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STUDIES ON LIQUEFACTION AND PYROLYSIS OF PEAT AND BIOMASS AT KTH

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Abstract

Thermochemical processes for conversion of peat and biomass have been studied at Kungliga Tekniska Högskolan, KTH, (Royal Institute of Technology, Stockholm) since the energy crisis in the seventies. Pyrolysis has mostly been studied as a tool for better understanding of both liquefaction and gasification of the fuels. Intensive work on the liquefaction has taken place mostly in the period between 1976 and 1990. The present activities are focused on the gasification and pyrolysis of biomass.

Introduction

The research on the thermochemical conversion of peat and biomass in Sweden was intensified after the energy crisis 1973 (Rensfelt et al., 1978; Björnbom, P., 1976). Intensive studies on peat liquefaction took place at KTH until 1990 (Björnbom, P., 1979, 1983; Björnbom, P. et al., 1981, 1987; Björnbom, P. and Björnbom, E., 1988; Björnbom, E. and Björnbom, P., 1988; Björnbom, E. et al., 1979 1980, 1986, 1988, 1991; Hörnell et al., 1985). The decrease of the oil prices in the eighties cooled down the interest of the authorities in Sweden in the development of a process for direct liquefaction of peat and biomass.

The activities on the gasification at KTH after the energy crisis aimed mostly the practical application of the process (Rensfelt et al., 1978). The present activities on the thermochemical conversion of solid fuels at KTH are focused on some research aspects of the pyrolysis and gasification of biomass as well as cracking of tar-rich gas (Sjöström and Chen, 1990; Sjöström and Björnbom, 1993; Sjöström et al., 1994; Chen et al., 1992; Liliedal et al., 1992; Zanzi et al., 1992, 1995).

Liquefaction of peat and biomass

There are two serious problems connected with the utilisation of peat for energy:

- *High moisture content in the natural peat deposits (approximately 90 %) and*
- *High oxygen content in the dry substance of the fuel (35-40%).*

Simultaneous dewatering and liquefaction of peat

The initial study on peat liquefaction aimed to test the possibility to achieve both liquefaction and dewatering of peat by a method proposed by Björnbom, based on F. Fischer's idea of using CO and H₂O in coal liquefaction (Björnbom, P., 1976). The wet peat was treated with CO without preliminary drying. The water present in the peat served as a reaction medium and as a source of hydrogen via the shift reaction. After treatment the water was phase-separated from the heavy oil product obtained from peat (Björnbom, E. et al., 1979). Thus, simultaneous dewatering and liquefaction of peat was achieved.

Deoxygenation of peat prior to liquefaction

The conversion of solid fuels to liquid and gas fuels requires increase of the ratio H/C in the fuel. If peat and biomass are directly hydrogenated to produce liquid fuels and the oxygen in them is transformed into water, by consumption of external hydrogen, this will be a serious drawback for the process. Our study has shown, however, that significant part of the oxygen in peat and biomass may be removed by thermal decomposition of these fuels prior to liquefaction and removal of carbon dioxide and water from the organic matter in them. The products obtained after the deoxygenation demands low consumption of external hydrogenation agent, because they are rich in hydrogen (*Table 1*).

Table 1. Comparison between coal, peat and its product obtained in the first step of the liquefaction (deoxygenation). The peat product is obtained by heating a slurry of 10 % peat dry substance for 30 min. at 300 °C in presence of CO with an initial pressure of 2.2 MPa (Björnbom, E., et al, 1986).

Material	H/C atomic	O/C	(H-2O)/C
Peat	1.46	0.42	0.62
Deoxygenated peat product	1.11	0.10	0.91
Lignites and brown coals	0.95	0.3-0.4	0.1-0.4
Bituminous coal	0.72	0.16	0.4

The data in Table 1 show that the product obtained in the deoxygenation of peat under the conditions applied in our study has the highest value of the ratio (H-2O)/C i.e. minimum demand of external hydrogen in the hydrogenation. The low consumption of hydrogen in the liquefaction of peat is confirmed also by dissolution of peat in H-donor solvents (Hörmell and Björnbom, 1989).

Some criteria for selection of peat as a raw material for liquefaction

Selection of peat as a raw material for thermochemical treatment is usually based on its *degree of humification (decomposition)*. Well humified peat is recommended for liquefaction, coking and gasification. The work on peat liquefaction at KTH showed, however, that the degree of humification is far from being a sufficient criterion for selection of peat for liquefaction (Björnbom, E. et al., 1988, Björnbom, E. and Björnbom, P., 1988).

It was found that the yield of the primary liquefaction products was linearly dependent on the total amount of *bitumen, humic acids and nonhydrolysables* in the peat (**B+HA+NH**). Thus, the latter was suggested as a criterion for the suitability of peat for liquefaction. Simple mathematical expressions were derived from literature data (Lishtvan, 1975), among which the following is of interest here (Björnbom, E. and Björnbom, P., 1988):

$$(B+HA+NH) = 0.29X_1 - 0.08X_2 + 4.80X_3 + 3.83X_4 - 85.7$$

where:

(B+HA+NH) is the content of bitumen, humic acids and nonhydrolysables in peat (%)

X_1 - degree of humification of peat (%). X_3 - calorific value, daf (daf) (Kcal. Kg⁻¹)

X_2 - ash yield of peat (wt %)

X_4 - pH of wet peat.

Analysis of the above equation based on the intervals of change of the independent variables in it, showed that the total amount of **(B+HA+NH)** may be better predicted using *the calorific value of peat (variable X_3)* instead of the *degree of composition (variable X_2)* (Björnbom, E., and Björnbom, P., 1988). This result was also tested and confirmed using experimental results obtained in the project. It was found that the yield of liquefaction products was linearly dependent on the calorific value of the peat samples.

Pyrolysis of peat and biomass

Equipment and experimental procedure

The free fall tubular reactor for rapid pyrolysis of solid fuels and the experimental procedure are described elsewhere (Zanzi et al., 1992). The maximum operating pressure is 5 MPa and the maximum operating temperature is 1100°C. The reactor is supplied with a screw feeder with capacity of 1 kg solid fuel/h. The maximum heated length of the reactor is 2900 mm. and the inner diameter is 40 mm. The char is collected in a char receiver situated below the reactor. The product gas passes a high-temperature metallic filter made of sintered metal, two tar condensers, a tar water condenser, dry ice traps and a cotton filter. The so purified gas is analysed by a gas chromatograph for CO, H₂, CO₂, N₂, aliphatic hydrocarbons C₁-C₅ and aromatic hydrocarbons (benzene and toluene).

Some of the fuel samples treated by rapid pyrolysis in the free fall reactor are additionally submitted to slow pyrolysis under atmospheric pressure in the thermobalance. The heating rate of the samples in the thermobalance is 20°C/minute. The treatment aims to complete the pyrolysis. The slow pyrolysis is interrupted when the weight of the sample acquires constant value. The reactivity of the char samples is determined by gasification with steam in the same thermobalance (Zanzi et al., 1992).

Effect of the treatment conditions under the rapid pyrolysis in the free fall reactor on the yield and the reactivity of char obtained after the final pyrolysis

Tables 2 and 3 show the effect of the treatment conditions under the rapid pyrolysis on the yield and the reactivity of the char obtained from peat and wood. Under the studied treatment conditions, during less than 1 second, peat and wood are transformed into pyrolysis products. Depending on the treatment conditions, 35-50 % of the moisture and ash-free peat and 70-80 % of the wood are converted into gaseous products. The char obtained in the rapid pyrolysis contains a fraction which can be further devolatilized by slow pyrolysis in the thermobalance with a heating rate of 20°C/minute. The time needed for the final pyrolysis is much longer (minutes) than the time for the formation of the primary products. High reactivity of char is favoured by lower pyrolysis temperature, shorter residence time and larger particle size of the fuel. The reactivity of the char samples can hardly be correlated to their surface areas.

Table 2 Effect of the treatment conditions under the rapid pyrolysis of peat in the free fall reactor at 1.5 MPa on the yield and the properties of char obtained after the additional slow pyrolysis at atmospheric pressure in the thermobalance.

Exp No	F070	F090	F0702	F0704	F0616	F0711	F0626	F0630
Reactor temperature, °C	970	970	770	770	770	770	630	630
Fuel particle size, mm	←-----0.9 - 1.0-----→				←-----0.32 - 0.5-----→			
Nitrogen flow, Nm ³ /h	0.45	0.7	0.7	1.1	0.45	0.85	0.55	1.05
Residence time of solids, s	0.64	1.06	1.07	1.68	0.41	0.90	1.58	2.45
Gas yield, wt % maf	49.7	55.3	42.7	45.6	38.2	42.1	37.2	34.7
Tar yield, wt % maf	1.6	0.2	0.9	2.2	2.3	1.5	1.6	1.4
Char yield, wt % maf	29.2	28.3	31.1	29.5	33.3	31.5	37.4	35.4
Char yield after additional slow pyrolysis at 800°C	21	22	22	22	23	23	23	24
Fraction of char removed by slow pyrolysis, wt %	28.1	22.3	29.3	25.4	30.9	27.0	38.5	32.2
<i>Properties of char :</i>								
Surface area, m ² /g	134	155	79	44	112	81	100	140
Reactivity, R ₁₀₋₅₀ (800°C), %/min	3.3	3.0	4.6	3.2	2.9	2.3	4.3	3.5

Table 3 Effect of the treatment conditions under the rapid pyrolysis of wood in the free fall reactor at 1.5 MPa on the properties of char obtained after the additional slow pyrolysis at atm. pressure.

Exp No	2703	1004	1303	1501	2901	3101
Reactor temperature, °C	750	750	750	900	900	900
Pressure, kPa	280	270	300	260	270	270
Residence time of solids, s	0.8	1.8	3.0	0.4	0.6	1.9
Gas residence time, s	5.6	8.2	11.9	2.6	3.7	6.8
Gas yield, wt % maf	73.2	73.0	73.5	81.6	81.3	81.1
Tar yield, wt % maf	1.7	1.2	1.1	1.2	1.1	1.1
Char yield, wt % maf	6.8	6.8	6.9	5.2	5.5	5.9
Char yield after final slow pyrolysis at 850°C in the thermobalance, wt % maf	5.1	5.5	5.8	3.6	3.8	4.4
Fraction of the char removed by slow pyrolysis at 850°C in thermobalance, wt %	29.7	23.9	19.3	31.1	30.7	24.6
<i>Properties of char:</i>						
N ₂ -surface area, m ² /g	0.3	ND	0.8	0.5	ND	0.9
CO ₂ -surface area, m ² /g	297	ND	332	386	ND	312
N ₂ -pore volume, mm ³ /g	3.2	ND	3.8	1.2	ND	2.7
Reactivity of char, wt %/min	4.1	2.7	2.3	5.0	4.2	3.0

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