

# Advanced Characterization of Biofuels for Combustion and Gasification Plants

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Detailed information on the biofuels is an essential requirement for the prediction of plant efficiency, carbon in ash, pollutant emissions, surface deposition and corrosion, in thermochemical processes. A fuel-specific comprehensive characterization is required to design, operate and model combustion, oxy-firing and gasification plants. At IFRF it couples fundamental analyses with advanced tests in the Isothermal Plug Flow Reactor (IPFR), which allows high temperature and heating rate, under programmed gaseous environments (N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O). The aim of this work is to:

- define the experimental procedures for testing biomass fuels in the IPFR;
- provide significant results of the recent experimental campaigns on biomass fuels;
- extrapolate the prerequisites and principles that could be in common with other test facilities (in the frame of the BRISK project) for an advanced characterization.

Particular attention is devoted to the qualification of the system and procedures used. Different sources of uncertainty (due to diagnostic limitations, segregation phenomena, fuel heterogeneity) affecting the operating parameters and test outputs (e.g., reaction conversion, obtained with the ash tracer method) are studied. The improvements in the experimental apparatus and procedures, as well as the support of CFD assisted diagnostics (e.g., to estimate the effective thermal history of the particles inside the reactor) have helped in quantifying and reducing the experimental uncertainties. The aim is to provide qualified data for the prediction of operational/design parameters for industrial-scale thermochemical systems. Uniform and reliable data will be finally inserted into the IFRF online Solid Fuel DataBase (SFDB).

## 1. Introduction

Detailed information on the fuel is an essential requirement for the prediction of pulverized combustion (but also co-combustion, gasification, oxyfiring) related issues by mathematical modeling. Due to the variety of biofuels, wide range of combustion properties and reactor configurations, many problems arise when changing the fuel, even in blends, or operating conditions. The increase in inefficiency, carbon in ash, tar and ash deposition, corrosion, pollutant emissions, can go out of control (with dramatic repercussions on plant efficiency and operation, costs, environmental impact) if not predicted and opportunely limited.

Typically, fuels are characterized by the use of proximate, ultimate and few more 'traditional' analyses, that give a useful fingerprint to estimate the behavior of a 'new' fuel by comparing the results with those of 'known' (or rather, already used in the same apparatus) fuels. Standard and laboratory analyses are performed under well controlled and generally mild conditions: relatively low temperature (<1000°C) and heating rate (<1°C/s). There is a general lack of quantitative information collected from reactors operating in conditions close to the actual environments encountered in pulverized fuel combustion. This is true especially for biomass and alternative fuels, for which a fundamental characterization is not sufficient to make good predictions. A fuel specific comprehensive characterization is required for designing and modeling combustion, oxyfiring and gasification on large scale applications. It is necessary to face the difficult reproducibility of severe conditions on laboratory scale equipment and the complex interpretation of raw data, that can be the sum of not-decoupled mechanisms.

Advanced solutions are developed and proposed to satisfy the need of fuel parameters in conditions similar to those encountered in full size plants. Drop tubes, entrained flow, moving and fluidized bed reactors on a laboratory or pilot scale are used to study the biofuels. However, standard solutions and uniform methodologies of investigation for the use of such apparatuses are not shared. It seems that due to the variety of the technical systems and configurations (concerning also the diagnostics), a standard solution (in terms of equipment) is not realistically achievable. It would be necessary, and this is indeed realizable, to share common prerequisites and investigation principles of apparatus and test qualification, even for different techniques. This aim falls within the WP6 (Development of new methodologies for the characterisation of 2<sup>nd</sup> generation biomass) of the 7<sup>th</sup> FP project BRISK (The European Research Infrastructure for Thermochemical Biomass Conversion), in which IFRF is involved ([www.briskeu.com](http://www.briskeu.com)). The objective of this work is to define the experimental procedures for testing solid fuels in the Isothermal Plug Flow Reactor of IFRF (that is an advanced tool for combustion related studies) and extrapolate the prerequisites and principles that could be common with other advanced equipment. The aim of the experimental campaigns (in the frame of the Joint Research and Transnational Access Activities programmed in BRISK) is also to provide qualified data for quantitative prediction of operational/design parameters of industrial-scale combustion systems through Computational Fluid Dynamics (CFD) simulations. Uniform and reliable data will be finally inserted into the Solid Fuel DataBase (SFDB) of IFRF.

## 2. Experimental section

IFRF avails itself of the collaboration of external labs (e.g., DICI-UNIFI, CRIBE Centro Ricerca Interuniversitario Biomasse da Energia, ENEL Engineering and Research labs) to get a complete characterization of the fuels, evaluate the characteristics of products, elaborate data and derive kinetic parameters. When a new material has to be characterized, a preliminary fundamental analysis (proximate and ultimate) is performed on the 'as received' sample or its sieved fractions. This is useful for the fingerprinting of the fuel and programming the experimental tests in the IPFR.

### 2.1 Traditional characterization

The characterization of solid fuels in the 'as received' form may be difficult for handling issues, because laboratory analyses and IPFR tests can be performed only on pulverized samples. Thus, some fuel pretreatments are necessary, such as drying, size reduction and sieving, to get a convenient particle size range. Fundamental and additional analyses (see Table 1) are performed on the as received samples, or its sieved fractions. The same analyses are carried out on the solid residues of IPFR tests (devolatilization, char oxidation, gasification). The standard procedures are applied according to the normative. In particular, the procedure for the determination of ash in the biofuels and its solid residues is reminded here because the conversion in the IPFR is calculated according to the ash tracer method. Shortly, it recommends the combustion in air of samples of around 1 g and maximum temperature of 550 °C.

### 2.2 Description of the IPFR

A detailed description of the geometrical, operating and diagnostic parameters of the new asset of the IPFR in the site of Livorno-IT can be found in Biagini et al. (2010). It is a drop tube (4.5 m total length x 0.15 m inner diameter, see Figure 1) in which solid fuel particles are pneumatically injected with a primary gas through a feeding probe inserted at different heights through one of the 19 ports available along the tube. A secondary gas flow (with the options of forming mixtures of N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O) is supplied from the top center of the reactor. The heating system is formed of the electrical resistances (globally 54 kW) located along the tube, and the hot gases coming from the 60 kW burner located at the top section of the reactor. The solid residues and gases are quenched at the bottom of the reactor and sampled in the collection probe for online and offline analyses. The residence time, temperature and combustion atmosphere can be varied to study the solid fuel under specified operating conditions. The fuel particles (in size fractions between 40 and 200 micron) are injected into the programmed combustion environment and collected after a residence time between 15 and 1500 ms. The maximum temperature achieved is 1400 °C, the heating rate of the particles (estimated on the basis of CFD analysis) is on the order of 10<sup>4</sup> K/s.

Table 1: List of traditional analyses

		Fundamental analyses	Additional analyses
IFRF DICI-UNIFI CRIBE ENEL Eng. Res. Lab.	SF-Lab  Solid Fuel characterization Laboratory	Determination of ash	Determination of moisture
		Proximate analysis	Density
		Ultimate analysis	Ash fusion analysis
		Ash analysis	Size and shape analysis
		Heating value	Chemical analysis

### 3. Description of the advanced characterization

The scheme of the advanced characterization method is shown in Figure 2. During the IPFR test, the nominal operating conditions are recorded and the solid residues collected and sent to the laboratories for the offline analyses. The operating conditions and lab results are elaborated to get the raw data (conversion vs thermal history) and more complex parameters (indexes and kinetics). All these data are then uniformed and inserted in the Solid Fuel Database.

#### 3.1 Experimental procedures in the IPFR tests

The nominal conditions of each IPFR test are defined by the reactor temperature, oxygen level (or gas concentration), residence time (calculated by the actual gas flow rate, the injection port and the position of the sampling probe). All the monitored test parameters are registered in a record system. The test archive file collects the average values of these variables (temperature, oxygen and CO<sub>2</sub> concentration), as well as the nominal conditions and all the information on the fuel. The solid fuel is fed dry and opportunely sieved to give a continuous and stable flow rate of 100 g/h. Indeed the behavior of the smallest fractions can be hardly standardized due to segregation phenomena in the IPFR (see below), whilst the largest particles show relevant internal gradients, complicating the interpretation of the raw data. Thus, a narrow range of particle size should be selected for the IPFR tests. The target for each test is to collect a sufficient amount of solid residue to be analyzed (few grams for determining at least the ash content). Ash is routinely determined on the fuel and IPFR residues to elaborate the conversion according to the ash tracer method. It is important to have a good reproducibility of this value.

The experimental campaign in the IPFR starts with explorative tests, consisting in studying the devolatilization of the fuel at different residence times and fixed temperature (900°C for biofuels). The results of the explorative tests (along with fundamental analyses) are important to define the entire campaign by comparing the reactivity to previous cases. Consequently, temperature and residence time for the following devolatilization and char oxidation tests are programmed. At least 5/6 points obtained by varying the particles' path inside the reactor at fixed temperature are recommended to reduce the effect of the (unavoidable) experimental errors, thus giving a clearer interpretation of the raw data.

The devolatilization has to be studied at least at two different temperatures. The residence time should be chosen to have a clear (increasing with time) trend in the conversion. Qualified data (verified by reproducible tests) and operating conditions with the specification of the experimental uncertainty should be considered for elaborating reliable parameters. The results at the highest residence times can be used to evaluate the High Temperature and heating rate Volatile Matter HTVM. The two sets of data should be considered to elaborate the kinetic parameters.

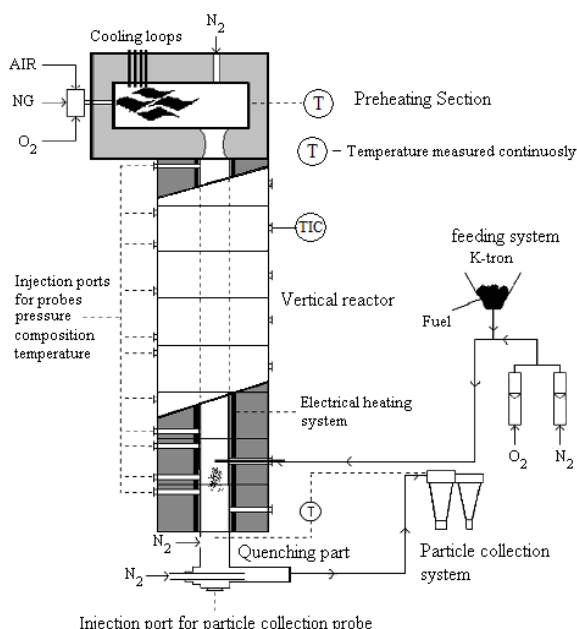


Figure 1: Scheme of the IPFR.

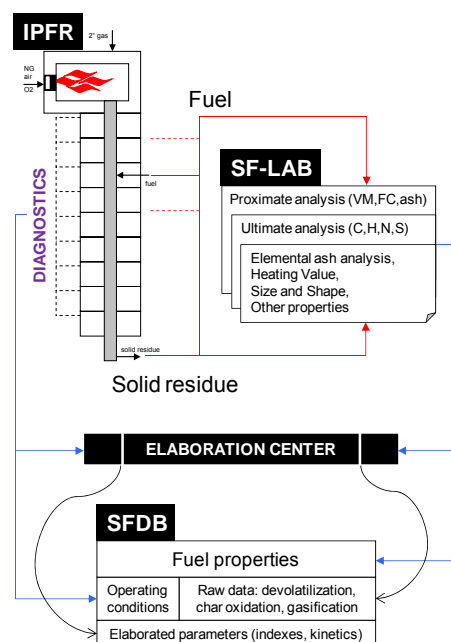


Figure 2: Advanced characterization method.

The char oxidation and gasification tests are carried out by varying the temperature (at least two values) and the oxygen (or gasifying agent) concentration (two or three values, like 3, 6 and 9% of oxygen). The results of the elaboration procedures give the char reactivity and kinetics of reactions.

### 3.2 Qualification of the IPFR

The high temperature and heating rate of IPFR (similar to those of large size plants) and the qualification activities make it a superior facility for providing fuel specific data and parameters for advanced models of pulverized fuel combustors as well as innovative plants (e.g., oxy-fuel combustion and gasification). The qualification of the IPFR consisted in improving the reactor characteristics, verifying the performance and validating the reliability of the results obtained. Some improvements were achieved, such as the optimization of the control system, introduction of advanced diagnostics, activities to eliminate or mitigate possible non-homogeneous sources in the temperature field inside the reactor. For instance, micro-suction pyrometers were used to measure the axial and radial temperature profiles inside the reactor and quantify the deviation from the nominal conditions. The IPFR-CFD model 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. Some general points are crucial for the qualification of tests under high temperature and heating rate:

1. In drop tube tests the sample is dynamic, so that the collection of solid products is problematic, since not all the particles can be collected. The conversion is generally estimated by analyzing samples of the collected solid. This procedure is inevitably a source of error, due to the fact that the collector probe acts as a selective sampler: a size fraction of the fuel is fed at the top of the drop tube, so that the smallest particles have an actual residence time and thermal history different from those of the largest ones. Some of them can go through unpredicted trajectories (the turbulence and radial gradients influence strongly the smallest particles, the particle shape is a further crucial aspect) and be selectively separated from the main particle stream. This is even more relevant when the particle mass decreases (in terms of density and/or size) because of the progress of the reactions or fragmentation phenomena. This segregation issue can be limited, by sieving particles into a narrow range of size, but cannot be completely solved.
2. A second source of error is given by the method used to elaborate the conversion. The most common way is to assume that a tracer, uniformly distributed within the sample, remained constant during the test, so that the determination of it in the fuel and solid residues is needed. If ash can be assumed thermally stable the ash tracer method can be applied. Otherwise, some elements can be used as tracers, like titanium, which is a thermally stable element, but the low amount found in biofuels limits its applicability. Different methods for determining the ash were compared at IFRF to optimize the sampling and analytical procedures, quantify and reduce the error deriving from the application of the ash tracer method.

Further sources of errors may derive from:

- the fuel, because of its origin and nature (it can be heterogeneous, ash can be thermally unstable or their distribution within the fuel particles can be non-uniform), or the preparation (e.g., grinding and sieving, which may concentrate the ash in the finest fractions);
- the test, because of the instrument uncertainties (the operating conditions, like temperature and oxygen concentration, may be not constant during the test or not uniform in the reactor), the intrinsic difference between nominal and effective thermal history, particle-to-particle differences;
- the off-line analysis, performed on the samples before and after the test, because of instrumental uncertainties or sampling operations.

## 4. Results and discussion

The research needs for solid fuel devolatilization include data and parameters on volatile products, time of reaction (kinetics) and char properties. The operating conditions strongly influence the devolatilization of biofuels and also the properties of the char for the subsequent steps. The parameters derived under mild conditions runs in lab-scale equipments can be unsuitable to predict the behavior of a fuel in full-scale practical applications. The volatile matter released at high HR and T results significantly higher than the one estimated from the standard proximate analysis (HTVM > STVM). The example given in Figure 3 (where the volatile matter released in the proximate analysis is compared with the one obtained in the IPFR devolatilization tests at the same final temperature of 900°C, for a biomass fuel and its torrefied samples) confirmed the observations made in literature works with different lab and pilot scale facilities (see for instance Biagini et al. 2004). It is important to have this information when a high volatile fuel is studied. Moreover, the time of devolatilization is a fundamental parameter for every comprehensive model,



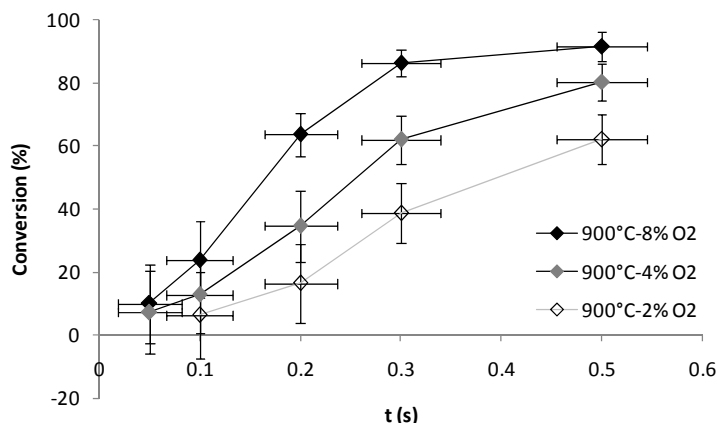


Figure 4: Oxidation of lignin char in the IPFR with the quantification of the experimental errors.

analyses. The first step in this process was the qualification of the experimental apparatus, diagnostic system (also aided by CFD model), test program and data elaboration. Some general prerequisites and principles in common with other test facilities (in the frame of the BRISK project) for an advanced characterization are summarized here:

- provided parameters (for modeling and practical applications) should derive from tests performed under conditions similar to those of use;
- samples in a narrow dimensional range should be tested, to limit the internal thermal gradients, segregation phenomena and errors due particle-to-particle differences;
- the effective thermal history of the samples during the experimental tests should be estimated with direct measurements (if possible) or interpretative models;
- raw data (test results and parameters) should be provided with the quantified uncertainty;
- uniform and reliable data organized in databases can be compared to engender practical indexes, validate empirical correlations and predictive models.

Some examples are provided in this paper and in recent IFRF reports ([www.ifrf.net](http://www.ifrf.net)). An exhaustive container of all IPFR results is the Solid Fuel DataBase of IFRF ([sfdb.ifrf.net](http://sfdb.ifrf.net)). It couples the fuel properties with the test parameters (devolatilization, char oxidation, gasification) from the high temperature and heating rate runs. In progress activities aims at equipping it with advanced tools for predicting qualified operational/design parameters for industrial-scale thermochemical systems (Biagini and Tognotti 2012).

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