Energy 87 (2015) 259–269

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

# Characterisation of renewable fuels' torrefaction process with different instrumental techniques

Małgorzata Wilk*, Aneta Magdziarz, Izabela Kalemba

*AGH University of Science and Technology, Al. Mickiewicza 30, 30-059 Krakow, Poland*

A R T I C L E   I N F O

*Article history:*
Received 11 December 2014
Received in revised form
10 April 2015
Accepted 28 April 2015
Available online 23 May 2015

*Keywords:*
Biomass
Sewage sludge
Torrefaction
TGA (Thermogravimetric characteristic)
SEM (scanning electron microscopy)
FTIR (Fourier Transform Infrared)

A B S T R A C T

The effects of the torrefaction process on two kinds of wood biomass materials (WB1 and WB2) and SS (sewage sludge) were analysed. The thermal conversion of wood biomass and sewage sludge was tested from ambient temperature to 700 °C in air and argon atmospheres using TG (thermogravimetric analysis) and DTG (derivative thermogravimetric)). The studied materials were characterised in terms of their proximate and ultimate analysis and HHV (higher heating value) before and after the torrefaction was investigated. The course of carbonising the tested biomass and sewage sludge in 230 °C, 260 °C and 290 °C temperatures under 0.5 h, 1.0 h and 1.5 h time of heating was carried out in an electrical furnace. The changes in the chemical structure (bonds) were conducted by the FTIR (Fourier Transform Infrared) method. The structural changes in the torrefied materials were examined by a SEM (scanning electron microscopy). The results showed the changes of biomass and sewage sludge properties towards coal (more carbon content fuel), and additionally low moisture content and better strength properties were obtained. Finally, the applied instrumental methods are necessary to describe torrefaction process in detail and confirm physical and chemical changes in raw biomass giving possibility to the application in industry.



## 1. Introduction

Operating difficulties concerning renewable fuel combustion caused by moisture content, easiness of biological degradation and the milling of raw, wet biomass require the pre-treatment of feedstock in pelletisation, drying, pyrolysis or torrefaction processes. Torrefaction is a process where raw biomass is heated under an inert atmosphere at a temperature range of 200–300 °C and the hydroxyl groups are removed, thus producing hydrophobic material. The great advantages of torrefied material in contrast to a raw one are a higher calorific value and energy density, and a lower O/C ratio and moisture content. Besides, the obtained product is brittle and, as such, is easier to grind. Moreover, the torrefied material is more resistant to biological degradation, and is safer to store and easier to transport. Handling biomass in large quantity raises big logistical questions – transporting the bulky crop with its significant water content is costly. It is necessary to mention that transportation and storage problems decrease because of hydrophobic properties and higher energy density of torrefied material allowing for reduced cost per Joule of fuel transported. Torrefied biomass has been proposed as suitable lower cost feedstock for thermochemical fuel production. Benefits result from significantly lower water content giving easily handled renewable fuel and can be successfully stored in outdoor places. The size of torrefied biomass is reduced more than half (50–85%) comparing to the amount of raw material. Giving its ability torrefied biomass have huge market potential. Torrefacion process due to its attractiveness can be used by industry and vastly improved the competitiveness of raw biomass. The increased homogeneity in solid product quality from different raw materials, as well as reduced seasonal influences, is also obtained in the course of the torrefaction process [1–3]. The most promising product is the solid part, which can be used to form torrefied pellets (second generation" pellets – TOPs (Torrefaction and Pelletisation Process)) alternatively as a fuel in heating sector and power generation. During torrefaction, in addition to a solid torrefied product, a condensed liquid and non-condensable gas mixture-torgas (CO, $CO_2$, $H_2$, and $CH_4$), are also formed. These properties are very promising in improving the quality of biomass for energy utilization [4–9]. The torrefied products from biomass torrefaction have been proposed as a successful feedstock for

* Corresponding author. Tel.: +48 126173198.
*E-mail addresses:* mwilk@agh.edu.pl (M. Wilk), amagdzia@agh.edu.pl (A. Magdziarz), kalemba@agh.edu.pl (I. Kalemba).

http://dx.doi.org/10.1016/j.energy.2015.04.073

combustion, co-gasification or gasification processes [10,11]. During torrefaction process pollutants emission is very low and $NO_x$ and $SO_x$ emissions should be negligible due to the low processing temperature and extremely low content of sulphur in lignocellulose biomass. Therefore, torrefaction process can be classified as friendly environment technology. According to the environmental impact analysis, the environmental impacts of torrefaction are rather positive taking into account replacing fossil fuels by renewable energy sources. The insignificant environmental effect of the torrefaction is emission to air. But the gases produced in torrefaction can be filtered for dust removal, and then burned in an incinerator. The concentrations of the substances in the exhaust gases are remarkably low, and thus impact to the environment is rather low. Advantages of torrefaction bring interest in industrial and researchers for energy production. The evaluation of torrefied biomass requires using several methods which are obligatory to fuel investigations. The essential analyses include proximate and ultimate analyses (volatile matter, ash content, fixed carbon and elemental analyses CHNSO (C – Carbon, H – Hydrogen, N – Nitrogen, S – Sulphur, O – Oxygen)) [4–6], as well as identifying wood composition (hemicellulose, cellulose, and lignin) [11–14]. Therefore, the thermal decomposition characteristics of these constituents play a dominant role in determining the performance of lignocellulose materials' torrefaction. In addition, other methods are needed to obtain the comprehensive characteristic of torrefied material. Both ICP-MS and ICP-OES (Inductivity Coupled Plasma-Mass Spectrometry, Optical Emission Spectroskopy) allow for the detection of the major elements (Na, Mg, K, Ca, Al, Mg, P, Fe, Ti) and heavy/toxic elements (Cr, Ni, Cu, Zn, Cd, Sn, Ba, Pb, As) [15]. XRF (X-ray Fluorescence Spectroscopy) identifies the mineralogical data ($SiO_2$, $Al_2O_3$, $Fe_2O_3$ CaO, MgO, $Na_2O$, $K_2O$, $TiO_2$, $Mn_3O_4$, $P_2O_5$, $SO_3$, SrO, BaO, ZnO, $V_2O_5$) [16]. A FTIR (Fourier Transform Infrared), Raman and NMR spectroscopy are used to investigate the changes in the chemical structure [14]. A GC-MS (Gas Chromatography-Mass Spectrometry) can identify the torrefaction condensable phases [16–18]. The microstructural characterisation of torrefied biomass is performed by a scanning electron microscopy and X-ray diffraction. SEM (Scanning Electron Microscopy) observation and EDS (Energy Dispersive Spectroscopy) analysis enables the characterisation of the material morphology [19–25]. Thermal analysis (TG, DTG and DTA) is a technique used for combustion and pyrolysis studies. TGA is a useful technique to investigate the thermal behaviour of fuels (the temperature at which a process starts and ends, the maximum reactivity temperature, the ash amount and the range of temperature). Numerous papers present results using thermal analysis that takes into account combustion, pyrolysis and the co-combustion of renewable fuels [24–32].

Similar thermochemical treatments and analysing techniques to those applied to biomass can also be satisfactorily used in the case of SS (sewage sludge) management, which is a significant challenge in modern society. SS is the major waste generated in the urban wastewater treatment process and gives not only a high organic matter content, but also heavy metals and organic contaminants. The most common disposal of sewage sludge is landfilling, farm applications and incineration. These days, European and Polish legislation concerning sewage sludge treatment has become very restrictive [33], imposing the rapid development of thermal methods of sewage sludge utilisation. There are several thermal technologies for utilising municipal sewage sludge to obtain useful forms of energy, such as pyrolysis, gasification, combustion, and co-combustion processes [10,15,16]. The advantages of thermal processes are the large reduction in volume, the thermal destruction of toxic organics and the recovery of the energy of organic sources in the sludge. One of the promising options is torrefaction technology based on the experience gained with biomass. The research concerning torrefaction is mainly focussed on lignocellulose biomass [34–42]. Accordingly, there is a great need to implement some more experimental studies to these few papers concerning sewage sludge torrefaction [17,18,43,44].

The main objectives of this research are to characterise the wood biomass and sewage sludge after the torrefaction process, and then evaluation of the candidacy towards renewable, more carbon content fuels. It is worth mentioned that in this study different renewable fuels in their chemical composition, character and reactivity were chosen. The torrefaction process carried out in special design laboratory set-up. The physical and thermochemical properties were studied by using advanced instrumental techniques (TA, SEM, FTIR).

## 2. Experiment

### 2.1. Materials

In this experimental study of the torrefaction process, two wood biomass samples, and raw and pre-dried sewage sludge were used as renewable sources. It is worth noting that biomass and sewage sludge characteristics depend on the local climate and production (sewage sludge is the residual matter from the treatment processes of household and industrial wastewaters). However, in this study, the wood biomass represents common wood species in Poland. Both kinds of biomass, WB1 and WB2, were taken from two different sawmills. The WB1 chips were crushed, milled and sieved to ≤5 mm screen size. The WB1 wood biomass was much more heterogeneous (leaves, stumps, barks and roots all milled together) than WB2, which was obtained in a powdery form and at the size of ≤1 mm, plus bright in colour. The sewage sludge samples were taken from a municipal wastewater plant. Part of the material was dried at room temperature for several days, resulting in 10.4% of moisture. Proximate and ultimate analyses of the biomass and sewage sludge were performed (Table 1). Studied biomass material is highly heterogeneous in quality and nature (springy, fibrous, bulky crop, significant water content), therefore it needs to be pre-treated to improve handling, milling and transport. That is why torrefaction is a promising technology which delivers densified, hydrophobic, non-biodegradable, brittle and easy to grind biofuel similar to coal.

The moisture content of the studied fuels was determined on the basis of weight loss during drying of a small sample using the thermo-gravimetrical method by means of AXIS ATS Precise Moisture Analysers, and by maintaining 1 g of the samples in the drying system at 105 °C to a constant mass according to EN 15934:2012, where both results were comparable. The ash content was determined by burning a 1 g sample of all studied solid recovered fuels in a muffle furnace at 250 ± 10 °C for 50 min and then at 550 ± 10 °C for 4 h, according to the EN 15403:2011 European Standard. In the case of sludge, EN 15935:2012 was applied. The volatile matter was determined by maintaining the 1 g of mass samples at 900 and 950 ± 10 °C for 7 min using the EN 15402:2011 method.

The fixed carbon content was calculated by difference using the balance:

$$FC = 100 - Ash - VM - M, \% \tag{1}$$

where: FC (%), Ash (%), VM (%), and M (%), respectively mean the mass percentages of fixed carbon, ash, volatile matter and moisture of the raw sample.

An Elemental Analyser Truespec CHN Leco was used to determine the carbon, hydrogen and nitrogen content. The LECO CHN628 is a combustion elemental C, H, and N instrument that utilizes only pure oxygen in a furnace, ensuring complete combustion and superior recovery of the elements of interest. A SC-