Vacuum Pyrolysis of Brazilian coal, peat and biomass - 2. Preliminary results from preparative liquid chromatography of feedstock bitumen and organic liquids generated

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ABSTRACT

Bench scale vacuum pyrolysis experiments showed that fossil fuels and biomass, including wood, peat, coal and bituminous shale, can be successfully converted to liquid and gaseous products as well as used to produce char as a solid residue. The present work aims to evaluate the conversion characteristics of Brazilian biomass, coal and peat, using individual samples of six different coals (Rio Grande do Sul, Paraná and Santa Catarina Mines), biomass (grass, sawdust, rice husk, wood chips, sugar cane bagasse, eucalyptus leaves, eucalyptus and pine chips) and coarse and fine peat. The experiments were carried out in a pyrolysis reactor (Pyrovac Inc., Canada, 1200 cm^3) using 90 to 200 g of previously dried samples with granulometry 2.8 mm. The samples were submitted to a temperature of up to 500°C, with mean average rate of 10°C/min and 2 h isotherm at final temperature under a pressure not superior to 1.0 kPa. Parallelly, the feedstock samples were extracted in a Soxtec^{TM} 2050 FOSS, with dichloromethane/methanol (93:7 v/v %), for 4 hours. The organic liquids (condensed in three traps) and solids (residue removed from the reactor) obtained from pyrolysis, after cooling to room temperature, were collected, weighted and treated to be submitted to liquid preparative chromatography to obtain aliphatic, aromatic and polar pure liquid fractions. The same procedure was carried out with the bitumen from Soxtec^{TM}. The conversion results (pyrolysis) showed that highest conversion was achieved with Braquiaria Grass (56%) while the lowest occurred with Cambui/Paraná coal (5%). Among the peat samples, fine peat presented the highest conversion (33%). Liquid preparative chromatography data show that for peat samples and for most of the coal samples the aliphatic fraction from pyrolysis process was higher than the soxtec extraction (bitumen), while among the biomass samples only the sugar cane bagasse sample presented this behavior. It was also verified that the polar fraction was predominant for all analyzed samples.

Key-Words: vacuum pyrolysis; biomass; coal; peat; preparative liquid *chromatography*

RESUMO

Experimentos de pirólise a vácuo, em escala da bancada (bench-scale), mostrou que combustíveis fósseis e biomassa, incluindo madeira, turfa, carvão e folhelho betuminoso, podem ser convertidos com sucesso para produtos líquidos e gasosos, bem como para a produção resíduos sólidos (char). O presente trabalho teve o objetivo de avaliar as características de conversão dos materiais biomassa, carvão e turfa brasileira, utilizando amostras, individuais, de seis distintos carvões (minas do Rio Grande do Sul (RS), Paraná (Pr) e Santa Catarina (SC)), biomassa (capim, serragem, casca de arroz, lascas de madeira, bagaço de cana de açúcar, folhas de eucalipto, lascas de eucalipto e de pinus) e de turfa fina e grossa. Os experimentos foram conduzidos em um reator de pirólise (Pyrovac Inc, Canada, 1200 cm^3), utilizando 90 a 200 g de amostra previamente seca com 2.8 mm de granulometria. As amostras foram submetidas a até 500°C, com taxa média de aquecimento de 10°C/min e isoterma de 2h na temperatura final, sob pressão não superior a 1.0 kPa. Paralelamente, foram realizadas extrações das amostras originais em equipamento SOXTEC^{TM} 2050 FOSS, com mistura diclormetano/metanol (93/7) v/v%, por um período de 4 h. Após o término dos experimentos, os produtos líquidos (condensados em três *traps* durante os experimentos*)* e os sólidos (resíduos removidos do reator), obtidos após resfriamento para a temperatura ambiente, foram recolhidos e pesados. A fração líquida da pirólise a vácuo, bem como os extratos obtidos do processo s*oxtec* (betumes), após devidamente concentrados, foram submetidos a cromatografia líquida preparativa, para obtenção de fração puras de composto alifáticos, aromáticos e polares. Os resultados mostraram que a maior conversão no processo de pirólise, foi obtida com a biomassa Capim Braquiaria (56%), enquanto que a menor ocorreu com o carvão de Cambui/Paraná (5%). Entre as amostras de turfa, a turfa fina foi a de maior conversão (33%). Os resultados da cromatografia a líquido mostraram que para as amostras de turfa e para a maioria das amostras de carvão, a fração alifática foi maior no processo de pirólise a vácuo do que para o processo por extração em soxtec (betume), enquanto que para as amostras de biomassa, somente a de bagaço de cana apresentou esse comportamento. Também foi verificado a predominância da fração polar em todas as amostras analisadas.

Palavras-chave: *pirólise a vacuo; , biomassa; carvão; turfa, cromatografia a líquido preparativa*

1 INTRODUCTION

Energy consumption in world scale grows continually. Brazil expects an annual increase of 4.4% projecting 128% growth between 2010 and 2030 (EPE, National Energy Plan, 2007). Furthermore, according to the National Energetic Balance (EPE, 2012), the 2012 energy consumption was 283.6 Mtep, with contributions of renewable sources, including biomass, in the order of 57%. On the other hand, there is a gradual decrease of non-renewable fuels like coal, natural gas and oil leading, therefore, to a growing demand of non-fossil renewable fuels (biomass). In Brazil the employed biomass includes sugar cane bagasse, rice husk, forest residues and sawdust. In the south states, coal reserves estimated as 32 billion tons (Inf. An. Indust. Carbonif., 2000) which are employed almost exclusively for electricity generation. Peat also presents potential as electricity producing material. Peat deposits are distributed all over the Country with estimated reserves of 486 million tons, being the larger deposits located in the south states (CPRM, 2005). According to Garcia-Perez et al., 2007, results of peat and lignin-cellulose vacuum pyrolysis showed potential to produce lipids and solid residues. However, in Brazil, peat has been employed only in agriculture not being considered as solid fuel source yet.

Due to the large coal and peat reserves of South Brazil as well as the abundance of biomass, the knowledge of coal, peat and biomass capacity for generating liquid and gaseous products by vacuum pyrolysis is highly desirable. Vacuum pyrolysis applied to these materials allows characterization and qualification of generated products, being the main technology for obtaining liquid and gaseous products (Kalkreuth et al, 1986a, 1986b, 1989a, 1989b, 1993; Roy et al, 1985, 1993, 1998; Pakdel et al, 1999), as well as for the generation of a solid residue (char).

2 EXPERIMENTAL

Bench extraction experiments with Soxtec and vacuum pyrolizer were carried out using coal, peat and biomass samples identified in Table 1.

2 1 SOXTEC EXTRACTION EXPERIMENTS

Coal, biomass and peat original samples (dried at 40°C and sieved to 4.76 mm particle size) were extracted (20 g) in a Soxtec™ 2050, from Foss, in cartridges pre-extracted with a mixture of dichloromethane (DCM)/methanol (Met) (pesticide degree) 93/7% v/v for a period of 4 hours. The obtained extracts (bitumes) were concentrated in a rotary evaporator and reserved for posterior treatment and analysis.

Table 1. Identification of samples used in Soxtec and vacuum pyrolysis experiments and respective origins.

Origin	Sample
Cambui-PR	Mina Cambui Coal
Rio Deserto - SC	Cruz de Malta Coal
Rio Deserto - SC	Mina 101 Coal
CRM - RS	São Vicente do Norte Coal
CRM - RS	Candiota Coal
Eco Fogo	Sugar Cane Bagasse
Eco Fogo	Rice Husk
Eco Fogo	Sawdust
Eco Fogo	Wood Chips
Águas Claras	Coarse Peat
Águas Claras	Fine Peat
Eco Fogo	Eucalyptus Bark
Eco Fogo	Eucalyptus leaves
Rio Deserto - SC	Fontanela Coal
Eco Fogo	Leaf and Castor stalk
Eco Fogo	Shrimp Grass
Eco Fogo	Braquiária Grass
Eco Fogo	Pine

2 2 VACUUM PYROLYSIS EXPERIMENTS

Vacuum pyrolysis experiments were carried out in bench scale reactor (Pyrovac, Canada) installed in the Geoscience Institute – UFRGS.

Coal, biomass and peat samples weighing between 80 and 250 g (dried at 40°C and sieve to 4.76 mm particle size) were transferred to a pyrolysis reactor placed in an oven heated up to 550°C with heating rate of 10°C/min and isothermal for 2 h at final temperature under absolute system pressure < 1 kPa. The residence time of vapors was 1-2 s, being the vapors and water condensed by a series of three sequential glass traps. After cooling the system, the condensed products were removed by a mixture of dichloromethane/methanol (1:1) to Erlenmeyers with glass stopcocks for posterior composition analysis.

2 3 ANALYSES OF OBTAINED EXTRACTS

Extracts resulting from Soxtec (bitumens) and condensed liquids from vacuum pyrolysis were submitted to elemental sulfur removal (only when needed) and liquid preparative chromatography to obtain pure compound fractions.

2 3 1 ELEMENTAL SULFUR REMOVAL

The elemental sulfur removal was carried out in an activated copper column [~5 g of copper washed with concentrated HCl (3x), acetone (3x) and DCM (3x) in a glass column of 1.5 internal diameter]. The sample, added to the top of the activated copper column was eluted with pesticide grade DCM and the sulfur free extract concentrated in rotary evaporator (~1.0 mL) for posterior preparative liquid chromatography.

2 3 2 LIQUID PREPARATIVE CHROMATOGRAPHY

The liquid preparative chromatography was carried out in a 1.0 internal diameter silica/alumina glass column [1.5 g silica, (70-230 mesh, Merck), 3.0 g neutral alumina (Fluka) pre-activated at 200°C for 3 h and 400°C overnight and 0.5 g of sodium sulfate]. The sample, added to the column top was eluted with a sequence of solvents (20 mL of n-hexane, 20 mL of a mixture n-hexane/toluene 3:2 v/v) to obtain pure fractions of aliphatic hydrocarbons, aromatic hydrocarbons and polar compounds (NOS), respectively.

3 RESULTS

Table 2 shows the extract masses of original samples obtained by Soxtec (bitumens) and vacuum pyrolysis condensable liquid products. According to Table 2 the masses generated by vacuum pyrolysis were significantly superiors than those obtained by Soxtec extraction (bitumen). This result was expected by taking into account that vacuum pyrolysis is a process involving transformation of organic matter and consequently higher formation of liquid products, while Soxtec removes only the solvent soluble organic fraction present in the original matrix.

Table 2. Extract masses obtained by Soxtec (bitumen) and the condensed liquid products generated in vacuum pyrolysis of the coal, biomass and peat samples.

	Soxtec	**Vacuum Pyrolysis**	
Sample	**bitumen (%)**	**Condensed Liquid Mass (%)**	**Condensed Liquid Mass(%)/ bitumen(%)**
Cambui Mine Coal	2.6	6.8	2.6
Cruz de Malta Coal	0.9	9.9	11.0
Fontanela Coal	1.1	27.0	24.5
Mine 101 Coal	1.1	25.1	22.8
São Vicente do Norte Coal	1.6	21.0	13.1
Candiota Coal	0.8	19.4	24.3
Sugar Cane Bagasse	1.2	18.2	15.2
Rice Husk	1.2	33.9	28.3
Sawdust	0.8	44.3	55.4
Wood chips	0.8	48.5	60.6
Eucalyptus Bark	1.0	21.1	21.1
Eucalyptus leaf	9.5	17.1	1.8
Leaf and Castor stalk	4.8	26.9	5.6
Shrimps Grass	2.5	23.7	9.5
Branquiara Grass	2.1	55.7	26.5
Pine	1.2	51.0	42.5
Coarse Peat	3.9	12.0	3.1
Fine Peat	2.9	33.1	11.4

The Table 3 shows the liquid chromatography data of the aliphatic (alif), aromatic (arom) and polar fractions (NSO) the coal and peat extract samples by Soxtec (bitumen) and Vacuum pyrolysis condensed liquid.

Table 3. The liquid chromatography data of the aliphatic (alif), aromatic (arom) and polar fractions (NSO) the coal and peat extract samples by Soxtec (bitumen) and condensed liquid from Vacuum pyrolysis.

Sample	Soxtec			Vacuum Pyrolysis		
	% alif.	% arom.	% NSO	% alif.	% arom	% NSO
Cambui Mine Coal	3.3	8.9	69.2	2.2	10.7	55.5
Cruz de Malta Coal	8.6	29.7	48.8	11.2	22.9	44.2
Fontanella Coal	5.9	17.5	23.5	2.0	8.8	25.0
Mine 101 Coal	2.3	14.3	75.3	7.0	19.1	50.7
São Vicente do Norte Coal	0.3	6.4	67.1	3.1	7.5	36.6
Candiota Coal	0.0	6.5	51.5	3.8	15.7	40.0
Coarse Peat	0.0	1.0	0.0	3.1	4.2	30.0
Fine Peat	0.0	0.0	0.0	2.5	2.7	14.0

Analyzing the data in Table 3, it can be verified that for condensed liquid vacuum pyrolysis fractions, for peat samples and for most of the coal samples, the aliphatic fraction increased when compared to the respective bitumen obtained from the original raw material samples. The maximum values of the aliphatic fraction occurred in vacuum pyrolysis of Santa Catarina coal. Percentage values of aliphatic fractions were 11.2% for Cruz de Malta coal and 7% for Mine 101 coal, values far superiors than those of the aliphatic fractions of corresponding bitumen: 8.6% and 2.3% respectively. Liquid samples derived from peat showed significant increase in aliphatic fraction (3.1% for coarse grain and 2.5% for fine grain), when compared to the bitumen samples. As far as the polar fraction is concerned very high values are encountered in all bitumen samples as well as in condensable liquids, indicating that those samples do not present good transformation for aliphatic compounds.

Table 4 shows data for liquid chromatography of extracts from Soxtec (bitumen) and liquid products from vacuum pyrolysis obtained from biomass samples. In biomass samples the aliphatic fraction is relatively enriched in the extract obtained from the raw material (bitumen), with a maximum value in Castor (4%). In condensed liquids, the aliphatic fraction has its maximum in the sugar cane bagasse sample (1.8%).

Table 4 - The liquid chromatography data of the aliphatic (alif), aromatic (arom) and polar fractions (NSO) biomass samples obtained by Soxtec (bitumen) and Vacuum pyrolysis.

Sample	Soxtec			Vacuum pyrolysis		
	% alif	% arom	% NSO	% alif	% arom	% NSO
Sugar Cane Bagasse	0.5	0.3	14.7	1.8	0.4	13.8
Rice Husk	0.7	0.4	3.7	0.2	0.2	28.5
Sawdust	1.2	1.,2	25.8	0.0	0.1	24.2
Wood chips	0.0	0.0	23.6	0.0	0.1	22.9
Eucaliptus Bark	0.5	0.3	71.6	0.1	0.0	56.1
Eucaliptus Leaf	0.4	0.0	74.6	0.6	0.5	60.6
Leaf and Castor stalk	4.1	0.2	75.9	0.9	1.2	57.8
Shrimp Grass	0.0	0.0	58.1	0.2	0.1	23.3
Braquiária Grass	0.4	0.1	51.3	0.2	0.4	72.0
Pine	0.0	0.4	75.3	0.0	0.2	66.0

From data in Tables 3 and 4 it can be verified that the polar fraction was predominant in all samples and that the sum of percentages does not add up to 100%. This can be explained by highly polar compound that might be adsorbed in the column not being eluted by the employed solvents, indicating a formation of highly polar liquids.

4 CONCLUSION

Vacuum pyrolysis preliminary data indicate a tendency of the aliphatic fraction increase for most of the analyzed matrices, as well as predominant formation of polar compounds in condensable liquids.

5 BIBLIGRAPHIC REFERENCES

EPE, 2007. Plano Nacional de Energia 2030. Rio de Janeiro, 408pp.

EPE, 2012. Balanço Energético Nacional 2012, Rio de Janeiro, 282pp.

Informativo Anual da Indústria Carbonífica., 2000.

CPRM. 2005. Seminário Carvão no Brasil, Criciúma, SC, Fevereiro 2005

GARCIA-PEREZ, M., ABELKADER C. and ROY, C., 2002. Co-pyrolysis of sugarcane bagasse with petroleum residue. Part II Products yields and properties, 893-907.

KALKREUTH, W., C. ROY AND M. HÉBERT. 1986a. Vacuum Pyrolysis of Prince Mine Coal, Nova Scotia, Canada. Chemical and Petrological Analysis of Feedstock and Reaction Residues. Erdöl und Kohle-Erdgas-Petrochemie vereinigt mit Brennstoff - Chemie. 39 : 213-222

KALKREUTH, W., D. BROUILLARD AND C. ROY. 1986b. Optical and Chemical Characterization of Solid Residues Obtained from Vacuum Pyrolysis of Poplar Wood. Biomass. 10 : 27-45

KALKREUTH, W., C. ROY AND M. STELLER. 1989a. Conversion Properties of Selected Canadian Coals Based on Hydrogenation and Pyrolysis Experiments. In Contributions to Canadian Coal Geoscience. Geological Survey of Canada. Paper 89-8

KALKREUTH, W., C. ROY AND M. STELLER. 1989b. Conversion Characteristics of Selected Canadian Coals Based on Hydrogenation and Pyrolysis Experiments. Advances in Western Canadian Coal Geoscience. Edmonton, Alberta. (101-114). April 24-25

KALKREUTH, W.D., H. PAKDEL AND C. ROY. 1993. Low Temperature Vacuum Pyrolysis of Canadian Solid Fossil Fuels. 7th International Conference on Coal Science. Banff, Alberta, Canada. September 12-17

PAKDEL, H., C. ROY AND W. KALKREUTH.1999. Oil Production by Vacuum Pyrolysis of Canadian Oil Shale and Fate of the Biological Markers. Fuel. 78 : 365-375

ROY, C., M. HÉBERT AND W. KALKREUTH. 1993. Vacuum Pyrolysis of Canadian Coals. Thermal De-composition Characteristics of Two High Volatile Bituminous Coals. Erdöl und_Kohle, Erdgas, Petrochemie. 46: 66-73

ROY, C., B. DE CAUMIA AND W. KALKREUTH. 1985. Vacuum Pyrolysis of Prince Mine Coal, Nova Scotia, Canada. Fuel. 64 : 1662-1666

ROY, C., M. HÉBERT, W. KALKREUTH AND A.E. SCHWERDTFEGER. 1998. Conversion Characteristics of Canadian Coals Subjected to Vacuum Pyrolysis Treatment. Fuel. 77: 197-208