ASSESSMENT OF THE MOISTURE EFFECT ON GASEOUS PRODUCTS OF SELF-HEATING OF WOOD CHIPS

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Research article

Abstract: Biofuels are stored in large quantities and may be susceptible to self-ignition. The possible methods of indication of temperature increase include the analysis of the gaseous products of heating where concentrations of certain gases may increase with increasing temperature. Gas release is also affected by the moisture of the material given that the moisture level changes surface accessibility for oxygen on the one side and serves as a catalyst of the oxidation reactions on the other. The present project analysed the effect of temperature and moisture on gaseous products of heating of wood chips, one of frequently used biofuels, with the aim to determine a suitable gaseous indicator of beginning self-ignition.

Keywords: Wood chips, self-heating, gaseous products, moisture effect.

Introduction

In the past decades the role of biofuels as a source of energy increased considerably. Unlike fossil fuels, biofuels represent a renewable energy source contributing to air pollution reduction and mitigation of the negative effect of combustion products on the environment. Solid biomass consisting of materials of organic origin generated mainly by photosynthesis is the most often used biofuel.

Wood chips represent the most frequently encountered type of solid biomass. Wood chips include crushed tree branches, roots and other wood residues with the usual particle size range from 5 to 100 mm. Wood chips can be divided to green, brown and white according to the raw material type used. While green chips, sometimes called forest chips, consist of waste of tree cutting in forests and include foliage and needles, brown chips only include residues of trunks and other wood cuttings and white chips do not contain any bark (Stupavský and Holý, 2015) .

Despite the benefits offered by biofuels their use is connected with certain disadvantages too. Their storage brings about the risk of self-ignition, which may in effect cause fires and subsequent property loss, human health damage and, in the worst case, casualties. This phenomenon is caused by exothermic chemical reactions, often preceded by micro-organism activity inside the accumulated material. These processes are indicated by temperature increase and if the heat is not sufficiently removed from the material, the heating process may result in the material ignition (Veznikova, 2016).

Krigstin and Wetzl (2016) present a survey of causes of self-ignition of biofuels, including wood. They determined respiration of the still living plant cells, biological degradation and thermochemical oxidation reactions as the main processes taking place in the stored biomass. These three causes differing in their mechanisms are responsible for transformation of mass to energy, thus contributing to self-heating of the stored biomass, which may lead as far as to its self-ignition.

Apart from that self-heating of the fuel, its heating capacity and therefore also its quality worsen. This process is connected with release of volatile compounds in the process of cell respiration and biodegradation and release of oxidation products in the thermochemical stage, mainly in the form of gases.

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The whole process of self-heating of plant products is accompanied with release of gaseous products. The products mainly contain carbon oxides, especially carbon dioxide, to a lesser extent carbon monoxide and to the least extent methane (Kuang, 2009; Malow, 2008). As the main products of the self-heating are represented by carbon oxides and water, the main reactions accompanying the self-heating process can be expected to be oxidation by air oxygen.

Some papers dealing with a more profound analysis of the products also detected presence of aliphatic hydrocarbons (Perdochova et al., 2014; Perďochová 2014a). The products may also include nitrogen oxides and possibly volatile substances resulting from oxidation of cellulose materials, such as acroleine.

According to Rowel (1984) temperature is an important factor. Upon heating up to 300 °C the macromolecule bonds split, water is eliminated together with carbon dioxide and carbon monoxide, free radicals are formed together with carbonyl, carboxyl and hydroperoxide functional groups. The last product is a very reactive carbon residue.

The above list indicates that biofuel storage represents not only the risk of fire of the material itself, but also the risk of release of toxic products of its self-heating. Their main components are hazardous substances: methane is an explosive gas, carbon dioxide is unbreathable and carbon monoxide is toxic and flammable.

Self-ignition of the stored material can be identified in time especially by periodic checks of its inside temperature. The temperature of biofuels at the same time affects the gaseous product composition. The effect of temperature on the composition of gaseous products of wood-based material heating is generally described by Ševěček and Netopilová (1986). Wood biomass mainly dries at the temperature of up to 100 °C. The decomposition itself begins at 130-150 °C, and intense degradation with release of large quantities of gases begins at 180-195 °C. Certain gas release was already noted at low temperatures, though. Exothermic decomposition occurs at 270 °C -280 °C (Ševěček and Netopilová, 1986).

In addition to temperature measurement, self-heating and its phases can also be identified by analysis of the gaseous products released from the material. However, the gaseous products released from the self-heating material depend on other factors too, in addition to temperature, for example on the material composition, moisture or oxygen concentration (Gray, 1984; Kuang et al., 2009; Pospíšilová, 2013; Věžníková and Hütter, 2008; Wilhersaari, 2005).

For the self-heating stage to be correctly identified and the appropriate safety measures to be specified it is necessary to analyse the effects of these factors on the gaseous product quantity and composition. Moisture in biofuel is one of the factors affecting composition of gaseous products of its self-heating. Moisture affects the progress of oxidation, the main reaction of the thermochemical stage of self-heating, and this makes it crucial for the self-heating products formation.

Relatively few papers have focused on an evaluation of the effect of moisture on the composition of gaseous products of self-heating of biofuels. These studies show that moisture accelerates the release of carbon dioxide, carbon monoxide and methane emissions, resulting in quicker consumption of oxygen from within the storage room. From the safety point of view the risk of explosion, fire and possibly employee suffocation thus increases (Guo, 2013; Malow and Kraouse, 2008; Soto-Garcia et al, 2015).

That is why this study aims at the evaluation of the effect of moisture on the gaseous products released by self-heating of wood chips. The measured experimental data will help study the issue of self-ignition of solid materials. The results are also usable in evaluation of the effect of moisture on toxicity of gaseous emissions into the occupational and living environment and may help select appropriate safety measures.

Materials and methods

Used materials

The subject of the experiments performed in the context of this study was forest chips, i.e. green chips containing waste wood as well as needles and foliage. The forest chips were sampled from an outdoor heap of an energy plant where the chips are used as fuel for burning together with coal.

The samples were taken with regard to possible heterogeneity of the stored material and its large volume pursuant to CSN EN 14778 - Solid biofuels - Sampling (CSN EN 14778, 2011). A subsample was obtained from the sampled materials pursuant to CSN EN 14780 - Solid biofuels - Sample preparation (CSN EN 14780, 2011), in which the moisture level was determined immediately after sampling with the help of the halogen moisture analyser METTLER TOLEDO HS 153.

The sample was further used to determine additional parameters characterising its composition. A survey of the results of the analysis is shown in Tab. 1.

Tab. 1 Basic parameters of the sample of forest chips (physical properties, proximate and ultimate analysis)

Parameter	Value	Units
Apparent density	320	kg.m^{-3}
Mean grain size	8.75	mm
Proximate analysis		
Moisture W^t	47.74	wt%
Ash A^d	11.90	wt%
Volatile matter V^{daf}	81.10	wt%
Fixed carbon C^{daf}	18.90	wt%
Ultimate analysis		
Carbon C_t^d	46.89	wt%
Hydrogen H_t^d	5.14	wt%
Nitrogen N_t^d	0.34	wt%
Sulphur S_t^d	0.04	wt%
Oxygen O_t^d	47.59	wt%

Wood chips differ from other chips in their lower level of volatile flammable materials, higher moisture and higher ash proportion, as follows from comparisons to other types of chips sampled in the same manner, see Tab. 2. No fundamental differences between this and other types of chips were found.

Tab. 2 Proximate analysis [wt%] of four types of wood chips (Perďochová, 2015)

Parameters	Forest chips	Deciduous wood chips	Timber chips	Poplar wood chips
Moisture W^t	47.74	43.35	41.02	44.23
Ash A^d	11.90	4.66	3.95	2.86
Volatile matter V^{daf}	81.10	82.93	83.38	85.07
Fixed carbon C^{daf}	18.90	17.07	16.62	14.93

Tab. 3 ltimate analysis [wt%] of three types of biofuels

	Forest chips	Wood chips[x]	Wood pellets[x]
Carbon C_t^d	46.89	42.20	46.79
Hydrogen H_t^d	5.14	5.51	6.13
Nitrogen N_t^d	0.34	0.13	0.60
Sulphur S_t^d	0.04	0.27	0.32
Oxygen O_t^d	47.59	51.88	46.15

[x] - source: García et al, 2014.

Also elemental composition of other types of wood-based biofuels from European forests and the analysed forest chips did not reveal any fundamental differences between these materials. A survey of elements contained in the forest chips analysed by this study and two wood-based materials analysed by García et al (2014) is shown in Tab. 3.

Used methods and equipment

Samples with three moisture values were prepared for the purpose of assessment of the effect of moisture on the composition and quantity of gaseous products of self-heating. In addition to the sample where the natural moisture level was preserved, the other two samples were dried at 105 °C in the BINDER FD 53 dryer for 15 and 30 minutes, respectively, to achieve two different levels of drying. Sample moisture was specified by weighing in the moisture analyser METTLER TOLEDO HS 153.

The mean values of total water content in the original sample and in the samples with modified moisture including the two-sided 95 % confidence interval are shown in Tab. 4.

Tab. 4 Mean values of total water content Mar in the samples after 15 and 30 minutes of drying

Sample condition	Total water content M_{ar} [wt%]
Original sample	47.74 ± 0.63
Sample after 15-minute drying	30.99 ± 0.41
Sample after 30-minute drying	21.12 ± 0.65

The thus prepared samples of wood chips were heated in the dryer under isothermal conditions in air at 50, 100 and 150 °C for one hour. Measurements at higher temperatures were not performed given that the subject of this study was to evaluate the effect of moisture on gaseous product composition during self-heating of stored biomass. At higher temperatures, around 200 °C, the material was already observed to flicker and burn, which was the reason why the measurements were performed at lower temperatures than that.

The technical parameters of the furnace and the measurements were based on the method described in EN 15188, i.e. specification of the tendency of solid materials to self-heating. Differently from the standardised procedure this trial was based on flow arrangement allowing for continual measurements of the products while heating under constant pressure. Temperature

homogenisation inside the furnace was assured by a circulation ventilator.

The samples were heated for 1 hour in a wire basket assuring air access to the material from all sides. The basked was cube-shaped with side length 7 cm. The air flow was maintained throughout the measurement at (2.5 ± 0.2) l.min^{-1} and the pump was placed behind the spectrometer burette.

The gases were analysed by an infrared spectrometer with the Fourier transform, NICOLET iS10. The tubes connecting the place of origin of the gaseous products and the measuring burette were heated and so was the burette, whose temperature was maintained at 165 °C. The purpose of the heating was reduction of the risk of condensation of the low-boiling components and their keeping in the gaseous state. This mainly concerned the large proportion of moisture in the gaseous products.

The FTIR spectrometer used for the heating product identification in the analysed materials and for determination of their levels was equipped with a gas burette with the optical length of 10 m, allowing for measurement of the gaseous components with the accuracy down to ppm to ppb. This instrument monitors the central area of the IR spectra within the range of 4000 cm^{-1} to 400 cm^{-1}. The spectrum measurements were controlled by software Omnic 9 in Series mode. The spectra were measured in the intervals of circa 30.98 s and 8 samples per measurement were processed. Substance identification in the spectrum was performed on the basis of a comparison of the measured spectrum with the spectra of pre-identified substances with the help of the libraries of Omnic Specta software and determination of the fundamental vibration peaks.

Quantitative analysis of the measured substances was performed with the help of the spectroscopic software TQ Analyst, where calibration curves were used for determination of concentrations of the components in time. The calibration curves were formed on the basis of the measurements at burette temperature 165 °C under normal pressure, i.e. under the conditions identical with the conditions of the measured gaseous product sampling.

Results and discussion

The analysis found that the gaseous products released during heating of the analysed samples of the forest chips mainly contained water, carbon dioxide and carbon monoxide and methane. The dependence of concentrations of the main heating products, i.e. carbon oxides and methane, on the sample moisture and temperature was evaluated quantitatively.

The analysis of the gaseous product composition showed that carbon oxides and methane were released in relatively high, well detectable concentrations.

That is why their usability for the evaluation of the progress of the self-heating process, especially for the temperature estimate and determination of the self-heating stage, was examined.

Further gaseous components of the mixture generated by self-heating were hard to identify given that a large part of the spectrogram was covered with the rotary-vibration strips connected with the presence of water. That is why probably just some of the generated components were detected.

Dependences of the carbon oxide levels on moisture and temperature

The effects of moisture and temperature on the concentrations of the main components of the gaseous products of forest chips heating are shown in the following Tab. 5 where arithmetic means of carbon dioxide, carbon monoxide and methane concentrations are shown. The arithmetic means are accompanied by selective standard deviations of the measurements.

Tab. 5 Mean concentrations of carbon dioxide, carbon monoxide and methane in dependence on temperature and moisture

Measurement temperature [°C]	47.74 [wt%]	30.99 [wt]	21.12 [wt]
CO_2 [ppm]			
50	20.7±3.5	11.9±1.5	10.8±0.7
100	756.4±764.6	227.3±20.0	247.4±23.0
150	5692.4±4811.0	3735.7±85.4	2286.8±134.0
CO [ppm]			
50	9.7±1.6	6.5±0.9	6.1±1.4
100	23.4±3.4	15.0±3.6	12.9±3.6
150	109.8±19.2	84.3±6.5	73.3±5.8
CH_4 [ppm]			
50	11.8±3.7	14.6±2.0	9.9±2.2
100	45.2±6.1	39.1±4.2	16.6±3.4
150	68.8±9.1	62.4±6.1	24.3±3.1

Concentration values mentioned in the tab. 5 are converted to release rate from weight unit of wood chips - see tab. 5A. This conversion allows comparison of different types of materials.

Tab. 5A Average value of release rate of carbon dioxide, carbon monoxide and methane converted to 1 kg of wood chips in dependence on temperature and moisture

Measurement temperature [°C]	47.74 [wt%]	30.99 [wt%]	21.12 [wt%]
CO_2 [ml.min^{-1}.kg^{-1}]			
50	0,49±0,08	0,28±0,04	0,25±0,02
100	17,78±17,97	5,34±0,47	5,81±0,54
150	133,77±113,06	87,79±2,01	53,74±3,15
CO [ml.min^{-1}.kg^{-1}]			
50	0,23±0,04	0,15±0,02	0,14±0,03
100	0,55±0,08	0,35±0,08	0,30±0,08
150	2,58±0,45	1,98±0,15	1,72±0,14
CH_4 [ml.min^{-1}.kg^{-1}]			
50	0,28±0,09	0,34±0,05	0,23±0,05
100	1,06±0,14	0,92±0,10	0,39±0,08
150	1,62±0,21	1,47±0,14	0,57±0,07

The measured data indicate that within the moisture range of circa 21 to 48 wt% the carbon dioxide concentrations grow with moisture increase at all temperatures. The growth of the concentration between 21 wt% and 31 wt% is very slow but between 31 wt% and 48 wt% it accelerates considerably, in the case of carbon dioxide to double the previous value. The relationship between the mean carbon dioxide concentration and moisture is quadratic.

The original forest chips sample (moisture level 47.74 / wt%) showed a large dispersion of the carbon dioxide concentration values in comparison to the pre-dried samples. In the course of the one-hour measurement the original wood chips sample released a very high quantity of carbon dioxide at the beginning of the measurement and the final quantities were low. This difference was manifested as a large dispersion of the measured values. The pre-drying of the other two samples may be considered the cause of this difference in concentrations.

The original sample was taken from the outdoor storage heap oxidised by air oxygen. The generated carbon dioxide, one of the main products of oxidation, might have remained partly absorbed in the wood particle surface. The gases absorbed in the solid surface or in the liquid are released at increased temperatures in the case of physical absorption.

Hence the lower dispersion of the values of the pre-dried samples, where the gases generated by oxidation under the given conditions were not enriched by the gases absorbed in the course of previous oxidation.

Carbon monoxide shows the same dependencies as carbon dioxide, meaning that within the moisture range of circa 21 to 48 wt% the carbon monoxide concentrations grow with moisture increase at all temperatures like in the case of carbon dioxide. The arithmetic mean increase, like in the case of carbon dioxide, is very high within the range of 31 wt% to 48 wt%. The relationship between the mean carbon monoxide concentration and moisture is also quadratic. The values of carbon monoxide are lower than the values of carbon dioxide, though.

In the case of carbon monoxide the value dispersion in the original sample is not considerably different from the value dispersion in the measurements of the pre-dried samples. This shows that in the case of carbon monoxide no significant absorption by oxidation under the given storage conditions takes place. Also, it cannot be excluded that the water solubility of carbon dioxide may also play a role in this context.

The results allow for the conclusion that the water level in the analysed biofuel substantially affects carbon dioxide and carbon monoxide concentrations. The higher the material moisture the larger the quantity of the gaseous carbon oxides released. Although the effect of temperature on the quantity of the generated reaction products was higher than the effect of moisture, the volumes of the generated oxides were still the highest in the highest concentrations.

This shows that oxidation is the dominant reaction in this process. This is clearly confirmed by the generated products - i.e. carbon oxides and the large quantity of water, originating in the moisture contained in the material but also being the product of the reaction. This also manifests one of the features of oxidation with air oxygen, whose speed increases at the presence of moisture.

Hydrocarbon oxidation by air oxygen is a process called autooxidation. Autooxidation, i.e. direct material oxidation by air oxygen under normal ambient temperature, i.e. without catalytic effects of other substances, is the most common type of oxidation. It is a radical chain reaction with the primary products represented by hydroperoxides and other radicals.

This type of oxidation first generates a radical from the oxidised substance molecule, which is one of the ways of overcoming the spin selection rule, for only the radical is able to react with the common triplet oxygen.

The generation of the radical from the molecule in a process requiring a large amount of energy and this is the reason why autooxidation is supported by temperature increase. (Věžníková, 2016) In addition, radicals may also be developed mechanically, i.e. by milling or crushing of the material, and in the case of biologically active systems also by peroxidases, i.e.plant-produced enzymes. Both these methods of free radical generation are possible in the studied material.

The confirmed dependencies between temperature, moisture and carbon oxide concentrations can be used for determination of preventive measures for increased safety of biofuel storage. Although accurate concentrations cannot be determined using laboratory methods, as they strongly depend on the local conditions of the material storage, the basic trends and dependencies are confirmed.

Carbon dioxide and carbon monoxide concentrations grow with temperature increase. The values are also affected by moisture but temperature plays the decisive role. Moisture increase by about 20 wt% doubles the concentration at the maximum but temperature increase by 50 °C increases the concentration ten times.

Carbon monoxide shows a weaker dependence on moisture than carbon dioxide, therefore its measurement is able to increase accuracy of the stored material temperature estimate. In addition its concentrations must mainly be monitored in closed spaces considering its toxicity. Accumulation of carbon monoxide in closed storage rooms is a serious threat to human safety.

For those reasons the increased concentrations of both gases can be considered a suitable indicator of temperature increase in the stored biofuel, i.e. an indicator of the beginning of its self-heating. When this increase of concentrations of both the gases is detected further measures should follow, such as heap monitoring, identification of places with possible temperature increase, their measurements and monitoring, and other active interventions as appropriate.

Dependencies of methane concentrations on moisture and temperature

Methane is another main gaseous product of biofuel heating in the air. Methane is one of gases used for indication of the risk of self-ignition of coal in heaps on the surface or in underground mines. The arithmetic mean of concentrations resulting from forest chips heating is shown in Tab. 5.

The measured values show that like carbon oxides methane too is released in larger quantities at higher temperatures. The nature of the dependence between moisture and the measured concentration is different from carbon oxides, though, and is not unambiguous either. At 50 °C the effect of moisture on the generated methane quantity is not manifested almost at all and the quantity increase between 31 wt% and 48 wt% moisture content is also very low.

To compare the dependencies, Fig. 1 shows the dependencies of the mean concentrations of carbon monoxide and methane at 150 °C.
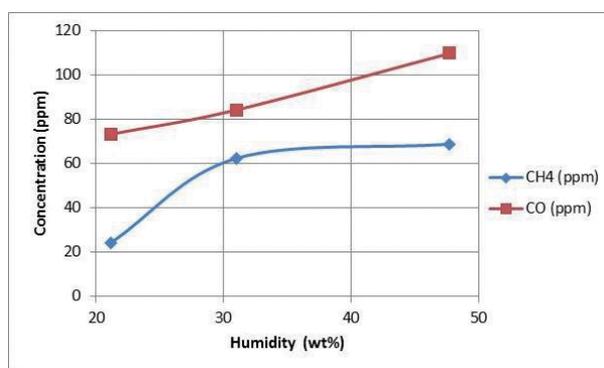

Fig. 1 Mean concentrations of carbon monoxide and methane in relation to moisture at 150 °C

The comparison of data obtained by measurement of carbon oxides and methane concentrations in relation to temperature and moisture shows that the mechanisms of generation of the oxides and methane are different, not showing clear signs of oxidation. In the case of methane only a small volume of the gas is generated at low temperatures and its increase with temperature is little distinct. Therefore the use of this gas for indication of self-heating appears inappropriate and impracticable.

Other gaseous products of heating

In addition to carbon oxides and methane, biofuel heating in oxidising environment resulted in generation of other gaseous products of the ongoing reactions. The main detected product was water, resulting from evaporation of the moisture contained in the material and as a product of the oxidation reactions.

According to Rowel (1984) the presence of carbonyl, carboxyl and hydroperoxide groups is assumed. In the case of biomass it is necessary to expect formaldehyde, or another aldehyde, such as acrolein, and also acetic acid and methanol. As regards these substances the applied measurement

method may only be used for detection of gaseous substances, whose vibrational-rotational spectra show strips in the areas not covered with other mixture components, mainly moisture.

Methanol belonged to the well detectable substances. Fig. 2 shows a strip of valence vibration of the C-O bond (C-O stretching vibration for methanol occurs at 1090-970 cm^{-1}) found in the area of 1090 to 970 cm^{-1}, with a clearly marked peak at 1033 cm^{-1}. This peak is characteristic for methanol.

Other oxygen compounds are present in the area around 1720-1760, according to the C=O valence vibrations, but they could not be accurately identified.

The quantity of the released methanol is affected by the measurement temperature. The values of intensity in relation to temperature and moisture are shown in Tab. 6. The table shows that temperature is the main factor affecting the quantity of the generated methanol. The dependence on the moisture content is clear only at 150 °C. At lower temperatures methanol release is probably affected by other influences. It is possible to consider oxygen access, i.e. its influencing for example by the bulk density.
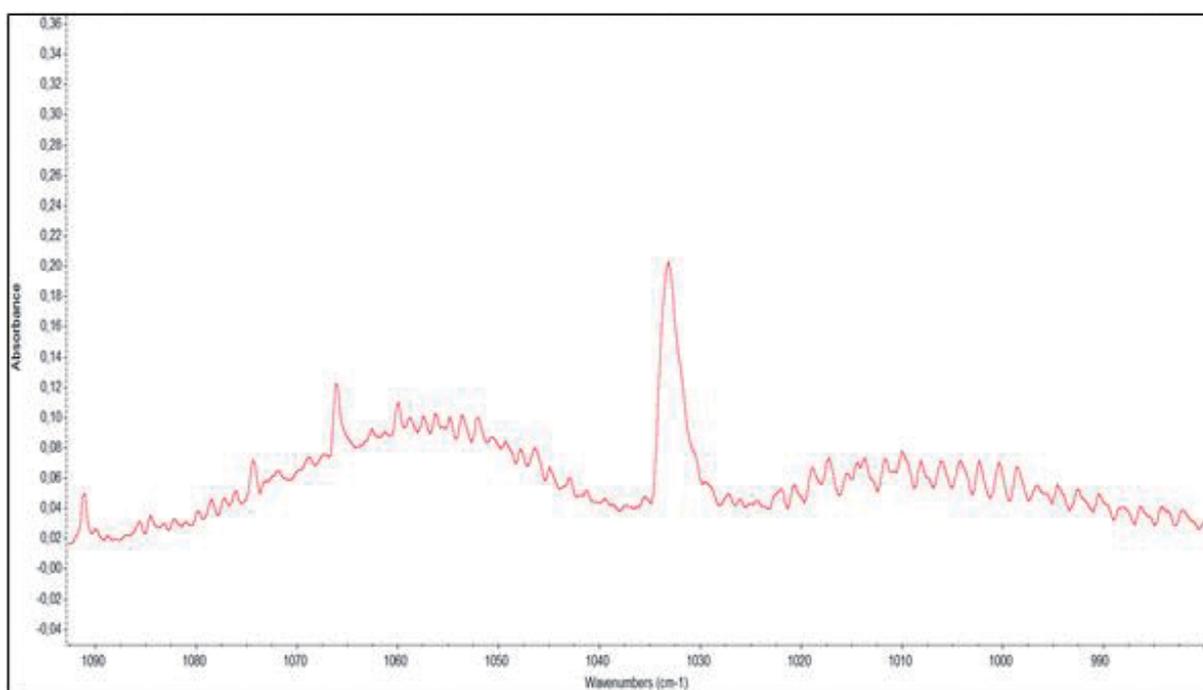

Fig. 2 C-O stretching vibration characteristic for methanol

Tab. 6 Dependence of methanol peak intensity on sample temperature and moisture

Temperature/°C	Moisture/wt%	Position/cm^{-1}	Intensity	Average intensity
150	48	1033.17	0.202	
150	31	1033.19	0.169	150 °C: 0.163
150	21	1033.16	0.119	
100	48	1033.21	0.0669	
100	31	1033.00	0.0920	100 °C: 0.079
100	21	1032.77	0.0794	
50	48	1033.23	0.0177	
50	31	1033.63	0.0026	50 °C: 0.019
50	21	1032.69	0.0367	

Conclusion

The present article demonstrated the possibility to use gaseous products of heating for indication of temperature of the stored biofuels, known by their tendency to self-heating, which may lead as far as their self-ignition. The method of material temperature evaluation for materials stored in large quantities on the basis of analysis of the gases generated by the material contact with air oxygen has been used for a long time for coal.

Biofuels are a relatively new fuel type used in large quantities. This fuel is from coal in many aspects. Biofuels, inter alia, easily absorb air moisture in relatively large quantities, and this may affect their behaviour towards oxygen. That is why this study evaluated the effect of moisture on the composition of gaseous products of heating in oxidising atmosphere.

The selected fuel type, the forest chips, with three different moisture values, was heated and the gaseous products were analysed by a FTIR spectrometer. The analyses showed that both carbon dioxide and carbon monoxide can be used for indication of temperature of the stored material. Both gases are generated by oxidation reactions accelerated by moisture content. However, temperature affects their concentrations more than moisture. Carbon monoxide shows a weaker dependence on moisture than carbon dioxide, therefore its measurement is able to increase accuracy of the stored material temperature estimate.

Methane was found to be affected by moisture only a little, which would be beneficial for temperature increase indication. However, the dependence of its generation on temperature is not distinct and clear and therefore the gas is not usable for indication of temperature changes in the stored biofuel.

With the aim to find other gases suitable for temperature indication further compounds found in the products of heating were analysed. The positive findings included methanol. Other chemical substances were not determined for the reason of the large quantities of water in the gaseous mixture spectrum. Their determination would require change in the measurement methodology. Their determination will be the subject of future research for the relevance of these gaseous components of the mixtures generated by cellulose-based fuel heating for the environment.

Acknowledgements

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