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FRACTION COMPOSITION AND CALORIFIC VALUE OF INDUSTRIAL BIRCH WOOD PYROLYTIC TAR

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A sample of industrial wood pyrolytic tar was separated by vacuum distillation into volatile products and pitch. The highest heating value (HHV) was determined by bomb calorimetry for condensed volatile products (summary oils) and for pitch. For summary oils the HHV was found to be 28 800 kJ·kg^{-1}, which can characterize these products as a fuel with high energy density.

Keywords: wood pyrolytic tar, calorific value

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Thermal processing of wood and wood residues is nowadays considered as one of promising direction for biofuel production [1]. It is known that the liquid products of conventional slow wood pyrolysis possess about 20% of the total energy stored in wood, whereas in the process of fast pyrolysis the energy stored in liquids increases up to 54%, mainly due to increase of the yield of liquids themselves. Despite the fact that fast pyrolysis continuously attracts more and more attention for investigation as a perspective method for biofuel production [2], the liquid tar is still produced on the industrial scale, for example in Amzya (Russia) plant.

Literature data for calorific values of bio-oils of different origin are presented in publication [3] and refer to the total amount of bio-oils without their separation. For our investigation we separated the pyrolytic tar, which was produced by pyrolysis of birch wood in vertical charcoal burning kiln of Amzya plant. To remove water the sample of pyrolytic tar was subjected to heating in rotary evaporator at 100 °C, and the reduced pressure of a water jet vacuum pump. The dried tar obtained with yield of 95% was then distilled on the rotary evaporator at heating from 110 to 250 °C and vacuum about 0,005 mm Hg. From 154 g of dried tar were obtained 86 g (56%) of summary oils fraction, 61 g (40%) of pitch, losses comprise 7 g (4%). For summary oils and pitch the elemental composition was determined (Table). The amount of oxygen was estimated using the usual assumption that all other elements (N, S) are absent.

A bomb calorimeter (IKA 200) was used for calorimetric combustion of summary oils fraction and pitch. Averaged calorific values are given in the Table as the highest heating values (HHV). Despite the relative simplicity and availability of calorimetric determination of HHV for liquid and solid fuels, in many publications empirical estimations are usually used to determine HHV. These estimations are based on the elemental composition of the fuel, and use the equations proposed by Mendeleev and Dulong [4, 5]. For us it was informative to compare the calorific values obtained by combustion and estimated by these two equations. Such comparisons for bio-oils are not commonly found in the literature. In our empirical estimations we assume that samples are free from water and nitrogen and sulfur containing compounds. The results are given in the Table as well.

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Elemental composition and highest heating values for summary oils and pitch from birch wood pyrolytic tar of Amzya plant

	Elemental composition, %			Highest heating value		
	C	H	O	Experimental, $kJ \cdot kg^{-1}$	Mendeleev equation, $kJ \cdot kg^{-1}$	Dulong equation, $kJ \cdot kg^{-1}$
Summary oils	58,40	5,79	35,81	28800	23200	20500
Pitch	66,75	5,72	27,53	27300	26800	24700

It can be seen that there are rather strong deviations of empirical determinations from those obtained by bomb combustion. These deviations are about 6,5% for Mendeleev equation and about 14% for Dulong equation, so the Mendeleev equation gives results closer to the experimental data. At present we can not offer any reasonable explanation for the observed differences. It is noteworthy that HHV values for the industrial samples of bio-oils Dynamotive (Canada), Ensyn (USA) and others lie in an interval of 15 400–17 600 $kJ \cdot kg^{-1}$ [3]. There are no indications how the authors take into account the amount of water present in these samples, but if one makes an appropriate correction, it will increase HHV for Dynamotive bio-oil only up to 21900 $kJ \cdot kg^{-1}$, a value still significantly lower than ours.

For the initial industrial pyrolytic tar and its derived summary oils NMR 1H spectra were recorded (Bruker AM-400 200 MHz, $CDCl_3$). The assignment of signals was done according to [6]. The examination of 1H NMR spectra of initial tar and summary oils displays close qualitative similarity. Using integral intensities, we estimate the relative amount of protons which belong to aliphatic and aromatic fragments (6,2–7,9 and 0,75–5,2 ppm, respectively). The main difference between initial tar and summary oils consists in a higher content of aromatics in the later. The amount of aromatic protons increases from 11,7% in initial tar to 26,3% in summary oils. Therefore we can conclude that in a course of distilling and accompanying heating the summary oils fraction enriches by aromatics by about two times.

Conclusions

1. The volatile fraction of industrial birch wood pyrolytic tar possesses high heating value of 28 800 $kJ \cdot kg^{-1}$.

2. Experimental heats of combustion are found to be consistently higher than those predicted by the empirical equations of Dulong and Mendeleev based on elemental composition.

3. By comparison of 1H NMR spectra for initial tar and the summary oils it was concluded that distillation the summary oils fraction enriches the aromatics by about two times.

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