

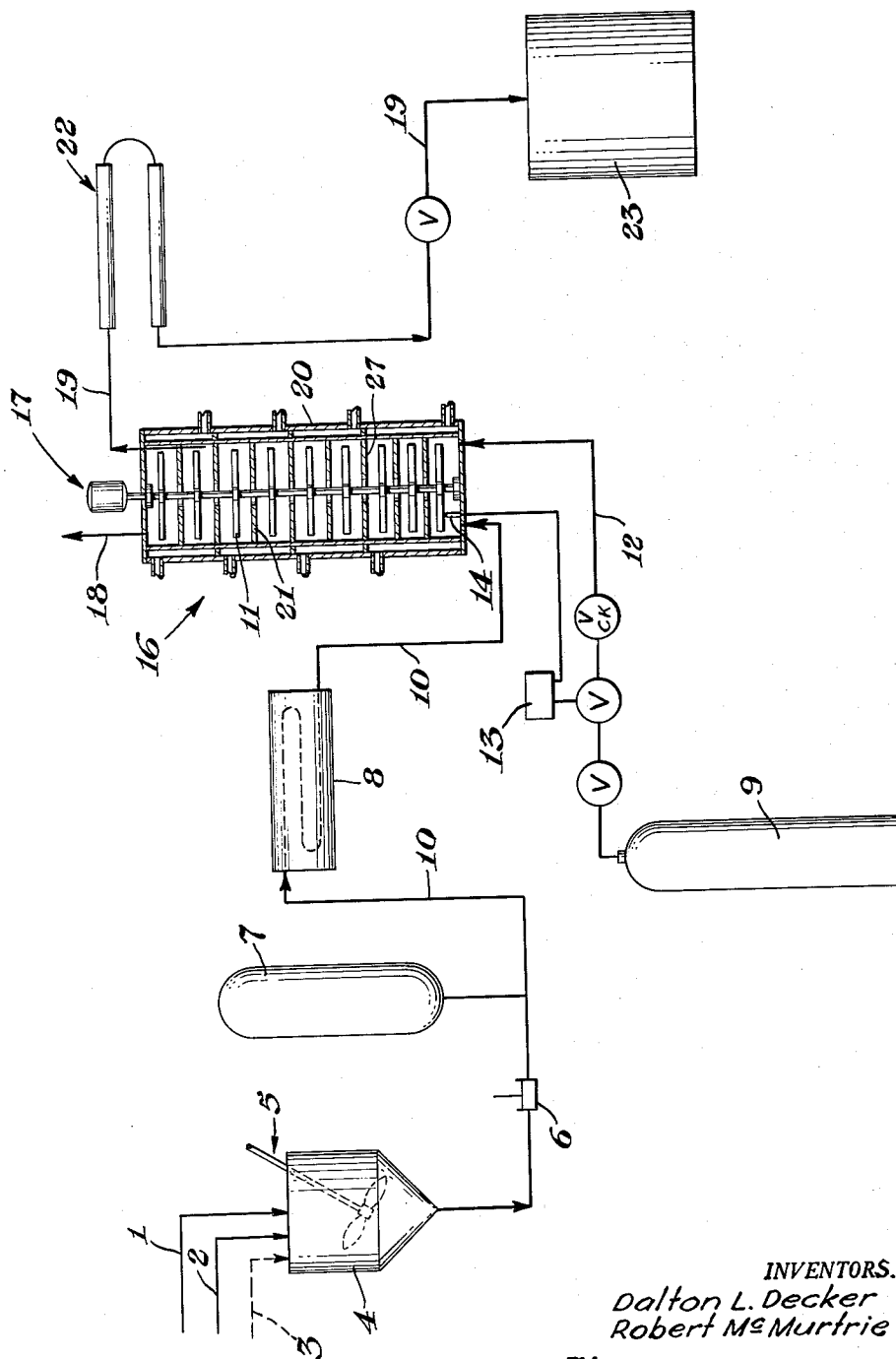
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D. L. DECKER ET AL

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OXIDATION OF CARBONACEOUS MATERIALS IN THE PRESENCE
OF A NON-ALKALINE MEDIUM TO PRODUCE COAL ACIDS

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INVENTORS.

Dalton L. Decker
Robert M. Murtrie

BY

Wriswold & Burdick
ATTORNEYS

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OXIDATION OF CARBONACEOUS MATERIALS IN THE PRESENCE OF A NON-ALKALINE MEDIUM TO PRODUCE COAL ACIDS**Dalton L. Decker and Robert McMurtrie, Midland, Mich., assignors to The Dow Chemical Company, Midland, Mich., a corporation of Delaware**

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6 Claims. (Cl. 260—515)

This application is a continuation-in-part of my co-pending application, Serial No. 5,307, filed January 28, 1960, and now abandoned.

The present invention relates to a method of making coal acids from carbonaceous materials and more particularly it concerns the production of coal acids mixtures by thermal oxidation of said carbonaceous materials in an aqueous slurry.

Coal acids obtained as a product of the partial oxidation of a carbonaceous material are predominantly mixtures of polycarboxylic aromatic acids. They are usually classified into two broad groups designated as the humic acids and water-soluble coal acids. The former are high molecular weight alkaline-soluble, acid precipitable materials believed to be intermediates in processes directed to the production of the lower molecular weight, water-soluble coal acids.

There are several known processes for the production of coal acids of which the water-soluble coal acids are of primary interest. These methods generally involve contacting a carbonaceous material at elevated temperatures with an oxidizing agent such as nitric acid, permanganate in an alkaline solution, or gaseous oxygen in an alkaline solution. These and other known processes employ large amounts of chemical reagents relative to the amount of water-soluble coal acids produced. Also, after obtaining the reaction product mixture, it is usually necessary to add further amounts of reagents before separation of the coal acids can be achieved.

It is, therefore, desirable, as an object of the present invention, to provide a direct process for the production of coal acids mixtures obviating the need to employ large quantities of chemical reagents. It is a further object of the present invention to provide a method whereby carbonaceous materials can be converted to a large proportion of water-soluble coal acids in an aqueous medium. Other objects will become apparent hereinafter as the invention is more fully described.

In accordance with the present invention, coal acids mixtures can be prepared by a process which involves the step of contacting a vigorously agitated aqueous slurry of a carbonaceous material with gaseous oxygen at an elevated temperature for a sufficient period of time to accomplish the formation of coal acids.

In carrying out the invention an aqueous feed slurry is prepared by any of a number of conventional methods. A carbonaceous feed material is subjected to grinding or other pulverizing treatment so as to provide a fine, particulate material which is easily dispersed in water. This material is supplied to a mixing vessel wherein it is dispersed in a sufficient quantity of water to provide the desired slurry concentrate substantially free of alkaline materials. If desired, a small amount of a viscosity-lowering agent may be added to the slurry to decrease pump-

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ing energy requirements. The prepared slurry is then pumped into a preheater wherein it is heated to a desirable pre-reaction temperature.

The preheated slurry of the carbonaceous material is introduced into a suitable gas-liquid phase reactor such as a mechanically stirred reactor or a turbulent flow reactor capable of maintaining vigorous agitation of the slurry. While therein the agitated slurry is contacted with gaseous oxygen at an elevated temperature for a sufficient period of time to accomplish the formation of coal acids. Generally, a residence time within the reaction zone, from about 4 to 30 minutes, preferably about 10 minutes, is desirable. Residence time refers to the period of time required for a particular portion of the slurry to pass through the reaction zone. By "reaction zone" is meant that portion of the reactor in which the agitated slurry is contacted with oxygen at an elevated temperature.

The reaction temperature can range from about 240° to about 320° C. with a temperature range from about 290° to about 300° C. being preferred. Since the oxidation reaction is exothermic, the necessary heat for maintaining the reaction mixture at these temperatures is supplied by the heat of reaction.

To initiate the oxidation reaction of the present invention, it is necessary to preheat the reactor feed slurry containing the carbonaceous material to be oxidized to about 280° C. During subsequent continuous operation, the preheat temperature is lowered to a range from about 240° to about 250° C.

Due to the importance of maintaining the reaction temperature within the aforementioned limits, it is generally desirable to provide cooling means for the reaction zone. Cooling of the reaction zone can be conveniently accomplished by providing a jacketed reaction vessel or reaction tube in which moderate cooling fluids such as saturated steam-water mixtures can be applied to the vessel or tube outer walls.

Reaction pressures required within the reactor to maintain an aqueous liquid phase therein, as a minimum, cannot be less than the vapor pressure of steam over water at the temperature of the reaction. Generally, over the reaction temperature range specified, the operating pressure may range from about 900 to 1,800 pounds per square inch absolute. The reaction can be carried out at substantially greater pressures, but this has little effect on the efficiency of the conversion of the carbonaceous materials to coal acids. Usually it is preferred to operate at pressures of from about 1,500 to 1,800 pounds per square inch absolute.

An operating variable of the present invention, which is interrelated with the residence time of the reactants (oxygen and carbonaceous material) within the reactor and the temperature maintained therein, is the extent of agitation of the reaction system. Vigorous agitation of the reaction mixture is critical for obtaining desirable yields of coal acids and such agitation must be maintained throughout the reaction zone in order to obtain suitable heat and mass transfer rates. If the reactor is of the type that relies on turbulent flow within a pipe to accomplish the desired state of agitation, Reynolds numbers within the turbulent flow zone should be at least about 20,000 and preferably about 75,000 for effective operation. Reynolds numbers within mechanically stirred reactors

at the tip of the impeller should be at least about 100,000 for effective operation.

The product removed from the reaction zone substantially comprises insoluble unreacted carbonaceous materials, alkali-soluble and acid-precipitable humic acids, water-soluble coal acids, carbon dioxide and water. By virtue of the varying properties of its components, the effluent product can be separated into its parts by methods well known in the art such as precipitation, filtration, liquid-liquid extraction, leaching, fractionation and the like. The particular method or combination of methods employed will depend upon the desired product separation and purity required.

Generally, the product of prime interest is the water-soluble coal acid mixture which, as a mixture, predominantly comprises polyfunctional polycarboxylic aromatic acids having an average carboxylic acid group functionality of about 2.5 to 5 and an average equivalent weight based on the carboxylic acid group functionality of about 75 to 90. This mixture can be separated in toto as a mixture with a solvent such as methyl ethyl ketone or it can be separated by various means into its individual components. O. H. Grosskinsky et al., United States Letters Patent 2,785,198, teaches a process for separating monocyclic aromatic polycarboxylic acids from a crude oxidation product of carbonaceous materials.

In some instances of application, the effluent product of the process of the present invention comprising both humic acids and water-soluble coal acids is a desirable utile product in itself without further separatory treatment. Such an admixture of coal acids is, for example, an effective additive for decreasing the viscosity of slurries such as drilling muds for use in the petroleum industry.

The aqueous slurries employed in the present invention contain a finely ground or pulverized carbonaceous material in an amount from about 2 percent to as much as 50 percent or more by weight of the total slurry. Preferably, the slurry contains from about 5 to 10 percent by weight of the carbonaceous material being oxidized. Slurries containing higher amounts of the carbonaceous material are oxidizable to coal acids but the percent yield of such acids from a single pass within the reactor is substantially decreased at higher slurry concentrations.

Carbonaceous materials suitable for oxidation by the method of the present invention for the production of coal acids include a variety of coals or other similar sources of condensed aromatic nuclei such as the anthracite coals, bituminous coals, lignites and the like, and includes carbonization products such as coke. By-product carbonaceous materials such as petroleum coke and charcoal are also operable. More particularly, Reading anthracite, Pocahontas No. 3 low volatile bituminous, Harmon medium volatile bituminous, Sunnyside No. 8 high volatile bituminous and Island Creek high volatile bituminous are exemplary of coals which can be employed in the present invention to produce coal acids.

Oxygen supplied to the reaction zone can be provided as in air or preferably as a relatively pure component. Generally, amounts of oxygen employed in the present invention to produce coal acids range from about 1.5 to about 4.0 times the weight of the carbonaceous material employed. Lesser amounts of oxygen can be employed when less than the maximum conversion of the carbonaceous material to coal acids is desirable.

A representative process for the production of coal acids incorporating the present invention is shown schematically in the accompanying drawing.

A finely ground carbonaceous material 1 and water 2 are introduced into a slurry feed tank 4 equipped with a mechanical mixer 5. Optionally a viscosity-lowering agent 3 may be introduced. The thoroughly mixed slurry is forced along a feed pipe line 10 by means of a positive displacement pump 6 into a preheater 8 operating on superheated steam. In order to alleviate pressure pulsations in the feed line 10, the latter is connected to

a surge tank 7. After leaving the preheater 8, the feed line discharges the slurry mixture directly into a multistage mechanically stirred reactor 16. Oxygen is supplied to the reactor from oxygen storage 9 through an oxygen line 12 equipped with valve regulator 13 responsive to a thermocouple 14 within the reaction zone of the reactor. The multistage reactor is equipped with a multiple turbine mixer 17 having turbine blades 11 mounted thereon which provide mixing for each stage of the reactor. Individual cooling jackets 20 are provided for four areas of the reaction zone in order to accommodate variances in cooling requirements. Stage dividers within the reactor vessel are flat ring baffles 21 and 27 with a center hole substantially larger than the mixer turbine drive shaft. Passage of materials from stage to stage within the reactor is effected through these center holes in the baffles. A safety discharge vent 18 and effluent product line 19 are provided at the top of the reactor 16. The effluent product line 19 passes through a cooler 22 and thence to a receiving tank 23.

In a representative operation, a feed slurry containing 5 percent by weight of pulverized Pocahontas No. 3 coal (200 mesh) in water was prepared in the mixing tank. This slurry was pumped by means of a positive displacement pump at a pressure of 1,500 pounds per square inch into a three-gallon, nitrogen-filled, surge tank and thence into the preheater comprising a 64 foot coil of ¼ inch I.D. tubing which is heated by saturated steam contained in a surrounding steam jacket. Within the preheater, the temperature of the slurry was increased to 270° C. for the start-up period and to about 250° C. after continuous operation conditions had been achieved. From the preheater the feed slurry passed into the bottom of the turbine-stirred reactor vessel at a rate of about 150 pounds of slurry per hour which provided a residence time within the reactor vessel of about 10 minutes. The feed slurry was contacted with oxygen introduced at a rate of about 19 pounds per hour through an opening in the bottom of the turbine-stirred reactor. The oxygen supply was regulated by means of a control valve device activated by a thermocouple located within the reaction zone.

The slurry and oxygen passed concurrently through a series of nine stages within the reaction vessel. The reaction vessel, which had a 5 inch inside diameter and a height of 5 feet, was divided into stages by means of a series of uniformly spaced flat ring baffles. Within each stage, the feed slurry and oxygen were mixed by turbines rotating at 600 r.p.m. providing Reynolds numbers of about 750,000. The pressure within the reaction vessel was maintained at about 1,500 pounds per square inch absolute and the temperature ranged during the course of the reaction from about 280° to 300° C. During operation, the reactor was run full to prevent the accumulation of explosive gas mixtures.

The effluent product taken from the top of the reactor was cooled and subjected to separatory treatment to recover the water-soluble coal acids component. The crude product was first acidified with sulfuric acid to a pH of about 1. The insoluble unreacted coal residue and acid-insoluble humic acids were then allowed to settle out of the crude product in a settling tank. Next, the water solution of the coal acids was concentrated by evaporation and subsequently subjected to liquid-liquid extraction with methyl ethyl ketone. The methyl ethyl ketone extract was then evaporated to dryness leaving a residue which was a substantially pure mixture of water-soluble coal acids in a yield of about 10 percent based on the total converted carbon.

Alternatively, the effluent product can be filtered to remove unreacted coal and insoluble humic acids to thereby provide a water solution of relatively pure water-soluble coal acids. The water-soluble coal acids can then be isolated as by evaporating such a solution to dryness.

Results of additional runs are tabulated below. These runs were carried out in a similar manner to that of the foregoing run with the exception of certain variations in pressure, temperature and feed rates as indicated.

TABLE

Run	Reactor Pressure, p.s.i.a.	Reactor Temp., ° C.	Coal Feed Rate, lb./hr.	Oxygen Feed Rate, lb./hr.	Reactor Effluent, lb./hr.	Pounds per Pound of Coal Input		
						Unreacted Material	Humic Acids	Water-Soluble Coal Acids
2-----	1,700	290-310	6.5	23	135	0.27	0.04	0.13
3-----	1,700	290-310	6.5	23	135	0.29	0.03	0.13
4-----	1,700	290-310	6.5	23	130	0.14	-----	0.17
5-----	1,700	290-310	6.5	23	130	0.39	-----	0.14

We claim:

1. A process for the production of coal acids which comprises the steps of forming a non-alkaline, aqueous slurry containing from about 2 to about 50 percent by weight of a finely divided carbonaceous material, vigorously agitating the slurry so as to achieve Reynolds numbers of at least 20,000 therein and simultaneously therewith, while maintaining the temperature of the slurry at a temperature within the range from about 240° to about 320° C., and under autogenous pressure, contacting the non-alkaline slurry with oxygen in an amount of from about 1.5 to about 4.0 times the weight of carbonaceous material present for a period of time from about 4 to 30 minutes, whereby coal acids are produced.

2. A process for the production of coal acids which comprises the steps of heating a non-alkaline, aqueous slurry containing from about 2 to about 50 percent by weight of finely divided carbonaceous material up to a temperature of from about 240° to about 280° C., vigorously agitating the slurry so as to achieve Reynolds numbers of at least 20,000 therein and simultaneously therewith, while maintaining the temperature of the slurry at a temperature within the range from about 240° to about 320° C. and under autogenous pressure, contacting the non-alkaline slurry with oxygen in an amount of from about 1.5 to about 4.0 times the weight of carbonaceous material present for a period of time from about 4 to 30 minutes, whereby coal acids are produced.

3. A process for the production of coal acids which comprises the steps of heating a non-alkaline, aqueous slurry containing from about 2 to about 50 percent by weight of a finely divided carbonaceous material up to a temperature from about 240° to about 280° C.; passing the heated slurry through a tube reactor at a rate such as to achieve Reynolds numbers of at least 20,000 therein and simultaneously therewith, while maintaining the slurry at a temperature from about 240° to about 320° C. and under autogenous pressure, contacting the non-alkaline slurry with oxygen in an amount of from about 1.5 to about 4.0 times the weight of carbonaceous material present for a period of time from about 4 to about 30 minutes, whereby coal acids are produced.

4. A process for the production of coal acids which comprises the steps of heating a non-alkaline aqueous slurry containing from about 2 to about 50 percent by weight of a finely divided carbonaceous material up to a temperature from about 240° to about 280° C.; passing the heated slurry through a turbine-stirred reaction zone wherein Reynolds numbers of at least about 100,000 at the tip of the impeller are maintained and simultaneously

therewith, while maintaining the slurry at a temperature from about 240° to about 320° C. and under autogenous pressure, contacting the non-alkaline slurry with oxygen in an amount of from about 1.5 to about 4.0 times the

weight of carbonaceous material present for a period of time from about 4 to about 30 minutes, whereby coal acids are produced.

5. A process for the production of coal acids which consists essentially of the steps of forming an aqueous slurry substantially free of alkaline materials and containing from about 2 to about 50 percent by weight of a finely divided carbonaceous material, vigorously agitating the slurry so as to achieve Reynolds numbers of at least 20,000 therein and simultaneously therewith, while maintaining the temperature of the slurry at a temperature within the range from about 240° to about 320° C., and under autogenous pressure, contacting the slurry substantially free of alkaline materials with oxygen in an amount of from about 1.5 to about 4.0 times the weight of carbonaceous material present for a period of time from about 4 to 30 minutes, whereby coal acids are produced.

6. A process for the production of coal acids which consists essentially of the steps of forming an aqueous slurry substantially free of alkali hydroxides and containing from about 2 to about 50 percent by weight of a finely divided carbonaceous material, vigorously agitating the slurry so as to achieve Reynolds numbers of at least 20,000 therein and simultaneously therewith, while maintaining the temperature of the slurry at a temperature within the range from about 240° to about 320° C., and under autogenous pressure, contacting the slurry substantially free of alkali hydroxides with oxygen in an amount of from about 1.5 to about 4.0 times the weight of carbonaceous material present for a period of time from about 4 to 30 minutes, whereby coal acids are produced.

References Cited by the Examiner

UNITED STATES PATENTS

2,193,337	3/1940	Leicester	-----	260—528
2,461,740	2/1949	Kiebler	-----	260—515
2,786,074	3/1957	Goren	-----	260—514

OTHER REFERENCES

60	Franke et al., "Industrial and Engineering Chemistry," vol. 44, No. 11 (1952), pp. 2784-2792.
65	Weissberger, "Techniques of Organic Chemistry," vol. III (1950), Interscience, New York, pp. 100-101.
	LORRAINE A. WEINBERGER, <i>Primary Examiner</i> .
	LEON ZITVER, <i>Examiner</i> .
	R. E. MESSA, T. L. GALLOWAY, <i>Assistant Examiners</i> .