Full Length Article

Direct primary brown coal liquefaction via non-catalytic and catalytic co-processing with model, waste and petroleum-derived hydrogen donors

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ABSTRACT

Direct coal liquefaction (DCL) seems to be a suitable way to convert low rank coals into liquid fuels, especially when problematic wastes are used together with this feedstock. It is also a solution to become energy independent for many countries which have significant coal resources and limited access to crude oil. The aim of this research was to investigate DCL process by the co-processing of brown coal with model-, petroleum- and waste-derived solvents. The brown coal with and without W, Fe and Mo metals supported on its surface was tested. Thirteen DCL tests with added hydrogen pressure were carried out in the autoclave. These tests were classified in two groups. First group covered reactions using model and petroleum-derived solvents (tetralin, 1-methylnaphthalene, light cycle oil (LCO), hydrotreated LCO, C9+ fraction and decalin) with non-impregnated brown coal. Then, LCO was chosen as solvent for carrying out three tests using the metals supported on coal. Finally, waste tires pyrolysis oil was used as a waste-derived solvent for other three tests with molybdenum supported on coal. For tests using LCO, the total amount of direct liquid and n-heptane soluble products was 20 wt% higher using metal covered brown coal in comparison to unmodified one. The test with the brown coal impregnated by 1% of molybdenum resulted in the best efficiency, thus this type of coal was chosen as a catalytic feedstock for the tests with waste tires pyrolysis oil.

1. Introduction

The coal liquefaction process has been developed since the 1930s; German army was using it to produce synthetic fuels because of the conflict restrictions [1]. The basics of the process are well known, however the process is being continuously investigated. Especially now, when the world's petroleum oil resources are located in unstable territories and the demand for petroleum is continuously increasing, processes such as coal liquefaction are coming back into the researchers interest. The coal can be converted into useful compounds by indirect coal liquefaction (ICL) which consists in the coal gasification followed by catalytic conversion of received synthetic gas into clean hydrocarbons and oxygenated transportation fuels, or by direct coal liquefaction (DCL) which can be performed using solvent under hydrogen atmosphere or donor-solvent under inert atmosphere. In both cases, high temperatures and pressures are used. DCL processes are able to generate wider spectrum of chemicals in comparison to the indirect route [2]. Coal liquefaction process strongly depends on the temperature and reaction time obtaining the best yields in the temperature range of 400–450 °C. However there are other factors which affect the DCL process yield such as type of solvent, reaction atmosphere or the coal itself. The solid residues produced after these processes are usually considered as less valuable products than the original coal used as raw material. Moreover, useful chemicals from the extraction of the solid residues can be done, although the obtaining of high liquid products yields are the main targets [3]. From the reaction mechanism's point of view, two major phenomena occurs during the coal liquefaction: cracking reactions of big structures generating radicals promoted by the high reaction temperature and then the saturation of unsaturated compounds by hydrogen derived from the donor solvent or directly from H_2. The use of catalysts in DCL process improves the hydrogenation, cracking and removing of heteroatoms from the coal structure [4].

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Hydrogen donors are used for these processes. These compounds can transfer the hydrogen to the final products. Many articles are describing applications in which the donor-solvents such as tetralin or decalin for DCL process are used. Nevertheless, those model-solvents are expensive and difficult to reuse. To overcome disadvantages related to the application of these liquid-donors, the use of hydrogenated polymer as solid-donor was considered. In addition, the co-processing of coal and petroleum- or waste-derived solvents is possible. This co-processing could be beneficiary in case of overall process economy and improve the ecological aspects of DCL. Thus, the need of research of easy affordable and cheap donor-solvent is a suitable target [5,6]. DCL process can be a great way of transformation possessed resources into useful fuels and to become energy independent for countries which have significant resources of coal and none or very small access to the crude oil. In addition, the use of waste derived materials such as the waste tires pyrolysis oil can improve definitively the energetic security in the world. Waste tires (WT) are a significant part of the urban waste that is growing and over 1 billion waste tires are generated each year in the world [7–10]. So, WT derived feeds such as WT pyrolysis oil could be used as affordable raw material for DCL reactions. The aim of this work was to explore the DCL by co-processing brown coal, model compounds, several petroleum fractions and pyrolysis tires oil with and without W, Fe and Mo metals supported on the coal.

2. Material and methods

2.1. Materials

The brown coal (BC) called SevEn X [11] (Table 1) was supplied by VUHU (Výzkumný ústav pro hnědé uhlí, Most, Czech Republic) and used in all tests. This BC was collected from the North Bohemian Basin located in Czech Republic. The proximate and elemental analyses of the sample are listed in Table 1.

For catalytic tests, metal/BC samples were ensured by the company IBERCAT S.L. where BC was prepared by impregnation with Fe, Mo and W producing three samples: Fe(1 wt%)/BC, Mo(1 wt%)/BC and {Fe (0.5 wt%) + Mo(0.5 wt%) + W(0.5 wt%)}/BC. In addition, a DCL test was carried out using a commercial NiW/SiO$_2$-Al$_2$O$_3$ catalyst (NiW). For non-catalytic reactions three model solvents were used: tetralin (Honeywell, ≥97%), 1-methylnaphtalene (1-MN) (Sigma Aldrich, ≥95%) and decalin (Honeywell, > 98%). Three industrial solvent-reactants were used: LCO, H-LCO (Hydrotreated LCO), both previously described in literature [12] and C9 + fraction.

LCO was also selected for the catalytic tests using metal/BC materials. Tetralin was selected for the commercial catalyst tests. Pyrolysis oil from waste tires was chosen as waste derived solvent for tests using the Mo/BC material.

C9 + fraction was supplied by UniCRE. Mono- (MA), di- (DA), poly- (PA) aromatic contents, densities and elemental analyses of the C9 + fraction and WT pyrolysis oil are presented in Table 2. In the case of

Table 1
Proximate and elemental analyses of the brown coal.

Brown Coal sample	SevEn X
Proximate Analysis (wt%)	
Moisture (as measured)	23.8
Ash Content (dry basis)	4.9
Volatiles (daf basis)	56.2
Fixed Carbon (daf basis)	43.8
Elemental Analysis (wt% daf basis)	
Carbon	75.3
Hydrogen	6.4
Nitrogen	1.3
Sulfur	1.0
Oxygen (by difference)	16.0

Table 2
Mono- (MA), di- (DA), poly- (PA) aromatics amounts, densities and elemental analyses of carbon (C), hydrogen (H), sulfur (S) and nitrogen (N) for the C9 + fraction and WT pyrolysis oil.

Analysis	C9 +	WT Pyrolysis Oil
MA (wt%)	38.1	20.9
DA (wt%)	4.2	1.7
PA (wt%)	0.1	6.8
Total amount of aromatics (wt%)	42.4	29.4
C (wt%)	89.9	86.8
H (wt%)	10.2	11.1
S (mg kg^{-1})	72.3	9900
N (mg kg^{-1})	14.7	4894
Density at 15 °C (kg m^{-3})	960.3	939.5

C9 + fraction, aliphatics and mono-aromatics were the dominant present species. For WT pyrolysis oil, the aromatics content was only 29 wt %, so lower than for C9 + fraction and the sulfur and nitrogen contents were much bigger. WT pyrolysis oil presented a bromine index of 68266.2 mg Br/100 g and iodine number of 41.98 g I$_2$/100 g.

Simulated distillation profiles showed that the C9 + fraction, as expected, was considerable lighter than the LCO. GC-MS results indicated that indanes and indenes were the major components present with lower concentrations of alkylbenzenes. No tetralins were identified in the C9 + fraction.

Calorific values of all used materials are grouped and listed down in the Table 3.

2.2. Tests

The autoclave 4575/76 with a "4848B" controller delivered by Parr Instruments Company was used for all tests. The experiment procedure was the same for each test and reaction conditions were as follows: the brown coal (40 g) and the solvent (100 g) were introduced into the autoclave according to solvent/coal ratio equaled 2.5 wt/wt. The total mass of reaction mixture was 140 g and reagents were mixed in closed autoclave container with a mixing velocity of 500 rpm during the heating-up stage as well as during the remained reaction time. The autoclave was pressurized to an initial pressure of 34.4 bars (H$_2$) and then hermetically closed and heated up from room temperature up to 420 °C with a heating rate of 8.3 °C/min (position II) or 5.6 °C/min (position I). The reaction time of 60 mins were used (except for test No. 12 with 120 min), measured since the required temperature was obtained. The type of the carried out tests are described in Table 4.

After each reaction, the autoclave was cooled down to ambient temperature by air flow and then a gas sample was taken. The mass balance was calculated by the weight of the total sediment and liquids filtrated (cold filtration). Gas composition was characterized by Agilent's "Refinery Gas Analysis" method. Liquid products analyses were: density at 15 °C measured using a semi-hydrometer KYOTO DA-645 (Kyoto Electronics Manufacturing co.).

Simulated distillation (SimDis) performed by gas chromatography following the ASTM D7169 [13]. The sample was injected onto a gas chromatographic column separating the hydrocarbons according to their boiling point. The column temperature is reproducibly increased during analysis and the area under the chromatographic curve is recorded. Based on the analysis of the known hydrocarbon mixture, covering the sample distillation range and carried out under the same conditions as the sample, the boiling point time points are assigned from the calibration curve. Based on this data, the distribution of boiling points in the sample is determined. An Agilent 7890 HT/SIMDIS system was used. The column installed was DBHT-SIMD, 5 m, 0.53 mm, 0.15 μm.

Elemental analysis (C/H) was done by elemental analyzer FLASH 2000 (ASTDM D5291 [14]), nitrogen and sulfur content in micro scale

Table 3
Gross and net calorific values of used materials.

	Coal types				Solvents						
	BC	1%Fe/BC	1%Mo/BC	0.5%FeMoW/BC	Tetralin	Decalin	1-MN	C9 + frac.	LCO	H-LCO	WT Pyr. Oil
Gross cal. val., MJ/kg	29.78	27.19	28.73	28.17	52.35	55.26	44.71	49.82	50.78	51.40	51.99
Net cal. val., MJ/kg	28.38	25.79	27.33	26.77	50.39	52.19	43.07	47.59	48.12	48.95	49.56

(ppm) was measured by Trace SN Cube Instrument (ASTDM D5453 [15], ASTDM D4629 [16]). Thermogravimetric analyses of the obtained direct liquids were performed by TGA Discovery series device delivered by TA Instruments, operating at heating rate of 10 °C/min from temperature 50 °C to 900 °C under N_2 or O_2 (20 mL/min flow rate).

The measurements of the gross and net calorific values of the materials and direct liquid products were performed by VUHU using bomb calorimeter Parr 6300, delivered by Parr Instruments Company according to CSN ISO 1928 and CSN DIN 51,900 norms [17,18].

The wt% of insoluble n-heptane impurities analysis in liquid-products was carried out according to the next procedure: A filter paper (A 589/3 blue tape) was dried in a furnace for 2 h at 110° C. After 2 h, the paper was placed into a desiccator at room temperature. After 40 min, the paper filter was weighed and re-dried for other 40 min. This operation was repeated until having constant weight (difference between two re-dryings less than 0.0008 g). Then, 10 g of sample were introduced into a 250 mL beaker and mixed with 40 mL of n-heptane. The mixture of 10 g sample and 40 mL of n-heptane was filtered and the filter paper was weighed.

As reported by other authors, the solid residues produced by DCL are less valuable products than the original coal used as raw material [3], so for this research proximate and elemental analyses of solid residues were skipped to focus mainly on theirs extraction for improvement of total liquid yield. The solid-product solubility in n-heptane was carried out according to the next procedure: The solid sample was weighed (2–2.5 g) into a composite filter paper. The paper was closed by a tuft of cotton wool and inserted into a glass extraction cartridge. Soxhlet extraction apparatus was used and the extraction device consisted of a broad neck conical flask with volume 500 (or 250 or 100) mL, and Dimitroth coolers of 300 mm length joined with a NZ 45/40 joint. The inner tube of the cooler was provided with two openings at the end-end to suspend a glass extraction cartridge. The paper was weighed after each extraction.

3. Results and discussion

Mass balances and elemental analyses are exposed in Figs. 1 and 2 and Table 5. In case of non-catalytic reactions, the best yield to direct
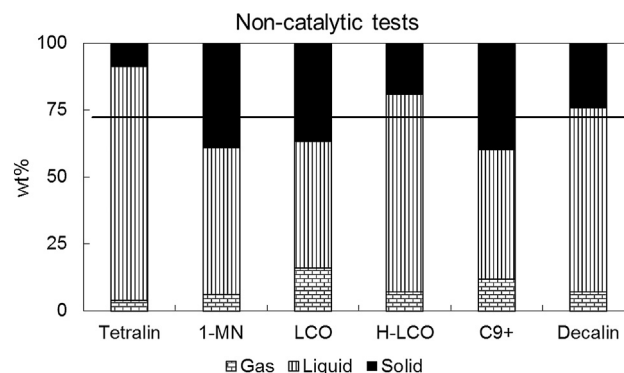

Fig. 1. DCL tests using model solvent (tetralin, 1-MN or decalin) or petroleum fraction (LCO, H-LCO or C9 +) and brown coal. Dash line is indicating the 28.6 wt% of initial solid content present in the feedstock.

liquids was obtained in reaction 1 when the model solvent tetralin was used. The highest solid-product content was found for the tests using 1-MN, C9 + fraction and LCO; moreover test with LCO produced the biggest amount of gas. These results are in agreement with literature considering the tetralin as a good hydrogen donor for DCL reactions [19]. However the 1-MN surprisingly was not an effective hydrogen donor. Due to a high content of tetralin-derived compounds, H-LCO resulted to be the second most effective hydrogen donor. While LCO, with a high content of diaromatic compounds, which were hydrogenated to monoaromatics during the test, was not able to donate more hydrogen atoms. Thus, the presence of tetralin type molecules, so partially hydrogenated naphthalene type molecules, resulted in an increment of liquid-products yield and in a decrease of solid and gaseous products yields. Test with decalin as hydrogen donor resulted in a much lower yield to liquids compared to the test performed with tetralin. For test No. 1 (tetralin) approximately 27 wt% of the total liquid product could be generated from the solid brown coal and the rest from the solvent (amount calculated from SimDis, Fig. 3). This type of approximate calculation from SimDis is possible only in case of pure solvents with singular boiling points. Thus, for those tests, it was possible to assume which amount of mixture was distilling in a different boiling

Table 4
Non-catalytic and catalytic tests conditions.

Non-catalytic tests						
Test No.	**1**	**2**	**3**	**4**	**5**	**6**
Reaction time, min	60	60	60	60	60	60
Heating rate, °C/min	8.3	8.3	8.3	8.3	8.3	8.3
Solvent	Tetralin	1-MN	LCO	H-LCO	C9 +	Decalin
Catalytic tests							
Test No.	**7**	**8**	**9**	**10**	**11**	**12**	**13**
Reaction time, min	60	60	60	60	60	120	60
Heating rate, °C/min	8.3	8.3	8.3	8.3	8.3	8.3	5.6
Solvent	Tetralin	LCO	WT Pyrolysis Oil				
Catalyst	NiW (5g)	Fe[1]	Mo[2]	FeMoW[3]	Mo[2]	Mo[2]	Mo[2]

[1] Fe(1 wt%)/BC.
[2] Mo(1 wt%)/BC.
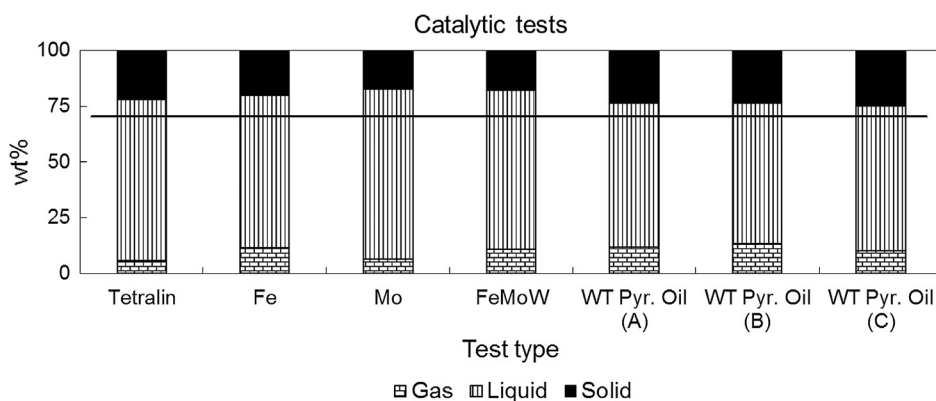[3] {Fe(0.5 wt%) + Mo(0.5 wt%) + W(0.5 wt%)}/BC.

Fig. 2. Catalytic tests using tetralin and NiW/SiO$_2$-Al$_2$O$_3$ (Tetralin), LCO and Fe(1 wt%)/BC (Fe), LCO and Mo(1 %wt)/BC (Mo), LCO and {Fe (0.5 wt%) + Mo(0.5 wt%) + W(0.5 wt%)}/BC (FeMoW). Three tests using waste tyres pyrolysis oil (WT Pyr. Oil A, B and C) were carried out with Mo(1 wt%)/BC during 60, 120 and 60 min at 420 °C with 8.3, 8.3 and 5.6 °C/min heating rates respectively. Dash line is indicating the 28.6 wt% of initial solid content present in the feedstock.

Table 5
Elemental composition of direct liquid-products obtained from all carried tests.

Non-catalytic tests

Test No.	1	2	3	4	5	6	
C, %	91.60	88.90	86.50	87.14	91.20	85.40	
H, %	8.48	7.60	7.39	10.20	8.10	11.08	
S, ppm	758	808	7636	849	11,000	662	
N, ppm	2336	761	1692	1131	802	663	
Density (15 °C), kg/m^3	1004.8	1040.9	1017	926.5	943	896.1	

Catalytic tests

Test No.	7	8	9	10	11	12	13
C, %	89.70	89.30	86.16	89.01	86.20	87	86.60
H, %	8.23	9.19	9.27	9.12	10.10	10.30	10.40
S, ppm	469	4646	4240	4478	5245	4777	5300
N, ppm	2085	1868	2525	2229	3578	3698	4349
Density (15 °C), kg/m^3	1004.8	984.6	988.3	981.2	943.9	938.6	942.7

range than the utilized solvent. Second best yield to total liquid products was obtained when H-LCO was used as solvent. However, SimDis results (Fig. 3) showed that approximately 8 wt% of the total received liquid product was originated from the solid coal. This assumption was based on differences in distillation curves shape between used solvent and liquid product.

Because partially hydrogenated compounds were considered as the best option for DCL reactions and with the aim of continuing catalytic tests without added cost to the process (H-LCO needed to be produced from LCO in a previous hydrotreatment [12]), LCO was selected as solvent-reactant for catalytic tests. LCO can also be obtained from refinery (easily affordable and a good solvent-reactant able to be partially hydrogenated, so a good candidate to be hydrogen donor for the catalytic DCL reactions). For the catalytic tests, the total liquid-products content was similar (slightly lower) compared to the total liquid-

product amount obtained after test No. 1. Nevertheless, test No. 3 (LCO) produced much lower amount of total liquid-products (Figs. 1 and 2) compared to the catalytic tests when LCO was used as well (especially using Mo/BC). For test using Mo/BC, SimDis results (Fig. 4), showed that approximately a 10 wt% of the liquid-products presented different boiling points range compared with the initial LCO. However, taking in account that LCO and H-LCO are a complex mixtures and not model solvents with a singular boiling points, separating the percent of liquid-product and initial liquid-solvent should be taken only as an indicative value.

Waste Tires Pyrolysis Oil was selected as waste derived solvent-reactant for DCL tests using Mo/BC as the best option after the evaluation of the catalytic trials (Mo/BC presented the highest yield of the liquid-products). In this case, all tests showed similar total liquid-product amounts and elemental analysis results (Table 5). The total amount of liquid, solid and gaseous products was similar to the amount obtained in non-catalytic test with decalin. However, the elemental composition of these products was different as a consequence of a different type of feedstock usage.

Interestingly for tests No. 8–10 (catalytic tests) the results were similar together with a slightly lower amount of direct liquids compared to test No. 1 according to the SimDis (Figs. 3 and 4). Approximately 10 wt% of produced direct liquids presented different boiling range than the hydrogen donor (tests No. 8–10). However in the case of using LCO, H-LCO or WT pyrolysis oil, the calculation of the direct liquid produced from the coal is more difficult due to their similar boiling range compared to the hydrogen donors. For catalytic tests No. 8–10, the increment in the direct liquids production was higher than 20% compared to test No. 3 (LCO was used as feedstock). As conclusion, the use of metal catalysts Fe, Mo or FeMoW supported on brown coal improved an increment in the final yield to liquid products.

Test using Mo/BC resulted to be the most effective in production of n-heptane soluble compounds (maltenes) (Table 6 and Fig. 5).
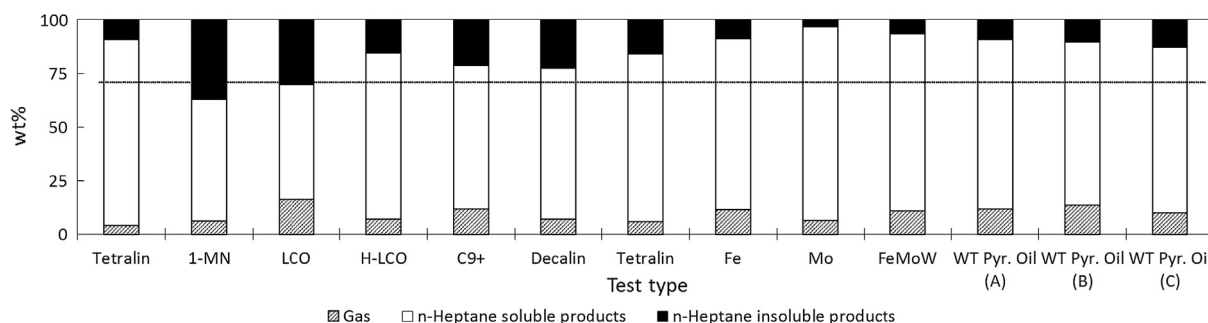

Fig. 3. Non-catalytic tests using tetralin, 1-MN, LCO, H-LCO, C9+, decalin and catalytic tests using tetralin and NiW/SiO$_2$-Al$_2$O$_3$ (Tetralin), LCO and Fe(1 wt%)/BC (Fe), LCO and Mo(1 wt%)/BC (Mo), LCO and {Fe(0.5 wt%) + Mo(0.5 wt%) + W(0.5 wt%)}/BC (FeMoW) respectively. Three tests using waste tires pyrolysis oil (WT Pyr. Oil A, B and C) were carried out with Mo(1 %wt)/BC during 60, 120 and 60 min at 420 °C with 8.3, 8.3 and 5.6 °C/min heating rates respectively. Dash line is indicating the 28.6 wt% of initial solid content present in the feedstock.
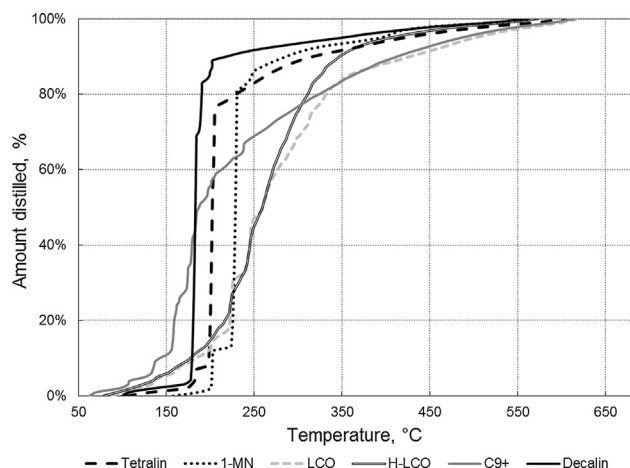
Fig. 4. SimDis for non-catalytic tests No. 1–6.

Table 6
n-Heptane insolubles for solid and liquid products having the total amount of gas + liquid + solid products = 100 wt% as reference.

Non-catalytic tests						
Test No.	1	2	3	4	5	6
Impurities insoluble in n-heptane, wt%[1]	5.73	1.91	0.94	1.49	0.02	0.34
Insoluble solid in n-heptane, wt%	3.40	35.10	29.51	14.06	21.36	22.34
Catalytic tests						
Test No.	7	8	9	10	11	12	13
Impurities insoluble in n-heptane, wt%[1]	1.35	0.02	0.05	0.01	0.57	0.38	0.35
Insoluble solid in n-heptane, wt%	14.60	8.85	3.18	6.46	8.62	9.89	12.54

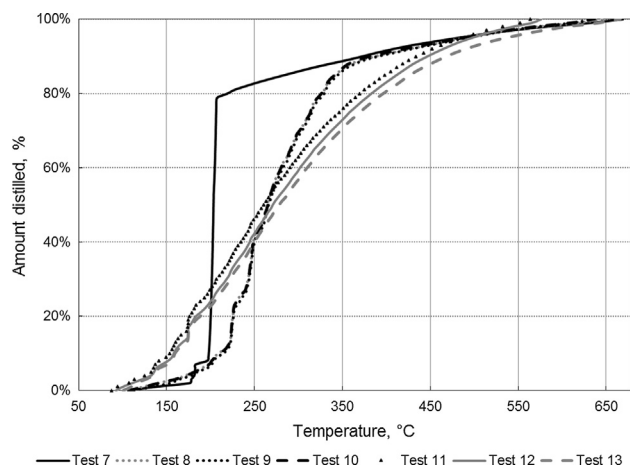[1] *Impurities present in the total liquid-product.*

Fig. 5. SimDis for catalytic tests No.7–13.

Moreover, the highest yields to liquid products and to n-heptane solubles were received together with the lowest production of gases. The use of 1-MN and LCO resulted in higher amount of solid product insoluble in n-heptane as expected. However, when metal supported on BC (catalytic tests) was used, the amount of n-heptane soluble solid product increased. Longer reaction time and decreased heating rate resulted in higher amount of n-heptane insoluble solids, so the test No. 11 was the best option for having the highest amount of n-heptane soluble compounds. However, the total amount of gases increased when the reaction time and the heating rate were higher in test No. 11 and 12

compared to the test No. 13.

Tests using Mo/BC and WT pyrolysis oil resulted in the liquid products with the highest H/C atomic ratios as shown in Table 7. The H/C ratio was calculated by molecular weight of carbon and hydrogen and percent content of those elements in the sample composition according to the equation below:

$$H/C = \frac{\frac{wt\%\,H}{atomic\,mass\,H}}{\frac{wt\%\,C}{atomic\,mass\,H}}$$

Predicted H/C ratios of mixed materials for each test were calculated by H/C ratios of substrates and applied solvent/coal weight ratio according to equation below:

$$H/C_{predicted} = \frac{2.5 * H/C_{solvent} + 1 * H/C_{coal}}{3.5}$$

In case of non-catalytic tests no clear trend was found for H/C ratios. The values were similar to predicted ones, only tests No.3 and No.5 presented significantly lower values compared to predicted ones. Test No. 7 (NiW/Tetr.) showed even lower H/C ratio than No.1 without catalyst, so possibly the commercial catalyst was apparently non-active. In case of tests with metals supported on coal, for tests with LCO, the highest H/C ratio was obtained when molybdenum supported on the coal was used. In all cases where WT pyrolysis oil and 1%Mo/BC were used, the H/C ratios were higher compared to the predicted H/C values. Nevertheless, as shown in Fig. 2, the total amount of solid and gaseous products was higher compared to the test using molybdenum covered coal and LCO as a solvent.

For all liquid products, the water content was lower than 0.2 wt%.

In terms of gaseous-products, their production was not accompanied with the highest amount of solid products and a no clear tendency was found for the gases production. However, the percentage of gaseous products was the lowest in two cases, non-catalytic test using tetralin and catalytic test using Mo/BC and LCO. For these two tests the highest yield to liquids and n-heptane soluble products was achieved.

The composition of gases (Table 8) showed that hydrogen, methane, carbon dioxide, ethane and propane were the main gaseous products detected. No carbon monoxide was found. This could be related to water–gas shift reaction because of partially wet coal usage, decarboxylation of carboxyl groups or reaction of methanation where carbon monoxide reacts with gaseous hydrogen producing methane and water molecules. At the beginning the water–gas shift (WGS) reaction was considered possibly as the main reason of the lack of CO due to the low water content in the products and the use of high temperatures during reaction, however the reaction equilibrium of WGS is shifted more preferably onto products side while the reaction temperature is low. In this case reaction temperature was 420 °C (693.15 K) and in the range of 600–2000 K the WGS reaction equilibrium is close to 1. Taking this fact in account the decarboxylation of carboxylic groups was considered as a second possible reason of no carbon monoxide in produced gas for current reaction set. It is highly probable that the lack of CO was found because of combination of many undesired reactions during DCL for example methanation of CO under high concentration of hydrogen combined with WGS as well as the effect of some spontaneous side catalytic processes due to many metals present in the coal structure like for example hydrodecarboxylation or hi-temperature WGS catalyzed by Fe,Cr,Mo metals which can be found in the coal structure [20–22]. Hydrogen sulfide was only detected in reactions using WT Pyr. Oil (tests No. 11–13) possibly due to the high amount of sulfur in the WT. The lower content of hydrogen sulfide in the gas obtained from test No. 12 (0.4 vol%.) can be related to the longer time of reaction, it was possible to assume that hydrogen sulfide reacted being included in the solid product as suggested by results in Table 5 presenting curiously lower sulfur content in the liquid products compared to tests No. 11 and 13.

TGA results (Table 9) for non-catalytic tests showed different weight losses at different temperature ranges depending on each reaction. Test

Table 7
H/C atomic ratios of pure solvents, products and feedstock mixtures (predicted).

Materials												
	Coal SevEnX	Solvents LCO	H-LCO	C9 + frac.	WT pyr. Oil	Tetralin	1-Mn	Decalin				
H/C ratio	1.01	1.35	1.50	1.35	1.52	1.2	0.91	1.8				

Test No.	Products												
	1	2	3	4	5	6	7	8	9	10	11	12	13
Solvent	Tetralin	1-MN	LCO	H-LCO	C9 +	Decalin	Tetralin	LCO			WT Pyr. Oil		
H/C ratio	1.10	1.02	1.02	1.39	1.06	1.55	1.09	1.23	1.28	1.22	1.40	1.41	1.43
H/C predicted	1.17	0.94	1.25	1.36	1.25	1.57	1.17	1.25	1.37				

Table 8
Main compounds detected in gas composition – level of significance > 0.5 vol%.

Compound	Test 1	2	3	4	5	6	7	8	9	10	11	12	13
	Volume %												
Hydrogen	74.1	48.1	30.0	64.0	38.4	63.6	78.6	58.4	57.1	67.6	47.4	49.1	48.8
CO_2	7.3	9.0	6.9	6.6	6.1	6.9	6.2	6.6	7.7	6.5	9.1	7.5	8.5
H_2S											0.8		1.0
Nitrogen	2.2		1.9	0.9	0.6	3.5	0.6	0.5					
Methane	12.4	37.9	43.8	22.5	39.3	21.7	10.9	18.9	24.5	19.1	25.0	29.6	26.7
Ethane	2.6	3.2	10.1	3.9	10.8	3.3	2.2	5.0	5.7	4.3	8.7	8.1	8.8
Propane	1.1	1.0	4.5	1.4	3.1	0.9	1.0	2.4	2.8	1.5	5.4	3.5	3.9
i-Butane			0.6								1.5	0.7	1.0
n-Butane			1.2					0.7	0.7		1.0	0.5	0.6

Table 9
TGA results for all carried reactions.

	TGA – N_2			TGA – O_2					
	Weight loss, wt%	Pol. Ar. [1] wt%	Dec. [2] °C	Weight loss, wt%			Ash, wt%	Dec. [2] °C	Comb. [3] °C
Test No.	50–200 °C			200–900 °C	50–200 °C	200–900 °C			
1	84.81	11.24	3.30	154.93	84.01	15.34	0.65	165.75	519.97
2	89.42	7.98	1.49	184.16	88.72	10.17	1.11	181.88	513.90
3	68.13	27.00	4.25	169.17	55.49	43.89	0.62	186.34	549.15
4	57.67	40.46	1.15	198.08	53.76	45.52	0.72	203.05	522.66
5	72.36	24.92	1.93	139.94	73.03	26.18	0.79	134.02	539.97
6	92.95	6.23	0.31	148.23	92.60	6.89	0.51	152.46	512.50
7	82.11	14.24	2.73	167.44	82.80	16.28	0.92	163.37	533.61
8	43.92	52.38	2.89	204.74	42.12	57.07	0.81	206.44	522.83
9	48.94	46.39	3.57	197.50	44.45	54.45	1.10	200.54	524.44
10	40.16	56.51	2.48	208.08	37.90	61.25	0.85	213.29	534.76
11	57.36	38.45	1.77	161.41	53.81	43.77	2.42	173.41	521.49
12	59.77	36.06	3.03	169.91	58.51	40.35	1.14	135.76	520.86
13	53.00	41.59	4.02	172.93	53.30	45.31	1.39	169.83	519.17

[1] Polycondensed Aromates.
[2] Decomposition maximum signal temperature, dwt/dT.
[3] Combustion maximum signal temperature, dwt/dT.

Table 10
Gross and net calorific values of direct liquid products from DCL tests (product of the test No.7 wasnt measured).

Non-catalytic							Catalytic					
Solvent	Tetralin	1-MN	LCO	H-LCO	C9 + frac.	Decalin	LCO			WT pyr oil		
Coal type	BC						1%Fe/BC	1%Mo/BC	0.5%FeMoW/BC	1%Mo/BC		
Test	1	2	3	4	5	6	8	9	10	11	12	13
Gross cal. val., MJ/kg	53.15	50.61	47.78	48.91	42.53	30.28	50.62	55.32	51.48	51.73	50.37	49.36
Net cal. val., MJ/kg	51.30	48.95	46.17	46.68	40.76	27.86	48.61	53.30	49.49	49.53	48.12	47.09

No.1 and 2 presented similar weight loss at 50–200 °C in oxygen or nitrogen, however for the test No. 1 the amount of polycondensed aromates (calculated from subtracting the amount of ash (TGA-O$_2$) to the final weight found on the end of the analysis at 900 °C under nitrogen) was 3.30 wt% compared to the 1.49 wt% for test No.2. For test No.1 (tetralin), the total liquid products content was higher than for the found for test No. 2 (1-MN). The highest ash content in the liquid products was found in the product obtained from test No. 11. No clear trends were found for catalytic or non-catalytic processes according to TGA results.

The calorific values of direct liquid products are listed in Table 10. In case of calorific values of the products from non-catalytic tests, the best result was obtained for test No.1 (tetralin) with a gross calorific value of 53.15 MJ/kg. This result was the only one in which a product of non-catalytic test showed a higher calorific value compared to the obtained one for the solvent used as a feedstock. This result was in agreement with the rest of analytical results, showing the highest direct liquid product yield and the highest calorific value for test No.1 from this group of tests (No. 1–6). In case of catalytic tests where LCO and different types of "catalytic" coals were tested (No.8–10), the best result was gained for test No. 9 with Mo/BC and at the same time the result of 55.32 MJ/kg of the gross calorific value was the highest compared to other direct liquid products from all carried tests. Test No. 9 resulted also in the highest yield to n-heptane solubles (maltenes). For tests included in the "factorial design" (No. 11–13), the best gross calorific value was received when reaction time of 60 min and higher heating rate of 8.3 °C/min were used. Thus, extending the reaction time (test No.12) and using lower heating rate (test No.13) negatively affected to the calorific values for liquid products.

4. Conclusions

Thirteen tests of direct coal liquefaction were carried out, seven catalytic and six non-catalytic ones. Model, industrial and waste solvents-reactants were tested to check their behavior, differences and similarities. Usage of brown coal which is impregnated by metals and can act as a catalyst itself is a novelty as well as innovative approach to co-process of this special coal with truly waste solvent. The highest amount of n-heptane soluble products was found for the test using molybdenum supported on the brown coal and LCO as a solvent, at the same time the direct liquid product obtained from this test showed the highest calorific values. Methane, carbon dioxide, ethane and propane were the main gaseous products in all cases. No carbon monoxide was found. The use of a product derived from a problematic waste, tires pyrolysis oil, was explored. It supposed an increment in the sulfur and nitrogen content in the final liquid products and a slightly lower amount of liquids and n-heptane soluble compared to the other catalytic processes.

Acknowledgements

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