solution of hydrocarbon extract, lowering the pressure on the solution while still hot and vaporizing a portion of the solvent therefrom by latent heat distillation while retaining a substantial portion of the solvent in the solution, condensing the vaporized solvent for re-use in the extraction step, and cracking the hydrocarbon extract in the presence of the unvaporized portion of the solvent.

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