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Influence of the different oxidizers on the composition of sulfur products at bitumen gasification process

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Abstract. In the article an influence of various oxidizers on the composition of sulfur products at bitumen gasification process are described. As an object of research the natural bitumen of Ashalchinskoe oil field of Tatarstan Republic (Russia) was chosen.

Introduction

At the present time the gasification process of hydrocarbon fuels belongs to clean technologies such as conversion of coal, heavy oil, peat and other solid and liquid fuels. According to data of [1] several hundred gasification plants which process the hydrocarbon fuels for production of chemicals, syngas and synthetic liquid fuels work worldwide.

One of the important sources of raw materials is high-viscosity hydrocarbons, including bitumen and oil sands. They are under study in Canada, Venezuela, Iran and other countries. In Russia a significant amount of bitumen is concentrated in the territory of the Republic of Tatarstan, where its reserves are 7 billion tons [2].

Gasification of bitumen would be allowed to produce syngas as alternative fuel source and attendant chemical products for various industries, as the methanol, ammonia or hydrogen production.

At gasification of hydrocarbon raw materials an air, oxygen, water steam or the mixtures of them use as the oxidizers. Their influence on the composition of sulfur products is not fully investigated. And this is the purpose of this work.

Materials and methods

Bitumen is a complex mixture of high-molecular hydrocarbons of oil and heteroatomic compounds, containing oxygen, sulfur, nitrogen and metals [3]. Chemical composition of bitumen is less studied than their physical, rheological and colloidal properties. Bitumen is considered like a complex of three components: oils, tars and asphaltenes [4]. Content of other substances is less 1% that is why we don't calculate them. Bitumen gasification process was considered using Texaco technology at a temperature of 1400 °C and pressure equal 1 MPa for heavy oil residues [5].

Bitumen gasification process can be considered as a complex of several stages. At first under temperature influence are heating and formation of microfractures due to water vaporization. As a result of chemical interaction between steam and surface of bitumen components under study appear light hydrocarbons. At the temperature over 900°C the oxidation-reduction reactions, steam-methane reforming and water-gas shift reactions are occurred, oxygen destroys benzene rings partially. During



at this time the solid residue (a soot) from unreacted hydrocarbons and chemical substances which are components of syngas are forming [6, 7].

The final composition of produced syngas depends from the equilibrium of reaction (1):



Results and discussion

This paper presents the results of numerical studies showing the effect of various oxidizers on the composition of the sulfur products formed from depending on the oxidizer/fuel ratio. Oxygen and steam were used as the oxidizing agent. The bitumen of the Ashalchinskoye oilfield of the Republic of Tatarstan was considered as fuel, the elemental composition of which is presented in the table 1. For comparing of results the oxidizer/fuel ratio was taken equal 0.4, 0.8, 1.2 and 1.8.

Table 1. Ultimate analysis of Ashalchinskoye oilfield bitumen

Carbon	83.6 wt.%
Hydrogen	12.1 wt.%
Oxygen	0.5 wt.%
Nitrogen	0.4 wt.%
Sulfur	3.4 wt.%

Using Comsol Multiphysics software, the dependences of sulfur gasification products on oxidizer type and oxidizer/fuel ratio were obtained.

As it was written above the choice of technological parameters was taken on the base of Texaco gasification technology, which is used for utilization of heavy oil residues. Figure 1 shows the results of calculations for bitumen gasification using oxygen blow. Figure 2 shows the results of calculations for bitumen gasification using steam blow.

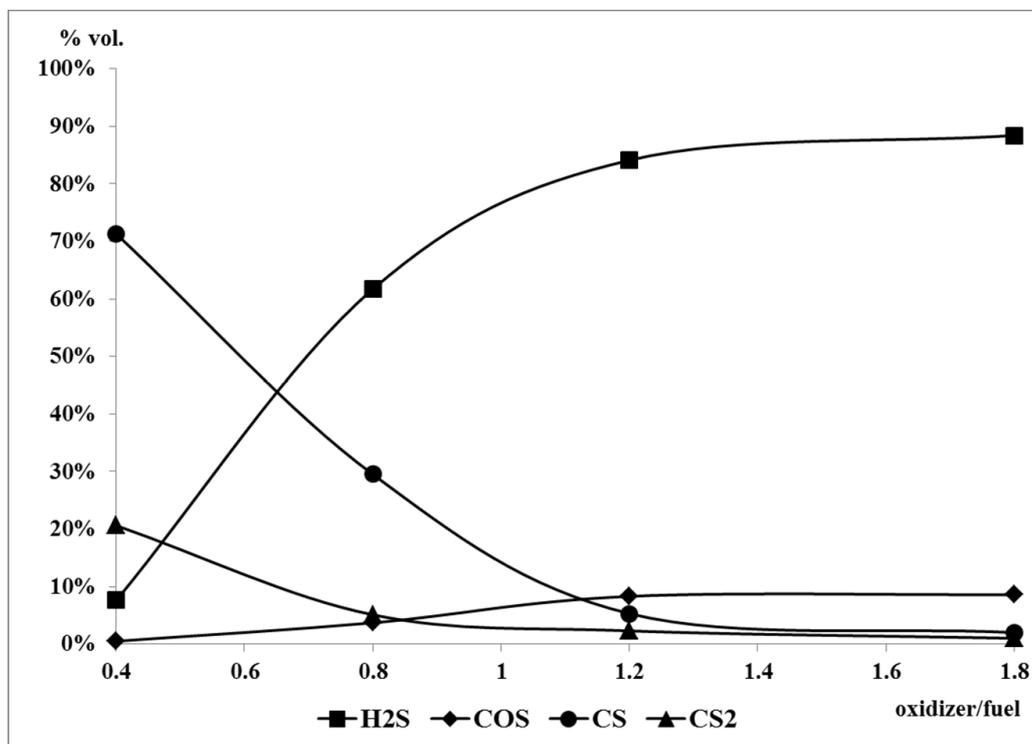


Fig. 1. Dependence of sulfur gasification products on oxygen blow

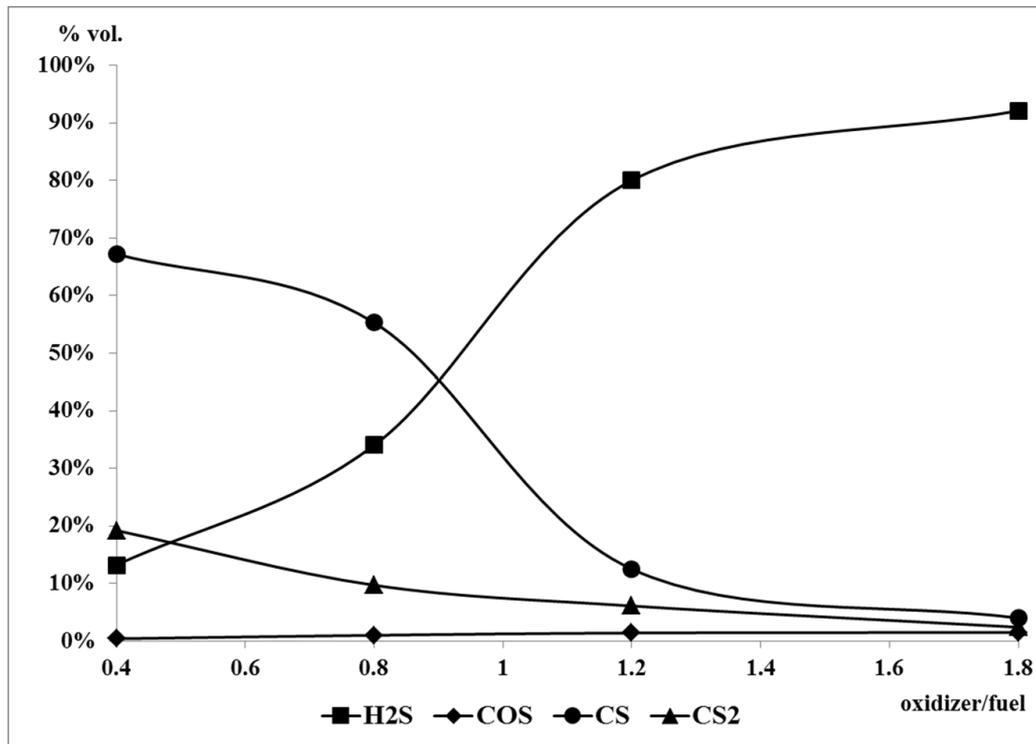


Fig. 2. Dependence of sulfur gasification products on steam blow

As you can see from figure 1, at an oxygen/bitumen ratio equal 0.4, a significant amount of sulfur from the bitumen in the gasification process proceed into the produced gas as carbon monosulfide CS and carbon disulfide CS₂. The rest of the sulfur forms a carbonyl sulfide COS and a small amount of hydrogen sulphide H₂S.

With an increase of oxygen/bitumen ratio to 0.8, a redistribution of sulfur compounds in the gas occurs: more than 60% is converted to hydrogen sulphide H₂S, about 30% of carbon monosulfide CS and rest of carbonyl sulfide COS and carbon disulfide CS₂. Further increase of oxygen/bitumen ratio leads to a significant increase in hydrogen sulphide and forming of sulfur dioxide SO₂, which amount are decreased with increasing pressure.

It can be seen from fig. 2 that with steam blow and small amount of steam/ bitumen ratio, the main amount of bitumen sulfur is converted to carbon monosulfide CS, the content of which in the produced gas decreases with increasing steam/bitumen ratio. In the same time, the amount of hydrogen sulphide H₂S is increased and at steam/bitumen ratio equal 1.8 this value is more than 90%.

The results of the calculations for the concentrations of sulfur compounds in the produced gas at steam-oxygen blow have shown that all the above-mentioned regularities remain for these conditions.

Comparing the obtained data with the results of experimental studies [8] it was obtained that in the real gasification process of sulfur liquid fuels, the sulfur contained in them is converted into the produced gas as a hydrogen sulphide H₂S (about 90%) and carbonyl sulfide COS (about 10%).

Conclusions

Based on the performed studies, the following conclusions were obtained:

- During the gasification process, the sulfur contained in the bitumen is converted in the syngas mainly in the form of hydrogen sulphide H₂S, carbonyl sulfide COS, carbon monosulfide CS and carbon disulfide CS₂;
- The distribution of sulfur amount between these compounds depends on the oxidizer/fuel ratio, temperature and pressure of gasification process;

- At low value of oxidizer/fuel ratio carbon monosulfide CS and carbon disulfide CS₂ are formed, at higher – a hydrogen sulphide H₂S.

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