THERMOGRAVIMETRIC BIOMASS-TO-LIQUID PROCESSES

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Abstract

The article presented forecasts for European biofuel production in processes BtL and WtL on the basis of thermochemical technological path. The paper presents the processes of pyrolysis and gasification of biomass leading to the preparation of liquid hydrocarbon fractions in the synthesis of Fischer-Tropsch and processes HTU. Based on the model Koufopanosa, made the right choice of methods to investigate the thermogravimetric kinetics of biomass gasification with a change of enthalpy and identification of degradation products in real time. Presents the results of preliminary tests conducted on the Simultaneous Thermal Analyzer STA 449 F3 Jupiter's Nietzsche. These studies were carried out for samples of cereal straw, crushed to a state of dry dust. Gasification process by subjecting the sample, the test set, recorded curves TG and DSC, and observing the changes in mass, temperature and enthalpy. These studies have been done to pre-determine the conditions under which it may begin the process of liquidation. The study was conducted in an atmosphere of argon / nitrogen and argon / carbon dioxide. The temperature regime provided that the samples were heated to the temperature of 500 °C at the heating rate of 3 K/min. Argon was used as protective gas, and N_2 and CO_2 – as purge gas with flow rates of 30 ml/min. The results, along with discussion, are presented in graphs - derivatograms and charts showing the cumulative weight changes and changes in enthalpy of individual samples.

Keywords: biomass, gasification, Thermogravimetric Analysiss, Differential Scanning Calorimetry, enthalpy

1. Introduction

Modern processes of obtaining biofuels should be carried out in conformity with the principles of sustainable development, taking into account the possibility of reducing carbon dioxide emissions and ensuring possibly high energy savings. Due to the limited availability of the raw material, which in this case is predominantly biomass, biofuels should be obtained from this resource with the maximum possible efficiency, with simultaneous complete treatment of the post-process residues in biorefining.

Currently research is being carried out in the EU countries with a view to obtaining second generation biofuels using biochemical and thermochemical methods. Pilot and demonstration plants already exist; a commercial application of the said technologies is also being planned. The pilot solutions under way related to the technology of producing second generation biofuels include predominantly the technology of producing bioethanol and attempts to transform biomass into DME.

For thermochemical processes to be performed, the thermodynamics of the BtL processes must be recognised, from the gasification process to the liquefaction stage, with a simultaneous identification of interim products.

The proposed technologies are mostly based on the following processes:
- biomass gasification into $CO+H_2$ synthesis gas, followed by Fischer-Tropsch synthesis, producing a mixture of liquid hydrocarbons as FT-diesel fuel,
- biomass pyrolysis, producing gases (methane, carbon dioxide and water vapour), a liquid fraction called bio-oil and solid residues containing charcoal and ash. The bio-oil is converted, in the process of gasification and Fischer-Tropsch synthesis, into FT-diesel hydrocarbon fuel fractions.

Reference literature also mentions a technology which may lead to the production of biofuel (HTU-diesel) for self-ignition engines. The technology involves a process of high-temperature depolymerisation of lignocellulose biomass into a liquid product which is a mixture of various organic compounds with high water content (HydroThermal Upgrading), and a process of catalytic hydrodeoxidation of the obtained product into a liquid hydrocarbon fraction – a form of fuel. The method may involve processing of biomass with high water content, and this, under certain conditions, may have an impact on the possibility of bond saturation.

Biomass gasification involves the breakdown of large and heavy molecules of solid or liquid hydrocarbons into simpler and lighter ones. The process generally occurs in the following sequential steps:
- pre-heating and drying,
- pyrolysis,
- char gasification and char oxidation.

Although these steps are frequently modelled in series, there is no sharp boundary dividing the steps and they often overlap. If the gasifying agent – oxygen – comes directly from air, the process is called „air gasification", which produces a lower quality gas in terms of the heating value. The process is referred to as „oxygen or steam gasification" if the gasification medium is pure oxygen or steam, respectively. Such gasification produces a relatively high quality gas without nitrogen, which is therefore suitable for use as synthesis gas for conversion to methanol and gasoline.

Pyrolysis is the first stage of thermal decomposition of the feedstock. When the dried fuel is heated in the range of 200 – 500 °C in absence of oxygen, it is decomposed into solid char, volatiles (condensable hydrocarbon or tar) and gases. The relative yield of gas, liquid and solid depends mostly on the rate of heating and on the final temperature of pyrolysis. The pyrolysis product then reacts with the gasifying medium (air, O2 or steam) to produce CO, CO2, H2 and lighter hydrocarbons. During pyrolysis heat is transferred first to the particle surface by radiation and convection, then into the pyrolysing particle through conduction, convection and radiation.

In 1989 Koufopanos et al. modelled the pyrolysis process by examining the decomposition of the three main components of biomass:
- cellulose,
- hemicelluloses,
- lignin.

The initial reaction (*k1*) represents the pyrolysis at low temperature (T < 200 °C), where transformation and modification of the biomass materials takes place. It is followed by an intermediate reaction (*k2, k3*), where decomposition occurs through two competitive reactions. The overall kinetic rate is given by:

$$Ki = \alpha k Ci + \beta k Hi + \gamma k Li,$$ (1)

where:

i - *r*eaction 1, 2 or 3,

C, *H* and *L* - stand for cellulose, hemicellulose and lignin, respectively,

α, β and *γ* - the weight fractions of the corresponding biomass components in the virgin material.

Koufopanos' model, modified by Babu and Chaurasia in 2004, introduces an intermediate step in pyrolysis that occurs at low (< 200°C) temperature, merely transforming and modifying the biomass.

The intermediate product undergoes two parallel competing reactions. The first produces volatiles and gas, the other – char. The volatiles and gas produced in reaction 2 react with char, producing different types of volatiles, gas and char. Thus, the products of primary pyrolysis react in a secondary reaction, which results in the final product.

2. Derivatography as an analytical method

The processes of biomass transformation into fluid (liquid or gaseous) components of engine fuels require a supply of energy in the form of heat in order to break the existent chemical bonds and create new ones. Therefore, in order to define the optimum conditions for the transformation processes it would be essential to define the kinetics of those processes. Due to the complex and varied chemical structures which form biomass, it is not fully possible to define the kinetics at each transformation stage. This may be analogous to natural processes of biomass transformation which result, in many transformations occurring under specific conditions and in a very long time, to produce oil and natural gas. Therefore, the choice of parameters of the biomass transformation processes is very important, and the values of the parameters result, for the time being, from technological practice and have not yet been determined unequivocally. It should be remembered that the process of biomass transformation into energy components (liquid and gaseous hydrocarbons, in BtL and BtG processes, respectively) is not a natural process, and it leads to an accelerated growth of entropy of the environment as a thermodynamic system.

The availability of biomass is not unlimited. The restriction of biomass availability results from the overriding necessity to use it in the food industry, which is particularly important in view of the fact that a relatively high proportion of the human population suffers from malnutrition. Independently, the progress of civilisation, or more specifically – the excessive consumerism it brings, causes an acceleration of the processes of energy conversion for consumption needs, which are not always related to he needs connected with keeping up the standards of living of the world's population. Therefore, with restricted biomass resources, new sources of energy should be looked for, such as all types of waste materials, which are also by-products of consumption processes (WtL processes). Taking into consideration the optimisation of the processes leading to the obtaining of energy carriers, it is now less significant to categorise raw materials according to their origin. It is much more important to use them as effectively as possible with the lowest possible values of energy put into the transformation processes. Consequently, the production of liquid energy carriers, i.e. fuels, should be treated as the XtL type of process, in which the materials transformed into liquid fuels can be any present or future waste materials, ensuring at the same time low-emissions transformation technologies and the value of the EROEI ("Energy Returned On Energy Invested") index substantially higher than one.

The selection of the optimum parameters of the BtL, and more generally – the XtL processes, calls for the recognition of the kinetics of transformation processes together with the determination of the intermediate products and their life during the process. It is also essential to determine the changes in enthalpy in the transformation process in the function of the variable state of matter, which could allow a development of the optimum conditions for liquefaction of the raw material. Due to the varied composition of raw materials in the BtL processes, an unequivocal determination of the optimum parameters of the transformation processes is rather complex and will require statistical processing.

For these reasons, the TGA *(Thermogravimetric Analysis)* method combined with DSC *(Differential Scanning Calorimetry)* was selected for preliminary exploratory research.

According to the *International Confederation for Thermal Analysis and Calorimetry (*ICTAC), thermal analysis (TA) means the analysis of the change in a sample which is related to an imposed temperature regime. Calorimetry means the measurement of heat. The kind of the property whose change is tested and analysed is assumed to be the basic classification criterion of thermoanalytical techniques.

Thermogravimetry is a technique used to define the change in the mass of a sample caused by a temperature regime imposed on the sample, or a technique used to measure the mass of the sample in the function of temperature. The ICTAC guidelines advise the use of the abbreviation TGA (Thermogravimetric Analysis). A thermogravimetric measurement results in a thermogravimetric curve (TG curve) – the dependence of the sample mass on time/temperature. Its derivative is the DTG curve.

Differential scanning calorimetry (DSC) means a technique in which the change of the difference in the heat flow rate to the sample and to the reference sample is analysed while they are subjected to a temperature regime, or a technique where the change of the difference in the heat flow rate to the sample and to the reference material is measured as a function of temperature.

$$\Delta\Phi_{SR} = \Phi_S - \Phi_R, \tag{2}$$

where:
S - sample,
R - reference sample.

3. Preliminary testing results

Preliminary thermogravimetric testing of samples of ground biomass (cereal straw) was, and still is, conducted on the Simultaneous Thermal Analyser STA 449 **F3 Jupiter**® of the Netzsch company. The grinding process, which is the subject matter of a patent application, yielded a homogenous granulometric composition of the cereal straw whose particles were of a very small size. In the analyser mentioned above the samples (S and R) were placed symmetrically in identical measuring vessels (Al2O3 crucibles) in the same furnace whose temperature was regulated according to an assumed temperature regime, regardless of the changes in the properties of the samples during the measurement. The temperature regime provided that the samples were heated to the temperature of 500 °C at the heating rate of 3 K/min. Argon was used as protective gas, and N2 and CO2 – as purge gas with flow rates of 30 ml/min.

The thermal analyser measured the difference in temperatures between the samples:

$$\Delta T_{SR} = T_S - T_R. \tag{3}$$

When the analyser furnace is heated and the system is thermally symmetric, an identical heat flux flows to both samples and their difference in temperature is then zero. If this state of dynamic equilibrium was disturbed by a change in either sample, or if there was thermal asymmetry of the system caused by a difference in the heat capacity of the samples, the DSC measurement showed differences in temperature, $\Delta T_{SR} \neq 0$, in proportion to the differences in the heat fluxes to the sample and to the reference sample, and then

$$\Delta\Phi_{SR} = -k\Delta T_{SR}, \tag{4}$$

where k is proportionality constant with the nature of the inverse of thermal resistance.

The results of the measurement made with the use of the DSC technique were DSC curves – the dependence of the measured difference in the heat fluxes on time/temperature.

The graphs in Fig. 1. and Fig. 2. present the course of derivatographic curves; the TG curves are marked in red, the DTA curves obtained by means of the DSC method - in blue, and the DTG curves are marked with a green broken line.

In the process of thermal decomposition of the biomass sample of 4.55 mg, in the atmosphere of nitrogen, the following stages can be isolated:
- evaporation of water to 100ºC with heat absorbed from the system,
- partial liquefaction in the very short period when the temperature grows from 271.6ºC to 298.4ºC,

- gasification reactions above 400ºC,
- above temperatures of 298.4ºC to 324.6ºC both the liquid and the gaseous state may occur; the thermal decomposition process becomes more intense, eventually leading to an intense mass loss of the sample.
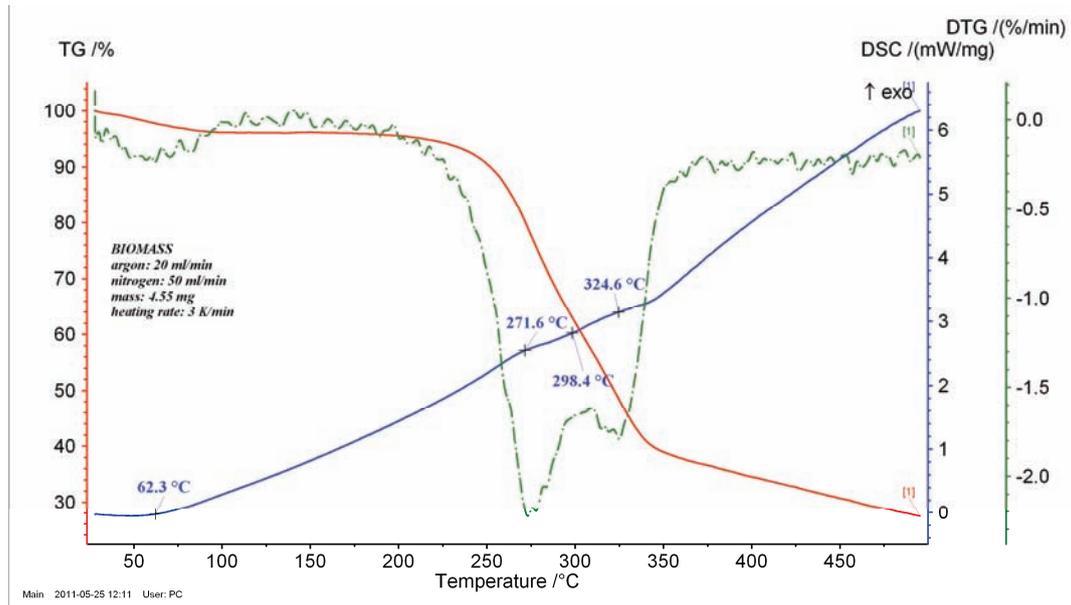

Fig. 1. Derivatogram of biomass sample tested in the atmosphere of nitrogen

The experiment repeated for the same kind of sample (ground cereal straw), similar weight, and conducted in the atmosphere of carbon dioxide shows a similar character of changes in individual curves. From the character of the course of the TG and DTG curves it can be concluded that CO_2 molecules join in the chemical processes which take place. A detailed interpretation of the process will be possible after the data concerning the kind of the arising chemical entities have been obtained.
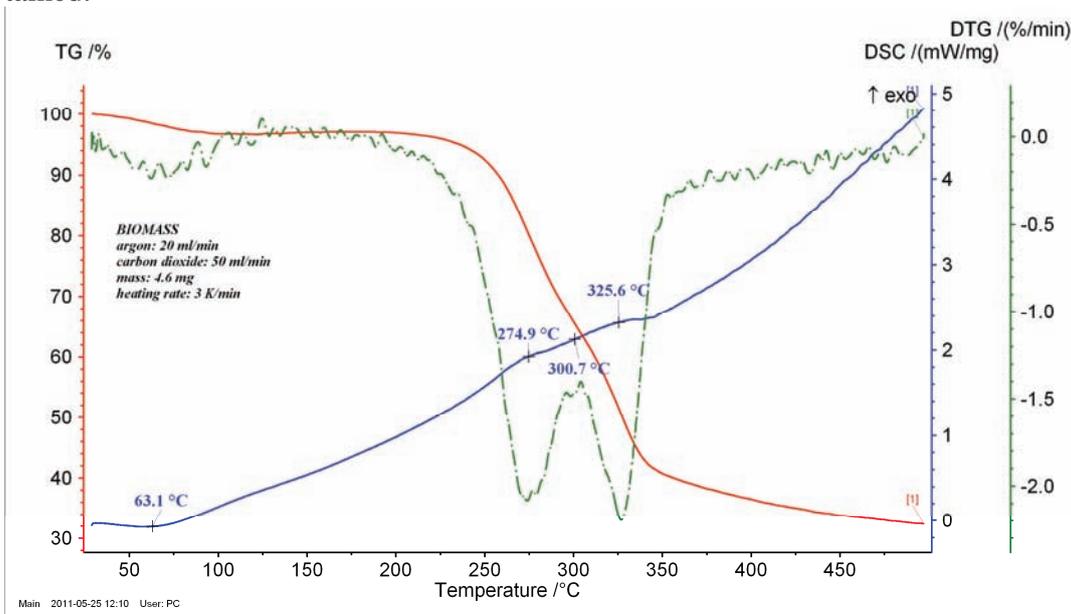

Fig. 2. Derivatogram of biomass sample tested in the atmosphere of carbon dioxide

Figure 3 illustrates the changes in enthalpy shown in the course of the DSC curve, for both biomass samples in different atmospheres.
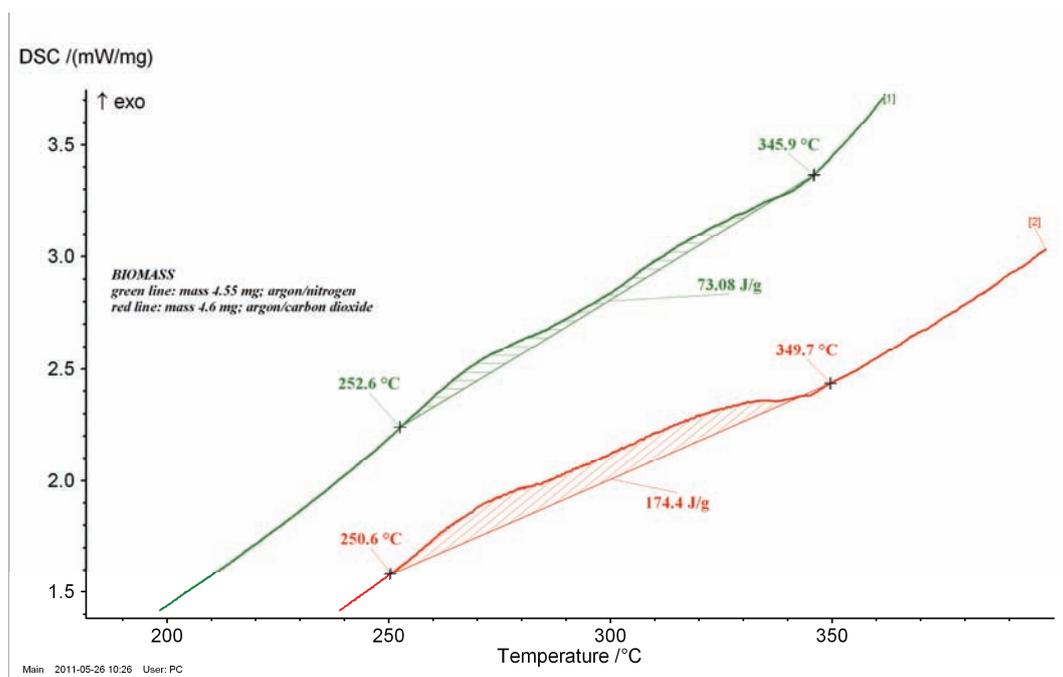
Fig. 3. Change in enthalpy for biomass sample tested in the atmosphere of nitrogen or of carbon dioxide

As it can be seen in Fig. 3, in the range of temperatures from 252.6 °C to 345.9 °C and from 250.6 °C to 349.7 °C, the decomposition process has an exothermic nature, showing two maxima. This confirms the conclusions drawn from the analysis of Fig. 1 and Fig. 2 because two processes can be observed in the range under consideration:
- the formation of the liquid phase bonds from resulting radicals, causing a partial reduction in the enthalpy change value,
- partial evaporation of the liquid phase, combined with decomposition.
  The total value of the enthalpy was: $-\Delta H = 73.08$ J/g or $-\Delta H = 174.4$ J/g.

Figure 4 illustrates the changes in mass shown in the course of the TG curve, for both biomass samples in different atmospheres.
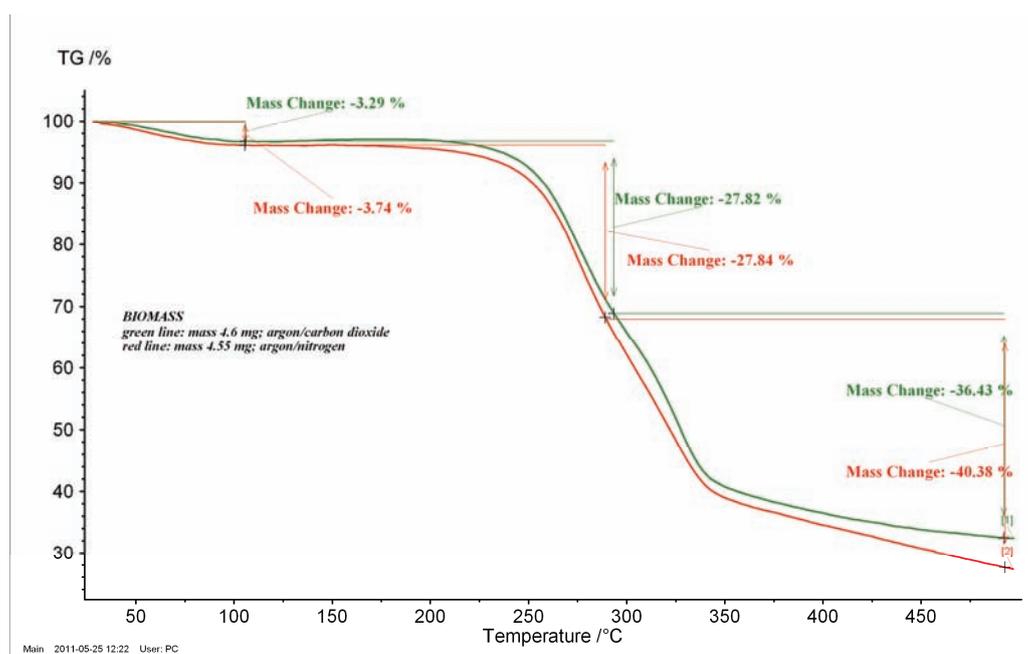

Fig. 4. Change in mass for biomass sample tested in the atmosphere of nitrogen or of carbon dioxide

Presented in Fig. 4, the differences in weight change of test samples may suggest the possibility of entry of carbon dioxide in response to emerging, in the process of decomposition, radicals. This assumption is further justified by the fact that the observable enthalpy changes for the test sample in an atmosphere of carbon dioxide, are larger and occur in a slightly broader range.

4. Conclusions

The conducted study shows that the adopted research method in the form of obtaining results of thermogravimetric testing for biomass samples of various origins can lead to a preliminary estimate of the optimum range of temperatures at which the process of liquefaction with the highest possible value of enthalpy can occur. The testing of many biomass samples with a parallel determination of their elemental constitution as well as structural-group composition should lead to the obtaining of empirical relationships allowing a selection of the parameters of the BtL processes depending on the kind of the raw material. An expansion of the research methodology is being planned to include an opportunity of on-line testing of the chemical composition and structure of the chemical entities arising at each stage of the thermal decomposition process with the use of the FT-IR and QMS.

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