

## CO-GASIFICATION OF RUBBER WITH BROWN COAL

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### ABSTRACT

On the basis of laboratory and industrial experiments it was found that rubber can be treated by co-gasification with brown coal, namely in the process of the oxygen-steam pressure gasification in a moving bed (Lurgi gasification process). Considering the very low reactivity of the residual char from rubber, the optimal content of the rubber particles in the mixture being gasified should probably not exceed 10 wt.-%, but short-term increases in the proportion of these particles (up to 20 wt.-%) will not cause technological problems or significant economic losses.

**KEYWORDS:** co-gasification, rubber, brown coal, moving bed, reactivity

### 1. INTRODUCTION

Rubber waste production is an increasing economical and environmental problem in all countries, especially in developed ones. The potential of rubber as a fuel has been defined recently, especially in connection with the rising cost of coal and the increased problems with landfill of rubber wastes. Basic studies of pyrolysis (Kaminsky, 1985) were recently updated and co-pyrolysis applications were published (Ucar et al., 2005). Moreover, products from pyrolysis of tire-derived fuels obtained under various final pyrolysis temperatures and heating rates were investigated (Unapumnuk et al., 2006) and gasification characteristics of waste tires powders were described (Leung and Wang, 2003). On the basis of co-gasification studies summarized in the work of Born (Born, 1998) and possibilities of oxygen-steam pressure gasification in a moving bed (Bučko, 2006) the capability of brown coal for thermal treatment of rubber by this Lurgi gasification process has been demonstrated (Kříž and Bučko, 2006). Important is that a) the moving bed pressure gasification of coal is a proven technology to produce, among others, gas suitable for combined cycle power generation and b) the raw gas yield and other gasification parameters of coal feedback can be predicted (Anjaneyulu et al., 1993). Moreover, the Integrated Gasification Combined Cycle appears to be emerging as the most important technology of powering due to its long term economic advantage and the least polluting compared to other technologies as atmospheric fluidized bed combustion and pulverized coal combustion with flue gas desulfurization, particularly when solid waste is considered. IGCC is the only technology that can

easily and inexpensively capture carbon dioxide, often for other uses (Lockwood, 2005).

The aim of this study is to determine the amount of waste rubber acceptable for its thermal treatment with brown coal by the steam-oxygen gasification in a moving bed in laboratory and industrial scales. The rubber needs to be added to the coal in an amount which will not impair the usual utility properties of the resulting energetic gas for power plant in the Integrated Gasification Combined Cycle and will not cause any operating problems.

### 2. EXPERIMENTAL

*Laboratory experiments.* Firstly, co-gasification of rubber with brown coal was carried out under well-defined conditions of gasification in a laboratory scale at a unit for the conversion of solid fuels at atmospheric pressure designed for the gasification of samples of a maximum weight of 100 g, capable of heating to a temperature of up to 900 °C and collecting gaseous products into a gas holder with a capacity of 130 dm<sup>3</sup>. The functional chart of the unit used can be seen in Figure 1.

The apparatus used consisted of the following parts: a furnace with a quartz reactor, a CO<sub>2</sub> and water-vapor (H<sub>2</sub>O(g)) feeder, a separator of liquid and gaseous products, a gas holder, and a unit for operation and data registration. The furnace core was formed by an electrically heated vertical ceramic tube placed in a stainless-steel shell. The main component of the furnace was a quartz reactor equipped with a temperature sensor in the axis of the reactor. The quartz reactor had a double jacket, thus forming an inner and an outer part. The outer part consisted of

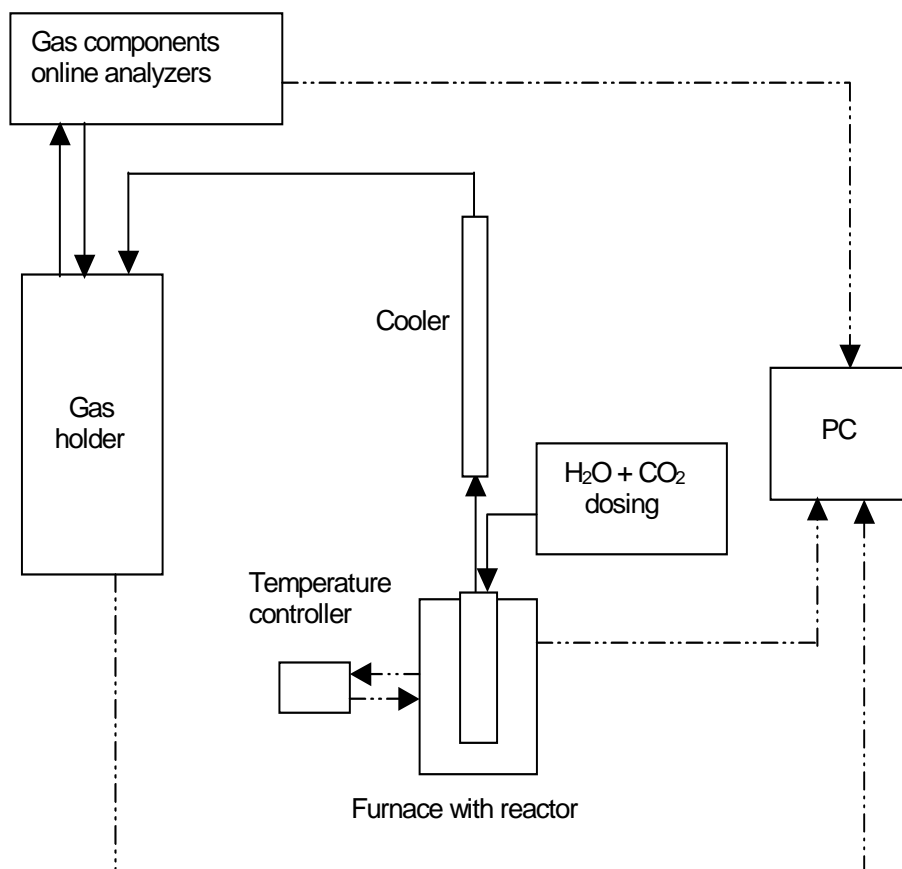


Fig. 1 Functional chart of the laboratory gasification unit.

a quartz tube of a diameter of 55 mm and a length of 450 mm with a sealed bottom, whereas the inner part also had a quartz tube but of a diameter of 40 mm and a length of 480 mm, with the bottom modified for the even distribution of the gasifying media (H<sub>2</sub>O(g) and CO<sub>2</sub>). The charge was placed in the inner part of the reactor. The gasifying media were being fed into the space between the inner and outer reactor. (The CO<sub>2</sub> being fed simulated carbon dioxide forming under operating conditions through combustion in the lower combustion zone of the industrial generator.) In the space between the tubes, the dosed media were being heated, which had reached the temperature of the charge being gasified prior to coming into contact with it. The temperature regime of the furnace was controlled by a program in a microprocessor-controlled regulator. A temperature regime with a linear temperature rise up to the final temperature was applied, with the temperature courses in the furnace and reactor being continuously registered. In the course of gasification, volatile products were being exhausted into the separator with a cooling circuit with ethanol (-10 °C). The gaseous products which had passed through the cooler were then fed into the gas holder and analyzed by the gas chromatographs of the Agilent Technologies, type 6890 N with the FID and TCD detectors.

*A temperature regime and separation of the products.* In all the experiments, a standard temperature regime was employed in the above-described tube furnace: a heating rate of 5 K/min to the final temperature of 900 °C with the soaking time at the final temperature being 30 minutes. So that the charge (30 g) would gasify, water was pumped into the reactor in the temperature range of 700–900 °C at an even flow of 30 cm<sup>3</sup>/h by a proportioning pump. In the temperature range of 750–900 °C, technical CO<sub>2</sub> was supplied from a pressure bottle, again at an even flow but this time of 5 dm<sup>3</sup>/h. Raw gas was exhausted from the reactor into the flask placed under the reflux cooler; the liquid products were collected in the flask, whereas the cooled gas was accumulated in the gas holder and analyzed after the experiment was completed. Amounts of ash and unburned carbon as the non-gasified solid residue in reactor were determined.

*Reactivity of the chars.* Chars from coal and coal with rubber were prepared and their reactivity was tested. Chars were obtained by heating of 30 g coal in reactor up to final temperature of 500 °C at the heating rate of 8 K/min, with the soaking time of 30 min at the final temperature. Reactivities of the chars towards carbon dioxide and steam were further tested by the thermal analysis method on a MOM

**Table 1** Laboratory experiments: proximate and ultimate analyses of the Jiří coal (wt.-%).  
VM – volatiles, S<sub>o</sub> – organic sulfur, O<sub>d</sub> – oxygen by difference.

Proximate analysis				Ultimate analysis (daf)				
moisture (air dry b.)	ash (db)	VM (daf)	total sulfur (db)	C	H	N	S <sub>o</sub>	O <sub>d</sub>
8.60	19.10	55.10	0.38	77.10	5.00	1.48	0.41	16.03

**Table 2** Laboratory experiments: proximate and ultimate analyses of the waste rubber used (wt.-%). For symbols see Table 1.

Proximate analysis				Ultimate analysis (daf)				
moisture (air dry b.)	ash (db)	VM (daf)	total sulfur (db)	C	H	N	S <sub>o</sub>	O <sub>d</sub>
0.90	5.31	68.90	1.12	85.59	7.65	0.57	1.04	5.15

**Table 3** Industrial experiment: proximate and ultimate analyses of the higher quality Jiří coal (wt.-%). For symbols see Table 1.

Proximate analysis				Ultimate analysis (daf)				
moisture (as received)	ash (db)	VM (daf)	total sulfur (db)	C	H	N	S <sub>o</sub>	O <sub>d</sub>
32.89	12.48	58.73	1.32	74.90	5.87	1.04	0.98	17.21

**Table 4** Industrial experiment: proximate and ultimate analyses of waste rubber particles (wt.-%). For symbols see Table 1.

Proximate analysis				Ultimate analysis (daf)				
moisture (as received)	ash (db)	VM (daf)	total sulfur (db)	C	H	N	S <sub>o</sub>	O <sub>d</sub>
5.92	3.66	65.71	1.48	85.28	7.20	0.24	1.37	5.91

thermal analyzer (MOM Budapest Comp.) with TERI electronics (TERI Praha Comp.). The thermal conditions of the measurement were similar to those of gasification, as the heating rate in the temperature range of 20–850 °C was 5 K/min, with a dwell at 850 °C until the maximum gasification of the tested char was achieved. During measurements, 10 dm<sup>3</sup>/h of carbon dioxide or 5 dm<sup>3</sup>/h of water vapor were fed into the apparatus.

*Materials.* For all the experiments, brown coal from the Jiří open-pit coal mine, Sokolov Basin, the same as under operating conditions in industrial scale, but with rather higher ash content. A grain size was of 0.5–4 mm, net (lower) calorific value was of 29.46 MJ/kg (daf basis), gross (higher) calorific value of 30.55 MJ/kg (daf basis). Analyses of the Jiří coal used are shown in Table 1. Furthermore, waste rubber was used with a grain size of less than 3 mm, supplied by the Pneucentrum Tasy Company. The analyses of the rubber are shown in Table 2.

*Industrial scale experiment.* Secondly, the rubber was co-gasified with brown coal in an industrial scale by pressure steam-oxygen gasification in a moving bed in the Lurgi gasifiers from the Sokolovská uhelná Company. The main resulting product was energetic

gas for a power-plant gas turbine working in the Integrated Gasification Combined Cycle. The composition of the raw gas obtained from the A gasifiers section, working with brown coal with the rubber particles, was compared with the gas from the B gasifiers section, working with coal alone. The percentage of rubber in the mixture being gasified was 20–40 %, mainly of 20 %. Coal was both gasified and co-gasified with the rubber under pressure of 2.7 MPa with the gasification generator output being approximately 10<sup>3</sup> m<sup>3</sup>/h.

*Materials.* It was used in operation dried brown coal, again from the Jiří open-pit mine, Sokolov Basin, of rather higher quality (lower ash content, Table 3). A grain size of the used coal was of 5–40 mm, gross (higher) calorific value was of 31.13 MJ/kg (daf basis). Further, rubber particles were used (in above-mentioned percentage). Waste rubber from waste tires was ground down to a grain size similar to that of the coal being gasified (3–40 mm). It is important that the water content in the particles themselves was 1.8–10 wt.-%, in average 5.9 wt.-% (Table 4), i.e. significantly lower than in the coal used (Table 3).

**Table 5** Composition (vol. %) of gas from gasification of coal alone and co-gasification of coal with rubber in a laboratory scale.  $Q_s$  – gross calorific value,  $s$  – gas density.

Gas component	the Jiří coal	coal + 10 % rubber	Coal + 20 % rubber
CH <sub>4</sub>	3.09	3.06	3.20
C <sub>2</sub> H <sub>4</sub>	0.07	0.08	0.14
C <sub>2</sub> H <sub>6</sub>	0.16	0.17	0.30
C <sub>3</sub> H <sub>6</sub>	0.03	0.06	0.34
C <sub>3</sub> H <sub>8</sub>	0.05	0.06	0.12
□C <sub>4</sub>	0.01	0.02	0.03
N <sub>2,r</sub>	0.26	0.53	0.43
CO	19.76	18.02	18.58
CO <sub>2</sub>	22.35	23.62	23.51
H <sub>2</sub>	54.220	54.38	53.35
$Q_s$ (MJ/m <sup>3</sup> )	10.90	10.76	11.22
$s$ (kg/m <sup>3</sup> )	0.768	0.776	0.789

**Table 6** Composition (vol. %) of raw gas from gasification of coal alone and co-gasification of coal with the rubber particles in an industrial scale.  $Q_i$  – net calorific value.

gas component	raw gas from the B gasifiers section (coal alone)	Raw gas from the A gasifiers section (coal with rubber)
CH <sub>4</sub>	10.44 – 11.94	10.43 – 11.71
CO	11.29 – 12.89	10.65 – 14.23
CO <sub>2</sub>	32.44 – 34.95	31.62 – 34.92
H <sub>2</sub>	39.79 – 42.28	38.90 – 41.03
C <sub>2</sub> H <sub>4</sub>	0.10 – 0.11	0.18 – 0.21
C <sub>2</sub> H <sub>6</sub>	0.54 – 0.63	0.69 – 0.75
C <sub>3</sub> H <sub>6</sub>	0.08 – 0.10	0.13 – 0.15
C <sub>3</sub> H <sub>8</sub>	0.14 – 0.16	0.17 – 0.18
ΣC <sub>4</sub>	0.09 – 0.10	0.06
ΣC <sub>5</sub>	0.06 – 0.10	0.12 – 0.16
ΣC <sub>6</sub>	0.03 – 0.05	0.03 – 0.06
O <sub>2</sub>	0.20	0.20
N <sub>2</sub>	0.40 – 0.50	0.40 – 0.80
$Q_i$ (MJ/m <sup>3</sup> )	10.67 – 11.32	11.02 – 11.78

### 3. RESULTS AND DISCUSSION

Only a few studies have been devoted to the gasification of rubber (as waste tires) in both laboratory and industrial scales (Leung and Wang, 2003; Lee and Kim, 1996; Raman et al., 1981). The waste tire/rubber gasification process is still in the development. In this work, both laboratory and industrial co-gasifications were carried out as complementary informations can be obtained in this way.

Essential findings. Basic data were acquired from laboratory co-gasification of brown coal with rubber at atmospheric pressure and from a comparison of the composition of the energetic gas obtained from brown coal alone on the one hand and with the admixtures of 10 and 20 wt. % of rubber on the other. During gasification/co-gasification, the decomposition

of the feedstock with CO<sub>2</sub> and H<sub>2</sub>O(g) were thought to begin at 300 °C; the formation of char at 420 °C; gasifying reactions of the char at 600 °C and intensive gasification of the char at 800/900 °C. The co-gasification of the mixtures in question at atmospheric pressure has proven that with the addition of up to 20 wt.-% of rubber in the charge, the composition of the obtained gas is practically the same when compared with the composition of the gas from coal alone, which is documented in Table 5. The same was found in the case of co-gasification of waste rubber with coal at a pressure of 2.7 MPa in an industrial scale (Table 6). Overall, it may be said that with appropriate dosing, the admixture of rubber does not considerably affect the composition and the heating power of the obtained energetic gas.

**Table 7** The temperature of the beginning of the char gasification and the rate of gasification at the temperature of 850 °C using CO<sub>2</sub>.

char from	beginning of gasification (°C)	rate of gasification (%/min)
the Jiří coal	820	1.54
coal with 20 % of rubber	830	1.39

**Table 8** The temperature of the beginning of the char gasification and the rate of gasification at the temperature of 850 °C using steam.

char from	beginning of gasification (°C)	rate of gasification (%/min)
the Jiří coal	730	1.88
coal with 20 % of rubber	786	1.21

*Evaluation of experiments in a laboratory scale in more detail.* A more detailed evaluation of the experiments in a laboratory scale has yielded the following results. With respect to the organic character of treated rubber, the main question which arises is that of the amount of unburned carbon. The amount of the unburned carbon is given, along with the processing conditions, by the reactivities of char towards H<sub>2</sub>O(g) and CO<sub>2</sub>. In this context, two reactivity parameters providing relevant information on the unburned carbon were evaluated: the temperature of the beginning of the char gasification and the rate of gasification at the temperature of 850 °C (determined by thermal analysis). The measured values are summarized in Tables 7 and 8. Table 7 shows the beginning of the gasifying reaction and the gasification rate using CO<sub>2</sub>, whereas Table 8 provides these parameters using steam.

The temperature of the beginning of gasification by carbon dioxide was higher in the case of the mixture with rubber than in the case of coal alone. The rate of gasification at 850 °C was lower in the case of the mixture with rubber (Table 7), which means that in this case, the gasification is slower, thus creating the possibility of more unburned carbon in the ash residue than in the common, low amount of unburned carbon from the gasification of coal alone. This conclusion has been corroborated by the results from gasification of chars by steam (Table 8). A considerable increase in the temperature at the beginning of gasification in the case of the mixture with rubber as compared with coal alone was determined, namely by 56 °C. At the same time, the rate of gasification at 850 °C decreased to 1.21 %/min as against 1.88 %/min in the case of coal alone. It may be presumed that the unburned carbon will be significantly higher in the case of co-gasification with rubber than in the case of gasification of coal alone. A solution may be a smaller grain size of the added rubber.

*Evaluation of experiment in industrial scale in more detail.* A more thorough evaluation of the

experiment in industrial scale has provided the following results concerning net calorific value of the raw gas obtained, sulfur in this gas, tar production, ash and unburned carbon, and content of the rubber particles in the gasified mixture.

*Net calorific value of the raw gas.* Based on Table 6, rubber particles are a material which can be treated by co-gasification in a moving bed as in the proportion of the particles in the fuel being gasified 20 wt.-% improve net calorific value of the raw gas on 3–4 % in comparison with that from gasification of coal alone.

*Sulfur.* Ratio of H<sub>2</sub>S concentrations in the raw gas from coal/rubber co-gasification ([H<sub>2</sub>S]<sub>A</sub>) and the reference coal gasification ([H<sub>2</sub>S]<sub>B</sub>) was determined as [H<sub>2</sub>S]<sub>A</sub>/[H<sub>2</sub>S]<sub>B</sub> = 0.90. Similarly, ratio of CH<sub>3</sub>SH concentrations was found as [CH<sub>3</sub>SH]<sub>A</sub>/[CH<sub>3</sub>SH]<sub>B</sub> = 0.63. It means that the H<sub>2</sub>S and CH<sub>3</sub>SH contents were lower in the case of co-gasification of the rubber-coal mixture in comparison with those from gasification of coal alone, in other words, the sulfur content was given by coal and not by rubber particles.

*Tar production.* A very positive feature of the co-gasification of rubber is more than a twofold increase in the production of tar, which is further workable.

*Ash.* Important results were provided by analyses of the resulting ashes. The ash from the B gasifiers' section, treating coal alone, showed an entirely standard composition and good properties – it was loose, without the slightest traces of slagging, light, with an unburned carbon of less than 3.5 wt.-%. The ash from the A gasifiers' section, treating coal with rubber, exhibited slight slagging tendencies on the one hand and a considerable increase in the content of unburned carbon as against the ash from coal alone. The increase in unburned carbon may be considered as a negative feature.

*Unburned carbon.* Although the increased content of unburned carbon in the ash of the generator could not cause further technological or ecological problems, it is evident that it causes a loss in the

useful energy from the system. Under normal operation conditions, when using fuel with an ash content not exceeding 26 wt.-% (dry basis), the contents of unburned carbon in the ashes are either 0–3 wt. %, which is low, ensuring very low energy losses, or 3–5 wt.-%, which is acceptable and does not cause any problems, or finally 5–7 wt.-%, which means an increased ash content and represents a higher chance of energy loss from the system. In this case, the determined contents of unburned carbon from section A were high – 10.5 wt.-% or higher. The cause seems to be the very significant difference between the reactivities of coal char and rubber char, as results from above-mentioned laboratory experiments. In the reaction zone, granular fuels in the mixture affect each other only to a minimum degree and gasify almost as if each component reacted individually. Should we substantially increase the proportion of rubber in the mixture and thus also the proportion of rubber carbon, the proportion of the unburned carbon will also increase. The penetration of carbon into the ash has a negative influence in two ways: a) in the reduction of the ash quality for its eventual technical application as well as for the maintenance of landfill and b) as a cause of the loss of energy invested in the process. This second factor is more important in economic terms. It seems that the grain size of just below 40 mm is too large for rubber and needs to be reduced. If finer granulometry of the rubber particles were used, it might improve the degree of conversion of residual carbon, in other words, to reduce the content of unburned carbon in ash the reduction of the maximum size of the grain to e.g. ca 15–20 mm is needed.

*Content of the rubber particles in the gasified mixture.* Considering the very low reactivity of the residual char from rubber, the optimal content of the rubber particles in the mixture with brown coal should probably not exceed 10 wt.-%, but short-term increases in the proportion of the particles in the fuel being gasified up to 20 wt.-% will not cause technological problems or significant economic losses.

#### 4. CONCLUSION

Rubber treated with brown coal in the process of the oxygen-steam gasification improved the net calorific value of the raw gas in comparison with that from gasification of coal alone. Considering the very low reactivity of the residual char from rubber, the optimal content of the rubber particles in the mixture with brown coal should probably not exceed 10–20 wt.-%. The optimum recommended grain size for rubber particles is 15–20 mm. The sulfur contents in gas were substantially lower in the case of co-gasification than in the case of gasification of coal alone. A very positive feature of the co-gasification of rubber is more than a twofold increase in the production of tar.

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