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A Comprehensive Approach to the Characterization of Second Generation Biofuels

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The thermochemical conversion of conventional and alternative biofuels is capable of supplying a wide range of energy vectors and chemicals. Peculiarities of such materials require a comprehensive and detailed characterization to provide the fundamental information and face with the issues of each process step. Innovative technologies, advanced model approaches, optimization procedures, need data which comply with relevant standards. The characterization tools described in this work range from lab-scale tools, used to provide the fuel fingerprint, to pilot scale facilities, which operate under industrial scale conditions. Protocols and procedures have been elaborated for all activities to provide reliable and qualified parameters for practical applications and comprehensive codes. The experimental activities have been supported with a broad set of on-line and off-line measurements and analyses, and coupled with modelling activities to qualify the experiments. Finally, a biofuel database, reporting the data collected in the last years, has been developed.

1. Introduction

The 20-20-20 targets adopted by the European Commission (a 20% reduction in greenhouse gas emissions from 1990 levels, raising the share of energy consumption produced from renewable resources to 20%, a 20% improvement in energy efficiency) represent a stimulus to optimise conventional biofuel production technologies and the conversion of the largest variety of fuels in the most efficient way. The growing interest in bioenergy and biofuels has led to a new range of solid biomass fuels such as hydrolytic lignin, distillers grains, torrefied biomass and gasification char whose properties may significantly differ from traditional biomass fuels. Thermochemical conversion can be considered a flexible conversion platform, capable of supplying a wide range of energy vectors. At all stages the different products and residues should be characterised to guarantee that they comply with relevant standards.

In this regard the detailed characterisation of selected new feedstocks, 2nd generation biofuels as well as residues from their production represents a relevant step in the whole bioenergy utilisation chain and provides the fundamental information for upstream and downstream process steps. There are required parameters and indices for the assessment of fuel behaviour, detailed fuel properties for utility designing, wide spectra of well-described experimental results for model validation in traditional, as well as innovative (like oxyfiring, Simone et al. 2009) combustion and gasification systems. A qualitative description of solid fuels should include detailed information on pyrolysis rate, devolatilization products (gas speciation, tar and soot formation), rate of char oxidation and gasification.

In the last years the Department of Civil and Industrial Engineering of University of Pisa, the International Flame Research Foundation (IFRF) and CRIBE have been contributing to fill the gap in the characterization of these materials. This experience has led to the development of several characterization tools and methodologies. The characterization tools range from lab-scale tools used to provide the fuel fingerprint to pilot scale facilities which operate under industrial scale conditions. Protocols and procedures have been elaborated for all activities to provide reliable and qualified parameters for practical

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applications. The experimental activities have been supported with a broad set of on-line and off-line measurements and analyses, and coupled with modelling activities to qualify the experiments.
This work is in the frame of the 7th FP project Biofuels Research Infrastructure for Sharing Knowledge (BRISK), in which IFRF is involved along with other 25 partners in Europe. It promotes the study of biofuel conversion by integrating research facilities in the European scientific community. Transnational Access and Joint Research Activities are coordinated to share knowledge on biofuel processes. Experimental campaigns, improvement of technical protocols, elaboration of practical parameters, development of solid fuel databases, are in progress or programmed activities in different facilities. IFRF, with CRIBE and DICI-UNIPI, contribute with an advanced drop tube for studying pyrolysis and oxidation, a fixed bed reactor for studying the tar formation, a downdraft reactor for studying the gasification of biomass fuels. Besides, it will improve and publish two solid fuel databases, containing data from literature, previous and BRISK experimental campaigns.

2. Development of procedures for solid fuel characterization

Typically, fuels are characterized on a lab scale by the use of fundamental analyses (proximate and ultimate), useful for fingerprinting and comparing the fuel with others. Additional analyses can be performed on solid fuels to give more information: heating value; ash analysis; ash fusion tests; pyrolysis gas speciation; chemical analysis. The evaluation of physical properties (size, shape, density, surface area, porosity, specific heat, conductivity) is also important. All these properties should be defined for fuel and char particles as average and representative values in a preliminary approach. However a distribution of values can be more appropriate for advanced models that can study the population of different dimensional classes (Biagini et al. 2009). Size, shape, swelling factors and their distributions can be obtained to estimate the heterogeneous nature of the fuel, particle-to-particle differences, effects of pretreatments (e.g., grinding and sieving).
The use of data obtained in mild conditions of temperature and heating rate, like those programmed in “traditional” lab scale apparatuses, is unsuitable for large scale plants applications. The effect of the operating conditions is not negligible, e.g., the volatile matter released during the devolatilization of coals and biomass fuels in drop tubes can be up to 30% higher than that measured in the proximate analysis (Biagini 2003). Therefore, experimental procedures which utilize advanced facilities, that more closely simulate the actual combustion environment, should be used to test solid fuels. There is a general lack of quantitative information collected in reactors which operate in these conditions. Also uniform methodologies with the use of such apparatuses are not standardized. Qualified procedures for solid fuel characterization are desired for providing useful parameters for large scale applications (advanced models, plant design and optimization).
IFRF, DICI-UNIPI and CRIBE virtually joined to constitute a Solid Fuel Characterization Laboratory, each institution providing specific competences and sharing facilities and protocols for experimental procedures and data elaboration. Expertise and specific activities are listed in Table 1. Protocols for each activity have been developed to assure reliable data by verifying the repeatability of the tests and reducing the experimental errors. Besides traditional lab-scale apparatuses, a pilot scale drop tube (Isothermal Plug Flow Reactor IPFR) is used at IFRF to give conditions similar to those of large scale furnaces. A pilot scale downdraft reactor is used to study the gasification of different biomasses at the CRIBE centre. Here, also a fixed bed reactor is available to study the pyrolysis of biomass fuels and obtain data on the pyrolysis products (char, tar, gas). Offline analyses on reaction products are carried at DICI-UNIPI.

Table 1. Activities of the virtual Solid Fuel Characterization Laboratory

Solid Fuel Characterization Laboratory			
Unit	DICI-UNIPI	IFRF	CRIBE
Expertise	Experimental characterization on a Lab scale	Experimental characterization on a pilot scale	Operation of plants for biofuels
Activities	- Traditional analysis (ultimate, proximate, ash, morphology) - Devolatilization tests (TG-FTIR) - Tar and char analysis - Kinetic models for devolatilization and char oxidation - CFD model as diagnostic tool	- Char preparation - High temperature and heating rate tests in IPFR (devolatilization, char oxidation, oxyfiring) - Solid Fuel DataBase	- Gasification in a downdraft reactor - Pyrolysis in a fixed bed reactor with tar sampling device and gas analysis

3. Equipment

3.1 The Isothermal Plug Flow Reactor at IFRF

The IPFR (Figure 1a) is a drop tube (4.5 m total length x 0.15 m inner diameter) with fuel particles fed pneumatically at a certain height through one of the 19 lateral ports along the tube, the heating system is formed of electrical resistances (54 kW) along the tube and hot gases from the 60 kW burner at the top section of the reactor, solid residues and product gas are quenched at the bottom of the reactor and sampled on the collector probe for online and offline analyses. The high temperature (1400 °C) and heating rate (evaluated on the order of 10^4 °C/s) of IPFR in the new asset of Livorno (IT), the qualification activities (upgrading of specific components and diagnostic tests) and the experimental procedures make it a superior facility for providing data and parameters for advanced models of pulverized fuel combustors as well as innovative plants (e.g., oxyfiring and gasification).

The qualification of the IPFR is a continuous activity consisting in improving the reactor characteristics, verifying the performance and validating the reliability of data obtained. For instance, activities to eliminate or mitigate possible non-homogeneous points in the temperature gradients inside the reactor have been carried out, like electrical heater improvement, automatic regulation of carrier gas mix, use of micro-suction pyrometers to measure the axial and radial temperature profiles. This was done because the isothermal conditions of the reactor are a crucial issue to provide reliable data for combustion related investigation. Finally, the CFD model of the IPFR during the devolatilization and combustion of fuel particles was developed and used as a diagnostic (to estimate the variables that can be hardly measured during the test, e.g., the effective thermal history of the particles), predicting and interpretative tool.

3.2 TG-FTIR analysis at DICI-UNIPI

Thermogravimetric (TG) analysis coupled with Fourier Transform InfraRed (FTIR) spectroscopy provides important information on the devolatilization of materials, that is the identification of major volatile species and the typical temperature range of release: while the sample weight loss is continuously recorded by the TG balance, the outlet gas is moved to a FTIR analyzer through a heated transfer line to limit the condensation of volatile products. The analysis of FTIR spectra allows for the identification of evolved species, and specific gas evolution profiles can be obtained.

The devolatilization in a TG-FTIR apparatus is fundamental as a preliminary characterization, for the fingerprinting of the fuel and the comparison with similar fuels. The analysis of weight loss rate curves and FTIR gas evolution profiles yields important information on the reactivity of the fuel during the devolatilization, and may be related to the chemical composition of the biomass fuel, namely, hemicellulose, cellulose and lignin, which represent the biomass macro-components (Biagini et al., 2006).

During the last years the TG-FTIR results of several lignocellulosic materials (of different origin, properties and composition) were analyzed, the main volatile compounds were identified and the main devolatilization steps characterized.

3.3 Biomass pyrolysis and gasification at CRIBE

CRIBE developed a pilot scale biorefinery in San Piero a Grado near Pisa with the aim of studying the production of biofuels and energy. It is formed of a syngas platform based on a biomass gasification plant, a bio-ethanol platform based on biomass fermentation, an oil platform for biodiesel production, a biomass combustion platform for the production of steam and electricity, and a biomass pyrolysis platform.

The gasification plant is based on a 200 kWth downdraft reactor, with a nominal input of 50 kg/h. The biomass bed is supported on a grate at the bottom of the reactor, while the syngas is transferred to the flare through the cleanup line, formed of a cyclone, a venturi scrubber, a chiller condenser, two sawdust filters and a bag filter. The plant is equipped with measuring devices to monitor the process variables: temperatures in the reactor and cleanup line, pressure drops across the gasifier bed, syngas flowrate and composition. Different biomass have been successfully tested in this plant (Simone et al. 2012).

The pyrolysis reactor (diameter 65 mm, bed length 400 mm) is formed of a steel basket and a steel case positioned in an electrical heater. The biomass is loaded on the basket. The inert conditions are guaranteed by a continuous nitrogen flow. The solid residue (char) is recovered at the end of each experimental run. The evolving gas is transferred to a tar sampling device through a piping, kept at 200°C to prevent tar condensation. During the pyrolysis tests the temperature, flow rate and outlet gas composition can be monitored. Three K-thermocouples are placed in the pyrolysis reactor within the biomass bed, and a K-thermocouple is positioned at the tar and gas sampling point.

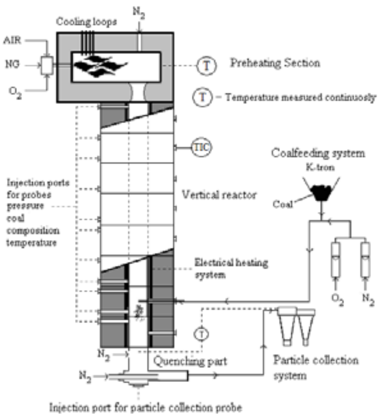
Two on-line instruments are available at CRIBE for gas sampling and analysis: a micro-gas chromatograph (micro-GC) and a Fourier Transform InfraRed Spectrometer (FTIR). They can be installed in both the gasification and pyrolysis lines. The micro-GC (equipped with a pump for gas sampling and a membrane filter) allows analyzing H_2, O_2, N_2, CO, CO_2 and C_1-C_2 hydrocarbons in less than 240 s. FTIR measurements are performed by using a FTIR spectrometer, installed in a specifically developed pressurized cabinet. The apparatus is equipped with a pump for gas sampling including valves and manometers for pressure control and a heated transfer line. A heated gas cell is used for gas analysis.

A tar sampling system was specifically developed for collecting the tar in the gas from either the gasification or pyrolysis lines (Simone et al. 2011). It is based on a solvent-free condensation method. Figure 1b reports a pictorial representation of the system. The gas is continuously blown into an impinger train through a pump positioned at end of the system. The tar sampling device separates the condensable species in 3 impingers kept at decreasing temperatures to allow for tar fractionation into 30×150 mm glass bottles. A particle filter made of syntherised steel, heated at 200°C, is used to remove solid particles. Ceramic rings and glass beads are used in the glass bottles to increase the contact surface. The first impinger (set-point temperature: from 100 to 200 °C) is devoted to the condensation of the heavy tars. The second impinger, whose temperature can be modulated from 0 to 40 °C, allows for the condensation of light tars and moisture. The third impinger (chilled from -15 to 0°C) is designed to recover the residual water and light organic components. A glass trap in an ice bath and a glass-fiber filter are positioned at the end of the line to prevent water or light components to be dragged from the gas flow to the pump.

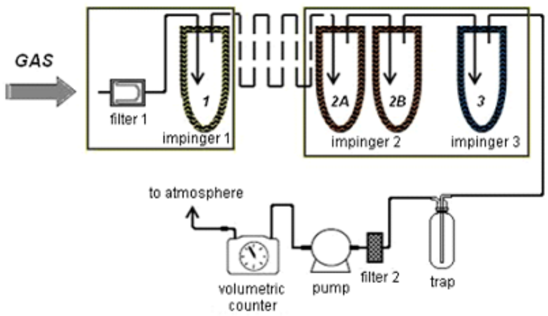
The main features of this system are: i) solvent free method, which allow for a straightforward gravimetric determination of tar content and/or tar yield; ii) reproducibility of sampling conditions due to an accurate control of the impinger temperatures by means of Peltier cells; iii) transportable and compact unit.

Different experimental techniques for offline tar characterization are used at DICI-UNIPI:

- TG analysis, to evaluate the boiling range of the different fractions of collected tar;
- TG-FTIR, to get a fingerprint of tar fractions and evaluate the water content;
- Ultimate Analysis, to obtain the CHN raw formula of the heavy tar fractions;
- Gas Chromatography – Mass Spectrometry (GC-MS), to identify the chemical compounds that constitute tar and thus provide qualitative information on tar reference compounds.



a)



b)

Figure 1. Sketch of (a) the IPFR reactor, and (b) the tar sampling device.

4. Description of protocols

4.1 General approach to the protocols

As said above, it is important to develop procedures for a fuel specific characterization. The first point (fundamental analyses) is to give a basic characterization of the solid fuel. Additional analyses can be performed, also based on the fingerprint of the material. Advanced analyses add value to the characterization by testing the fuels under conditions similar to those of large scale applications (high temperature and heating rate) and give significant fuel specific parameters.

Specific procedures have been developed and applied for:

- the operation of every plant,
- testing biofuels in devolatilization, combustion and gasification,
- monitoring the process variables,
- sampling and analyzing the test products,
- elaborating the raw data and provide useful and reliable parameters.

The description of one protocol is given in the next subsection as an example, while some results obtained from tests with biofuels are shown in the next section.

4.2 Protocol of high HR pyrolysis tests

The high Heating Rate (HR) pyrolysis tests are performed in the IPFR. The experimental conditions of each test are defined by the nominal temperature, nominal oxygen level (or gas concentration), injection port and sampling probe height. The power of the burner and the resistances are programmed to achieve the nominal temperature. The gas flowrate is programmed to adjust the oxygen level, even though the respect of the thermal balance depends also on this variable, so the stabilization of the reactor temperature have to be monitored. The reactor length derives from the difference between the injection port and the sampling probe height. It is used to estimate the nominal residence time, referred to the gas in the actual conditions. The fuel particle flowrate is fixed around 100 g/h. A sieved and dry sample is suitable for a continuous operation. The maximum flowrate (300 g/h) is programmed for char production. The target for each test is to get a sufficient amount of residue to be analyzed (few grams for determining at least the ash content) and this is generally done in 30 minutes.

All monitored parameters of the IPFR are registered in the historical file of the instrument. The test archive file collects the average values of these variables (temperature, oxygen and CO_2 concentration), the nominal conditions and the information on the fuel.

The aim of the IPFR devolatilization tests is to evaluate the Volatile Matter released at High Temperature and high heating rate (HTVM) in an oxygen free atmosphere and elaborate global kinetics for solid fuels. Tests at two different temperatures are necessary for studying the devolatilization. Explorative tests (under fixed values of temperature and time) are carried out to estimate the reactivity of the fuel. The results of these tests are useful to refine the program in case the reactivity of the fuel resulted different from that expected.

5. Results

Different experimental campaigns have been carried out on biofuels in the frame of the BRISK project and previous activities. Agricultural residues (straw), wood (pellets) and torrefied biomasses (from palm kernel) have been studied. Here some examples of a completely characterized biomass are shown. It is a black pellet that gave these fundamental results:

- proximate analysis: moisture 4.2 wt%(as received), VM 78.79 wt%(dry), ash 2.78 wt%(dry);
- ultimate analysis: C 50.32 wt%(dry), H 6.02 wt%(dry), N 0.26 wt%(dry), S 0.028 wt%(dry);
- heating value: LHV 18 MJ/kg (dry).

The results of the pyrolysis study under low HR are shown in Figure 2a. The derivative weight loss curve and the FTIR profiles of some gaseous products are compared. The TG curves under different heating rates are used to calculate the low heating rate kinetics according to the isoconversional method of Friedman (1965), as shown in Figure 2b. These results are used as preliminary results to calculate the kinetics from the high HR tests in the IPFR according to the two step reactions model. The graph in Figure 3a shows the comparison between the experimental tests and the model results for different temperatures and residence times. Finally, the experimental and model results of the char oxidation in the IPFR are compared in Figure 3b.

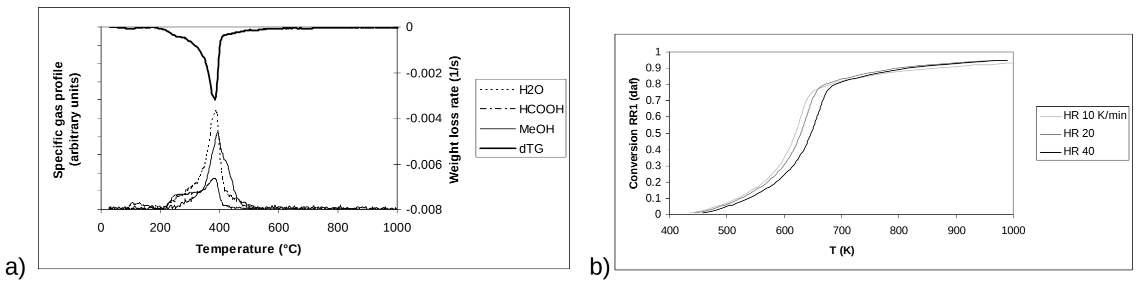


Figure 2: a) Derivative weight loss curve and FTIR profiles of some gaseous products during the pyrolysis of black pellets in TG balance. b) Conversion curves from the devolatilization of black pellets in TG balance under different Heating Rates.

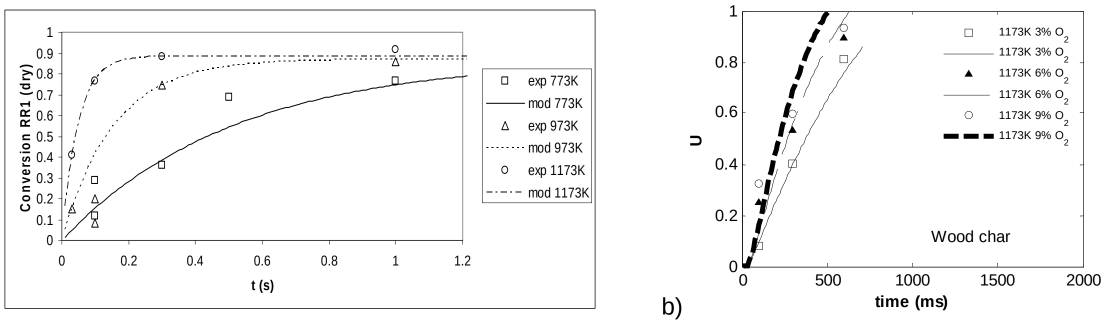


Figure 3: Comparison of model results (continuous curves) and experimental data (symbols) for (a) the devolatilization of black pellets in the IPFR, (b) the char oxidation tests in IPFR of black pellet.

6. Conclusions

Alternative fuels (biofuels, wastes, torrefied biomasses) and innovative processes (gasification, oxy-fuel and flameless combustion) are a challenge for mathematical modelling. Submodels accounting for solid fuel particle devolatilization and char oxidation, particle size and shape variations, tar/soot formation and oxidation, fate of ash and heteroatoms (N, S) should be developed and coupled in a comprehensive CFD model that must balance the sophistication, introduced by the submodels, with the computational capability. It is therefore desirable to provide reliable and qualified parameters for model validation. A comprehensive and detailed characterization of solid fuels can be performed in the Solid Fuel Characterization Laboratory, ranging from lab to pilot scale facilities, able to perform fundamental, additional and advanced analyses, and develop simple to complex models. Procedures for elaborating reliable and qualified indexes and model parameters have been developed and shared between experimenters and modellers in the frame of the activities of the BRISK project. Some protocols and examples have been described in this paper. The data will be included in two databases:

- the solid fuel database SFDB of IFRF, originally developed for coals (it contains approximately 100 coals, with data of devolatilization, char oxidation and nitrogen partitioning in the IPFR) and thus to be extended to biofuels;
- the biomass devo database BDDB of DICI-UNIPI, originally developed for literature data (150 biomasses with 1200 devolatilization tests in different facilities) and thus to be adapted for including the IPFR data.

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