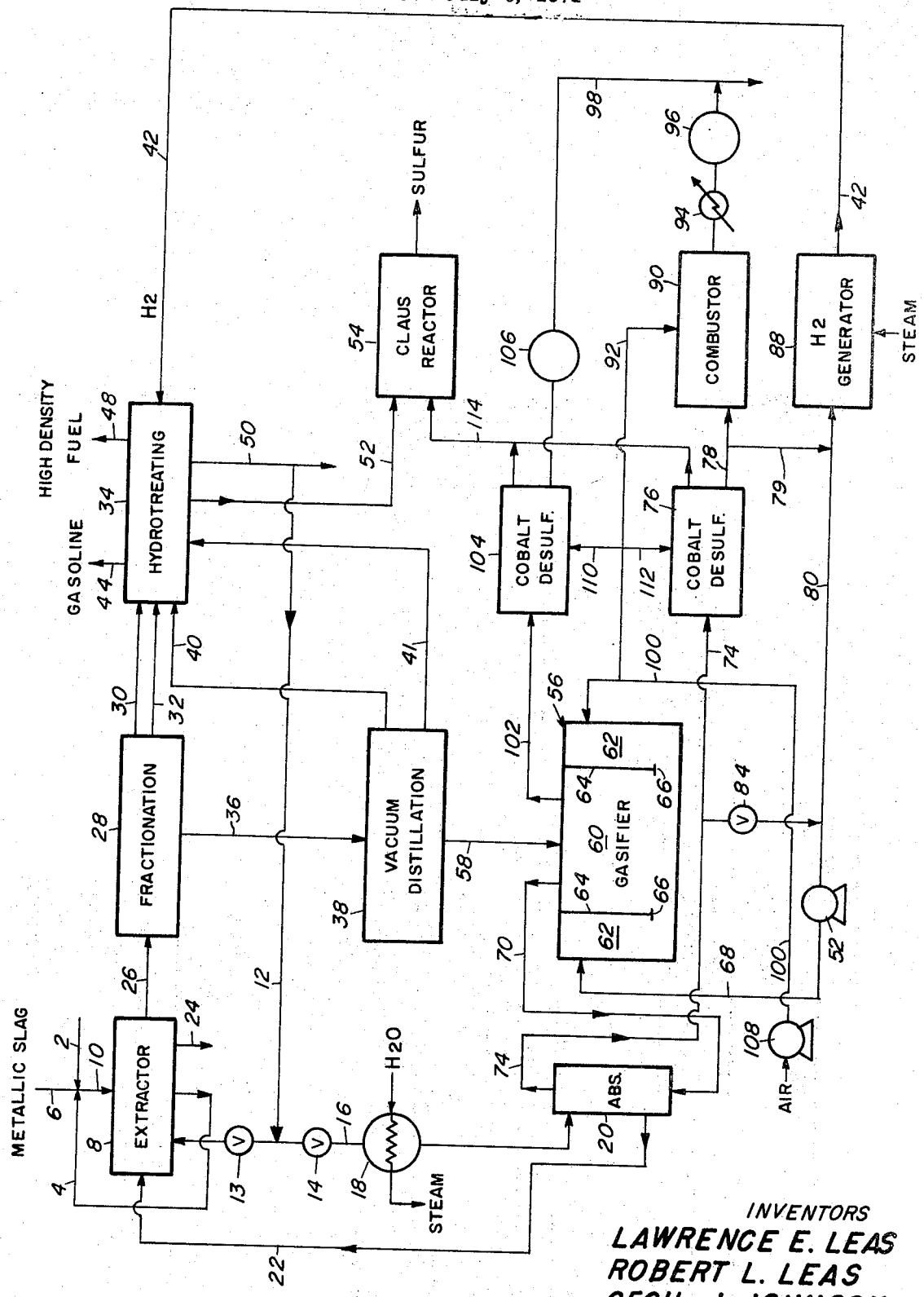
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POLLUTION-FREE FUELS

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POLLUTION-FREE FUELS

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ABSTRACT OF THE DISCLOSURE

The production of liquid and gaseous fuels from coal including the use of a metal oxide for desulfurization.

This invention relates to the production of fuels from coal and more particularly to the production of desulfurized and pollution-free fuels.

It is desirable from an economical standpoint to use coal for producing both liquid and gaseous fuels since coal is relatively inexpensive compared to petroleum crude oil, and is quite abundant in contrast to our rapidly dwingling domestic supply of the petroleum natural resource. One of the biggest drawbacks in using coal as a source for gasoline, or the like, or for gaseous fuels, is its high sulfur content. This problem is of even greater significance today where much emphasis is being placed on improving the environment by reducing air pollution.

It is an objective of this invention to provide a process for producing sulfur-free liquid and gaseous fuels from coal in a unitary process.

It is a further objective of this invention to extract coal liquids from dried coal with a hydro-treated solvent, fractionating the extracted coal liquids, and treating them with hydrogen whereby the sulfur contaminants therein are taken from the liquids as hydrogen sulfide.

It is a further objective of this invention to coke and then gasify the residual coal liquids from the extraction and fractionation operation in a combined coker and gasifier wherein the coal liquids are gasified with hot carbon dioxide to form a carbon monoxide-rich gas, which is then introduced to a metal oxide bed, whereby any sulfur contaminants in the carbon monoxide reacts with the metal to form a metal sulfide, and is thereby removed from the gases resulting in a substantially sulfur-free carbon monoxide-rich gaseous product. In alternate cycles air is introduced to the gasifier to burn the materials therein to a higher temperature and air is also introduced to the desulfurizer metal oxide bed to oxidize it back to its higher oxide form and liberate the sulfur therein as sulfur dioxide which is sent to a sulfur recovery system.

It is another objective of this invention to perform the coking and the gasifying operation in the same reactor thereby eliminating excessive handling of the residual liquids and solids.

It is another objective of this invention to combust the carbon monoxide product of the gasification step in a combustor in the presence of heated air at a temperature not to exceed 2500° F. whereby the production of nitrogen oxides in the combustion gases is minimized.

These and other objects of the invention will become more apparent to those skilled in the art by reference to the following detailed description when viewed in light of the accompanying drawings wherein:

The single figure is a diagrammatic illustration of the process of this invention.

As shown in the drawing, coal from line **2** and make-up slag and recycle slag from lines **4** and **6** respectively, are mixed together and introduced into an extraction unit **8** via line **10**. The extraction unit is shown diagrammatically and it is to be understood that it is of conventional construction and operation and may include a plurality of extractors. Hydro-treated solvent is introduced to the extraction unit via line **12** and valve **13**. A portion or all of the hydro-treated solvent may be bypassed through valve **14** and line **16** to a heat exchanger **18** and absorber unit **20** and then sent to the extractor via line **22**, as will be explained more fully hereinafter. Ash is taken from the extractor via line **24** and slag is recycled, as mentioned earlier, via line **4**. By recycling the slag, only a fraction thereof needs replacing during each cycle. Extracted coal liquids and solvent leaves the extraction unit **8** vita line **26** and enter fractionation unit **28** wherein the lighter distillates in gases are taken off via lines **30** and **32**, respectively, and sent to hydro-treating unit **34**. The heavy residues from the fractionation unit leave from the lower end thereof via line **36** and are subjected to vacuum distillation in distillation unit **38**, with the distillates being taken therefrom via line **40** and introduced to the hydro-treating unit **34** along with the lighter distillates and gases from the fractionation unit **28**.

In the hydro-treating unit **34**, hydrogen is introduced via line **42** from hydrogen generator **44**. Gasoline exits from the hydro-treater via line **46** and high density diesel fuel is taken off via line **48**. The heavier fuel oil leaves the hydro-treating unit via line **50** with a portion thereof being recycled back as solvent to the extraction unit **8** via line **12** and the rest being taken off for storage. Additionally, any sulfur in the coal liquids is reacted with the hydrogen in the hydro-treating unit to form hydrogen sulfide which is taken off via line **52** and sent to a Claus reactor **54** for the production of elemental sulfur.

It is to be understood that the extraction, fractionation and hydro-treating units, and the vacuum distillation unit, are conventional items in the art.

The heavy residues from the vacuum distillation unit **38** leaves distillation unit and are introduced to a combination coker-gasifier **56** via line **58**. The unit **56** is illustrated diagrammatically. However, it is to be understood that it is to be of the type disclosed in applicant's copending application Ser. No. 162,180, filed July 13, 1971, entitled Reactor. The reactor unit disclosed therein comprises concentric chambers with the central chamber **60** containing materials to be gasified, and the outer concentric chamber **62** receiving a metal oxide preferably cobalt oxide. The inner and outer chambers are separated by an annular divider wall **64** having passageways **66** in the bottom thereof permitting gases to flow from the outer chamber to the inner chamber. The combination coker-gasifier operates on alternate cycles of (a) air feed to preheat the bed and, (b) carbon dioxide feed to gasify the carbonaceous materials therein to a carbon monoxide-rich gas.

Carbon monoxide is introduced to chamber **62** via line **68** and reacts with the cobalt oxide therein in an endothermic action to produce superheated carbon dioxide. The carbon dioxide enters the central chamber **54** by means of the passageways **66** and gasifies the coke therein to additional carbon monoxide-rich gases in the ratio of approximately 2:1 with regard to the initial carbon monoxide infeed. The gas leaves via line **70** entraining some vapor therein due to the incomplete removal of the liquids from the feed residue. The gaseous stream with the vapors enters an absorber **20** wherein these vapors are removed by the incoming solvent stream from line **16**. The carbon monoxide-rich gas then leaves the absorber via line **74** and is sent to a desulfurizing unit **76**.

The desulfurizing unit **76** comprises a bed of metal oxide, preferably cobalt oxide in its higher oxide form. The ratio of cobalt oxide to the amount of carbon monoxide introduced to the desulfurizing unit **76** is such that only a portion of the carbon monoxide reacts to form carbon dioxide, yet substantially all of the sulfur contaminants

in the carbon monoxide-rich gas reacts with the cobalt to form cobalt sulfide thereby removing the sulfur from the gas. The amount of carbon monoxide that goes to carbon dioxide can also be controlled by regulating the velocity of the gases flowing therethrough.

The desulfurized carbon monoxide gases including some carbon dioxide leave the desulfurizer **76** via line **78** wherein a portion thereof is taken off via lines **79** and **80** and recycled via compressor **52** and line **68** to the coker-gasifier for the carbon monoxide production stage. Additional carbon monoxide can be provided prior to the desulfurization step via shunt line **84**. Still another portion of the carbon monoxide is introduced from line **80** to hydrogen generator **88** wherein it is reacted with steam for the production of hydrogen which is then introduced to the hydro-treating unit via line **42** in the manner heretofore described. The remainder of the carbon monoxide-rich gases are introduced to a combustor **90** and are combusted with heated air under compression introduced via line **92**. The exhaust gases are passed through heat exchanger **94** giving up process heat, and are then expanded through power wheel **96**. The exhaust gases therefrom are taken off via line **98** and may be used for drying or stripping operations.

The materials in the combined coker-gasifier are preheated in an alternate cycle by an introduction of excess air to the cobalt oxide chamber **62** by means of line **100**. The metal therein, having been reduced to a metal or a lower oxide during the previous cycle by the introduction of carbon monoxide, is then oxidized back to its higher oxide form by the introduction of excess air with the remaining air being introduced to the chamber **64** via passageways **66** for burning the materials therein to a higher temperature. The nitrogen-rich gases from the air-burn stage are taken off via line **102** and introduced to a second desulfurizing unit **104** also containing a metal oxide, preferably cobalt oxide in its higher oxide form. The sulfur in the nitrogen-rich gases reacts with the cobalt to form cobalt sulfide thereby removing the sulfur from the stream. The desulfurized nitrogen is then expanded through a power wheel **106** and combined with the exhaust from the combustor **90** in line **98** for use in drying and stripping operations.

The reduced cobalt oxide in the desulfurizing units **104** and **76** are oxidized to their higher oxide form during alternate cycles by the introduction of air from compressor **108** via lines **110** and **112**. The sulfide reacts with the oxygen in the air to form sulfur dioxide which is taken off from the desulfurizing units with the nitrogen via line **114** and introduced into the Claus reactor **54** along with the hydrogen sulfide from the hydro-treating unit for the formation of elemental sulfur.

It is to be understood that in this process multiple units in parallel may be used to render the process continuous. For example, two combination coker-gasifiers may be used with one being in the air-burn stage while the other is in the carbon monoxide production stage. The same is true for each of the cobalt desulfurizing units **76** and **104**, with one being in the desulfurizing stage while the other one is in the regeneration stage. Further, a Rankine cycle fluid system may be used for cooling the various liquid and gaseous streams with the heat taken from the system being used for additional power generation.

The combined coker-gasifier is operated cyclically to produce primarily three separate products, (a) a high purity carbon monoxide gas, (b) a nitrogen-rich gas, and (c) volatile hydrocarbons that are recycled with the fresh solvent to the extractor section. In this three-cycle operation: (a) the coal liquids or tar coking takes place by injecting the liquid tar on the hot packing within the gasifier at the end of the cobalt reduction step to facilitate the then recycled carbon monoxide to strip the volatiles out through the transfer line to be recovered as a liquid in the solvent absorber, while the solid coke is retained within the gasifier as a thin deposit on the packing for the heating and gasification cycles to follow; (b) the deposited coke is then superheated by the hot compressed air that burns the residual carbon from the extractor operation and also burns a small portion of the coke within the gasifier, with the exhaust air from the carbon burning containing primarily superheated nitrogen, carbon dioxide, and some oxygen; and, (c) carbon monoxide gas is recycled to the then oxidized cobalt in the annular space thereby reducing the cobalt, generating superheated carbon dioxide which with its entrained oxygen flows directly through ports into the bottom of the gasifier, which in turn generates carbon monoxide. Therefore, the combined coker-gasifier virtually eliminates the otherwise need for a separate coking unit with its associated solids handling problem.

The following are examples illustrative of the process of this invention:

EXAMPLE 1

50 pounds of coal and 50 pounds of slag were mixed and placed inside an extractor reactor. This mixture was placed on a bed of 4" depth of small slag to serve as a filter for the liquids. The coal was crushed before mixing with the slag and the particles of coal used varied in diameter from 1/16" to 3/8". The slag was approximately 1/4" diameter. The proximate analysis of the coal used was as follows:

Wt. percent basis:	Percent
Moisture	6.4
Volatile matter	30.9
Fixed carbon	51.2
Ash	11.5

The coal and slag were dried with 350° F. nitrogen to remove most of the moisture. Solvent was pumped into the reactor and the extractor pressure was maintained at 300 p.s.i.a. for the run. The solvent used was tetralin. After introduction of the solvent to fill the extractor, heat was applied and heated to 850° F. The solvent was circulated until the 850° F. was obtained in the extractor and then this solvent was accumulated and solvent entered the top of the extractor at 800° F. and exited the bottom of the extractor. The feed rate was maintained at 30 #/hr. and all the solvent was accumulated. A total of 50 pounds of solvent was used during the extraction run. 80.4 pounds of solvent plus extracted coal liquids were obtained after the product output was cooled to 100° F. 3.1 pounds of gases were obtained from the vapor-liquid separator after cooling. The analysis of the gases on a volume basis was as follows:

	Percent
Carbon dioxide	30.2
Carbon monoxide	5.5
Hydrogen	19.8
Methane	40.1
Hydrogen sulfide	2.4
Ethylene	0.6
C_3's and C_4's	1.4

Some water was present in the solvent and coal liquid phase. After the extracting run was completed, nitrogen at 500° F. was admitted into the extractor to remove any other liquids. The gaseous product was cooled and 0.7 pound of liquids were obtained. This was added to the other coal liquids and solvent for a total of 81.1 pounds of solvent and coal liquids. Air at 780° F. was injected into the extractor to burn off any coke deposits. The carbon dioxide and water concentrations of the exit gases were observed and by back calculations it was found that 4.2 pounds of material were burned to carbon dioxide and water. After cooling, the ash was separated from the slag. 6.2 pounds of ash remained after the extraction and coke combustion.

The solvent and extracted coal liquids were fractionated at 850° F. and at low pressure to remove any remaining gases and liquids from the residue or heavy fraction. 0.5 pounds of gases (90% methane by volume) was obtained and 0.6 pounds of water was condensed from the gas stream. 70.2 pounds of solvent and extracted liquids were obtained as well as 8.7 pounds of heavy material after the fractionation was completed. This material (residue from the fractionation unit) was subjected to a vacuum distillation at 5 p.s.i.a. and 800° F. and an additional 0.7 pounds of liquids were obtained which were mixed with the 70.2 pounds of liquids for a total of 70.9 pounds of liquids for hydrotreating. 7.6 pounds of residue were obtained from the vacuum fractionation unit for use in the coker-gasifier.

The 70.9 pounds of liquids (solvent and extracted coal liquids) were hydro-treated at 950° F. and 2000 p.s.i.a. using a cobalt molybdate catalyst on an alumina carrier. Hydrogen consumption was 0.72 pounds. The amount of gases obtained during hydro-treatment was 1.8 pounds. The material was fractionated and the following yields were obtained on a solvent free basis.

Yields on MAF Basis (after solvent removed)	Wt. percent
Gases from extractor	7.5
Gases from hydro-treater	4.4
Heavy material to coker-gasifier	18.5
Gasoline	10.2
Fuel oil	38.5
Coke burned in extractor	10.2
Fractionation gases	1.2
Unaccounted	9.5
Total	100.0

Enough gases are available to produce the necessary hydrogen.

Assuming that the net process heat or heat recovery (net) can be used in a Rankine cycle power generator, that the coke is burned with air at 300 p.s.i.a. and expanded in a gas turbine, that the material sent to the gasifier is burned and gasified with carbon dioxide, the desulfurizers are operated at 1000° F., the gasifier is operated at 2000° F., the carbon monoxide not required for recycle carbon dioxide is burned with air in a combustor at 300 p.s.i.a. and expanded through a gas turbine, and the gases are used for hydrogen production—this calculation gives a calculated electrical generation product output of 20.5 k.w. hr. using the above example feed and products.

EXAMPLE 2

60 pounds of the same coal as in Example 1 were mixed with 40 pounds of slag and placed inside the extractor as described in Example 1. The coal was crushed before mixing with the slag and the particles of coal used varied from 1/32" diameter to 1/2" diameter. The slag was approximately 3/8" diameter. The coal had the same proximate analysis as the coal used in Example 1. Drying of the coal and slag was accomplished by nitrogen at 360° F. to remove most of the moisture. Solvent was pumped into the reactor and 200 p.s.i.a. pressure was maintained on the extractor for the duration of the run. The temperature of the extractor and solvent was maintained at 800° F. The feed rate of the solvent was maintained at 25#/hr. and the liquids and gases were cooled to 90° F. and the gases were vented through a wet test gas meter and analysis were taken of the gases. The liquids were accumulated. In all, 65 pounds of solvent was fed into the extractor. 3.2 pounds of gases were obtained during extraction with the following volumetric analysis:

	Percent
Carbon dioxide	38.7
Carbon monoxide	8.3
Hydrogen	25.2
Methane	22.4
Hydrogen sulfide	4.2
Ethylene	0.3
Ethane	0.1
C_3's & C_4's	0.8

98.2 pounds of solvent and extracted coal liquids were obtained from the extractor.

After the extraction was completed, 600° F. nitrogen was injected into the extractor to remove any liquids which may be present. The stream was cooled and 0.5 pounds of liquids were obtained and added to the other liquids for a total of 98.7 pounds of solvent and extracted liquids from the extractor. The coke deposits were burned with 660° F. air and by analysis of the combustion stream for carbon dioxide and water vapor. 6.1 pounds of this material was calculated to have been burned. After cooling, the ash was separated from the slag. 7.05 pounds of ash were removed.

The solvent and extracted coal liquids were fractionated at 800° F. and at low pressure to remove any remaining gases and also to remove the liquids from the heavy fraction. 0.4 pounds of gases (91% methane) was obtained as well as 0.7 pounds of water. 86.8 pounds of liquids and 10.6 pounds of heavy material were obtained. The 10.6 pounds of heavy material was vacuum fractionated at 750° F. and 5 p.s.i.a. and an additional 0.4 pounds of liquids were obtained which were added to the 86.6 pounds for a total of 87.2 pounds of liquids for hydrotreating. 9.9 pounds of heavy material suitable for the coker-gasifier were obtained from the vacuum fractionator.

The 87.2 pounds of liquids were hydro-treated at 900° F. and 2000 p.s.i.a. pressure over a cobalt molybdate catalyst on an alumina carrier. Hydrogen consumption was 0.91 pounds. The amount of gases obtained (not including the hydrogen recycle) was 1.87 pounds. The liquid material was fractionated for solvent recovery and the following materials were obtained on a solvent free basis:

	Pounds
Gasoline	4.7
Fuel oil	20.1

Enough gases were available to produce the required hydrogen.

Yield obtained on MAF Basis (not incl. solvent):	Wt. percent
Gases from extractor	6.5
Heavy material to coker-gasifier	20.1
Gases from hydro-treater	3.8
Gasoline	9.6
Fuel oil	40.8
Coke burned in extractor	12.4
Fractionation gases	0.8
Unaccounted	6.0
Total	100.0

Making the same assumptions as in Example 1 except the coke is burned at 200 p.s.i.a. and not 300 p.s.i.a. and the combustor is operated at 200 p.s.i.a. instead of 300 p.s.i.a., a calculated electrical generation output of 27.6 k.w. hr. was obtained.

EXAMPLE 3

100 pounds of Venezuela crude oil with the following analysis were charged into the fractionator and fractionated at 800° F. and at low pressure.

Crude oil analysis:
Gravity—16.5° API, Specific gravity—0.9561,
Sulfur content—3.2%, wt.

Distillation analysis using Bureau of Mines routine

Crude oil analysis, vol. percent:

Light gasoline	1.8
Total gasoline & naphtha	7.2
Gas oil	40.2
Residuum	51.1
Distillation loss	1.5

4.8 pounds were taken off overhead into a flash chamber wherein 0.7 pounds of light gasoline were vented and 4.1 pounds of liquids remained. An additional 17.3 pounds of liquids were taken off for a total liquid output of 21.4 pounds. 77.8 pounds of this material remained at this condition and this was fractionated in a vacuum fractionator at 750° F. and 5 p.s.i.a. A total of 22.2 pounds of liquids were obtained and added to the other liquids for a total of 43.6 pounds of liquids for hydro-treating. 54.6 pounds of material from the vacuum distillation were suitable for feed to the coker-gasifier unit.

The 43.6 pounds of liquids were hydro-treated at 900° F. and 2000 p.s.i.a. pressure over a cobalt molybdate catalyst on an alumina carrier. Hydrogen consumption was 1.32 pounds. The product was sent to a vapor-liquid separator whereinn 3.4 pounds of gases were recovered with the following analysis: (not including the hydrogen recycle).

Analysis, wt. percent:	Percent
Hydrogen sulfide	50.2
Nitrogen	9.4
Water vapor	0.1
Methane	27.2
Ethylene	0.3
Ethane	12.1
C_3's & C_4's	0.7

After separating the liquid fraction, the following were obtained:

	Pounds
Light gasoline	3.3
Gasoline	5.8
Fuel oil	30.3

Yields, wt. percent of total feed:	Percent
Light gasoluine	4.0
Gases	3.4
Gasoline	5.8
Fuel oil	30.3
Heavy material to coker-gasifier	54.6
Unaccounted	1.9
Total	100.0

The hydrogen could be made from the gases after desulfurization and the light gasoline, additional hydrogen, if required, could be obtained from part of the gasoline fraction.

Assumingthe gasifier-coker and the carbon monoxide operate at 300 p.s.i.a. and making the other assumptions as made in Example 1, with the exception of the extractor burning of the coke and this power wheel, a calculated electrical generation product output of 104 k.w. hr. was obtained, using the material to the coker-gasified. Part of the coke will be burned with air to heat up the bed and to furnish the endothermic heat of reaction and this will be expanded through a gas power wheel.

In a general manner, while there has been discolsed an effective and efficient embodiment of the invention, it should be well understood that the invention is not limited to such embodiment as there might be changes made in the arrangement, disposition, and form of the parts without departing from the principle of the present invention as comprehended within the scope of the accompanying claims.

We claim:

1. A method of producing desulfurized fuels comprising the steps of:
feeding coal to an extractor wherein coal liquids are extracted therefrom with a hydro-treating solvent;
distilling off the lighter hydrocarbon distillates from the coal liquids and leaving a coal liquid residue having a sulfur content;
passing the liquid residue through a coker-gasifier wherein the liquid is coked and the coke formed is then gasified to a carbon monoxide-rich gas; and
contacting the carbon monoxide-rich gases with a metal oxide wherein any sulfur in said carbon monoxide reacts with the metal to form a metal sulfide thereby removing the sulfur from the gases.

2. The method of claim 1 wherein said metal oxide is cobalt oxide.

3. The method of claim 1 wherein a portion of said desulfurized carbon monoxide is mixed with heated air in a combustor and combusted, and the product gases from said combustion are expanded through a power generating wheel.

4. A method as in claim 1 and wherein the carbon monoxide is burned at a temperature less than 2500° F. to avoid the production of nitrogen oxides.

5. The method of claim 1 wherein a portion of said desulfurized carbon monoxide is treated with steam to produce hydrogen, and reacting said hyrdrogen with said distillates in a hydro-treating step wherein any sulfur in said distillates is reacted with the hydrogen to form hydrogen sulfide.

6. The method of claim 1 wherein said coke is gasified with carbon dioxide.

7. The method of claim 5 including forming a second metal oxide bed, recycling a portion of said carbon monoxide through said second metal oxide bed instead of said first metal oxide bed wherein the carbon monoxide reduces said metal oxide and is oxidized to superheated carbon dioxide which is introduced to said coker-gasifier for gasifying said coked coal liquids.

8. The method of claim 6 wherein excess air is introduced to said second metal oxide bed in an alternate cycle to oxidize said reduced metal oxide back to its higher oxide form, and then passing said excess air including a high nitrogen content to said gasifier for coking said liquids, and burning said coked coal liquids to a higher temperature, and desulfurizing the nitrogen-rich product gases in a third metal oxide bed.

9. The method of claim 7 wherein said first and third metal oxide desulfurizing beds are on alternate cycles purged with air to oxidize the bed back to its higher oxide form and to react with the sulfide theerin to form sulfur dioxide which is taken off to a pure sulfur recovery system.

References Cited

UNITED STATES PATENTS

3,128,164	4/1964	Moritz et al.	48—212
3,117,921	1/1964	Gorin	208—8
2,830,883	4/1958	Eastman	48—206
3,708,269	1/1973	Linden	48—197 R

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