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ESTABLISHMENT OF CORRELATION BETWEEN CALORIFIC VALUE AND IR-SPECTRA CHARACTERISTICS OF WOOD PYROLYTIC TARS BY MULTIDIMENTIONAL ANALYSIS METHOD

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Fractional distillation of industrial wood pyrolitic tar in the temperature range 125–265 °C was performed and highest heat of combustion for each fraction was determined by combustion bomb calorimetry. It was demonstrated that multidimentional analysis method could reveal a good correlation with $\rho = 0,99$ between calorific value and Near-IR-spectra characteristics which were recorded for each fraction. Application of this method to a large-scale production of wood pyrolytic biofuels could serve as a new analytic method for fuel calorific value determination.

Keywords: biofuels; calorific value.

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Elaboration of new types of liquid biofuels becomes one of the challenging concerns of industrial society [1, 2]. It is obvious that calorific value is the one of the important characteristics of a fuel which determination should be a facile not time-consuming procedure. The most exact method of calorific value determination represents by bomb calorimeter combustion [3]. Such combustion is a time consuming procedure therefore calculating methods based on element analysis data are usually applied for determination a calorific value of liquid biofuels. As a rule Dulong or Medeleev empiric formulae are used for this purpose [4, 5]. For us it seems interesting to develop new applicable in analysis of large series of samples method for experimental determination of liquid biofuels calorific value. It is known that application of multidimensional analysis method to large enough array of experimental data, including the FT-IR spectral ones, can reveal the correlation between spectral characteristics and investigated physical value [6]. Recently a successful application of this method was demonstrated for calorific value determination of willow wood [7].

For investigation we take a sample of industrial pyrolytic tar produced in Amzya wood pyrolysis plant (Russia). Initial pyrolytic wood tar was preliminary dried by heating in rotary evaporator at 100 °C. under reduced pressure of water-jet pump. Dried tar was then subjected to vacuum distillation (about 0,01 torr). This distillate hereafter named as "wood oils" was then distillate to a separate fractions in accordance with GOST 2177-99 in a manual operated instrument ARN-LAB-03. Heating of the sample up to boiling point took 5–15 min. Rate of distillation in the range 5–95% tar volume was 4–5 mL min^{-1}. Total amount of the wood oils subjected for fraction separation was about 100 mL. The results of fractional separation are presented in a Table.

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Fraction separation and highest heat of combustion for the wood liquid distillates

No	Fraction temperature, °C	Yield from total wood oils, %	Highest heat of combustion, MJ/kG
1	125–160	8,3	18,189
2	160–180	6,0	21,879
3	180–195	7,6	24,529
4	195–215	18,5	26,191
5	215–220	8,6	26,565
6	220–235	11,0	…
7	235–260	30,6	25,484
8	260–265	9,4	25,200

Energies of combustion (highest heat of combustion at constant volume) were measured in bomb isoperibolic calorimeter V-08MA [3]. Thermometric measurements in vessel and jacket of calorimeter were carried out by Pt-resistance thermometers. The energy equivalent (15021,0 ± 8,6 Дж °C^{-1}) was determined in experiments with a reference sample of benzoic acid (trade mark K-3). Samples were burnt in stainless steel crucible in terylene ampoules. 1 ml of water was placed in calorimetric bomb, than bomb was filled with oxygen under pressure 3,04 MPa without air displacement.

For each fraction IR spectra were recorded using FT IR-spectrometer Infralume FT-08. The instrument was equipped with frustrated total internal reflection (FTIR) accessory MIRacle ATR and sampler. Spectra were recorded in the range of 400–8000 cm^{-1} with resolution of 4 cm^{-1} using SpectraLUM program (Lumex). This accessory allows to record a sample with constant depth *ca* 2 micrometers. This allows to shorten the time of analysis because it is enough to wipe an accessory glass plate. For each fraction three spectra were recorded. The data thus obtained were treated with "Parsel" software worked out in "Lumex" company [8]. This software makes it possible to choose the spectral region which gives the best correlation. In our case such region was in the range of 2824–2860 cm^{-1} where the best correlation of IR band intensity with biofuel calorific value was found.
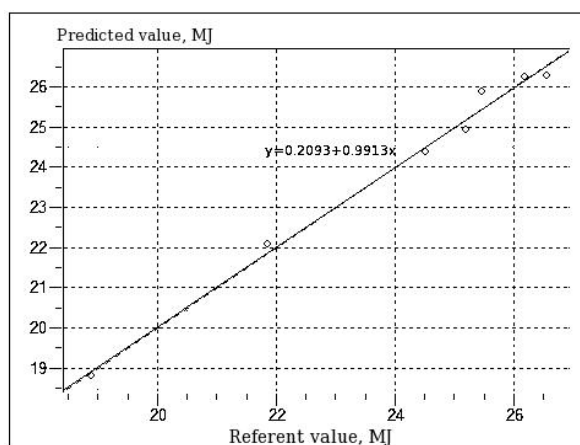
Correlation between experimental and predicted values of high heat of combustion for wood liquid distillates

The results of our correlation are presented on the Figure. Experimental values obtained by calorimeter combustion are given on the X-axis and those predicted by the "Parsel" software are given on the Y-axis. As it can be seen from the picture there is a good correlation with the correlation coefficient $\rho = 0,99$ between experimental and predicted data. We think that in the laboratory where the large series of calorific value determination are performed for pyrolytic biofuels the application of proposed FTIR spectral analysis can be useful being less time-consuming procedure than conventional bomb calorimeter analysis. It is noteworthy that present work does not give an answer about applicability of this method to other products of wood thermal or thermochemical treatment.

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