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Fluidized bed gasification of coal-oil and coal-water-oil slurries by a gas containing CO_2-oxygen mixture

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Laboratory fluidized bed (FB) gasification of coal-vegetable oil slurries (COS) with 50 mass % of coal by CO_2-O_2 mixtures (ER $\approx$ 0.2, CO_2/dry fuel mass ratio = 1 – 2.4) at temperatures around 850 – 900 ^oC produced fuel gas with LHV values about 8 – 12 MJ/kg fuel. Composition of producer gas was studied by GC (major and minor gas components). The yield of heavier tar components (excluding BTX) exceeds 20 g tar/kg of dry German (lignite) coal and 36 g tar/kg of dry Polish bituminous coal. FB gasification of coal-oil in water emulsion slurry (COWS) prepared from the Polish coal and containing 47 mass % of coal, 40 mass % of water and 12 mass % of vegetable oil by CO_2-O_2 mixtures at similar operating conditions moderately reduces heating value (LHV) of dry, N_2 free producer gas in comparison with gasification of COS, elevates H_2 concentrations and substantially reduces yield of tar. Excessive entrainment of char particles from the FB can be solved by recirculation (circulating FB gasification).

1. Introduction

The coal slurries can be divided into three kinds: coal-water slurry (CWS), coal-oil slurry (COS) and mixed coal-oil in water (COWS) or coal-water in oil slurry (CWOS) utilizing emulsions either oil in water or water in oil. Coal-oil slurries have generally higher LHV than CWS and even higher than the parent coal alone. Coal slurries as fuels have been used preferably for pressurized entrained flow gasification (Collot, 2006) and fluidized bed (FB) combustion/gasification (Takeuchi and Myiadera, 1987) mainly due to possibility of smooth feeding of coal into pressurized reactors. Preparation of ternary coal slurries with a mixture of water and oil requires formation of emulsion of water with oil by means of emulsifiers, additives, surfactants and indispensable irradiation by ultrasound. Direct use of CO_2 instead of steam or as a partial substitute for steam in coal and biomass direct gasification processes (Butterman and Castaldi, 2007; Ye et al 1998) is one of possibilities of potential useful application of CO_2. Based on the above stated facts we concentrated in our study on FB gasification of COS and COWS slurries with

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gases containing higher concentrations of CO_2. Our attention was particularly devoted to effects of CO_2 concentrations and gasification temperature on producer gas composition, heating value, energy yield, tar and BTX yields in comparison with FB gasification with steam-O_2 mixtures.

2. Experimental

2.1 Coal-oil slurries and coal-oil in water slurry preparation

We have prepared and used for gasification experiments three kinds of coal-slurries: subbituminous (German) coal-rape seed oil slurry, bituminous (Polish) coal-rape seed oil slurry and bituminous coal-oil in water emulsion slurry. The coal used for preparation of the slurries had in all cases bimodal PSD. 70 mass % of coal particles had diameter below 80 μm and 30 mass % of particles had diameter between 125 and 315 μm. The coal-oil slurries contained 50 mass % of coal and 50 mass % of the rape seed oil. The ternary slurry involved Polish coal, rape seed oil, water and food oil emulsifier Tween 80 (polyoxyethylene (20) sorbitan monooleate, molecular formula $C_{64}H_{124}O_{26}$). The composition of the final slurry: coal 47 mass %, water 39.75 %, oil 12.19 % and emulsifier Tween 80 about 1.06 mass %. The composition data and LHV for the three slurries are given in Table 1.

Table 1: Composition data for the coal slurries

Components (mass %)	German coal-oil slurry (50/50)	Polish coal-oil slurry (50/50)	Polish coal-oil-water slurry (47 % coal)
Water (raw)	4.50	3.85	43.370
Ash (raw)	1.9	4.33	4.07
Combustibles (raw)	93.6	91.83	52.565 (incl Tween)
C (dry)	70.94	75.98	73.42
H (dry)	8.18	7.88	5.76
O (dry)	18.46	10.86	12.42
N (dry)	0.347	0.552	0.88
S (dry)	0.084	0.22	0.326
LHV – raw (MJ/kg)	29.75	32.26	16.8 (estimated)

2.2 Experimental facility for FB gasification and feeding of coal slurries

Gasification experiments were carried out in the atmospheric FB reactor (Svoboda et al., 2010; Pohořelý et al., 2006). The main part of the reactor, the reaction zone, is 2200 mm high tube with the inner diameter of 51 mm in the lower section and 99.0 mm in the upper section. Size reduction is placed in the height of 540 mm above a grate. Electrical heating of the gasifier consists of three independent sections along height of the reactor. The slurry feeding line is described elsewhere (Svoboda et al., 2010).

2.3 Producer gas analyses

The producer gas was analyzed (Svoboda et al., 2010; Pohořelý et al., 2006) both on-line and off-line. The presented data are, however, based on the off-line GC analysis of the producer gas (gas chromatograph HP 6890 equipped with two analytical channels). The details of the GC analyses for gas components can be found elsewhere (Pohořelý et al., 2006). A standard sampling line was used for tar collection according to the Tar protocol (BTG biomass technology group, 2004).

2.4 Experimental condition for FB gasification of coal-oil slurries

The experimental conditions for the FB gasification of the German coal-oil and Polish coal-oil slurry are given in *Table 2*. The samples of gas for GC analyses have been taken at steady state FB gasification at 850 °C used generally as the basic reference temperature. The producer gas compositions and characteristics in all presented figures are based on dry, nitrogen free conditions.

Table 2: Experimental conditions for FB gasification of German COS and Polish COS

Material of fluidized bed	Sand 0.25 – 0.5 mm
Gasification agent	CO_2/oxygen
Studied effects	Temper. of the FB reactor, CO_2/fuel ratio
Coal slurry feeding rate (g/h)	1153 (German COS) 1049 (Polish COS)
CO_2 for gasification	1001 g/h, 1.36 m^3/h
Basic CO_2/dry fuel ratio (molar CO_2/C)	2.22 kg/kg (0.85) 2.43 kg/kg (0.87)
Equivalent oxygen/fuel ratio ER	0.23 (German) 0.20 (Polish)
Reactor temperature	800–900 °C 800–925 °C
Approx. content of N_2 in dry gas	Approx. 40 – 60 vol. %

Experimental conditions for FB gasification of Polish coal-oil-water slurry are summarized in Table 3**.**

Table 3: Experimental conditions for FB gasification of Polish coal-oil-water slurry

Material of fluidized bed	Sand 0.25 – 0.5 mm
Gasification agent	CO_2/oxygen
Studied effects	Temp. of the FB reactor, CO_2/fuel ratio
Coal slurry (COWS) feeding rate	1050 g/h
CO_2 for gasification	1423 g/h 0.79 m^3/h
Basic CO_2/dry fuel mass ratio	2.39 (molar CO_2/C ratio = 0.89)
Steam/dry fuel ratio (molar H_2O/C ratio)	0.77 (0.70)
Equivalent oxygen/fuel ratio ER	0.19
Reactor temperature	800–900 °C

3. Results and discussion

3.1 FB gasification of German coal-oil slurry by a CO_2 containing gas

Producer gas yield and LHV values of the produced gas (related to 1 m^3) depend significantly on temperature in the FB gasification reactor. The dependencies of gas yield, LHV of the gas produced and concentrations of main gas components on mean reactor temperature are shown in Figure 1. The main gas components in the producer gas are CO_2, CO, and H_2. The CH_4 concentrations are relatively low (below 4.5 vol. %). At reactor mean temperature 850 °C, in a range of CO_2/dry fuel mass ratio 0.9 – 1.9 kg/kg, the effect of this ratio on gas yield and LHV of the producer gas was mainly given by the diluting effect of CO_2. The gas yield increased from 1.44 to 1.98 m^3/kg (dry fuel) due to increase of CO_2/dry fuel ratio from 0.9 to 1.91. LHV values of the gas produced decreased in the same interval of CO_2/dry fuel mass ratio from 13.1 to 9.6 MJ/m^3. Comparison of tar and BTX (benzene + toluene + o, m, p xylene) yield from FB gasification of German coal with gasification of the German COS is shown in Figure 2.

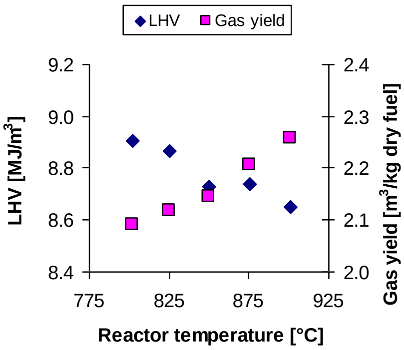

Figure 1: Effect of mean reactor temperature on gas yield and LHV of the producer gas (N_2-free, dry gas conditions) in FB gasification of German COS a CO_2-oxygen mixture (ER = 0.23, CO_2/C molar ratio = 0.85).

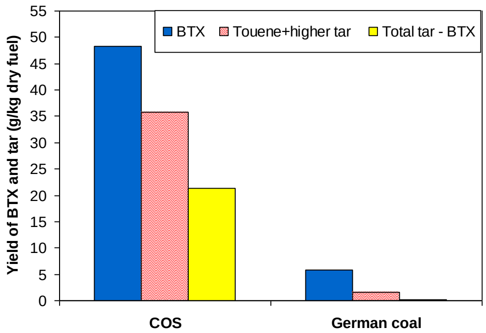

Figure 2: Comparison of BTX and tar yield from FB gasification of the COS (ER = 0.23,CO_2/dry fuel mass ratio = 2.22) and of the German coal alone (ER = 0.20, CO_2/dry fuel mass ratio = 1.89) at 850 °C.

3.2 FB gasification of Polish coal-oil slurry

The Polish bituminous coal is generally less reactive in FB gasification than the German subbituminous coal. Producer gas yields and LHV values of the produced gas depend only slightly on temperature in FB gasification reactor. The gas LHV values are about 8.3 MJ/m^3 with very weak decreasing trend with increasing temperature. The effect of CO_2/dry fuel mass ratio on gas yield and LHV of the gas produced is shown for Polish coal-oil slurry in Figure 3. The attained values of LHV of the dry producer gas from CO_2 gasification are generally significantly lower in comparison with the LHV values of dry producer gas from steam-O_2 gasification. The relative yields of BTX and total tar – BTX compounds are slightly higher for Polish COS in comparison with the German COS: BTX yield attains values about 61.65 g/kg of dry fuel. Total tar yield, excluding BTX, is about 23.8 g/kg.

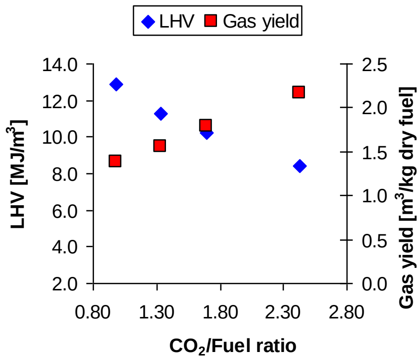

Figure 3: Effect of CO_2/dry fuel mass ratio on gas yield and LHV of the producer gas in FB gasification of Polish COWS by a CO_2-oxygen mixture (ER = 0.20, t = 850 °C).

3.3 FB gasification of Polish coal-oil in water slurry (COWS)

Producer gas yield (in m^3/kg of dry fuel) and LHV values of the produced gas (related to 1 m^3) for the COWS gasification increase with temperature in FB gasification reactor. Dependence of concentrations of main combustible components on reactor temperature is shown for Polish coal-oil in water slurry in Figure 4.

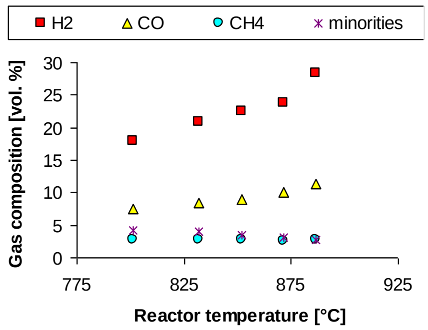

Figure 4: Dependence of producer gas composition (major gas components) on temperature in FB gasifier for Polish coal-oil-water slurry FB gasification by a CO_2-oxygen mixture (ER = 0.19, CO_2/C molar ratio = 0.89, H_2O/C molar ratio = 0.7).

LHV values of the gas produced decreased in the given range of CO_2/dry fuel mass ratio (at 850 °C) from 14.6 to 7.0 MJ/m^3. The attained values of LHV are moderately lower in comparison with gasification of Polish COS. The relative yields of BTX and tar compounds are about 50 % lower for Polish coal based COWS in comparison with the Polish coal-oil slurry

4. Conclusions

COS with 50 mass % of coal and 50 mass % of rape seed oil proved to be efficient, dense fuel with LHV about 30 MJ/kg. Their gasification in fluidized bed of quartz sand at temperatures between 800 and 925 °C with mixtures of oxygen and CO_2 (ER = 0.19–0.23, CO_2/dry fuel mass ratio ≈ 2.0) can generate producer gas with LHV values about

8–10 MJ/kg. The heating values of dry, N_2-free producer gas are affected by diluting effect of CO_2 and by relatively high content of ethylene, BTX and tar compounds. The heavier tar compounds yield (excluding BTX) is high, exceeding 20 g tar/kg of dry German coal based COS and exceeding 36 g/kg of fuel for Polish coal based COS. In the case of German COS the tar and BTX yield is roughly 1 order of magnitude higher than the tar yield in FB gasification of the same single coal. FB gasification of the COWS with content of water about 40 mass % and content of oil about 12 mass % (LHV $\approx$ 17 MJ/kg), reduces tar yield approximately to an half (related to FB gasification of the corresponding COS), but simultaneously moderately reduces the heating value of the producer gas. Application of calcined dolomite as fluidized bed particulate material and higher ER would cause substantial reduction of tar content in producer gas and reduction of total yield of tar and BTX compounds.Total energy yield from FB gasification of COS and COWS by CO_2-oxygen mixtures is slightly or moderately higher than the energy yield from FB gasification by steam-O_2 mixtures.
Expected problem with excessive entrainment of unreacted small coal-char particles in FB gasification (consequence of coal PSD in slurries and lower degree of coal-char gasification in oil slurries) can be solved by recirculation of coal-char particles (circulating FB gasification). Reactivity of coal is very significant factor in carbon loss from FB gasification of COS and COWS.

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