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CO-PYROLYSIS OF BROWN COAL AND BIOMASS MIXTURES AND LIQUID PRODUCT TREATMENT

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The brown coal pyrolysis was estimated on pilot unit at 650°C to produce liquid product (organic and water parts). The mass balance of pyrolysis products and analysis of gas composition and liquids composition were carried out. The mass balance showed that the highest yield had coke (43 % wt.). The pyrolysis gas contained mostly methan, hydrogen and carbon oxides. The organic part was separated out of the liquid product by sedimentation. Water part contained mostly oxygen organic compounds like phenols and carboxylic acids. Organic part contained mostly aliphatic hydrocarbons, mono and polycyclic aromatic hydrocarbons. The content of oxygen in organic part of liquid pyrolysis product was rather high and therefore the subsequent treatment of this product is necessary to produce liquid fuels.
Key words: pyrolysis, co-pyrolysis, brown coal.

Kopiroliza smeđeg ugljena i smjesa biomase te obrada tekućeg produkta. Piroliza smeđeg ugljena provedena je na pilot postrojenju na 650 °C pri čemu nastaje tekući produkt (organski i vodeni dio). Određena je masena bilanca produkata pirolize i analiza sastava plina i tekućina. Masena bilanca pokazuje da najviše iskorištenje ima koks (43 mas. %). Plin koji nastaje pirolizom većinom sadrži metan, vodik i okside ugljika. Organski dio je sedimentacijom izdvojen iz tekućeg produkta. Vodeni dio sadrži uglavnom kisikove organske spojeve, kao što su fenoli i karboksilne kiseline. Organski dio sadržava uglavnom alifatske ugljikovodike, mono i policikličke aromatske ugljikovodike. Udio kisika u organskom dijelu tekućeg produkta pirolize bio je prilično visok, zbog čega je nužna naknadna obrada tog produkta da bi se proizvelo tekuće gorivo.
Ključne riječi: piroliza, kopiroliza, smeđi ugljen.

INTRODUCTION

Pyrolysis is a physico-chemical process. This process is isolated from air and the material is decomposed at temperatures higher than the limit of its thermal stability. Pyrolysis products are: solid pyrolysis residue, liquid product and a gas [1]. The solid residue is called coke or semi-coke and is used as fuel or adsorbent. The liquid product contains an organic and a water part. The organic part can be utilized after refining as a fuel. The gas is often used to heat a reactor [2].

The highest yields of liquid product can be achieved by fast pyrolysis and quickly removing of products from the pyrolysis reactor [3]. The liquid product properties are closely related to material properties and process conditions [4]. In contrast with yield of coke, the yield of volatile matter increases as the pyrolysis temperature increase. The increasing residence time of volatile product in the hot area leads to secondary reactions, such as thermal cracking, polymerization, condensation... These reactions reduce the yield of liquid product [5, 6]. Substances containing sulfur, nitrogen and oxygen allow easier thermal decomposition, all of which leads to the formation of CO_2, CO, NH_3, H_2S, pyrogenetic water and other products. During pyrolysis many chemical reactions occur, including polymerization, polycondensation, condensation, fission, cyclization, isomerization, dehydrogenation and hydrogenation [1].

Coal is heterogenic mixture with mostly organic character. Brown coals and lignites are appropriate to liquefaction because of high content of hydrogen and reactive maceral groups. Biomass has high content of volatile compounds and therefore is also appropriate to liquefaction [7, 8].

Brown coal pyrolysis requires elevated temperatures to produce the liquid product that can be converted into fuel. By co-pyrolyzing brown coal with biomass, liquid product can be produced at lower temperatures [9].

Brown coal for ours pyrolysis tests was chosen based on the by Safarova and Kusy's research. Brown coal from mine CSA was evaluated as suitable for pyrolysis with purpose of further refining process [10]. Rape meal was chosen as suitable for pyrolysis because it is waste product from rape processing and withal has goodenergy-potencial [9].

The organic part of the liquid can be used for the fuel production. After pyrolysis, the organic part must be separated out of the liquid product. The organic product must be hydrogenated to decompose the compounds with a high molecular weight. After hydrogenation, the organic liquid product possesses similar properties to petroleum. This suggests that these products could also be processed in refineries for conversion to fuel [3].

MATERIALS AND METHODS

Pyrolysis pilot unit

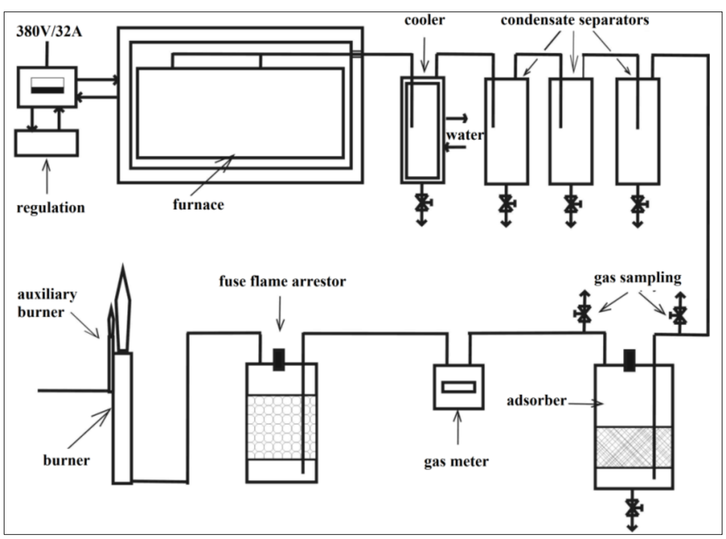

Figure 1. Scheme of the pyrolysis pilot unit
Slika 1. Shema pilot postrojenja za pirolizu

The figure 1 shows the scheme of the pilot unit, which was used for pyrolysis.

The batch (15 kg) was poured into a metal retort (71x51x6 cm) that was placed in an electrically heated furnace. Generated volatile compounds were conducted in a water cooler, then into three serial connected separators where the liquid product was accumulated. Pyrolysis gas went to an adsorber (activated carbon) where the rest of the liquids and sulphurous compounds were removed. Then the gas went through gas meter into burner.

The retort was heated up to 650 °C for 2 hours and the temperature was kept for next four hours. After that the system was cooled naturally to ambient temperature.

After each pyrolysis test the mass balance and analysis of the products were performed.

Off-line gas analysis

The pyrolysis gas was collected in sampling bags every hour and analysed immediately by using GC 82TT LabioPraha with dual thermal conductivity detector (TCD). Hydrogen, oxygen, nitrogen, methane and carbon monoxide were determined by the first TCD (150 °C, stainless steel column – length: 2 m, diameter: 3,2 mm, stationary phase: molecular sieve 5A, carrier gas: argon). Carbon dioxide was determined by the second TCD (150 °C, teflon column – length: 2 m, diameter 3,2 mm, stationary phase: Porapak Q, carrier gas: helium).

Off-line liquid products analysis

The liquid products were analysed by using the gas chromatographer HP 6890 with mass detector (MSD 5973). The gas chromatographer had metallic column MTX-1 (length: 30 m, diameter: 250 μm, carrier gas: helium). The column had 50 °C for first two minutes, than the temperature increased to 320 °C (15 °C·min^{-1}). The temperature 320 °C was kept for the next five minutes.

Pyrolyzed material

Brown coal (ČSA mine) and rape meal (the rest after extraction of the residue from pressing the rapeseed oil) were used as a feedstock. For tests on the pilot unit was used mixture 2:1 (brown coal:rape meal). The basic properties of feedstocks are in the table 1.

Table 1. The feedstocks properties
Tablica 1. Svojstva sirovina

parameter	*brown coal, ČSA*	*rape meal, Preola.s.*
W^a [% wt.]	6,9	11,75
A^a [% wt.]	5,31	6,85
S_t^d [% wt.]	0,95	0,68
C^d [% wt.]	74,6	49,12
V^d [% wt.]	57,7	78,37
Q_s^d [MJ·kg^{-1}]	31,33	20,99

W^a – water, A^a – ash, S_t^d – sulphur, C^d - carbon, V^d – volatile, Q_s^d – heat of combustion

RESULTS AND DISCUSSION

Mass balance

The results of mass balance are shown in the table 2.

Table 2. Mass balance
Tablica 2. Bilanca mase

	g	*% wt.*
batch	15000	100
solid residue	6454	42,0
water + organic part	4603,3	31,3
organic part	1801	12,3
water part	2756,8	18,8
distribution loss	45,5	0,2
gas	4010 l (3510 g)	24,0
loss	20,7	2,7

Gas amount and temperature in the retort during pyrolysis

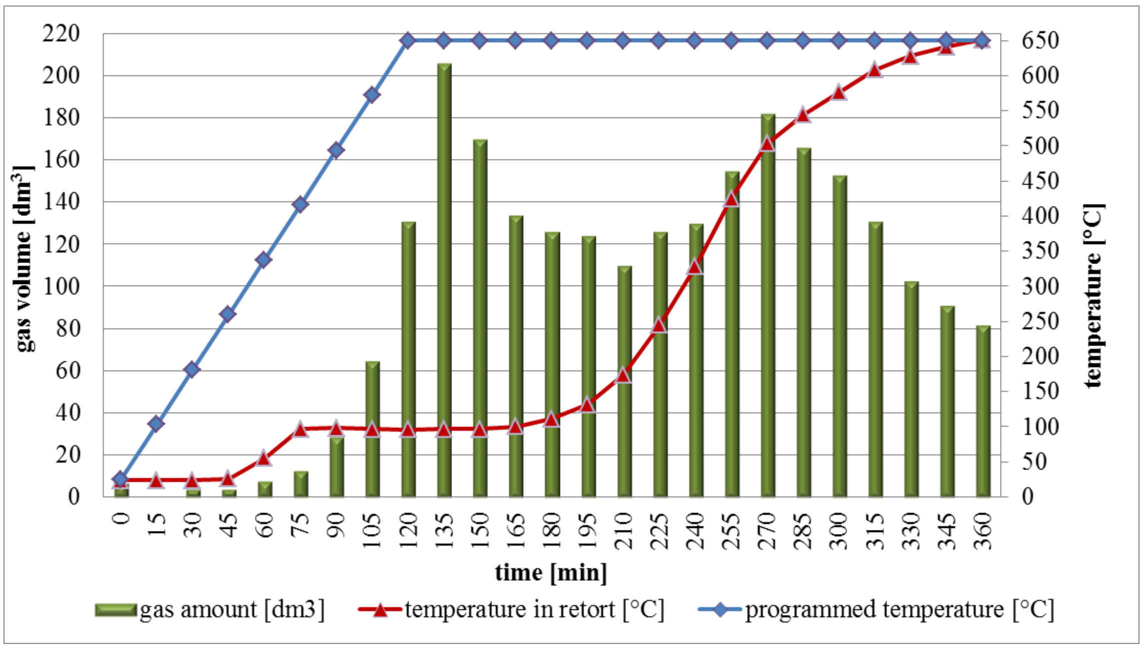

Figure 2. Gas amount and temperature in the retort during pyrolysis
Slika 2. Količina plina i temperature u retorti tijekom pirolize

The gas amount had two maximum, the first for the water vapor and adsorbed gases release (100 °C) and the second for the tar vapors release (about 500 °C).

Composition of pyrolysis gases

The following table shows the composition of pyrolysis gases.

Table 3. The composition of pyrolysis gases
Tablica 3. Sastav plinova nastalih pirolizom

% vol.	*after 1 h.*	*after 2 h.*	*after 3 h.*	*after 4 h.*	*after 5 h.*	*after 6 h.*
	55 °C	*96°C*	*111°C*	*328°C*	*576°C*	*651°C*
hydrogen	0,03	17,88	22,37	22,06	31,68	41,46
oxygen	20,3	0,09	<0,01	<0,01	<0,01	<0,01
nitrogen	76,32	1,18	0,43	0,51	0,54	1,31
carbon monoxide	<0,01	10,86	6,87	6,23	6,29	13,03
methane	<0,01	37,3	35,24	34,46	37,91	31,2
carbon dioxide	0,09	7,19	6,73	5,38	5,14	3,12
ethene	<0,01	0,71	0,86	1,14	0,52	<0,01
ethane	<0,01	6,77	2,07	2,04	1,22	<0,01
propene	<0,01	0,54	0,59	0,72	0,29	<0,01
propane	<0,01	1,21	1,75	1,61	0,92	<0,01
residue to 100%	3,2	16,27	23,08	25,84	15,48	9,83

The main components in pyrolysis gases were methane, hydrogen and carbon dioxide. In contrast with hydrogen, the content of methane decreased as the pyrolysis temperature increased.

Composition of organic part of the liquid product

During the pyrolysis the liquid product (condensate of volatile products from reaction area) was connected in condensate separators. After pyrolysis the condensate was separated into organic and water part during different density. Both phases were analysed by GC-MS.

It was identified cca 140 compounds in total. Table 4 contains typical identified compounds of organic part and shows their portion in organic part according to their peak area toward total peak area.

Table 4. Most important compounds of organic part
Tablica 4. Najvažniji spojevi organskog dijela

retention time	*compound*	*content [%]*
2,288	toluene	2,626
4,623	phenol	4,185
6,060	4-methylphenol	4,119
7,179	2,4-dimethylphenol	1,888
7,781	naphthalene	3,211
9,456	2-methylnaphthalene	1,902

The highest portioins had phenols and substited mono and diaromatic hydrocarbons in organic part. The next identified compounds were aliphatic hydrocarbons (saturated and unsaturated), benzene and polyaromatic hydrocarbons.

Composition of water part of the liquid product

By GC-MS analysis was identified cca 40 compounds in total. Table 5 contains typical indentified compounds of water part and shows their portion in water part according to their peak area toward total peak area.

Table 5. Most important compounds of water part
Tablica 5. Najvažniji spojevi vodenog dijela

retention time	*compound*	*content [%]*
1,747	acetic acid	24,144
2,001	propanoic acid	3,654
2,477	2,3-butanediol	4,021
3,391	1-(dimethylamino)butan-2-ol	7,647
4,628	phenol	7,869
6,065	4-methylphenol	3,434
7,909	1,2-benzenediol	3,639

The highest portioins had phenols, theirs derivates and organic acids.

CONCLUSION

Pyrolysis of brown coal and rape meal mixtures were performed on the pilot unit. The yields of the liquid product were about 31 % wt. and the yield of organic part of liquid product was 12 % wt.

The gas amount during pyrolysis had two maximum, the first maximum for the water and adsorbed gases release (about 100 °C) and the second maximum for the tar vapors release (about 500 °C).

The pyrolysis gases contain primarily methane, hydrogen and carbon dioxide. In contrast with hydrogen, the content of methane and carbon dioxide decreased as the temperature in the retort increased.

In the organic part were identified aliphatic hydrocarbons (saturated and unsaturated), benzene and its derivates, phenol and its derivates and aromatic hydrocarbons with one and more than one aromatic ring. In the water part from liquid product were identified phenols,theirs derivates and organic acids.

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