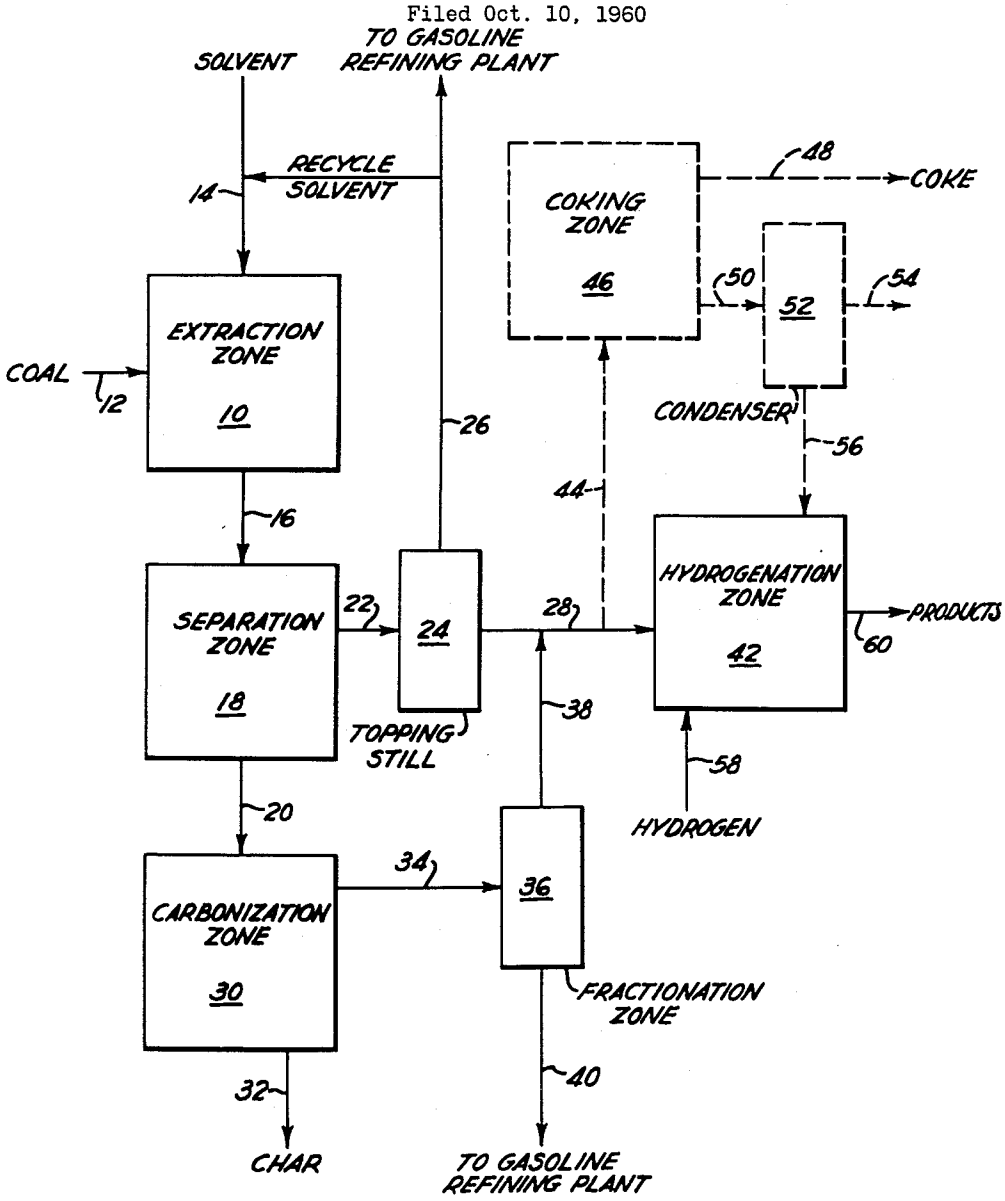
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PRODUCTION OF HYDROGEN-ENRICHED HYDROCARBONACEOUS LIQUIDS

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PRODUCTION OF HYDROGEN-ENRICHED HYDROCARBONACEOUS LIQUIDS

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This invention relates to the conversion of bituminous coal to a hydrogen-enriched hydrocarbonaceous liquid suitable as feedstock to a gasoline refining plant.

This application is a continuation-in-part of my copending application Serial No. 802,768, filed March 30, 1959, now abandoned, which is a continuation-in-part of my application Serial No. 735,177, filed May 14, 1958, the latter application being abandoned on April 2, 1959, each of the above applications being assigned to the assignee of the present invention.

Coal is normally converted to gasoline by a two-step process which comprises initially converting the coal to a hydrogen-enriched hydrocarbonaceous liquid and then converting the latter to gasoline in a conventional type gasoline refining plant. Prior investigators, however, have failed to develop an economical process for converting the coal to the hydrogen-enriched hydrocarbonaceous liquid, and as a result there is no commercial coal-to-gasoline plant in this country today.

The primary object of this invention is to provide a process for the conversion of bituminous coal to a hydrogen-enriched hydrocarbonaceous liquid suitable as feedstock to a gasoline refining plant.

Another object of this invention is to provide a process for the conversion of bituminous coal to a gasoline refining plant feedstock at a cost comparable to that of producing an equivalent petroleum derived material.

A further object of this invention is to provide a process for the conversion of bituminous coal to a hydrogen-enriched hydrocarbonaceous liquid, which process comprises a novel combination of processing steps.

A still further object of this invention is to provide a process for the conversion of bituminous coal to a hydrogen-enriched hydrocarbonaceous liquid, which process includes solvent extraction of the coal whereby the products obtained therefrom are utilized in a novel manner heretofore not appreciated.

In accordance with my invention, bituminous coal is converted to a hydrogen-enriched hydrocarbonaceous liquid by a process which comprises subjecting the coal to a solvent extraction treatment, whereby a mixture of extract and undissolved coal is obtained. The undissolved coal will sometimes hereinafter be referred to as residue. The solvent extraction is conducted under conditions to yield an extract amounting to between 50 and 70 percent by weight of the MAF, i.e., moisture-free and ash-free, coal, hereinafter more fully explained. The extract is separated from the residue and the residue is then introduced into a devolatilization retort from which is recovered a distillate tar and a solid material. The solid material is hereinafter referred to as char. At least a portion of the distillate tar and at least a portion of the extract are subsequently subjected to catalytic hydrogenation under hydrogenation conditions, whereby a hydrogen-enriched hydrocarbonaceous liquid is obtained.

For a better and more complete understanding of my invention, its objects and advantages, reference should be had to the following description and to the accompanying drawing which is a diagrammatic illustration of the preferred embodment of this invention.

In order to understand and fully appreciate the present invention, a brief discussion of certain facts implicit

in the invention follows. Heretofore investigators generally attempted to obtain as much extract as possible during the solvent extraction of coal, i.e., up to 90 percent by weight of the MAF coal or more. They would separate the extract from the undissolved coal, i.e. residue, and then hydrogenate the extract. The residue, on the other hand, was considered to be of little value by these investigators who usually treated the residue to recover adherent solvent, if any, and then employed the remaining residue as a boiler fuel. Contrary to the teachings of these investigators, however, I have unexpectedly discovered that particular residues possess very valuable components.

The prior investigators generally concluded that as the amount of extract obtained from the solvent extraction of coal increased, the amount of tar recoverable upon subsequent low temperature carbonization of the residue correspondingly decreased. Specifically, it was thought that once the amount of extract exceeded about 50 percent by weight of the MAF coal, essentially no tar remained in the residue. I have found, however, that a substantial amount of tar remains in the residue even when as much as 70 percent by weight of the MAF coal is recovered as extract.

In order to obtain more than about 40 percent by weight of the MAF coal as extract during the solvent extraction of coal, it is normally necessary that hydrogen be added to the coal. The hydrogen is usually added by employing a so-called "hydrogen-transferring" hydrocarbonaceous solvent such as tetrahydronaphthalene or specific extract hydrogenation products. As the amount of extract obtained by the solvent extraction is continuously increased above about 40 percent, the amount of hydrogen transferred markedly increases. It is known that the transferred hydrogen usually reacts with the extract as well as unites with carbon contained in the coal to form gas. The gas is generally methane and ethane, these gases being of relatively little value as compared to the extract. It is my belief that the hydrogen also reacts with the residue, thereby accounting for the unexpected amount of tar obtained from the residue upon subsequent low temperature carbonization. It is important to note, however, that as the amount of extract approaches 70 percent by weight of the MAF coal the transferred hydrogen tends to produce an increasing amount of gas rather than reacting with the residue. Specifically, once the amount of extract obtained by the solvent extraction of the coal exceeds 70 percent by weight of the MAF coal relatively little, if any, tar is recoverable from the resulting residue upon subsequent low temperature carbonization. In addition, I have also found that when the amount of extract exceeds about 70 percent by weight of the MAG coal the cost of the transferred hydrogen becomes economically prohibitive.

The following, with reference to the Figure, is a description of the preferred embodiment of this invention. The process of the preferred embodiment primarily comprises introducing bituminous coal, such as Pittsburgh Seam coal, in contact with a hydrocarbonaceous solvent in a solvent extraction zone **10**, to yield an extract amounting to between 50 and 70 percent by weight of the MAF coal. The extract is a liquid, dissolved in the solvent, at the conditions of extraction. Substantially all of the extract and the hydrocarbonaceous solvent are separated from the residue in a separation zone **18**, whereupon a mixture of the extract and the solvent is then introduced into a topping still **24**, while the residue is introduced into a low temperature carbonization retort **30**. Distillate tar which is recovered from the retort **30** is fractionated in a fractionation zone **36**. A portion of the tar is withdrawn from the zone **36** and combined with

a portion of the extract in a conduit **28**, and the mixture is then introduced into a catalytic hydrogenation zone **42**. A hydrogen-enriched hydrocarbonaceous liquid is obtained from the catalytic hydrogenation zone **42**, a portion of which is subsequently employed as a gasoline refining plant feedstock.

SOLVENT EXTRACTION ZONE

Bituminous coal is introduced into a conventional type solvent extraction zone **10** via a conduit **12**. Preferably, the bituminous coal is a high volatile bituminous coal. By high volatile I means bituminous coal having a volatile content of greater than about 20 percent by weight of the MAF coal. Hydrocarbonaceous solvent is introduced via a conduit **14** into the solvent extraction zone **10**. The coal and the solvent react therein to yield an extract comprising between 50 and 70 percent by weight of the MAF coal. Since the main purpose of this invention is to obtain as much hydrogen-enriched hydrocarbonaceous liquid as economically possible from the coal, it is necessary that the extract comprise at least 50 percent by weight of the MAF coal. For reasons previously stated, the amount of extract must not exceed 70 percent by weight of the MAF coal. A mixture of extract, solvent, and residue is withdrawn from the extraction zone **10** via a conduit **16**, and the mixture is then introduced into a conventional type separation zone **18**. The above solvent extraction process may be any of the processes commonly employed by those skilled in the art, e.g., continuous, batch, countercurrent, or staged extraction at a temperature in the range of 300° C. to 500° C., a pressure in the range of 1 p.s.i.g. to 6500 p.s.i.g., a residence time in the range of one minute to 120 minutes, a solvent to coal ratio of from 0.5/1 to 4/1, and, if desired, a catalyst and/or up to 50 standard cubic feet of hydrogen per pound of MAF coal.

Suitable solvents for the coal in the extraction step are those which are predominantly polycyclic hydrocarbons, preferably partially or completely hydrogenated aromatics, including naphthenic hydrocarbons, which are liquid under the temperature and pressure of extraction. Mixtures of these hydrocarbons are generally employed, and are derived from intermediate or final steps of the process of this invention. Those hydrocarbons or mixtures thereof boiling between 260° C. and 425° C. are preferred. Examples of suitable solvents are tetrahydronaphthalene, decalin, biphenyl, methylnaphthalene, and dimethylnaphthalene. Other types of coal solvent may be added to the above-mentioned types for special reasons, but the resulting mixture should be predominantly of the types mentioned, that is, should constitute more than 50 percent by weight of the solvent used. Examples of additive solvents are the phenolic compounds, such as phenol, cresols, and xylenols.

A preferred solvent is a portion of the product obtained from a previous catalytic hydrogenation of extract, normally comprising a blend of two high boiling distillates, preferably a 260° to 325° C. fraction and a 325° to 425° C. fraction, at a feed ratio in the range of 1/1 to 3/1, respectively. The solvent is obtained in this manner primarily to enhance the economics of the over-all process.

SEPARATION ZONE AND TOPPING STILL

Substantially all of the extract and the solvent are separated from the residue in the conventional type separation zone **18**, which is preferably a filtration zone. If desired, however, a cyclone, centrifuge, or a conventional type settling zone may be employed in place of the filtration zone. The residue, substantially free of solvent and extract is withdrawn from the separation zone **18** via a conduit **20**, while a mixture of the extract and the solvent is withdrawn via a conduit **22**. The solvent and extract mixture is introduced into a conventional type topping still **24**. The mixture is separated therein into a first fraction comprising substantially all of the hydrocarbonaceous solvent and some low boiling extract and a second fraction comprising the major portion of the high boiling extract. The separation is usually made at 325° C., corresponding to the boiling point requirements of gasoline refining plant feedstock. The first fraction is withdrawn from the topping still **24** via a conduit **26**, part of which is subsequently reintroduced into the extraction zone **10** as a portion of the solvent therein. The rest is preferably introduced into a gasoline refining plant (not shown). The second fraction is withdrawn from the topping still **24** via a conduit **28**.

If desired, the extract and solvent mixture obtained from the separation zone **18** may be treated prior to the topping still **24** in a deashing zone wherein solid contaminants which are not removable by mechanical separation methods are removed. If these contaminants are not removed from the extract, they tend to deposit on the catalyst maintained in the catalytic hydrogenation zone, thereby causing a more rapid decrease in the activity of the catalyst than would otherwise be experienced. Such decrease in activity forces resort to more frequent replenishment of the catalyst with either regenerated or fresh catalyst. The deashing zone may be any one of those which are generally employed by persons skilled in the art, e.g., an acid treating zone.

CARBONIZATION RETORT

The residue withdrawn from the zone **18** via the conduit **20** is introduced into a conventional type low temperature carbonization retort **30** which is maintained at a temperature in the range of 425° C. to 760° C. Preferably, the retort **30** is a fluidized low temperature carbonization zone however, if desired, other conventional devolatilization zones may be employed, e.g. a rotary kiln. Solids, i.e., char, are withdrawn from the retort **30** via a conduit **32**, while vapors and any solvent that may have adhered to the residue subsequent to the separation zone **18** are withdrawn via a conduit **34**. The vapors and any solvent that adhered to the residue are introduced into a conventional type fractionation zone **36**. If necessary, the tar vapors and the solvent are freed of any entrained solids before entering the fractionation zone **36** by any suitable means such as an electrostatic precipitator or a micrometallic filter. The material introduced into the fractionation zone **36** is preferably separated therein into a fraction boiling above 325° C., which is withdrawn via a conduit **38**, and into a fraction boiling below 325° C., which is withdrawn via a conduit **40**. The latter is introduced into a gasoline refining plant (not shown), while the former fraction is combined in the conduit **28** with the extract fraction removed from the topping still **24**. The mixture is then introduced into a conventional type catalytic hydrogenation zone **42**.

If desired, however, prior to introducing the mixture of extract and tar into the hydrogenation zone all or portions of the mixture may be introduced via a conduit **44**, into a conventional type coking zone **46**. Coke is recovered from the coking zone **46** via a conduit **48**, while a coker distillate is recovered via a conduit **50**. The coker distillate is condensed in a condenser **52** from which noncondensable gases are discharged via a conduit **54**. The condensate is withdrawn from the condenser via a conduit **56** and then introduced into the hydrogenation zone **42**. Coking the mixture of extract and tar tends to enhance the quality of the feed to the hydrogenation zone thereby decreasing the frequency of regeneration of the catalyst.

HYDROGENATION ZONE

Hydrogen is introduced into the catalytic hydrogenation zone **42** via a conduit **58** in contact with the tar and the extract mixture such that the mixture is hydrogenated therein. Hydrogenation products are withdrawn via a conduit **60**, from which is subsequently obtained a hydrogen-enriched hydrocarbonaceous liquid suitable for use as a gasoline refining plant feedstock. A portion of the hydrogenation products may be recovered and thereafter

introduced into the solvent extraction zone **10** as a portion of the hydrocarbonaceous solvent. In addition, portions of the higher boiling products of hydrogenation may be reintroduced into the hydrogenation zone and/or introduced into a conventional type coking zone (not shown).

The conditions generally employed during the catalytic hydrogenation of extract are a temperature in the range of 400° C. to 550° C.; a pressure in the range of 1000 p.s.i.g. to 10,000 p.s.i.g.; a hydrogen feed rate of from 5 to 100 standard cubic feet per pound of extract; and a liquid feed rate of from 10 to 100 pounds per cubic foot of reaction volume. The catalytic hydrogenation zone may be any one of the conventional hydrogenation zones employed by those skilled in the art such as a liquid phase or a vapor phase hydrogenation zone employing catalyst in the form of a fixed, gravitating, or fluidized bed therein. In addition, the catalyst may also be dispersed within the mixture of tar and extract in the form of a slurry and then introduced into a slurry phase, catalytic hydrogenation zone such that the catalyst is introduced into, maintained therein, and withdrawn therefrom in the form of a slurry or a suspensoid. Suitable catalysts are, for example, metals of sub-groups 5 to 8 of the periodic chart, preferably oxides or sulfides in combinations thereof. A preferred catalyst is one containing a metal oxide or sulfide of sub-group 6 of the periodic chart, i.e., molybdenum combined with a relatively minor amount of a transition group metal oxide or sulfide such as cobalt. The active hydrocracking metals are preferably supported on a hydrous oxide support such as alumina gel.

Example

The following is an example of the use of the process described in the preferred embodiment of this invention. Pittsburgh Seam coal was treated in a solvent extraction zone with a solvent recovered from a previous hydrogenation of extract under the following conditions:

Process conditions:	
Temperature	380° C.
Pressure	70 p.s.i.g.
Solvent/coal ratio	1.0
Residence time	1.0 hour.

The solvent comprised a mixture of a 260° to 325° C. fraction and a 325° to 425° C. fraction in the ratio by weight of 1 to1 respectively. The yields of the extraction treatment were:

Yields:	Wt. percent original MAF coal
Extract	57.8
Gases + H_2O	7.3
Residue	34.9

The extract was separated from the residue by filtration and the extract then introduced into a topping still, while the residue was carbonized in a fluidized low temperature carbonization retort under the following conditions and giving the following yields:

Process conditions:	
Temperature	510° C.
Residence time	20 minutes.
Sweep gas rate	4 cu. ft./lb.

Yields:	Wt. percent MAF residue
Gas + C_4	2.8
Liquor	2.8
Tar + light oil	16.4
Char	78.0
	100.0

The portion of the extract and the tar plus light oil boiling above 325° C. were introduced in admixture with a catalyst into a liquid phase catalytic hydrogenation zone under the following conditions and giving the following yields:

Process conditions:	
Temperature	441° C.
Pressure	3500 p.s.i.g.
Residence time (on fresh feed)	2.8 hours.
Catalyst	MoS_2

Yields:	Wt. percent fresh feed
C_1–C_3	12.5
C_4	5.2
C_5–325° C. distillate	80.6

According to the provisions of the patent statutes, I have explained the principle, preferred construction, and mode of operation of my invention and have illustrated and described when I now consider to represent its best embodiment. However, I desire to have it understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically illustrated and described.

I claim:

1. A combination process for the production of hydrogen-enriched hydrocarbonaceous liquid from bituminous coal, which comprises subjecting the coal to solvent extraction under conditions to yield an extract amounting to between 50 and 70 percent by weight of the MAF coal, separating the extract from the residue, subjecting at least a portion of said residue to devolatilization under conditions to yield a tar distillate, subjecting at least a portion of said extract and at least a portion of said tar distillate to catalytic hydrogenation under conditions to yield a hydrogen-enriched hydrocarbonaceous liquid, and thereafter recovering said hydrogen-enriched hydrocarbonaceous liquid.

2. A combination process for the production of hydrogen-enriched hydrocarbonaceous liquid from high volatile bituminous coal, which comprises subjecting the coal to solvent extraction under conditions to yield an extract amounting to between 50 and 70 percent by weight of the MAF coal, separating the extract from the residue by filtration, carbonizing said residue in a fluidized low temperature carbonization retort under condition to yield a tar distillate, combining at least a portion of said extract with at least a portion of said tar distillate, subjecting the resulting mixture to catalytic hydrogenation under conditions to yield a hydrogen-enriched hydrocarbonaceous liquid, and thereafter recovering said hydrogen-enriched hydrocarbonaceous liquid.

3. A combination process for the production of hydrogen-enriched hydrocarbonaceous liquid from high volatile bituminous coal, which comprises subjecting the coal to solvent extraction in a solvent obtained from a previous catalytic hydrogenation of extract under conditions to yield an extract amounting to between 50 and 70 percent by weight of the MAF coal, separating said extract from said residue by filtration, subjecting said residue to carbonization in a fluidized low temperature carbonization retort under conditions to yield a tar distillate, hydrogenating said extract and said tar distillate in a catalytic hydrogenation zone under conditions to yield a hydrogen-enriched hydrocarbonaceous liquid, and thereafter recovering said hydrogen-enriched hydrocarbonaceous liquid, a portion of which is subsequently introduced into said solvent extraction zone.

4. A combination process for the production of hydrogen-enriched hydrocarbonaceous liquid from bituminous coal, which comprises subjecting the coal to solvent extraction under conditions to yield an extract amounting to between 50 and 70 percent by weight of the MAF coal, separating said extract from said residue, carbonizing said residue in a fluidized low temperature carbonization zone under conditions to yield a tar distillate, treating said extract in a deashing zone to remove ash from said extract, catalytically hydrogenating the deashed extract and said tar distillate under conditions to yield a hydrogen-enriched hydrocarbonaceous liquid, and thereafter recovering said hydrogen-enriched hydrocarbonaceous liquid.

5. A combination process for the production of hydrogen-enriched hydrocarbonaceous liquid from bituminous coal, which comprises subjecting the coal to solvent extraction under conditions to yield an extract amounting to between 50 and 70 percent by weight of the MAF coal, separating said extract from said residue, devolatilizing said residue under conditions to yield a tar distillate, coking at least a portion of said extract and at least a portion of said tar distillate under conditions to yield a coker distillate, catalytically hydrogenating at least portions of said liquid products from the aforesaid process steps under conditions to yield a hydrogen-enriched hydrocarbonaceous liquid, and thereafter recovering said hydrogen-enriched hydrocarbonaceous liquid.

No references cited