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BIOPITCH PRODUCED FROM EUCALYPTUS WOOD PYROLYSIS LIQUIDS AS A RENEWABLE BINDER FOR CARBON ELECTRODE MANUFACTURE

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Abstract - Interest in biomass as a clean source of fuel, chemicals and materials is growing fast. What is attractive about biomass is its renewability and that it is CO_2 balanced and sulfur-free. Biomass pyrolysis produces charcoal, bio-oil and gases in different proportions, depending on the technology and raw material used. In this study biopitch, a substitute for fossil pitches in electrodes, was produced from bio-oil distillation in bench-scale equipment. Biopitch and charcoal were mixed and thermically modified to give prebaked electrodes. The physico-chemical and mechanical properties of the biopitch and final electrodes were measured and compared with those of coal tar and petroleum materials. Despite their similar application, biomaterials are structurally and chemically different from minerals. The oxygen content in biopitch is *ca* 20 wt% and in mineral pitches it is no more than 2 wt%. Characterization experiments for electrode samples measured electrical resistivity, Young's modulus, rupture strength, density, porosity and proximate analysis.
Keywords: biopitch, biomass, pyrolysis, bio-oil, electrode

INTRODUCTION

Probably the biggest challenges for industrialized society will be to decrease pollutant emissions and spread development more homogeneously throughout the world. But how can this occur when energy consumption is extremely concentrated and based mainly on fossil sources? Biomass (crops, forests, etc.) can provide a solution. It is worldwide available. It is the oldest source of energy used by humans; and it is able to supply all kinds of fuels, chemicals and materials, which we currently obtain from petroleum, coal or natural gas. The conversion of biomass feedstock into valuable products is now feasible due to new technologies. New concepts in fast pyrolysis and bio-oil catalytic upgrading are examples of processes suitable for thermochemical conversion of biomass (Hall, 1997; Rocha and Luengo, 1998).

The economies of many developing countries are based on the use of biomass as the primary source of energy; however, in most cases obsolete conversion processes are still used. Firewood and sugar cane are important feedstocks in the Brazilian economy, which has undergone huge technological improvements over the past years (Freitas and Moreira, 1997).

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The use of organic liquids from carbonization of the wood to produce biopitches, which can then be mixed with charcoal to make electrodes, is a creative way to replace both pitch and coke from fossil sources. Data on H^1 and C^{13} NMR and FT-ir show that the oxygenated groups in bio-oil are mainly carbonyl, hydroxyl, carboxyl and metoxyl (Pasa *et al.*, 1997; Rocha, 1997). Also, high polar compounds were found in biopitches by HPLC and liquid chromatography. They are mainly substituted monoaromatics, while the most abundant species in coal tar pitches are polyaromatics (Luengo *et al.*, 1995; Coutinho and Luengo, 1997; Carazza *et al.*, 1994).

There are already many applications for materials from biomass. Charcoal is widely used as activated carbon. Every year about 130,000 tons of wood and 35,000 tons of coconut shells are transformed into activated carbon worldwide (Rodríguez-Reinoso, 1997). Charcoal is used as an iron reducer for the production of pig iron and high quality steel and as a metal reducer for the production of iron alloys, particularly in Brazil and Australia (Fung, 1997; ABRACAVE, 1996). The use of wood tar in the naval industry dates back to the 17^{th} century, but it was replaced by bitumen in the last century (Newman and Newman, 1997). More recently, phenolic derivatives from bio-oil were found to partly replace petrochemical phenol in PF resins (Chum *et al*., 1993; Rocha *et al*., 1999).

There is a wide range of industrial applications for carbon electrodes from traditional materials. Prebaked electrodes are used in electric furnaces to reprocess scrap steel and melt metal alloys and nuclear reactors use high purity graphite to absorb neutrons. The aluminum industry consumes many tons of pitch and coke annually as a green electrode to transform bauxite ore by the electrolytic process. Silicon for semiconductors, new batteries, aircraft structures and composite-like metal intercalated with graphite are some specific applications where a high degree of purity is required and metal or sulfur impurities from oil and coal can contaminate the final product. In these cases, biomass-derived carbons may have important and successful applications (Marsh, 1997; Luengo *et al.*, 1994; Coutinho and Luengo, 1994).

EXPERIMENTAL

The eucalyptus wood bio-oil used in this study was produced by slow pyrolysis in a continuous retort. It is insoluble in water and had previously been separated from the acidic aqueous phase by decantation. It has a density of 1.163 $g.cm^{-3}$, a higher heating value of 21.3 $MJ.kg^{-1}$ (5,100 $kcal.kg^{-1}$), a viscosity of 43.5 cP at 40^{o}C, a pH of 2.75 at 25^{o}C and a humidity of 15% (Rezende et al., 1994).

Heat treatment of the bio-oil was carried out in the equipment shown in Figure 1, a 10-liter bench distiller/polymerizer. It consists of a resistively heated and well-swept stainless steel reactor (D-01) equipped with a mixer (G-01), temperature control (A-01), a thermocouple to measure the temperature inside the liquid (F-01) and a valve to discharge the material (E-01). The volatile material is condensed in a heat exchange (C-01) and recovered in a 5-liter reservoir (D-02). A vacuum pump (B-01) maintains the system at a low pressure. A liquid nitrogen trap (C-02) protects the pump against oil vapors and a pressure gauge (H-01) monitors reactor pressure. E-02, E-03 and E-04 are valves for distilled light-fraction discharge, closing the pump circuit and opening the system to atmospheric pressure, respectively. The temperature, heating rate and pressure were controlled during biopitch production. Temperatures in the range of 250 to 270^{o}C, heating rates of 2 to 50 C. min^{-1} and reduced pressures up to 0.05 MPa were applied. Once the system reached the final temperature, biopitch was discharged at room temperature with no residence time. Each run processed about 7 kg of bio-oil and yielded an average of 50 wt% in biopitch. Experimental conditions for the samples are shown in Table 1.

Biopitch is a residual fraction; it is black and solid at room temperature. Characterization experiments for this material measured softening point (ring & ball method, ASTM D36-70), specific gravity (displacement method, ASTM D71-72a), ash content (ASTM D2415-66), Conradson cooking value (ASTM D2416-73), quinoline insoluble (ASTM D2318-66), toluene insoluble (ASTM D2317-66), acetone insoluble (DIN 53700), higher heating value and elemental analysis.

Green carbon electrode samples were prepared with a mixture of biopitch and ground charcoal in a hot modeling under 60 MPa of pressure (Coutinho and Luengo, 1994). Biopitch as the binder and charcoal, also from eucalyptus wood, formed a compact cylindric electrode calcined at 1000^{0}C followed by graphitization at 2700^{0}C. Electrical resistivity, Young's modulus, rupture strength, density, porosity and proximate analysis were determined for the final electrodes (Coutinho et al., 2000).

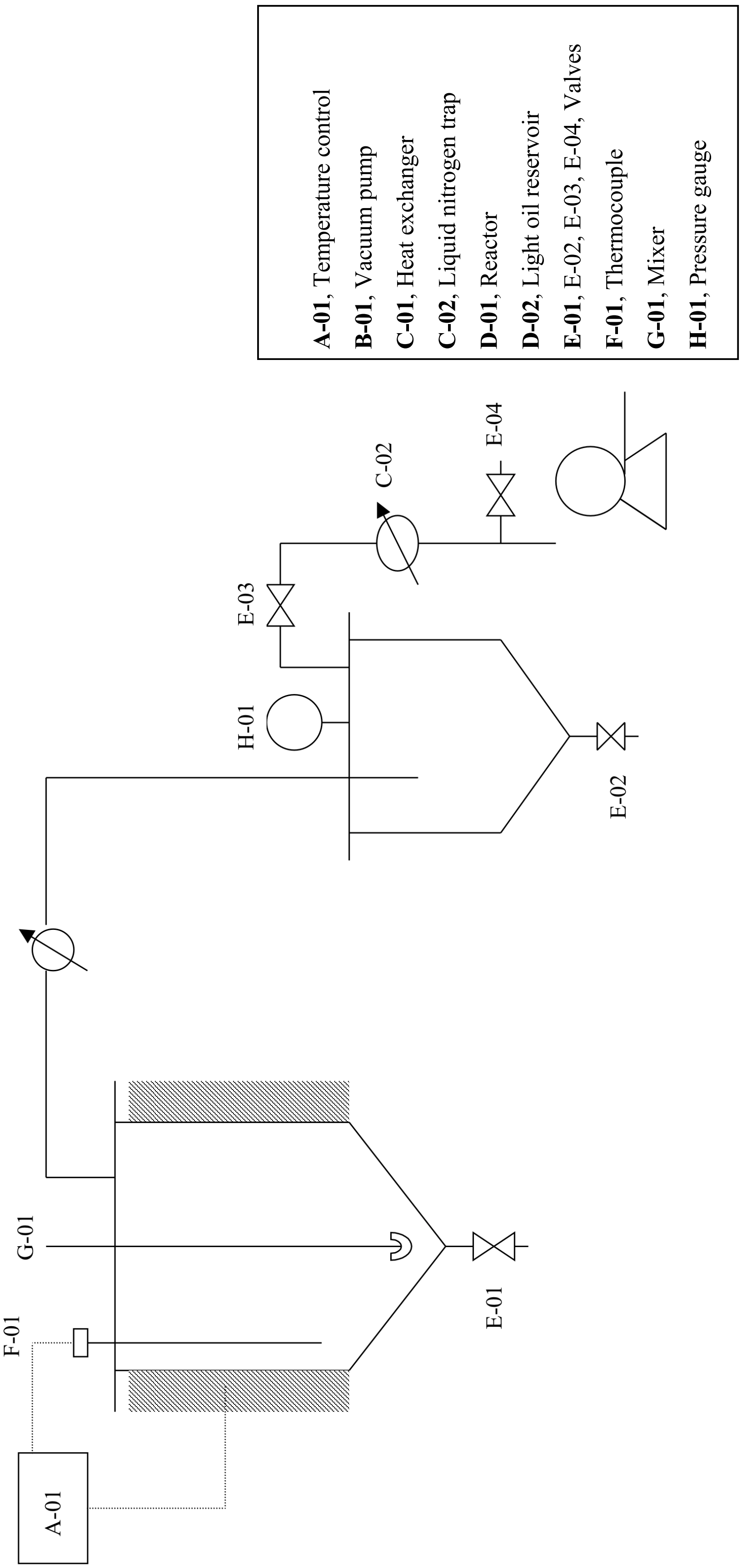

Figure 1: Flow chart of the equipment for bio-oil processing.

Table 1: Experimental conditions for obtaining biopitch samples.

Experimental Conditions	Biopitch # 01	Biopitch # 02	Biopitch # 03	Biopitch # 04	Biopitch # 05
Final temp., ^{o}C	250	250	270	270	270
Heating rate, ^{o}Cmin^{-1}	5	2	2	3	2
Pressure, MPa	0.1	0.07	0.1	0.1	0.05

RESULTS AND DISCUSSION

The properties of a series of five biopitch samples are reported in Table 2. The distilled fraction gave an aqueous phase and light oils. The low temperature the bio-oil can withstand is remarkable. For instance, coal tar and petroleum pitches are usually produced at 360^{o}C in open vessels (Newman and Newman, 1997). This temperature is too high for bio-oils and 270^{o}C was found to be the highest temperature for them. When the temperature is raised above this, bio-oil reacts fast to form a solid thermofix carbonaceous residue. This high reactivity is attributed to the high oxygen content in bio-oil, ca 20 wt%. In contrast, fossil pitches are very low in oxygen, around 2%.

The softening point (SP) for the biopitch samples ranged from 56 to 108^{o}C, the values comparable to those currently used in industry. The increase in SP is a result of polymerization (condensation reaction) and vaporization water and some volatile organics during the heating treatment.

As expected, the ash content in biopitch was very low due to the very low ash content in the raw material, i.e., the biomass. The mineral matter in the wood was almost negligible with a concentration between 0.3 and 1 wt%.

The residual carbon, measured by the Conradson test, is below 50 wt% for biopitches. In the case of coal tar pitches, it is usually above 50 wt% with elemental carbon at about 90 wt% in contrast to 70 wt% in biopitches.

Biopitches are highly soluble in quinoline. Quinoline insoluble (QI) was found to be less than 1 wt%. Biopitch # 03 had the highest SP and also the highest QI content, 1 wt%. QIs in fossil pitches are classified as primary when they come from the transported coke particles and secondary for the carbonaceous mesophase produced during heating. Biopitches are unable to generate mesophase, so the nature of their QI must be some charcoal particles carried during the wood carbonization process (Otani et al., 1990).

Toluene insoluble (TI) found for biopitch was very comparable to those for coal tar and petroleum pitches. A maximum value of 48 wt% for biopitch # 04 and a minimum of 26 wt%, for biopitch # 01, were found. β-resin, defined as TI minus QI for each sample, is responsible for the binder power of the pitch. It is very high in biopitches because of the very low QI and high TI (Marsh, 1997).

Acetone insoluble (AI), generally related to the degree of polymerization, was very high for biopitch # 03 (56 wt%); it also had the highest SP. In contrast AI was very low (concentration of 5-6 wt%) for the low SP biopitches, # 01 and 02. More severe heat treatment resulted in more condensation reactions, raising the molecular weight, the degree of polymerization and the SP.

The elemental composition of biopitches showed a carbon content of about 70 wt%, a hydrogen content between 6 and 6.5 wt%, a nitrogen content less than 1 wt% and an oxygen content greater than 20 wt%. The highly oxygenated nature of these materials causes the carbon content to be lower than the 90 wt% found in fossil feedstocks. An average H/C ratio of 0.9 is typical for biopitches.

An average higher heating value of 30.1 MJ.kg^{-1} (7,200 kcal.kg^{-1}) and specific gravity in the range of 1.24 to 1.26 were found for the biopitch samples. For a coal tar pitch sample, the heating value found was of 37.5 MJ.kg^{-1} (8,970 kcal.kg^{-1}) and the specific gravity was of 1.32.

Data from HPLC confirmed that biopitch molecular compounds are mostly polar (80-86%) and FT-ir of the same sample showed decreases in aliphatic hydrogen content when the SP increased. TGA/DTG analysis showed greater weight losses for low SP samples, indicating a higher degree of condensation for those samples obtained under more severe conditions (Luengo et al., 1995).

Electrode samples produced with the procedure described above had an electrical resistivity of 10^{-4} Ωcm when the temperature of heat treatment was higher than 900^{o}C, similar to that of commercial graphite (Coutinho and Luengo, 1994). Young's modulus and the rupture strength reach their highest values for samples obtained at about 1000°C, with values of 3.0 GPa and 50 MPa, respectively.

Density, porosity and proximate analysis for calcined (at 1200°C) and graphitized (at 2700°C) electrodes are summarized in Table 3. Density, porosity and residual carbon increased with the increasing temperature. A loss of volatile mass occurred, causing electrodes to become more porous. An assessment showed that only about 30% of the biopitch remained in the electrode as a binding element.

Table 2: Properties of biopitch.

Property	Biopitch # 01	Biopitch # 02	Biopitch # 03	Biopitch # 04	Biopitch # 05
SP, °C	56	65	108	73	97
Ash content, %	0.15	0.13	0.2	0.14	0.05
Conradson, %	35	43	47	42	47
QI, %	0.8	0.7	1.0	0.9	0.4
TI, %	26	31	39	48	35
AI, %	5	6	56	17	13
Carbon, %	70.3	69.9	70.5	71	71
Hydrogen, %	6.5	6.3	6.3	6.5	6.1
Nitrogen, %	0.6	0.7	0.6	0.6	0.6
Oxygen, %	22.6	23.1	22.6	21.9	22.2

Table 3: Properties of the calcined and graphitized electrodes.

Property	Calcined	Graphitized
Density ($g.cm^{-3}$)	1.1	1.3
Porosity (%)	17.0	35.0
Residual carbon (%)	95.2	99.0
Volatile matter (%)	3.8	0.9
Ash content (%)	1.0	0.1

CONCLUSIONS

This study shows an application for bio-oil from slow carbonization or from fast pyrolysis. The charcoal sector in Brazil is in need of much improvement. The recovery and processing of bio-oil must be implemented to increase overall yields. Some Brazilian companies have already begun bio-oil recovery and offered it on the market at a competitive price. The quality of bio-electrodes is comparable to that of commercial ones; they can function under severe conditions, thus avoiding carbon and sulfur oxide (SO_x) contamination. Non-conventional materials can be used to replace conventional fossil sources in similar end-use products and to avoid emissions. Bio-oil proved to be an alternative to coal tar and petroleum pitches as a binder in carbonaceous electrodes.

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