Combustion of foamed emulsion containing biochar microparticles: Foam as a medium for incomplete hydrocarbons oxidation

B V Kichatov, A M Korshunov, A D Kiverin and E E Korshunova
Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya 13 Bldg 2, Moscow 125412, Russia
E-mail: korlex@yandex.ru

Abstract. The paper studies experimentally and analyzes the effect of biochar microparticles on the process of foamed emulsion combustion. Combustible foamed emulsion is a new promising type of fuel, which distinctive feature is that it could contain a significant amount of water (about 80 wt %) and it would be still combustible. In the process of experimental study we measured the speed of flame propagation through the foamed emulsion with the use of high-speed camera. It is obtained that the dependence of total burning rate of the foam on biochar content is non-monotonic and characterized by a maximum at certain biochar content. This is due to the effect of biochar microparticles on the heat losses from the flame front. By means of chromatographic analysis of combustion products it is shown that the use of biochar as a part of foamed emulsion favors the increase in syngas yield while the yields of methane, propane, ethylene and acetylene decrease. Structural characteristics of foamed emulsion were determined on the basis of microphotography while coefficients of surface and interfacial tensions were measured using a duNouy ring tensiometer.

1. Introduction
Foamed emulsion is foam consisting of gas bubbles dispersed in the emulsion. Foamed emulsions are widely spread in our everyday life that provides a wide research interest to their study [1]. For the first time it was proposed to utilize foamed emulsion as a fuel in [2]. Combustible foamed emulsion represents a multiphase mixture of oil droplets and oxygen bubbles distributed in the water solution of stabilizer, figure 1. The interest to study such systems is determined by their possible utilization for issues of chemical technology related with incomplete hydrocarbon oxidation. Due to the high water content in the foam and as a result due to the low temperature in the combustion zone the incomplete hydrocarbon oxidation could lead to the formation of significant amount of syngas (mixture of CO with H₂) and another valuable chemical products. Moreover, the interest to study such systems is related with the opportunity to use them to solve ecological problems related with the utilization of oil products spill on the water surface via burning. An important advantage of foamed emulsions as the type of fuel is the opportunity to control the flame speed in rather wide range. This can be achieved via variation in tube diameter and set up of obstacles inside the tube [3], via addition of magnesium oxide microparticles into the foam and varying the stabilizer concentration [4], via ultrasonic processing of the initial emulsion [5]. The mechanism of foamed emulsion combustion is rather complex and
ambiguous. It depends in many ways on the foam stability [6] and on the possibility of explosive boiling of liquid phase of the foam [7]. Often the foamed emulsion combustion proceeds in the non-stationary manner [8]. Experimental and theoretical results on the combustion of foamed emulsions are generalized in [9].

Nowadays an important problem arises concerning the use of renewable fuels. This paper is devoted to solve the problem of combined use of bio fuel and hydrocarbon fuel. The paper studies experimentally the process of combustion of the heptane-based foamed emulsion containing the microparticles of birch char. One obtained data on the influence of biochar microparticles on the total burning rate of the foam and on the combustion products composition. It is shown that the dependence of total burning rate on the biochar particles concentration in the initial emulsion is non-monotonic and characterized by the maximum at certain biochar content. On the basis of chromatographic analysis of combustion products it is established that the use of biochar particles as a part of foamed emulsion could favor the significant increase in syngas yield. We also present the data on the influence of biochar concentration on the yield of acetylene, propane, methane and ethylene.

2. Experiment

Foamed emulsion was prepared in two stages. At the first stage, the emulsion was made ready via the stirring of heptane with water solution of stabilizer, see figure 1. Average diameter of heptane droplets was equal to 48 µm. As a stabilizer we used commercial detergent representing a mixture of anionic and nonionic stabilizers. Coefficient of surface tension of water solution was 29.3 mN/m, that of heptane—19.5 mN/m. On the interfacial surface oil–water, it was 3.4 mN/m. Biochar microparticles (birch char, average size of particles 52 µm, porosity 75%, specific heat of combustion $3.1 \times 10^6$ J/kg) were added into the prepared emulsion. Particles content in the emulsion was varied in the range from 0 to 35 g/l.

At the second stage the hydrogen peroxide was added to prepared emulsion-suspension blend. Hydrogen peroxide decayed under the effect of catalyst (ammoniac solution of copper sulfate) that leaded to oxygen release. Foaming of the emulsion resulted in the formation of the foam with average diameter of oxygen bubbles of the order of 153 µm, see figure 1(b). The foam was prepared exactly inside the tube where the combustion process was considered and the flame speed was measured. Semi-opened tube of 27 mm diameter and 245 mm length was setup vertically. The foam was ignited by the pilot flame at the top open end of the tube. To analyze the combustion products the chromatograph Crystal 5000 was used. To measure the flame speed the high-speed camera Photron FASTCAM SA-4 (10 000 fps, 99.3 µs shutter speed) was used. Here, term “flame speed” is used to determine the velocity of flame leading point propagation [7]. Term “total burning rate of the foam” is used to determine the flame speed averaged over the whole tube length. The error of flame speed measurements was 7.4%.

![Figure 1. (a) Emulsion-suspension blend; (b) structure of foamed emulsion.](image-url)
3. Results and discussion

The use of biochar microparticles as a part of foamed emulsion could lead to significant changes in the total burning rate of the foam, figure 2. Thus, the increase in biochar particles concentration from 0 to 20 g/l causes the increase in total burning rate of the foam by the factor of 1.7. After the total burning rate achieves its maximum value at about 20 g/l concentration of biochar particles in the foam, the further increase in biochar content leads to the decrease in the burning rate. Thereby, one can observe maximum in the dependence of total burning rate of the foam on the biochar particles concentration, see figure 2. To substantiate such experimental data it is necessary to analyze the histories of flame speeds at different conditions, figure 3. As one can see, instantaneously the flame speed could achieve the values of the order of 100 m/s. This clearly indicates that an important role in the process of flame propagation belongs to the gas-dynamical factors. If the flame speed is determined by the heat transfer or by the diffusion of active centers then its value will be smaller by the order of magnitude compared with that observed in the experiments, see figure 3. The mechanism of flame acceleration is a quite complex phenomenon. Note here, that in considered case the ignition of the foam was carried out at the open end of the tube, therefore the expansion of combustion products could not lead to such significant flame acceleration.

One of the possible mechanisms of flame acceleration in the process of foam combustion is related with the phenomenon of explosive boiling of the liquid phase [9]. The essence of this phenomenon is the following. The heat flux from the combustion zone to the cold layers of the foam could lead to the liquid phase superheating relative the saturation temperature. Nucleation mechanism causes formation of supercritical vapor bubbles in the superheated liquid [10]. As soon as the vapor content achieves a certain critical level the foam decays. Herewith, the flow of vapor and droplets is formed. This flow drags the reacting mixture into the cold layers of the foam. As a result, scattered burning kernels are formed in the foam. The ignition pulse spreads from these kernels over the whole width of the tube, figure 4. Velocity of reacting mixture ejection determines the velocity of flame leading point propagation. In such a way, the processes associated with the water boiling determine the flame speed. Exactly this principle underlies the basis of flame speed control in the foam via addition of magnesium oxide microparticles [4].
Figure 3. Histories of flame trajectory and flame speed. Volumetric content of heptane in the emulsion is 17.7%. Biochar particles content in the emulsion: (a) 17.5; (b) 8.8 g/L.

Figure 4. Structure of the combustion zone in the foamed emulsion containing biochar particles. All the parameters correspond to the case of figure 3(a). Time instants are counted from the moment of foam ignition.

Magnesium oxide is the inert compound which does not take a part in the chemical reactions. However, due to the fact that microparticles represent centers of nucleation for vapor bubbles one is able to vary the flame speed in the foamed emulsion by the order of magnitude via addition of MgO particles [4].

The fact that the instantaneous flame speed changes in the oscillating manner, see figure 3, is due to the incomplete evaporation of fuel droplets in the convection-diffusion zone of the flame front [2]. In the process of flame acceleration there is a certain decrease in time during which fuel droplets are found inside the preheat zone of the flame. This leads to the decrease in the concentration of fuel vapors in the flame front and therefore to the decrease in temperature. As a result there is a certain decrease in the intensity of explosive boiling of the liquid phase. Due to this the flame decelerates. In the process of flame deceleration there is an increase in the completeness of fuel droplets evaporation in the preheat zone of the flame. This favors repeated increase in temperature and subsequent flame acceleration. Thus, the oscillating regime of flame propagation through the foam is realized.

The burning time of biochar particles is much longer compare with burning time of heptane droplets. Since the size of biochar microparticles is approximately the same as the heptane droplets diameter ($\approx 50 \, \mu m$) the difference can be estimated as a factor of 30 [10]. Due to this the combustion zones of heptane droplets and biochar particles occur to be split in space. The vapor heptane–oxygen mixture burns down inside the flame front while biochar particles burn in the region of combustion products. In the process of combustion the water droplets are
formed with characteristic diameter of the order of Plateau border of the foam. In the considered case the diameter of water droplets is of the order of 100 µm that is twice larger compare with heptane droplets (≈ 50 µm). Therefore, water droplets are mainly evaporated in the region of combustion products. The intensity of water droplets evaporation affects in many ways the heat losses from the flame front and, as a result, the temperature at the flame front. Due to the fact that primary reactions of carbon oxidation are exothermic

\[ C + O_2 = CO_2 + 395 \text{ kJ/mol}, \]  
\[ 2C + O_2 = 2CO + 219 \text{ kJ/mol}, \]

the biochar particles combustion causes the decrease in heat losses from the vapor flame front. Since in considered experiments the combustible foam was prepared with excess oxygen which is required for complete oil combustion then the process of biochar particles burning in the region of combustion products is exothermic. This leads to the increase in temperature at the flame front and, as a result, to the increase in intensity of explosive boiling of the liquid phase and certain increase in reacting mixture ejection velocity. Finally, the total burning rate of the foam increases, see figure 2. The fact that total burning rate decreases at significant increase in biochar concentration in the emulsion, see figure 2 is related with the effect of biochar microparticles on the process of liquid phase fragmentation. Biochar particles represent heterogeneous centers of vapor bubbles nucleation. Therefore, their presence in the emulsion favors finer dispersion of liquid phase of the foam in the process of foam decay. The decrease in water droplets diameter leads to the increase in the intensity of their evaporation that in turn causes the increase in heat losses from the flame front. The decrease in the temperature at the flame front favors decrease in explosive boiling intensity and, as a result, to the decrease in flame speed. In the region of combustion products biochar particles reacts in accordance with the integral heterogeneous reactions of gasification

\[ C + CO_2 = 2CO - 175.5 \text{ kJ/mol}, \]  
\[ C + H_2O = CO + H_2 - 130.5 \text{ kJ/mol}. \]

This leads to the additional formation of CO and H_2 compare with the case of pure foam without biochar particles, figure 5(a). Note that in the foam with oxygen deficit the endothermic reactions (3) and (4) would be much more probable inside the region of combustion products. Therefore, the use of biochar particles would cause opposite effect leading to the increase in heat losses from the vapor flame front.

Methane formation, figure 5(b), is related with the integral reaction

\[ C + 2H_2 = CH_4 - 74.9 \text{ kJ/mol}. \]

According to the data by Rusinko and Walker [11] the rate of reaction (5) is lower by 3–4 orders compared with reaction (4) rate. This leads to the significant decrease in methane yield which does not achieve even 1%. Note, that the concentrations of methane and ethylene, see figure 5(b), as well as concentrations of acetylene and propane, figure 6, in the combustion products decrease with the addition of biochar microparticles. One of the possible reasons defining this phenomenon is related with the fact that the use of biochar particles in the foam favors finer fragmentation of liquid phase. Smaller water droplets evaporate faster [12] that leads to the increase in water vapors concentration in the combustion products. Therefore, carbon mainly reacts via the gasification channel (4).

In case of biochar particles combustion in the environment with high humidity the reaction (4) is more probable than reaction [11]:

\[ C + 2H_2O = CO_2 + 2H_2 - 132 \text{ kJ/mol}. \]
Figure 5. (a) Dependencies of hydrogen and carbon monoxide on the concentration of biochar microparticles in the emulsion; (b) dependencies of ethylene and methane on the concentration of biochar microparticles in the emulsion (index 0 corresponds to the foam without biochar particles). Volumetric content of heptane in the emulsion is 17.7 vol%.

Figure 6. Dependencies of acetylene and propane on the concentration of biochar microparticles in the emulsion (index 0 corresponds to the foam without biochar particles). Volumetric content of heptane in the emulsion is 17.7%.

Analysis of combustion products shows that hydrogen yield occurs to be smaller than carbon monoxide yield that contradicts with reaction (4). This is due to the following reason: in the process of hydrogen diffusion out from the particle surface hydrogen reacts with oxygen via the reaction:

\[2H_2 + O_2 = 2H_2O + 231 \text{ kJ/mol.}\]

(7)

Herewith, the rate of reaction of carbon monoxide afterburning in the boundary layer near the particle

\[2CO_2 + O_2 = 2CO_2 + 571 \text{ kJ/mol}\]

(8)

occurs to be lower by several orders of magnitude compare with reaction (7) [11]. So, carbon monoxide content in the combustion products occurs to be higher compared with predictions on the basis of reaction (4).
4. Conclusions

Thus, we can draw the following conclusions:

- Despite significant water content in the foamed emulsion (volumetric water content in the initial emulsion is 82.4%) the flame propagation is possible in such a system.
- In such combustible system the conditions occur to be favorable for incomplete oxidation of hydrocarbons (the quenching of intermediate oxidation products takes place).
- The use of biochar microparticles as a part of foamed emulsion favors the increase in syngas yield that is related with reaction of gasification.
- In the case of foamed emulsions containing biochar microparticles, the yields of acetylene, methane and propane can be decreased almost twice.
- The dependence of total burning rate of the foam on the biochar microparticles content is characterized by the maximum at certain biochar concentration that is related with the influence of particles on the intensity of heat losses from the flame front.

Acknowledgments

The work was funded by the grant of the Russian Science Foundation No. 17-19-01392.

References

[1] Denkov N D *Langmuir* 20 9463–505
[2] Kichatov B, Korshunov A, Son K and Son E 2016 *Combust. Flame* 172 162–72
[3] Kichatov B, Korshunov A, Kiverin A and Son E 2017 *Combust. Sci. Technol.* 189 2095–114
[4] Kichatov B, Korshunov A, Kiverin A and Son E 2017 *Fuel Process. Technol.* 166 77–85
[5] Kichatov B, Korshunov A, Kiverin A and Ivanov M 2018 *Fuel Process. Technol.* 169 178–90
[6] Kichatov B, Korshunov A, Kiverin A and Son E 2017 *Fuel* 203 261–8
[7] Kichatov B, Korshunov A, Kiverin A and Saveliev A 2018 *Int. J. Heat Mass Transfer* 119 199–207
[8] Kichatov B, Korshunov A, Kiverin A and Son E 2017 *Energy Fuels* 31 7572–81
[9] Leont'ev A I, Kichatov B V and Korshunov A M 2017 *Combustion of Foamed Emulsions* (Moscow: Russian Academy of Sciences)
[10] Blander M and Katz J L 1975 *AIChE J.* 21 833–48
[11] Pomerantsev V V, Aref'ev K M, Akhmedov D B, Konovich M N, Korchunov Yu N, Rudigin Yu A, Shagalova S L and Shestakov S M 1986 *Fundamentals of Practical Combustion Theory* (Leningrad: Energoatomizdat)
[12] Spalding D B 1979 *Combustion and Mass Transfer* (London: Pergamon Press)