

Aug. 16, 1960

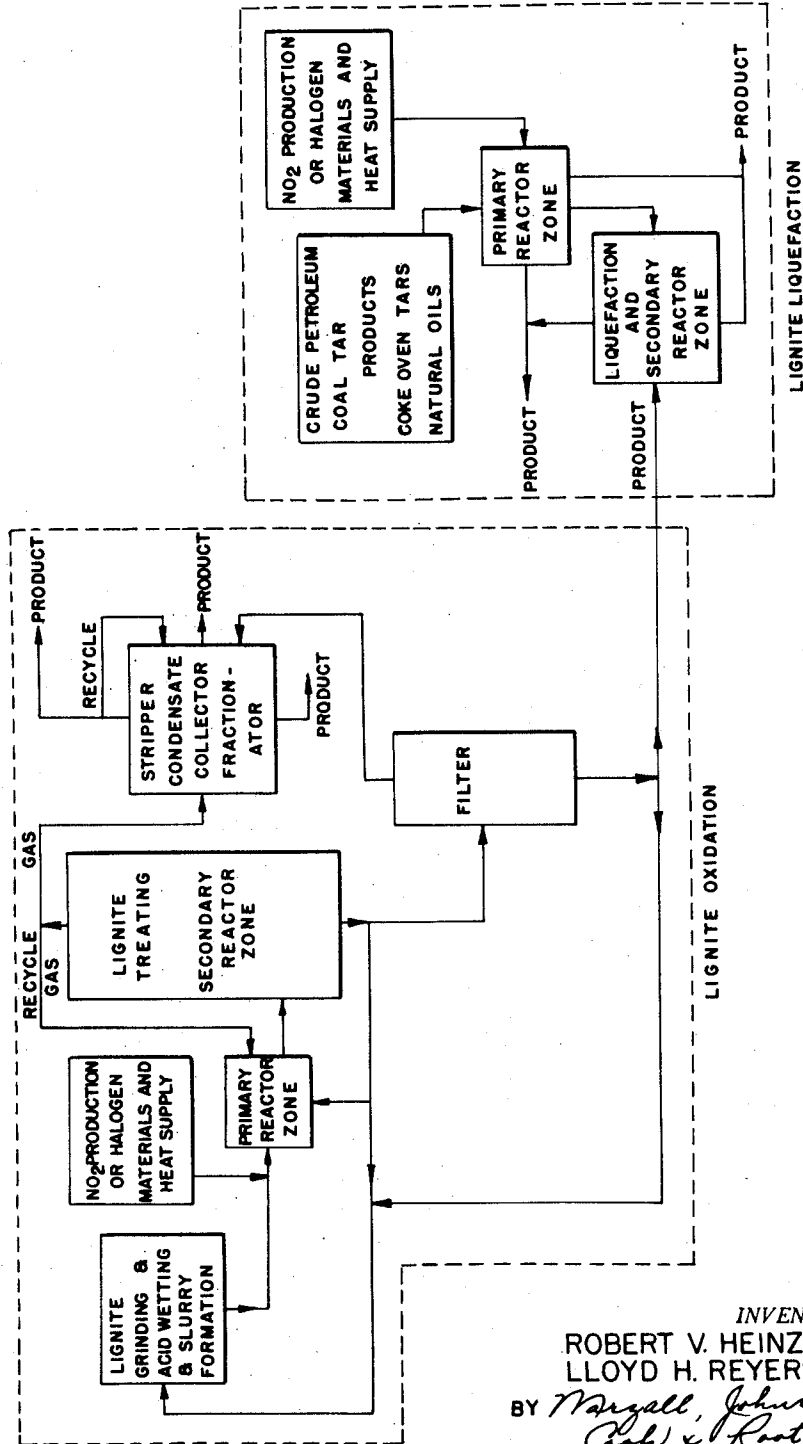
R. V. HEINZE ET AL
PROCESSING OF LIGNITE

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3 Sheets-Sheet 1

FIG. 1



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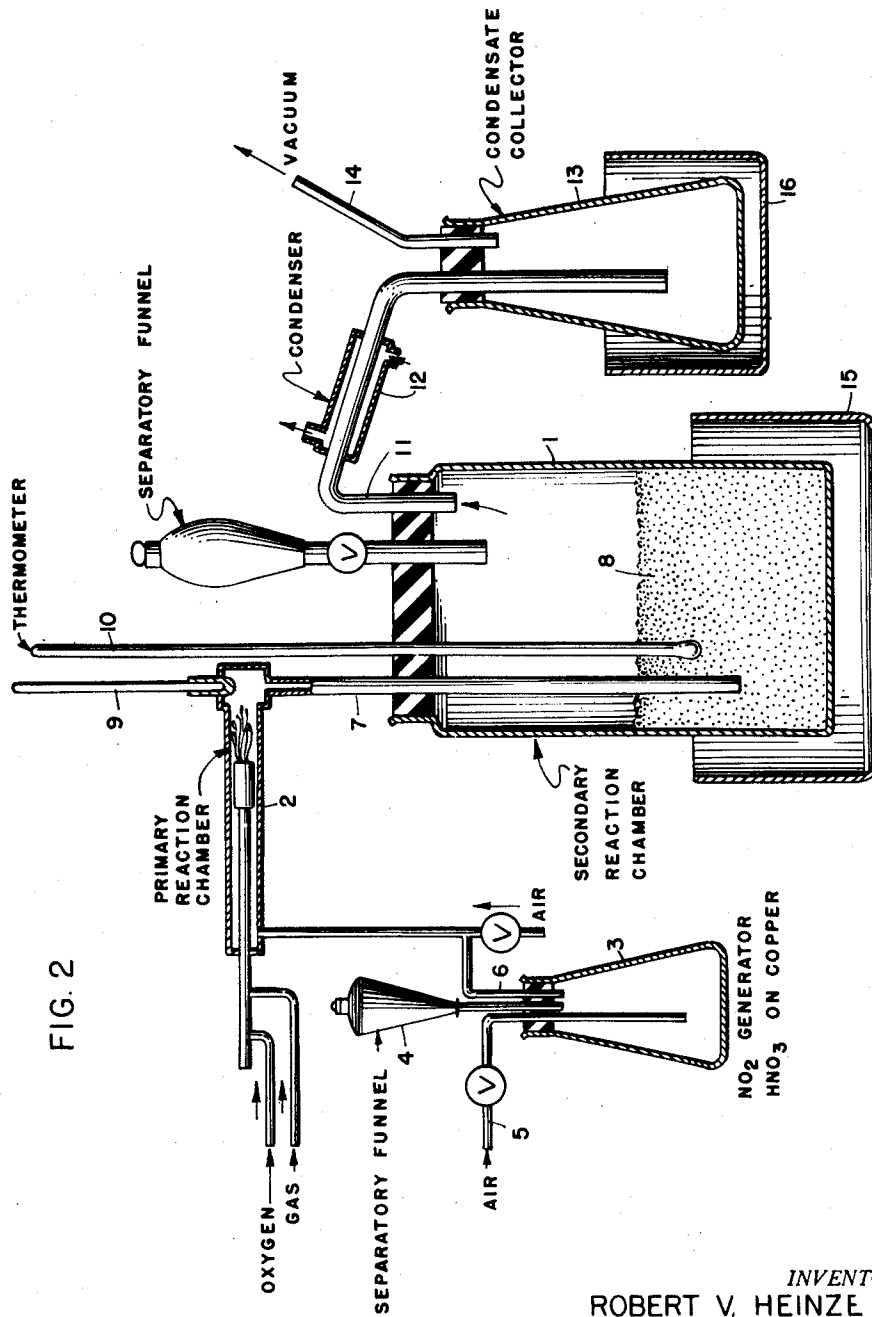
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3 Sheets-Sheet 2



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FIG. 3

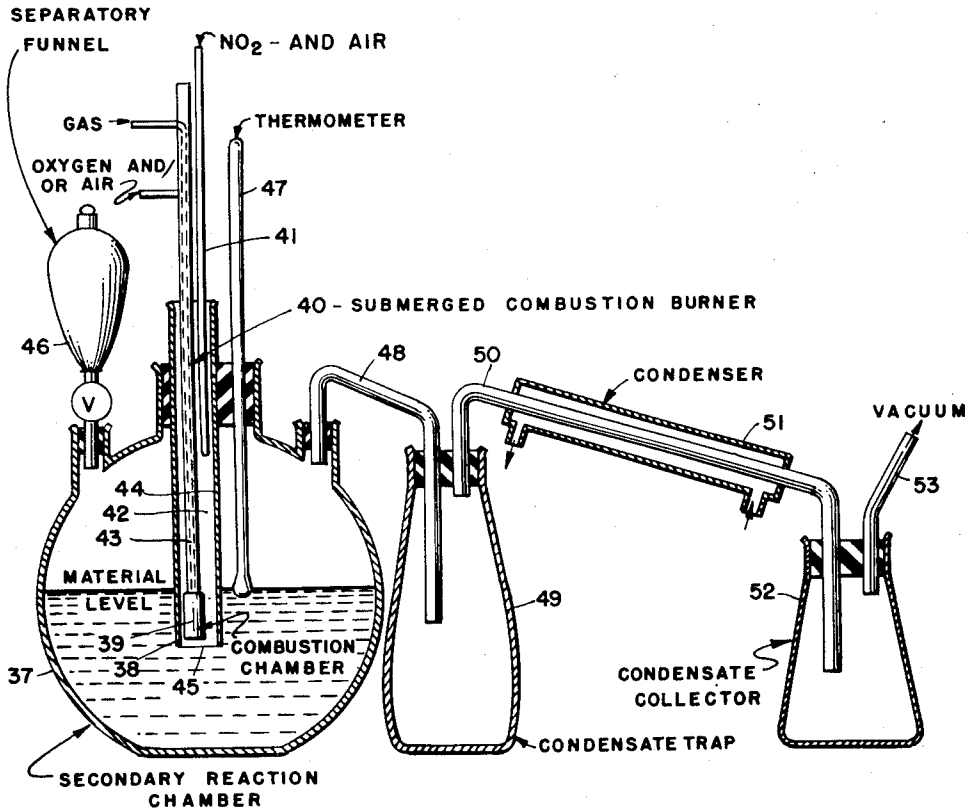
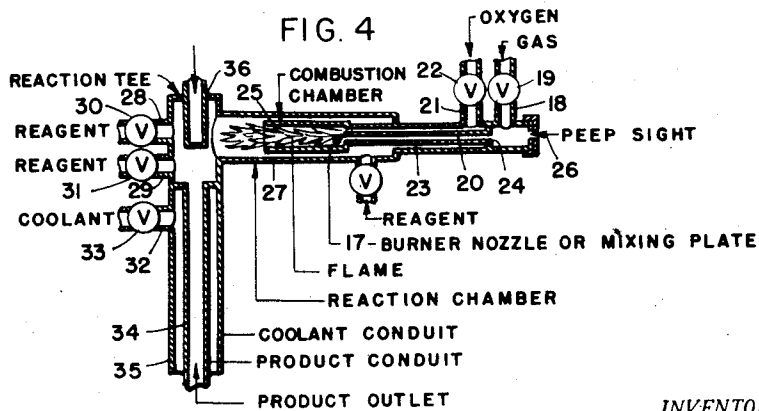


FIG. 4



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PROCESSING OF LIGNITE

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6 Claims. (Cl. 44—50)

This invention relates to a new and improved method of processing lignite and to the products resulting therefrom.

Lignite is a carbonaceous material found in large quantities in North Dakota, South Dakota, Montana and other parts of the United States and Canada. In general, lignite may be described as a brown coal in which the original structure of the wood is still recognizable. It usually contains 25% to 45% water. Geocerinic acid ($C_{28}H_{56}O_2$) is an unsaturated aliphatic acid obtained from lignite. Montan wax is a hydrocarbon soluble in chloroform or benzene which is obtained from lignite.

It is estimated that there are six hundred billion tons of lignite in North Dakota alone. This vast deposit of lignite is estimated to represent one-seventh of the world's reserve of fuel existing as coal, gas, petroleum and oil shale. Lignite is believed to consist of sheets of cyclic compounds of hydrogen and carbon. Most of the lignite today is converted into a fuel by drying it to about 5% by weight water content where spontaneous combustion is not so likely to occur. The drying of the lignite has heretofore been considered to be desirable in order to convert it into a useful product, otherwise it tends to disintegrate into a fine, thin powder on exposure to the atmosphere.

One of the objects of the present invention is to provide a new and improved method for processing lignite which does not involve an initial drying step but, on the contrary, utilizes the lignite in a wet form.

Another object of the invention is to provide a new and improved process for the treatment of lignite which results in new and useful by-products.

Still a further object of the invention is to provide a new and improved process for changing lignite to a liquid state in which it can be used as a fuel or further processed to obtain various by-products therefrom.

Other objects and advantages of the invention will be apparent by reference to the following description in conjunction with the accompanying drawing in which:

Fig. 1 represents a flow sheet of a process embodying the invention for altering and/or liquefying lignite;

Fig. 2 represents one form of apparatus for processing lignite in accordance with the invention;

Fig. 3 represents another form of apparatus for processing lignite in accordance with the invention, and

Fig. 4 illustrates a portion of the apparatus shown in Fig. 2.

In general, the invention involves a process in which lignite is first partially oxidized. By-products are recovered from the oxidized product. The oxidized product can also be converted to a liquid state by mixing it with cycle stock obtained from the catalytic refining of petroleum or by mixing it with other materials which are essentially hydrocarbon in nature, such as the tars and heavy residues obtained from coke ovens.

The preferred method of procedure is illustrated in Fig. 1. According to this procedure, lignite is ground in the presence of water to form a slurry. It is then par-

2

tially oxidized and/or halogenated by bringing the slurry of lignite into contact with an oxidizing agent such as oxides of nitrogen (e.g., NO), and /or a halogen (e.g., chlorine or bromine) in a primary reaction zone. The residue from the primary reaction zone is passed to a secondary reaction zone. Gases which are given off in the secondary reaction zone are at least partially recycled to the primary reaction zone. The gases given off from the secondary reaction zone can also be passed to a fractionating column where the lower boiling portions are stripped off and removed and a condensate is collected. The condensate can be collected in various fractions of different boiling points. The residual product can be used as such for a fuel or can be mixed with crude petroleum, coal tar products, coke oven tars, and/or natural oils. The residual product from the secondary reaction zone can also be filtered out and converted to a liquid state by further treatment with oxides of nitrogen and then mixing it with crude petroleum, coal tar products, coke oven tars and/or natural oils. The crude petroleum, coal tar products, coke oven tars and/or natural oils can also be partially oxidized, for example, by treatment with HNO_3 , NO, NO_2 , chlorine or other halogen prior to mixing them with the partially oxidized lignite.

In the initial stages of the process it is frequently desirable to mix the lignite with an oxidizing acid, such as nitric acid, in order to accelerate the lignite oxidation.

The products of the process include polycarboxylic acids which can be obtained by crystallization, solvent extraction, or other suitable treatment of the condensates and/or of the residues obtained in the lignite oxidation. The products of the lignite liquefaction can be used as fuel oils or can be further processed by solvent extraction methods, cracking, hydrogenation, dehydrogenation, hydrofining and reforming, utilizing processes known in the petroleum industry.

The invention will be further illustrated by the following examples in which the quantities are stated in parts by weight unless otherwise indicated. It will be understood that these examples are exemplary only and do not represent all possible methods of practicing the invention.

Example I

An apparatus of the type shown in Fig. 2 was employed. 589 parts of 20 mesh lignite (Peerless) was charged into the secondary reaction chamber 1. The burner 2 (Subcomco made by Submerged Combustion Company of America) was ignited using natural gas as a fuel and oxygen to support the combustion. Nitrogen dioxide (NO_2) was generated in vessel 3 by allowing nitric acid to drop from separatory vessel 4 on to copper contained in vessel 3. Air was drawn in at the T in conduit 6 and, when desired, air under pressure was forced through tube 5 in order to sweep the NO_2 gas through tube 6 and the outer casing of burner 2 where the NO_2 was heated and mixed with the combustion gases. The resultant gases consisting essentially of NO_2 , nitrogen, oxygen and carbon dioxide, were passed through tube 7 into the lignite 8 contained in vessel 1. The temperature of the gases and of the lignite were observed by thermometers 9 and 10, respectively. The gases in the primary reaction chamber were at a temperature of about 240° F. (120° C.). The gases above the lignite in the secondary reaction chamber were at a temperature of about 120° F. (49° C.).

The blowing of the gases into the lignite was continued for 4 hours at which time the product was a slightly darker brown than the dark brown lignite in the original charge. At the end of 4 hours, 13 parts of the reaction product remaining in vessel 1 were removed. Ten of the thirteen parts were washed with distilled water and filtered. The filtrate was acidic and yielded a considerable

quantity of a white solid material with a slightly yellow tinge which consisted essentially of small crystals, irregular in shape but flat and thin. This material appeared to be a cyclic polycarboxylic acid. It was hygroscopic and soluble in water.

The vapors evolved during the reaction were passed through conduit 11, cooled by condenser 12 and the condensate collected in a vessel 13. A tube 14 connected vessel 13 to a source of vacuum. Vessels 15 and 16 were provided to contain a cooling medium such as water, which was cooled with ice or solid carbon dioxide, for the desired control of the reaction temperature. This variation in control varies the types of chemical reaction products being produced in the lignitic material during processing.

Ten parts of condensate were withdrawn from vessel 13 after 4 hours. The condensate was contaminated with some of the reaction product from vessel 1 which was removed by filtration. The filtrate on crystallization yielded a considerable quantity of white, slightly yellow tinged solid containing small, irregular, flat, thin crystals similar to those recovered from the reaction product obtained from the reaction chamber 1.

In this example, the burner 2 was provided with a burner nozzle or mixing plate 17, Fig. 4. Fuel gas (e.g., methane or hydrogen) was introduced through a conduit 18 controlled by a valve 19 and passed through an inner tube 20 to the burner nozzle or mixing plate. Oxygen was introduced through conduit 21 and controlled by valve 22 to the concentric outer space 23 which was sealed from the outer space 20 at a point 24 so that mixing of the oxygen and the combustible gas occurs at the mixing plate or burner nozzle 17. The mixture of oxygen and gas was ignited in any suitable manner and flame was propagated in combustion chamber 25. After the burner was ignited it was inserted and fastened into the reaction chamber 27. The flame was observed through the peepsight 26. The flame size was regulated so as to control the heat generation and thereby the reaction temperature. Inlet passageways 28 and 29, controlled by valves 30 and 31, respectively, were provided for the introduction of NO_2 or other oxidizing gases. Inlet passageway 32, controlled by valve 33, was provided for the introduction of other gases, such as air, nitrogen or carbon dioxide, to act as additional chemical reagent or as a coolant. The mixture of oxidizing gases was introduced into the secondary reaction chamber 1 through conduit 34 and the coolant was introduced through conduit 35. A temperature well 36 was provided to receive the thermometer 9 in order to determine the temperature of the mixed gases. The outer shell 27, as well as the other tubular parts of the apparatus from the peepsight 26 to the temperature well 36, were constructed of stainless steel. The remainder of the apparatus was constructed of iron or brass. The pressures of the gases used in this apparatus were nominal and within the limits of the fragile equipment into which they were being introduced. For plant scale operations, the pressures are varied in accordance with the end products to be produced in the lignitic material.

Example II

The apparatus shown in Fig. 3 was employed. 848 parts of $\frac{1}{8}$ inch mesh lignite (Peerless) was placed in the glass reaction chamber 37. Lignite was covered by water to the approximate level shown in Fig. 3 so that the water level was above the upper end 38 of the combustion chamber 39 of the submerged combustion burner 40. Hydrogen was used as the fuel and oxygen was employed to support combustion in the burner. NO_2 and air was introduced into the burner through conduit 41 and passed downwardly in the concentric space 42 between the inner tube 43 carrying the oxygen and hydrogen and the primary reaction chamber or outer shell 44. The flame is generated inside of the combustion chamber

39 and must be submerged in material (liquid or gas) that carries away the heat so as to prevent sintering of the combustion chamber 39. In this case, the heat was carried away by the NO_2 and air introduced by tube 41 into the annular space 42 between tubes 43 and 44 which were installed concentric with each other.

The NO_2 , air, and the products of combustion were simultaneously mixed as they entered the water containing the lignite at point 45. Additional water was added from a separatory funnel 46 in order to maintain the liquid level above the upper end 38 of the burner housing. The temperature was observed by means of thermometer 47. Reaction vapors were passed upwardly through tube 48, thence from condensate trap 49 to condenser tube 50 where they were cooled by condenser 51 and the condensate was collected in vessel 52. The vessel 52 was subjected to vacuum through a tube 53. This vacuum subjected vessels 49 and 37 to vacuum also.

Example III

The apparatus was similar to that shown in Fig. 2 except that a condensate trap was employed between the secondary reaction chamber and the condensate collecting vessel as in Fig. 3. 848 parts of lignite were saturated with water and placed in the secondary reaction chamber. The oxygen-hydrogen flame was lit and NO_2 gas was passed into the wet lignite. The temperature in the secondary reaction chamber was held at around 100°C . to 120°C . for about $1\frac{1}{4}$ hours. The hydrogen and oxygen were then shut off. NO_2 and air were continuously passed through the lignite. Grey brown fumes arose and went through the condensing apparatus. This was continued for another $1\frac{1}{4}$ hours. The gas in the secondary reaction chamber had a temperature of 360°C . before the oxygen-hydrogen flame was shut off, then the temperature dropped to 180°C . The liquid in the condensate collector turned red litmus paper blue and had a strong burnt wood odor resembling creosol. The secondary reaction chamber was lined with a dark brown condensate having a greasy characteristic.

Example IV

100 parts of lignite having an average particle size of about $\frac{1}{8}$ inch was wet with water and then placed in a reaction chamber. Chlorine and air were passed into the reaction chamber. The wet, almost black lignite dried and turned a lighter brown as the water was removed and as the reaction took place. The reaction chamber was heated until the gases in the chamber above the lignite were at a temperature of about 40°C . 83.5 parts of reacted lignite were recovered from the reaction chamber.

Example V

The chlorinated lignite material produced as described in Example IV was mixed with catalytic cycle stock, a petroleum product which had been treated with nitric acid. Nitric acid forms two distinct products with catalytic cycle stock. One is a clear, usually red, rather viscous oil. Depending on the treating conditions, in some of these stocks this oil is yellowish. Under this oil and on top of the acid there is the very viscous, dark red, gummy material. Both the oil and the red gummy material combine with lignite which has previously been partially oxidized by reaction either with NO , NO_2 , nitric acid or a halogen (such as chlorine or bromine).

The mixture was mixed with methanol. This dissolved out the water soluble products and the water remaining in the chlorinated lignite. The methanol was decanted off and contained water soluble products. This resultant, decanted product was evaporated to obtain a homogeneous lacquer-like fluid which was a compound of lignite and petroleum stock. This lignite-oil material was soluble in benzene and acetone.

5

Example VI

100 parts of water-leached lignite having an average particle size of $\frac{1}{8}$ inch were placed in the secondary reaction chamber of an apparatus similar to that used in Example III. Bromine and air were passed through the lignite. The temperature started at 16.8° C. and bromine was introduced until the temperature rose to 30° C. The quantity of air was increased until the temperature dropped to about 20° C. The damp, almost black lignite, lightened until slightly brown in color, indicating the desired reaction had occurred.

Example VII

About 15 to 20 parts of lignite were mixed with 10 parts of concentrated HNO₃. About 20 parts of high sulfur crude and 10 parts catalytically clarified petroleum oil were mixed with 5 parts of concentrated HNO₃. The nitric acid treated lignite was then mixed with the nitric acid treated petroleum. The mixture was dissolved in benzene. The entire mixture became a smooth, thin liquid suitable for use as a fuel and capable of being subjected to cracking, hydrofining, reforming and other operations known in the petroleum industry.

Example VIII

A quantity of lignite was ground to about 25 mesh size, wetted thoroughly with water and after stirring a like quantity of strong nitric acid equal to the amount of water that was used for the wetting was added to the wet lignite. This was stirred thoroughly and heated to a temperature of about 150° F. The lignite become soft and some of it was quite tarry in nature. This product was suitable for conversion to a liquid mixture by mixing it with a catalytic cycle stock. The addition of the powdered lignite to the catalytic cycle stock appeared to promote cracking when the resultant mixture was subjected to cracking temperatures. No coke was formed during this operation.

Example IX

40 parts of raw, undried 20 mesh lignite (Peerless) were treated two hours with NO₂ and air (2% NO₂ and 98% air) at about 85° F. The lignite remaining in the reaction chamber was washed with water and then dried on filter paper. 31 parts of solids remained as a dark brown material after filtration. The filtrate on heating to dryness yielded a considerable quantity (about 10% of the charge) of a white, slightly yellow solid substance. The residue of reacted lignite showed by its appearance that it was no longer ordinary lignite. Subsequent treatments produced several other products quite varied in appearance.

Example X

589 parts of raw undried 20 mesh lignite (Peerless) were treated with NO₂ at temperatures as high as 235° F. using a system similar to that described in Example I. The resultant material was brown but obviously was no longer a true lignite. This altered lignite produced products varying widely in appearance.

While the preferred method of heating involves the direct introduction of hot combustion gases into the reaction zone, it will be understood that indirect heating methods can also be employed.

The temperature at which the lignite is subjected to treatment with oxidizing agents is subject to variation and a substantial variation in the results can be obtained by employing different temperatures. Good results have been obtained at temperatures of 0° C. or below. Good results have also been obtained at room temperatures and at higher temperatures as high as 360° C.

The pressures employed during the treatment of the lignite can be atmospheric, subatmospheric or super-atmospheric pressures. Good results have been obtained at pressures varying from a high vacuum to as much as 125 pounds per square inch gauge.

6

The invention is not limited to the employment of any specific oxidizing agent but especially good results are obtained with nitric acid, nitrogen oxides and free halogens. It will be understood that other oxidizing agents, such as free oxygen, sulfur dioxide, sulfur trioxide, hydrogen peroxide, sodium peroxide, manganese dioxide and potassium permanganate can also be employed.

In the practice of the invention it has been discovered that the presence of moisture promotes the oxidation reaction. Lignites having a water content of from 30% to 40%, or even greater amounts of water, are more reactive toward chemical agents than is the case for the more consolidated coals. The water apparently first serves to dissolve the chemical reactants and then, as the reaction and the passage of gases and chemicals through the lignite removes much of the water, the freshly exposed surfaces of the lignite constitute a large reactive area. The usual practice of drying lignite at high temperatures glazes the surface of the lignite particles. These glazed surfaces tend to slow the reaction times and to cause less complete chemical change within the molecular structure of the lignite when the latter is treated with an oxidizing agent.

If desired, the lignite can be washed with water to remove certain extraneous materials such as inorganic compounds containing calcium, sodium, and sulfur.

The oxidizing and acidifying chemicals alter the chemical composition of the lignite so that a part of the sulfur content can be removed by washing with water after the oxidation. The sulfur washes out mostly as calcium sulfate. Thus, the invention provides a means for removing materials that may be more desirable when separated out before later refining and chemical synthesis. By washing at this stage the ash-producing substances of the lignite can be reduced very substantially, or in many cases, practically eliminated.

After this washing, or directly after acidifying and/or oxidizing, it is sometimes desirable to treat the reacted material with a series of solvents such as water, methanol, benzene, acetone, furfural and/or carbon tetrachloride, to extract and separate out solvent soluble materials for further refinement.

After such refinement and separation, the residual lignite can be further oxidized by the use of oxygen, nitrogen oxides, chlorine, bromine, oxides and other chemicals of the type previously described to bring about additional and more complete chemical changes and rearrangements within the lignite. In fact, it is usually desirable to carry out the oxidation and separation of by-products from the lignite in stages. By the practice of the invention more than 90% of the carbon and hydrogen compounds present in the lignite can be altered to produce desirable and useful products.

The acidic materials obtained by the practice of the present invention can be used as such or esterified with alcohols to produce esters. They can also be converted to other oxygen-containing compounds. The more desirable and useful products produced in and obtainable by further treatment of materials resulting from the invention are compounds containing carboxyl, hydroxyl, carbonyl and aldehydic groups, including polycarboxylic acids, halogenated derivatives of the humic acids, alcohols, ketones, aldehydes, nitrated or nitrited compounds, and unsaturated tarry asphaltic-type compounds. The products of the oxidation, halogenation or nitration treatments can be converted to other desirable and useful products by hydrogenation, which under controlled conditions, causes the reduction of certain groups in the molecular structure.

One of the principal uses for the acidified and oxidized lignite compounds is the production of liquid lignite products with petroleum fractions, such as common fractions known as catalytic cycle stock. Petroleum cycle stock is a petroleum oil which is withdrawn from the cycle during the catalytic cracking of petroleum. These newly

compounded materials can be made viscous and ductile or short and brittle.

Other materials, especially hydrocarbons, including benzene and xylene, can be mixed with the partially oxidized lignite to produce liquid products. For the purpose of the present invention all of these materials, including benzene, xylene, crude petroleum, coal tar products, coke oven tars, natural oils, partially oxidized crude petroleum, partially oxidized coke oven tars, partially oxidized coal tar products, and partially oxidized natural oils are referred to herein as solvents for the partially oxidized lignite because the resultant product is more or less a homogeneous liquid. The formation of the liquid, however, may be due to some synergistic action.

The relative proportions of the partially oxidized lignite and the solvent employed in the preparation of liquid products are subject to variation, depending upon the particular solvent, but are preferably within the range corresponding to a weight ratio of 1:9 to 9:1, and in most cases the optimum results are obtained where the weight ratio is within the range of 2:3 to 3:2.

The invention is hereby claimed as follows:

1. A process of preparing lignite products which comprises subjecting lignite containing its natural moisture to partial oxidation with an oxidizing gas selected from the group consisting of oxides of nitrogen and halogens, to produce water-soluble carboxylic acids, and recovering said carboxylic acids.

2. A process of preparing lignite products which comprises subjecting lignite containing its natural moisture to partial oxidation with an oxide of nitrogen and air to produce water-soluble carboxylic acids, and recovering said carboxylic acids.

3. A process of preparing lignite products which comprises partially oxidizing lignite containing its natural amount of water to water-soluble polycarboxylic acids

with an oxide of nitrogen, heating the lignite during said oxidation, at least partially condensing the gases and vapors given off by the heated lignite and recovering polycarboxylic acids from the resultant condensate.

4. A process of preparing lignite derivatives which comprises subjecting particles of lignite in an aqueous slurry to direct heating by a flame submerged beneath the liquid level of said slurry, introducing an oxidizing gas selected from the group consisting of oxides of nitrogen and halogens into said slurry around the submerged flame to produce water-soluble carboxylic acids, and recovering said carboxylic acids.

5. A process as claimed in claim 4 in which NO_2 and air is introduced into the submerged flame.

6. A process of producing chemicals from lignite which comprises contacting particles of lignite containing at least its natural moisture with nitrogen dioxide and air at an elevated temperature of about 49°C . to 360°C . to convert said lignite to water-soluble carboxylic acids, and contacting the resultant reaction product with water to extract said carboxylic acids.

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