

EFFECT OF CATALYSTS ON TAR CARBONIZATION

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1. Introduction

One of the most economically feasible routes for processing heavy oil residues is delayed coking, which yields additional valuable petroleum products and more advanced oil processing at a minimum cost. The carbide cycle mechanism opens new opportunities for enhancement of the delayed coking technology. Nickel metal has the highest activity in the formation of carbon nanostructures. One can expect that the addition of nickel catalysts to the carbonization feedstock will result in the interaction of the active catalyst particles with the hydrocarbons present in the heavy oil residues yielding oil coke reinforced with carbon materials. Furthermore, nickel catalysts are widely used in oil desulfurization.

The present study was devoted to catalytic tar carbonization in the presence of Ni/Sibunit, Cu/Sibunit and Ni-Mo/Sibunit catalysts. Particular attention was paid to the contents of sulfur compounds in the reaction products.

2. Experimental

Carbonization was performed in an autoclave (fig.) 350-550 °C and 1 MPa pressure. A tar sample (~ 10 g) or a tar sample (~ 10 g) with a catalyst (0.8 g) was loaded in the sample holder basket. Then the autoclave was heated to the desired temperature and maintained at it for 3 h. The 8%Ni/Sibunit catalyst was added to the tar. The catalyst concentration was 4 wt.%.

3. Results and discussion

The data on the coke yield and sulfur concentration in it are reported in Table. The 8%Ni/Sibunit catalyst addition to the tar led to an increase of the coke yield and decrease of the sulfur concentration in it, i.e. improvement of the coke properties. However, no carbon nanostructures (carbon nanofibers or nanotubes) were observed in the carbonization products. About 1.5 wt.% S was present in the tar. Its presence leads to the formation of hydrogen sulfide and COS in the cracking products. The sulfur-containing compounds react with nickel metal yielding nickel sulfide.

Fig. Scheme of the autoclave unit. Three zones where Ni/Sibunit, Cu/Sibunit and Ni-Mo/Sibunit catalysts were placed are indicated with numbers.

Zone 1: tar + 8% Ni-2.5%Mo/Sibunit catalyst;
zone 2: 2.5%Mo/Sibunit catalyst;
zone 3: 8% Ni /Sibunit catalyst.

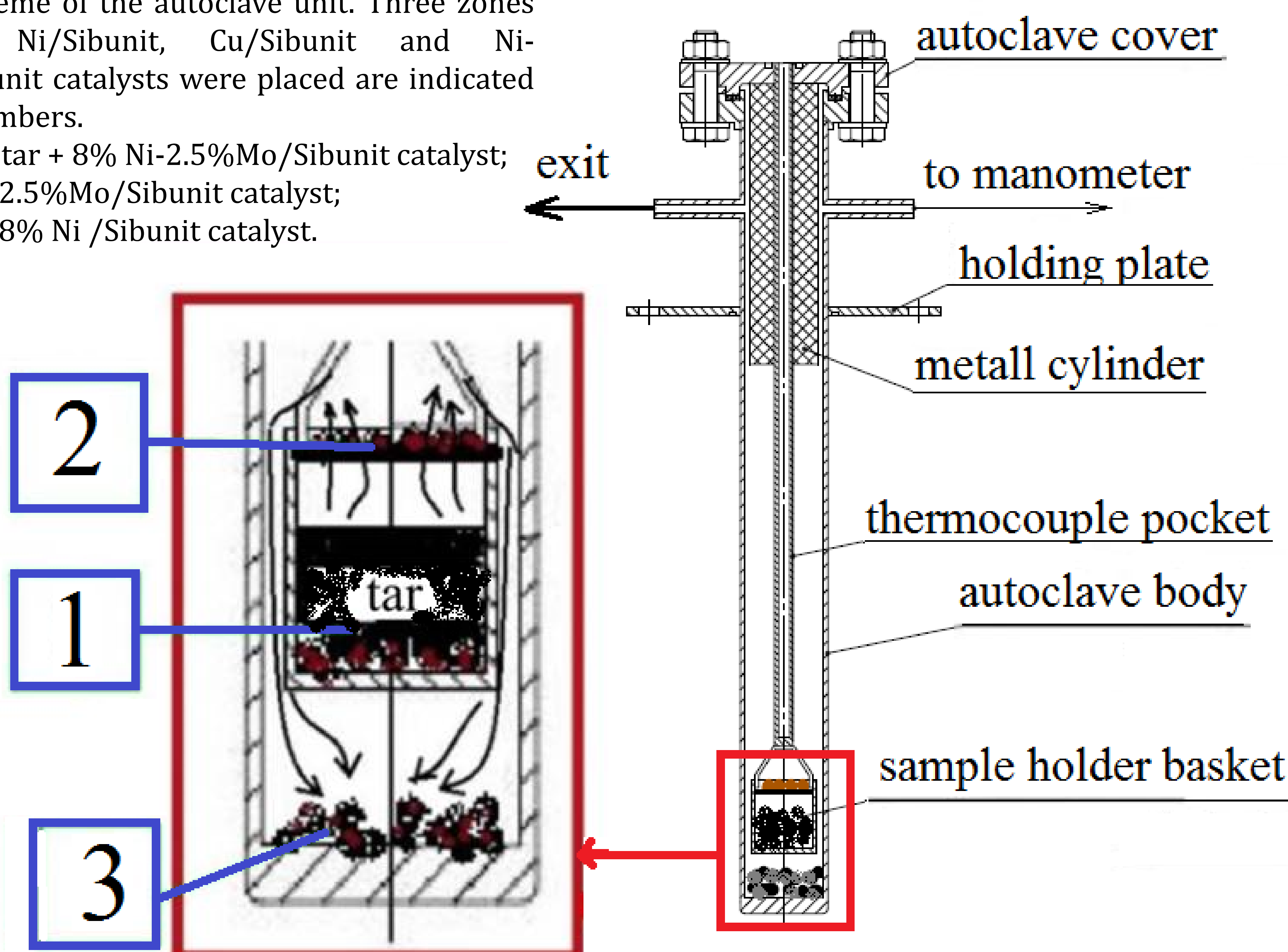


Table. The composition of main gaseous products formed during tar carbonization at 450 °C.

Hydrocarbons	Feedstock	
	Tar	Tar- Ni/Sibunit
Concentration, %		
H ₂	18.7	31.8
CH ₄	44.4	36.8
C ₂ H ₆	10.4	10.2
C ₂ H ₄	1.3	2.6
C ₃ H ₈	8.8	8.1
C ₃ H ₆	1.9	2.5
i-C ₄ H ₁₀	0.8	0.9
n-C ₄ H ₁₀	4.0	3.4
1-Butene	1.2	0.6

Table. Effect of 8%Ni/Sibunit catalyst addition to tar on the coke yield and sulfur concentration

	Tar	Tar- 8% Ni/Sibunit
Coke yield, wt. % of the initial tar	28%	33%
Sulfur content in the coke, wt. %	1.28	1.11

To improve the carbonization efficiency and properties of the produced coke, we used a three-zone arrangement of three different catalysts. The tar and the 8% Ni-2.5%Mo/Sibunit catalysts were loaded in zone 1.

4. Conclusions

The tar carbonization was studied in the temperature range of 350-500 °C. The gaseous products formed during the tar carbonization at 450 °C were analyzed for the concentration of sulfur-containing compounds. H₂S and COS were observed in the reaction products. So, sulfur was partially removed from the tar with the gas phase during its thermal carbonization. An increase of the carbonization temperature from 450 to 550 °C led to the decrease of the coke yield due to deeper cracking of the tar components and simultaneous decrease of the sulfur concentration in the coke.

The addition of the Ni/Sibunit catalyst to the tar improved the properties of the obtained oil coke. The coke yield increased to 33% whereas the sulfur concentration in the coke decreased.

The efficiency of the carbonization process and the properties of the obtained coke were further improved by placing three different catalysts Ni-Mo/Sibunit, Cu/Sibunit and Ni/Sibunit in different zones of the autoclave where the tar carbonization was performed. In zone 1 the tar was subjected to hydrocracking and desulfurization over the 8%Ni-2,5%Mo/Sibunit catalyst. In zone 2 sulfur was trapped by the Cu/Sibunit in the form of copper sulfide. In zone 3 coke was formed over the Ni/Sibunit catalyst predominantly from the gases formed by the tar cracking. Due to such catalyst arrangement, the coke yield in zone 1 was 27% of the initial tar weight, whereas its yield in zone 3 was as high as 18%. So, the total coke yield was equal to 45%. Meanwhile, its yield during the thermal carbonization was only 28 wt.%. The three-zone arrangement of the catalyst also led to a substantial decrease of the concentration of sulfur-containing compounds in the gaseous products of the tar carbonization affecting the sulfur concentration in the solid reaction products. Thus, the coke in zone 3 of the autoclave contained only 0.56% S.

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