Plasma decomposition of pyrolysis oil to synthesis gas and carbon black

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Abstract: Pyrolysis oil produced from waste tires was decomposed in a reactor equipped by dc water/argon plasma torch. Atmosphere in the reactor was controlled by the adding of oxygen, carbon dioxide and water so that the overall amount of oxygen enables the entire gasification of oil. Synthesis gas with the high content of hydrogen and carbon monoxide and carbon black particles with the size of several hundreds of nm were produced.

Keywords: pyrolysis oil, decomposition, pyrolysis, plasma, carbon black, nano-sized

1. Introduction

Plasma technologies are used for decomposition processes particularly due to higher reaction temperature than those are usually achieved in conventional reactors. It brings the advantages of lower content of unwanted species such as tar or dioxins, higher reaction rates etc. This paper deals with the decomposition of pyrolysis oil produced from waste tires to synthesis gas (syngas) that is formed mainly by hydrogen and carbon monoxide but also by solid residue – carbon black powder. Since there are many areas where carbon black is used (total production in 2006 was 8,100,000 metric tons [1]) the new ways how to produce carbon black powders with higher efficiencies have been studied intensively during last decades. Carbon black manufacturing processes can be splitted into two basic groups: (a) the thermal black process where natural gas is thermally decomposed, or (b) the furnace black process where heavy aromatic oil plays the role of a carbon carrier [2]. Some applications (polymer electrolyte membrane fuel cells, supercapacitors etc.) need particles with minimum size, so called nano-sized particles. Plasmas, mainly thermal plasmas, are nowadays frequently used for carbon black production [3, 4].

2. Experimental

A plasma torch with DC supply was used as the main source of energy for the decomposition. The plasma torch involves the combination of arc stabilization by gas (cathode part), where the cathode is protected against oxidation by Ar flow, followed by water stabilization of the arc. Water is injected tangentially to the arc chamber of the torch and forms a vortex that surrounds the electric arc. An anode is a water cooled rotating copper disc.

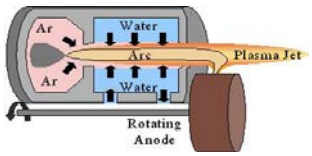

Fig. 1. Schema of the argon/water DC plasma torch.

The arc power was 110 kW during experiments. The simplified schema of the torch is in Fig. 1. Produced plasma features extreme parameters such as very high bulk temperature (18 000 K) together with low mass flow rate (typically around 0.3 g/s of H_2O + 0.2 g/s of Ar), however, due to combined stabilization, wide range of plasma properties can be adjusted [5]. The plasma torch is mounted at the top of a reactor. The reactor has ceramic thermal insulation with the thickness of 400 mm and inner volume of 0.22 m^3. The inlet of pyrolysis oil was on the top part of the reactor and the outlet of produced gas is in the upper side of the reactor. The mass flow rate of oil was controlled by overpressure in an oil reservoir and manually adjusted valve. Produced syngas enters a quenching chamber, where the produced gas is cooled down to 300°C by water spray then enters a filter chamber and subsequently is burnt (Fig. 2). A water ejector installed between the filter chamber and the syngas burner maintains the reactor at the slight underpressure of several hundreds of Pa. Reaction temperature is monitored by thermocouples and ranged between 1 200°C and 1 400°C during experiments. The measuring system included monitoring of plasma torch operation parameters, temperatures of inner walls in the reactor, calorimetric measurements of cooling water loops and the flow rate of produced syngas as well as its composition. A sampling probe for composition measurements was located at the reactor output in front of the quenching chamber. This set-up enables the fast quenching of the sampling gas that is similar to the quenching of the main flow of produced gas. A quadrupole mass spectrometer Pfeiffer Vacuum Omnistar GSD 301 with direct inlet was used as a main gas analyzer. A freezing unit is placed between the mass spectrometer and the sampling probe to avoid water condensation and the damaging of the mass spectrometer. From this reason, the efficiency of the gasification process is preferably calculated as a carbon yield. Particle images were taken using a scanning electron microscope EVO MA 15 (Carl Zeiss SMT, Germany) with LaB6 cathode.

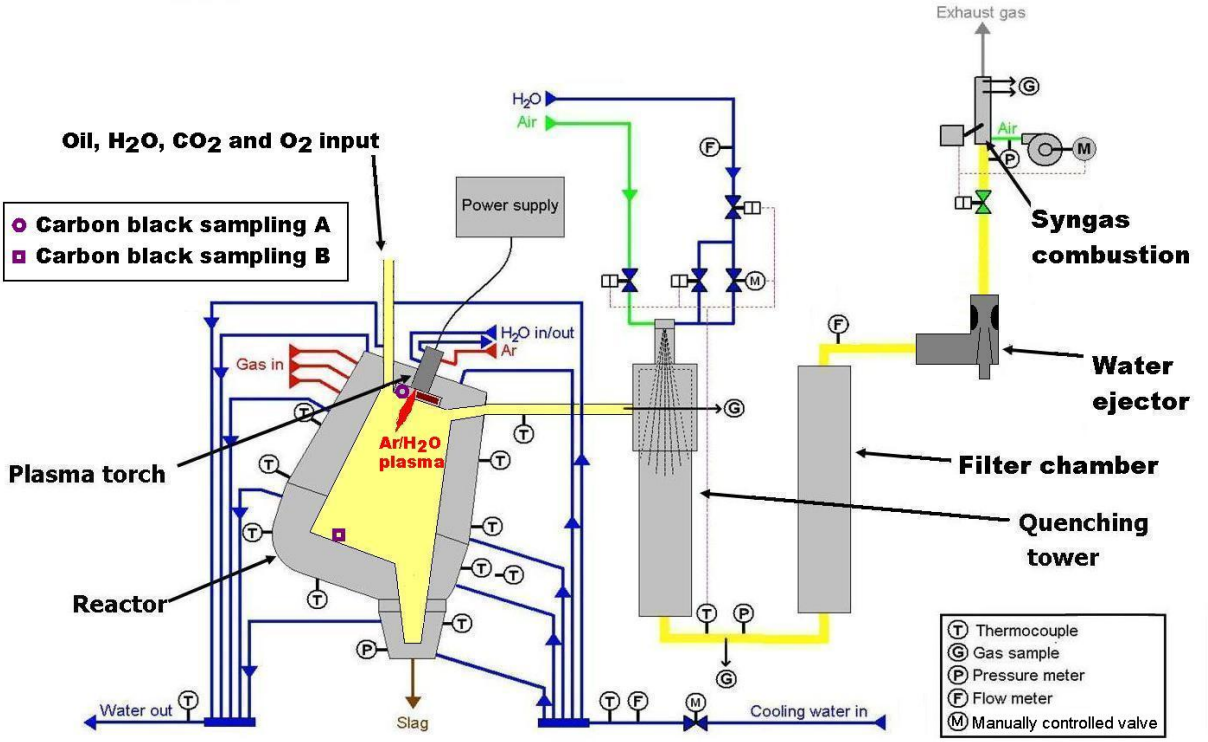

Fig. 2. Schema of experimental reactor.

3. Results and discussion

Pyrolysis oil used in the decomposition process was produced from waste tires. Compositional analysis of the oil showed the high content of aromatic and polyaromatic hydrocarbons as well as 21 wt. % of water. The elemental analysis of the water-free fraction of the oil was as follows: C – 87.6, H – 10.7, S – 1.01 and N – 0.66 (wt. %). The low heating value and the density measurements of the water-free fraction were carried out as well - 42.1 MJ/kg and 926 kg/m^{-3} (15°C), respectively.

The main point of the experiment was to produce syngas with the maximal content of H_2 and CO so oxidizing media (H_2O, CO_2, O_2 and the mixture of CO_2 and O_2) due to the composition of the oil had to be added. The flow-rates of the oil and oxidizing media are summarised in Table 1.

Table 1. Experimental conditions – flow-rates of pyrolysis oil and oxidation media, calculated carbon yield.

Type of oxidation	Oil [kg/h]	H_2O [kg/h]	CO_2 [slm]	O_2 [slm]	C_{out}/C_{in}
H_2O	8.8	10.6	-	-	0.64
CO_2	10.6	-	182	-	0.58
O_2	10.6	-	-	92	0.73
$CO_2 + O_2$	10.6	-	182	92	0.85

Produced syngas was leaving the reactor at temperature of approximately 1 200°C. There is also the position of gas sampling between the reactor and a quenching tower (see Fig. 2.). Syngas analysis revealed high concentrations of H_2 and CO. Argon from the plasma torch is neglected (the concentration of Ar varied under 1 vol. %). Main syngas components for different types of oxidation can be seen in Fig. 3.

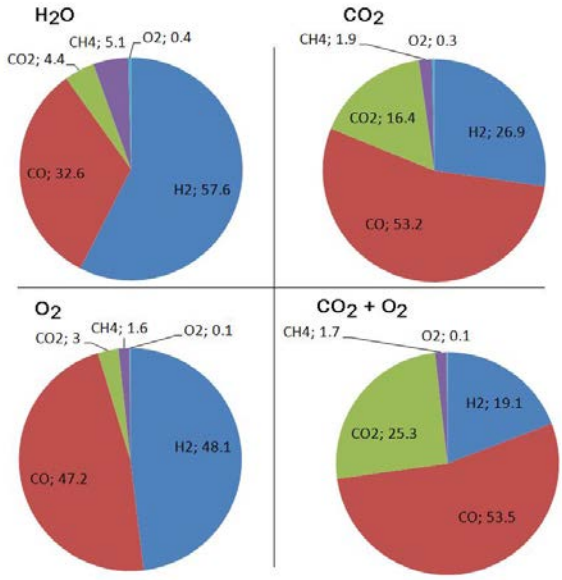

Fig. 3. Gas compositions of syngas for different types of oxidation (values in vol. %).

The highest value of LHV showed the experiment with H_2O (12.2 MJ/Nm^3) as an oxidizing medium although the surplus of oxygen during this experiment was higher by

30 % in comparison with the case of the stoichiometric amount of oxygen. Carbon yield is for this experiment also quite low so it can be deduced that the part of H_2O (added as an oxidizing medium) is evaporated and it does not participate the gasification process (water in syngas is not analysed).

The surplus of oxygen in the cases of oxidation by CO_2 and O_2 were much lower 3.7 and 7.1 respectively. CO_2 confirmed much lower affinity for the gasification process (caused especially by much higher energy demand in comparison with O_2) by low carbon yield and high CO_2 content in syngas.

The surplus of oxygen in the case when the mixture of CO_2 and O_2 was used reached 32.4 %. The highest carbon yield was achieved but LHV is low due to the partial oxidation of the oil and therefore high CO_2 content in syngas.

The reactor was opened after all experiments with the oil and carbon black samples were withdrawn from two different positions – from the upper (A) and the bottom (B) part of the reactor (see Fig. 2). The elemental analysis of the samples proved high carbon content (98.5 wt. %). Particle size ranged between 100 and 1000 nm and it can be seen that in the case of the sampling closer to the plasma torch (A) the particles seem to be more various in shape and size.

Described decomposition process could be utilized for syngas production as well as for the production of spherical nanosized black carbon parictles with above-mentioned size.

4. Acknowledgement

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5. References

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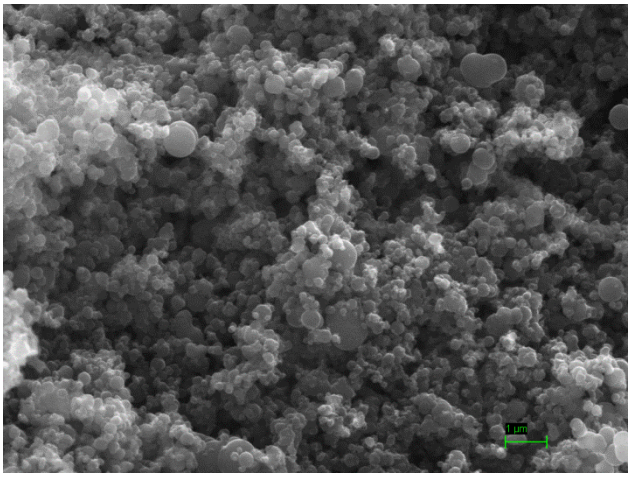

Fig. 4. Carbon black particles, sampling position A, particle size 100 - 800 nm.

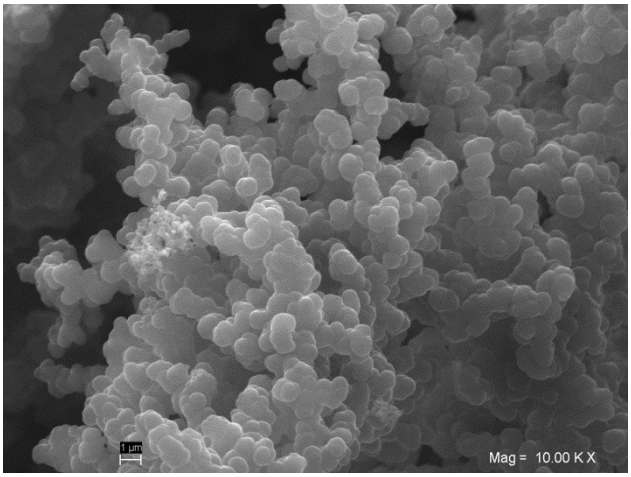

Fig. 5. Carbon black particles, sampling position B, particle size 400 - 1000 nm.

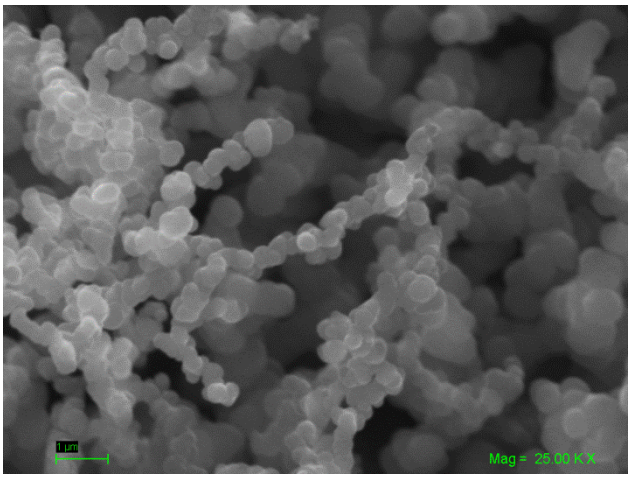

Fig. 6. Carbon black particles, sampling position B, particle size 180 - 600 nm.