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Production of Organic (Carboxylic) Acids from Coals Through Liquid-Phase Oxidation of Coals: New Route for Utilizing Low-Rank Coals

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Abstract: The potential of producing organic carboxylic acids from low-rank coals (lignite) using an oxidizing agent, hydrogen peroxide (H_2O_2) has been investigated. Five samples of pulverized lignite coal (C = 65.2-74.8% on d.a.f. basis) of different sizes were contacted with 20 volumes of 30% H_2O_2 at different constant temperatures and residence times to yield organic acids of varying yields and concentrations. The analytical and graphical results indicate that an increase in reaction temperature and residence time and a reduction in particle size increases the yield; selectivity and carbon conversion to the organic carboxylic acid with a maximum at a temperature of 60°C, a residence time of 24 h and a particle size range of 0.1-0.5 mm beyond which they (optimum reaction variables) reduce rapidly. The production at these optimum conditions permits the carbon conversion to water-soluble organics to reach 0.75 with a selectivity of 3.0 in which about 50% were small molecules: methanol, formic acid, acetic acid, glycolic acid and malonic acid with a yield of approximately 9.72 g /20 g of coal as is shown in the study. The high yields, selectivity and conversion to organic carboxylic acids are closely related to the structure of the low rank coals and the strength of the aqueous hydrogen peroxide (H_2O_2).

Key words: Oxidation of coals, liquid-phase, low-rank coals, conversion, organic acids, Nigeria

INTRODUCTION

The term low-rank coals as used in the international classification system is defined as coals with a gross calorific value of <5700 kcal kg^{-1} (10260 Btu/lb or 23.86 MJ kg^{-1}) on a moisture and ash-free basis. Low-rank coals according to the American Society of Mechanical Engineers (ASME) are primarily sub-bituminous and lignites coals which are generally, low in sulfur (Onwu, 1999). The structures, constituents and properties of low rank coals have imposed serious problems and limitations on their utilization and uses. However, their low sulfur content makes them very useful as power plant fuels in place of high-sulfur Eastern coals (Nickels, 1993; Sheldon, 1995; Derbyshine and Stansberry, 1987). Also, chemical studies carried out on low-rank coals show that they have high oxygen contents in which about two-third are bonded carboxyl, acetyl, hydroxyl and methoxyl groups that exist in low rank coals (brown and lignite) (Kent, 1992). Approximately 90%, about 1000×10^6 ton of the proven total coal reserves in Nigeria for instance is low-rank coals (Onwu, 1999). Coals in the country are underdeveloped and underutilized. Even though, the proven coal reserve is vast and enormous, there is no consistent and comprehensive energy policy on the part of government. Coal has been abandoned and cancelled as a current primary energy resource only because of lack of ways for utilizing it. There are numerous methods of producing organic carboxylic acids, viz. Oxidation of primary alcohols or aldehydes; hydrolysis of esters, amides, acid chlorides and acid anhydride; hydrolysis of nitriles which are prepared from alkyl halides; reaction of Grignard reagents with CO_2; acetoacetic ester synthesis; malonic ester synthesis; liquid-phase catalytic hydrocarbon oxidation; methanol carbonylation, vapour-phase catalytic oxidation of aldehydes diluted with steam at 250°C; liquid-phase catalytic ethylene oxidation using sulfate compounds (Seghin and Bresler, 1981; Lowry, 1963; Cundy and Maples, 1982; Sheldon, 1995; Nickels, 1993). Among all these methods, liquid-phase oxidation of low-rank coals using H_2O_2 is the most economical in terms of raw material utilization and production costs (Emanuel *et al*., 1967). The sole aim of this research is to develop a new route for the utilization

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of low-rank coals (Given, 1961; Dryden, 1963; Wender *et al.*, 1981; Dry, 1987; Wender, 1987; Kirk-Othmer, 1947; Anderson and Tillman 1979; De Levie, 1997; Fieser and Fieser, 1961; Ike, 2001; Suubera *et al.*, 1977).

The route is the production of small molecular weight carboxylic acids (formic acid, acetic acid, glycolic acid and malonic acid) from low-rank coals (lignite) at low temperatures and under ambient pressure, through liquid-phase oxidation (oxidative degradation) using hydrogen peroxide solution, H_2O_2. In the liquid-phase oxidation of coals, there exists a series of complex, homogeneous and heterogeneous, exothermic and endothermic reactions simultaneously. These are reactions of carbon with volatile matters, hydrogen peroxide, reactive intermediate products and oxidation products, mainly low-boiling constituents. The reactions involve aldehydes, formic and acetic acids, acetone, water, methanol and methyl ethyl ketone, oxygen, hydrogen, carbon oxides, methyl formate, etc., produced at the earlier stages. The reactions involved are as follows:

$C+H_2O_2 \quad HCOOH$ 1
$C+H_2O_2 \quad CO+H_2O$ 2
$C+2H_2O \quad CH_3OOH$ 3
$CO+3H_2 \quad CH_4+H_2O$ 4
$2C+3H_2 \quad C_2H_6$ 5
$CH_4+H_2O \quad CH_2O+2H_2$ 6
$CH_4+H_2O_2 \quad CH_3OH+H_2O$ 7
$2CH_4+H_2O_2 \quad 2CH_3OH+H_2$ 8
$CH_2O+H_2O_2 \quad HCOOH+H_2O$ 9
$C_2H_6+H_2O_2 \quad CH_3COOH+2H_2$ 10
$CH_3COOH+H_2O \quad HOCH_2COOH+H_2$ 11
$CH_3COOH+HCOOH \quad H_2C(CO_2H)_2+H_2$ 12

The extent and rates of the above reactions are dependent on certain conditions, primarily; temperature, pressure, gaseous environment and hydrodynamic conditions which have been of considerable interest for years now. The developed reactive fragments react homogeneously with other fragments or heterogeneously with the remaining coal structure.

MATERIALS AND METHODS

A logical step-by-step approach was adopted in the laboratory manufacture of low molecular weight organic acids from a pulverized coal through liquid-phase oxidation. Five samples of pulverized lignite coal each of different particle sizes 3.0, 1.0, 0.8, 0.5 and 0.1 mm were used. Five 20 g samples of one particle size were each contacted with 400 cm^3 of 30% H_2O_2 in an isothermal stirred batch reactor maintained at one particular constant temperature. The five reactors were monitored at five different residence times (6, 12, 18, 24 and 28 h). This procedure was repeated with other samples in five reactors maintained at another constant temperature and monitored for the same five different residence times until five constant temperatures (40, 60, 80, 100 and 120°C) were considered. The entire process was repeated using five 20 g samples of the remaining four particle sizes for the five different constant temperatures and monitored at each temperature for the five different residence times. At the end of each residence time experiment, 56 cm^3 of water was added to dilute and dissolve all the water-soluble organics so as to enhance their separation. The mixtures were transferred into a separating vessel where separation was achieved by differences in density after strong agitation.

The coal residue in each case was weighed after drying with air and the weights were recorded. About 5 mL each of the various water soluble and insoluble and 25 or 10 cm^3 of the various specimens (water soluble organics) were used for the standard qualitative and quantitative analytical tests, respectively (De Levie, 1997). The results of the quantitative analysis (yield, selectivity and conversion to organic carboxylic acids) were found and various graphs were plotted as shown in the results (Fig. 1-9).

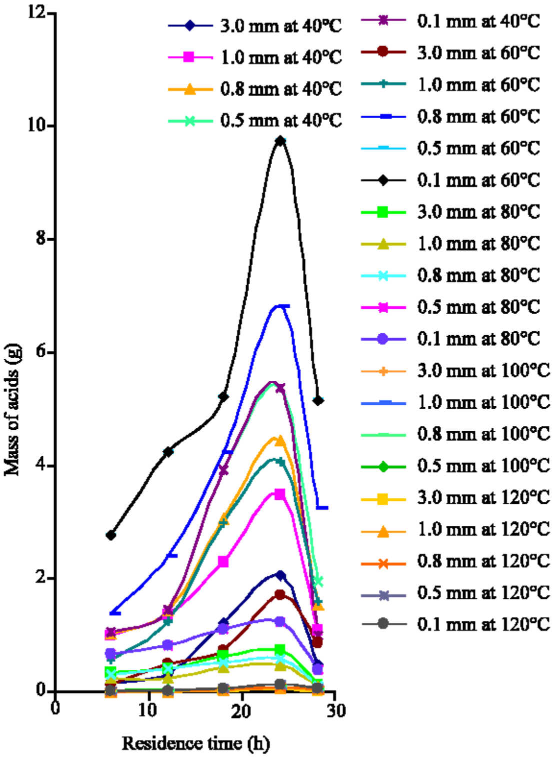

Fig. 1: The mass of carboxylic acid against residence time at 40, 60, 80, 100, 120°C

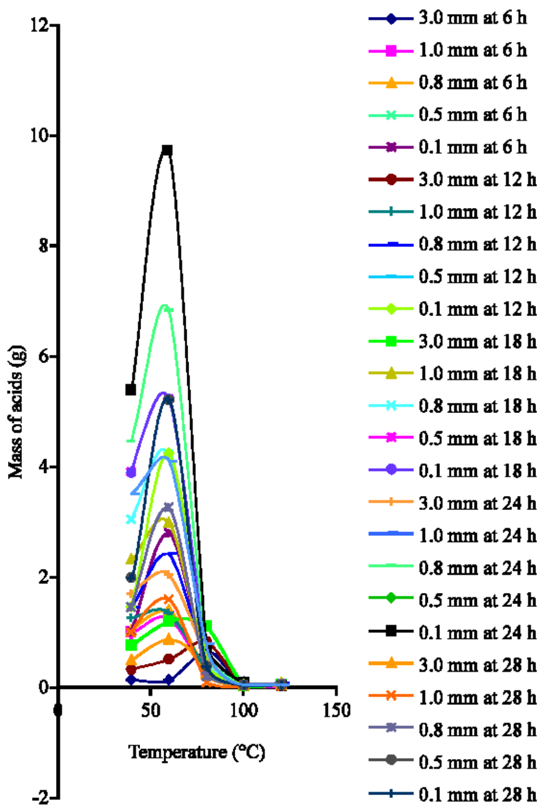

Fig. 2: The mass of carboxylic acid against temperature (°C) for 6, 12, 18, 24 and 28 h

RESULTS AND DISCUSSION

Within 3 min of contacting the pulverized lignite coal with 30% H_2O_2 at a constant temperature, the volatile matters (hydrogen, carbon monoxide, methane, other hydrocarbons, air vapours, carbon dioxide and water vapour) were expelled. Colour changes occurred basically as a result of both thermal and chemical bleaching which reach a maximum at longer residence times (18-28 h) when reactions must have been completed at low temperatures.

The low boiling constituents earlier formed are readily oxidized to acetic and formic acids. The biacetyl which is noticeable in the products, even in extremely low concentrations are oxidized to acetic acid by H_2O_2 at reduced temperatures.

The malonic and glycolic acids which are thermally unstable are mainly formed by the replacement of one Hydrogen atom (H) of acetic acids with carboxyl and hydroxyl groups (COOH and OH), respectively. At temperatures of 40, 60 and 80°C with particle sizes of 0.1-0.5 mm, the carbon conversion to water soluble organics was up to 0.3 for residence times between 0-18 h.

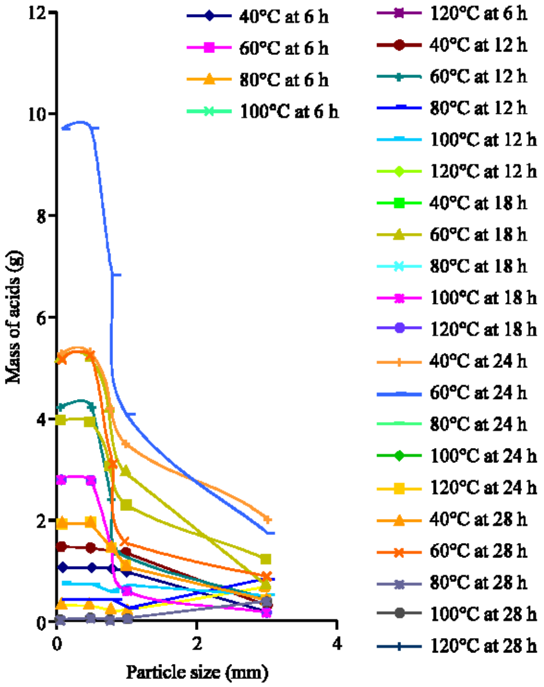

Fig. 3: The mass of carboxylic acid against particle size (mm) for 6, 12, 18, 24 and 28 h

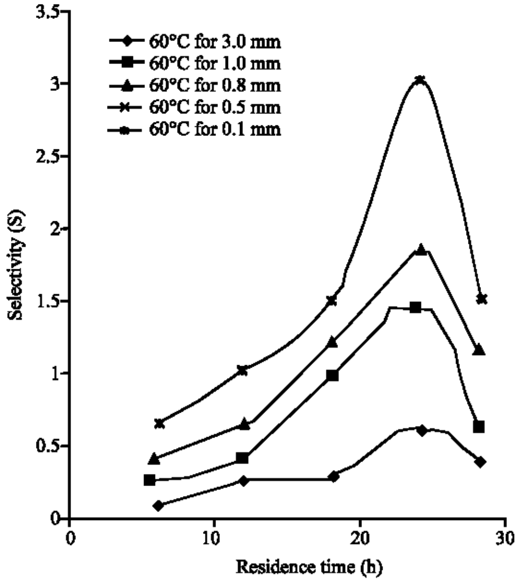

Fig. 4: The Selectivity (S) against residence time at 60°C

The carbon conversion to water soluble organics rose to 75% within 24 h residence time. Longer residence times are needed for complete reaction at low temperatures. At a temperature of 100°C, 50% of the carboxylic acid functions, oxygen functions, thermally unstable fatty acids (glycolic and malonic) and hydroxyl functions of coals and earlier formed unstable acids are

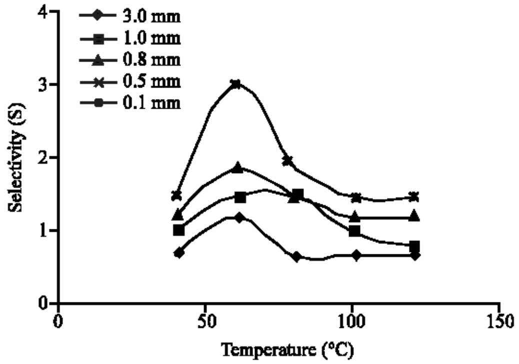

Fig. 5: The Selectivity (S) against temperature for 24 h

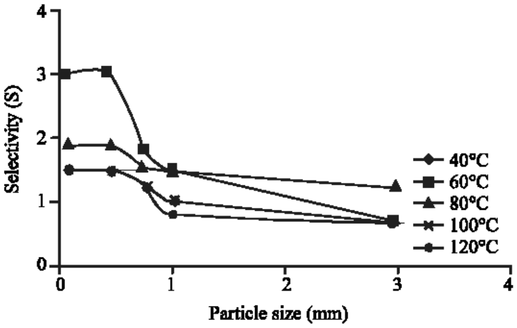

Fig. 6: The Selectivity (S) against particle size for 24 h

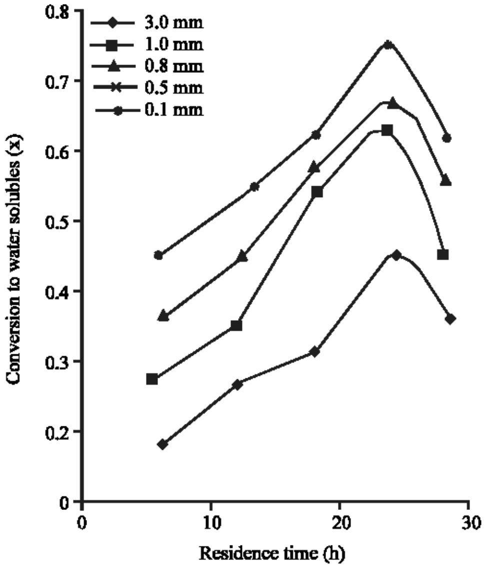

Fig. 7: The conversion to water soluble against residence time at 60°C

lost as oxides of carbon and as water, through thermal decarboxylation and dehydration which reduce the yields and selectivity of the organic carboxylic acids. The graphical and analytical results obtained show that the amount (mass) of organic carboxylic acids produced is directly proportional to the temperature and residence time and indirectly proportional to the particle size but attains the maximum at optimum temperature of 60°C, residence time of 24 h and particle size range of 0.5-0.1 mm beyond which it starts reducing. These optimum conditions allow the fractional conversion of water soluble organics, XA to reach 0.75 with selectivity of 3.0 g/20 g of coal in which about 50% were small molecular weights; methanol, formic acid, acetic acid, glycolic acid and malonic acid. The optimum yield of the low molecule carboxylic acid obtainable at this optimum process condition is 9.72 g/20 g of coal (Fig. 1).

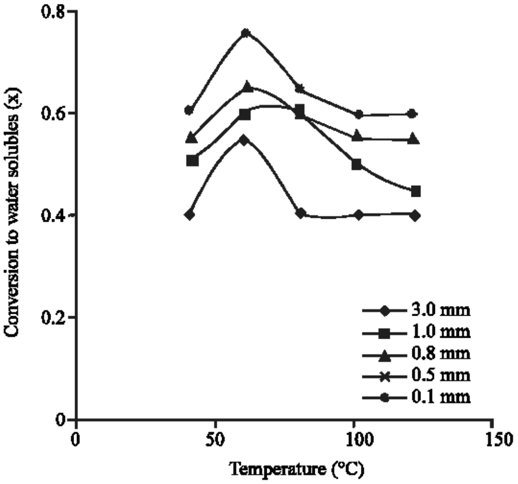

Fig. 8: The conversion to water soluble against temperature at 24 h

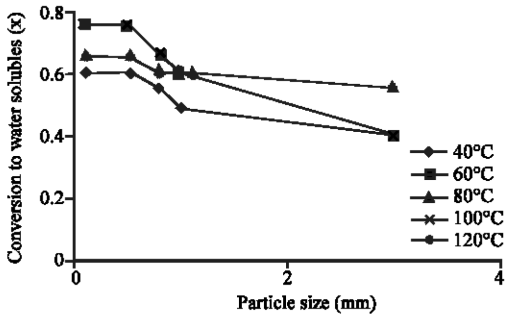

Fig. 9: The conversion to water soluble (X) against particle size for 24 h

As the optimum process variables, especially the temperature are exceeded, the conditions then favour the yield and selectivity of many by-products. The decomposition of the fatty acids and secondary reactions are favoured. Decarboxylation and dehydration reactions predominate, liberating carbon oxides and water lower molecular weight organics especially, aliphatic compounds are lost. Also, the coal structures are destroyed by heat to produce methane, other alkanes, polycyclic aromatics, phenols and nitrogen-containing compounds, etc. The losses in weight of coal residues is a result of chemical conversions and the removal of volatile matters which increase with increase in temperature and residence time and also increase with reduction in particle size of the coal sample.

CONCLUSION

Low molecular weight organic carboxylic acids are produced in appreciable quantity from low-rank coals through liquid-phase oxidation and degradation of coals by low strength aqueous hydrogen peroxide, H_2O_2 at relatively mild reaction conditions. The optimum process conditions for optimum conversion of 75%, yield of 9.72 g/20 g of coal and selectivity of 3.0 g/20 g of coal are 0.1-0.5 mm particle size range, 60°C temperature and 24 h residence time. The high yield of these compounds is primarily related to the structure of low-rank coals and the strength of the aqueous hydrogen peroxide, H_2O_2 hence, a low strength of about 30% H_2O_2 and a low-rank coal are to be used. This process route is well suited for industrial manufacture of low molecular weight organic carboxylic acids. Thus, this is a new viable route for utilizing abundantly available and abandoned low-rank coals in Nigeria.

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