



Major challenges and recent advances in characterizing biomass thermochemical reactions

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ABSTRACT

Thermochemical conversions are pathways for biomass utilization to produce various value-added energy and chemical products. For the development of novel thermochemical conversion technologies, an accurate understanding of the reaction performance and kinetics is essential. Given the diversity of the thermal analysis techniques, it is necessary to understand the features and limitations of the reactors, ensuring that the selected thermal analysis reactor meets the specific need for reaction characterization. This paper provides a critical overview of the thermal analysis reactors based on the following perspectives: 1) gas flow conditions in the reactor, 2) particle's external and internal heat and mass transfer limitations, 3) heating rate, 4) temperature distribution, 5) nascent char production and reaction, 6) liquid feeding and atomization, 7) simultaneous sampling and analyzing of bed materials, and 8) reacting atmosphere change. Finally, prospects and future research directions in the development of analysis techniques are proposed.

Abbreviations

DSC	differential scanning calorimetry
DTA	differential thermal analysis
EGA	evolved gas analysis
FTIR	Fourier transform infrared spectrometer
GC	gas chromatograph
IHMFB	induction heating micro fluidized bed
MFB	micro fluidized bed
MFBR	micro fluidized bed reaction analyzer
MW-TGA	microwave-powered thermal gravimetric analyzer
HP-TGA	high-pressure thermogravimetric analyzer
MS	mass spectrometer
Py	pyrolysis
RKA	reaction kinetic analysis
SPI	single photoionization
TGA	thermal gravimetric analyzer

1. Introduction

Biomass is an abundant, renewable, and natural resources with a multitude of applications. Bio-based fuels, chemicals, and energy can be produced, directly or indirectly, from biomass materials via various thermochemical routes [1–3], including mainly pyrolysis or carbonization, gasification, and combustion. Biomass pyrolysis involves a series of physical changes and chemical reactions activated by heating the fuel in the absence of oxygen or the presence of sub-stoichiometric amounts of oxygen to a preferential temperature. The pyrolysis reactor can be heated to a preset temperature at various heating rates from 0.01 to 10⁵ °C/s. The selection of the heating rate, the peak reaction temperature, and the residence time is determined based on the preference for the yield of gas, liquid (i.e., tar), or solid (i.e., char, semi-coke, or coke). In practice, the pyrolysis products are often further processed or refined by various catalytic or non-catalytic processes.

Pyrolysis is also an intermediary reaction step through which gasification and combustion must go [4,5]. As pyrolysis simultaneously

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produces gas, liquid, and solid products, the reaction performance of gasification or combustion is greatly dependent on the characteristics of these intermediates [6–8]. For example, the process of char gasification or combustion has been recognized as the rate-limiting step, which is significantly affected by char characteristics such as specific surface area and pore structure [9,10]. Therefore, understanding the characteristics of these intermediary products and accompanying reactions is vital for the comprehension of global gasification or combustion reactions.

Although biomass thermal conversion reactions are highly complex and diverse, they can be decoupled to a series of reaction pathways, as schematically shown in Fig. 1 [4,11]. It is worth noting that these thermochemical conversion pathways and many of the technical issues or challenges encountered in analyzing or characterizing them are also applicable to other carbonaceous materials, such as coal, oil shale, and organic waste.

Additional challenges for characterizing biomass thermochemical reactions also come from the fact that biomass materials are of great complexity and variability in chemical structures (e.g., contents and compositions of cellulose, lignin, and ash) and physical properties (e.g., moisture, particle size, density, and shape). Furthermore, biomass materials sometimes are co-processed (e.g., co-pyrolysis, co-gasification, co-combustion) with other feedstocks to increase product yields or to achieve some preferred synergetic effects [12–17]. This makes the reaction characterization even more complex and challenging. Moreover, some reactions require changes in reactants or reacting atmosphere (e.g., oxidation, reduction, reforming, with oxygen and steam as reactants). However, it has been difficult for thermal analytic reactors to change the reacting environment flexibly and smoothly. Therefore, analyzing biomass thermochemical reactions requires special knowledge of reaction characteristics and analytical instruments, as well as the properties of feedstock materials and conditional parameters. Past experiences have shown that gathering reaction performance accurately and effectively has never been an easy task.

Over the years, various thermochemical conversion technologies have been developed to convert a variety of biomass feedstocks into a wide range of products [2,18,19]. The pioneering experiments used a diversity of thermal analysis instruments, which are commercially available or self-made in individual laboratories, to develop a better understanding of reaction mechanisms and kinetics. The results from such research have been useful for creating valuable knowledge about complicated thermochemical conversion technologies. However, the research outcomes often provide inconsistent conclusions or views owing to not only the complexities in biomass feedstocks and diversity in conversion technologies but also the differences in thermal analytic instruments.

So far, a limited number of studies have looked at the issues concerning various thermal analytic techniques for accurately measuring the intrinsic kinetics of different thermochemical reactions. Most recently, Saadatkhah et al. [20] have conducted a comprehensive

overview of the basic principles, advantages, and limitations of the thermogravimetric analyzers (TGAs), and SriBala et al. [21] have presented a state-of-the-art review of the experimental techniques used to develop biomass fast pyrolysis kinetics. It is important to note that for accurately measuring reaction kinetics, the reactor configurations, analytical techniques, and reaction conditions need to be carefully considered. However, for other biomass thermochemical conversion reactions shown in Fig. 1, such as nascent char gasification, tar conversion, and real-time catalytic performance in gas-phase catalytic reactions, a comprehensive overview of the issues and challenges of the available analytical techniques is lacking.

This paper critically reviews the major thermal analytical techniques used for biomass thermochemical conversions. The technical challenges, issues, and recent advances in characterizing the major thermochemical reactions are identified and further discussed. In addition, future research and development prospects for the continuous innovation of thermal analysis sciences and technologies are proposed.

2. Challenges for thermal analysis

The ultimate goals of thermal analysis of a sample undergoing thermochemical conversion include 1) determination of the profiles and yields of the products or the sample variation and 2) understanding the reaction mechanism and kinetics. The former is usually referred to as the evolved gas analysis (EGA) and the thermogravimetric analysis (TGA), which can be achieved by the incorporation of a gas chromatograph (GC) together with other appropriate analytic instruments (e.g., IR, FTIR, MS) and by the thermogravimetric analysis instruments (i.e., the TGA instruments), respectively. On the other hand, the latter can be accomplished only with an appropriate analytic instrument, such as a mass spectrometer (MS) rather than a GC. Of all thermal analysis instruments, their reactors initiating the thermal reactions of a sample are various and critical to the results of analysis. Depending on how a sample (usually particles) is loaded and heated, the typical experimental reactors by far used for thermal analysis, both commercially available and self-made, can be classified and listed as shown in Table 1.

Detailed descriptions and some of their applications of the reactors listed in Table 1 have been provided in the literatures cited. Although so many thermal analysis reactors are available (Table 1), one must understand the characteristics of these analytical instruments based on these micro reactors, especially their technical limitations and challenges. First, regardless of what thermal analysis method is used and what reactions are involved, the product gas from its production to detection must be or close to a plug flow in order to accurately capture the production dynamics (i.e., time-dependent sequence and intensity). Another ideal gas flow condition is the requirement of minimizing or eliminating the possible secondary reactions among primary products. Secondly, the effects of heat and mass transfer on reaction kinetics must be reduced to ensure the measurements of the approximate intrinsic

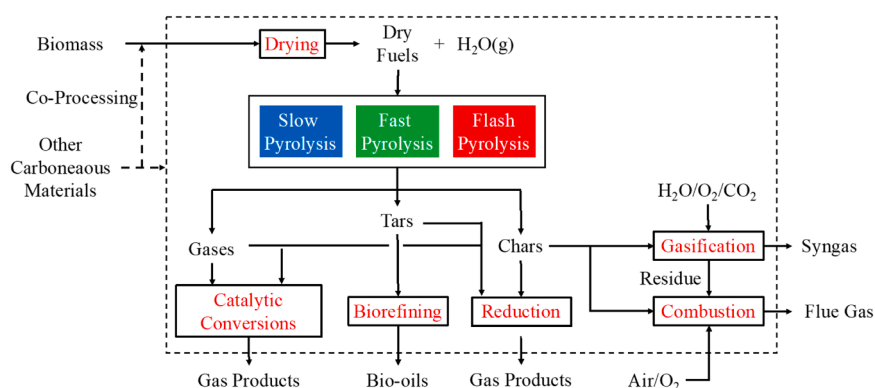


Fig. 1. The representative pathways of biomass thermochemical conversions.

Table 1
Typical experimental reactors for thermal analysis.

Heating method	The sample loaded before the reactor is heated	The sample loaded when the reactor is heated
I: Sample particles stacked		
Furnace heating	<ul style="list-style-type: none"> Thermogravimetric analyzer [20,22] Micro fixed bed reactor [23–25] Gas-pulsed microreactor [26] 	<ul style="list-style-type: none"> Microtubular reactor (μ-reactor) [27] Py-GC/MS [27–30] Tandem microreactor [27,31,32]
Resistively / Inductively heating	<ul style="list-style-type: none"> Wire mesh reactor [33] Heat grid reactor [34] Screen heater reactor [35] Curie point reactor [36,37] Pulse-heated analysis of solid reactions reactor [38] 	<ul style="list-style-type: none"> Pyroprobe reactor [39, 40]
Nonconventional heating	<ul style="list-style-type: none"> Microwave reactor [41,42] Laser ablation reactor [43] 	
II: Sample particles fluidized		
Furnace heating	<ul style="list-style-type: none"> Micro fluidized bed reaction analyzer [44] Micro spouted bed reactor [45] Modified Linkam CCR1000 microreactor [46,47] Micro fluidized bed thermogravimetric analyzer [48–50] 	<ul style="list-style-type: none"> Drop-tube reactor [51, 52] Micro fluidized bed reaction analyzer [53–55]
Resistively / Inductively heating		<ul style="list-style-type: none"> Induction-heating micro fluidized bed reactor [41,56]
Nonconventional heating	<ul style="list-style-type: none"> Jet-stirred reactor [57] 	

kinetic parameters. Third, depending on whether the reaction is slow, moderate, or fast in the reaction rate, appropriate sample heating rates that best meet the reaction's characteristic needs should be selected. Besides, because the reaction kinetics, specifically the activation energy, is a function of temperature, the presentation of temperature must be sole and accurate. This presents another challenge for any thermal analytic reactor since achieving and maintaining a uniform temperature distribution (or zero-dimension) is not straightforward for many actual reactors. In case there is a spatial temperature distribution, the experimental data has to be analyzed using non-isothermal and non-differential approaches, which complicates the thermal analysis and may also reduce the reliability of the results.

In addition to the above four general challenges, there are additional challenges faced by characterizing specific reactions shown in Fig. 1. The first is related to char reactions. Producing a nascent char by pyrolysis and continuing its reaction (such as gasification or combustion) under the same temperature and atmosphere in one reactor, which approximates what is occurring in actual reactors, is a difficult task that has been rarely successfully achieved [58]. Secondly, acquiring the kinetics of tar conversion in a fashion that mimics the real reactor environment, i.e., instantaneously feeding and atomizing the liquid samples, requires special considerations and designs. The third challenge arises from gas-phase reactions when rapid and precise catalyst screening is concerned. It would be more direct, accurate, and efficient if the catalyst samples could be taken and characterized in-situ during the actual reaction. Once the time-dependent variations in both the catalyst characteristics and gas productions are directly linked and compared, it offers a powerful diagnostic tool for in-depth investigation of both catalytic and non-catalytic reactions. Lastly, for both gas-phase reactions and char conversions, changes in the reacting atmospheres are often desired during the reaction processes. For example, varying the atmosphere from a reducing one to an oxidation condition, from CO₂ to steam, and from an inert to a reactive gas stream. This would facilitate investigations of reactions under different conditions without the necessity to interrupt the operations. All these technical challenges have

remained for a long time and motivated the community to a number of technological advances, as is detailed below in this article.

3. Advances in thermal analysis approaches

3.1. Gas flow condition

A near-plug flow of gas is an essential requirement for accurately detecting and measuring the sequence and dynamics of the product gas released from sample particles. Experimental research has confirmed that deviation from the plug flow increases the activation energy of a reaction [59]. Reviewing the configurations of all the reactors listed in Table 1, it is reasonable to assume that nearly plug flow conditions are to prevail at all times inside the reactors. In practice, it may be necessary to examine the effects of the gas flow rate to ensure that the near plug flow conditions are attained. According to Geng et al. [60,61], a near plug flow of gas can be assured if the standard deviation or the peak height of the measured gas residence time distribution functions is smaller than 0.25 or higher than 1.0, respectively.

It needs to be pointed out that a plug flow alone is not enough to ensure the accuracy of the obtained reaction kinetics and mechanism. An ideal plug gas flow condition shall also prevent secondary reactions from taking place either among the tar molecules or between the tar vapors and char particles. In this regard, the use of reactors with thick sample packing and high mass transfer inhibition should be avoided. Additionally, an ideal gas flow condition should be able to reduce the time delay for the product gas from the reactor to the gas detector. This objective can be readily achieved by careful design of gas transporting conduit and selection of gas flow rate.

3.2. Mass/heat transfer effect

Mass/heat transfer effects occur both outside and inside of sample particles. Internal mass/heat transfer effects can be significantly reduced by using smaller sample particles, such as <100 μm [21,62,63]. Reactor designs have no impact on the intragranular transport effects; therefore, this will not be discussed further. Actually, reactor designs can appreciably affect the external mass/heat transfer during thermal analysis [64]. External transport effects may be significant when sample particles are loaded in a reactor in stacked or packed form, especially in a cup (e.g., microtubular reactors), as conceptually illustrated in Fig. 2. For TGAs, the mass/heat transfer limitations have been well recognized and analyzed [49,64,65].

To reduce the transport effect for TGA, Zeng et al. [66] recommended keeping the sample amount not higher than 1 mg, the crucible height not over 2 mm, the carrier gas flow rate higher than 300 mL/min, and the sample particle size below 100 μm . For all other types of reactors with sample particles stacked, such as micro fixed bed reactors, wire mesh reactors, heat grid reactors, screen heater reactors, microprobe reactors, pulse-heated reactors, and laser ablation reactors, the operating conditions must be carefully selected to ensure minimized transport effects on the process and kinetics of measured reactions. Placing a small sample amount in a shallow layer can indeed minimize the transport effect, but it cannot be presumed that this can ensure the accuracy of the experimental results. As reported by Hoekstra et al. [67], the yield and composition of oil obtained from the fast pyrolysis of biomass in an advanced wire mesh reactor changed with the sample loading. However, the sample amounts were already very small. The possible reason includes the nonuniform sample placement and the temperature distribution. Additionally, the use of a too-small amount of sample may reduce the repeatability and reliability of the experimental results, especially for heterogeneous feedstock materials.

When transport effects become a concern, fluidized bed reactors are recommended. Recent advances made in the development of the so-called micro fluidized bed reaction analyzer (MFBRA) have confirmed that the effects of mass/heat transfer can become negligible when the

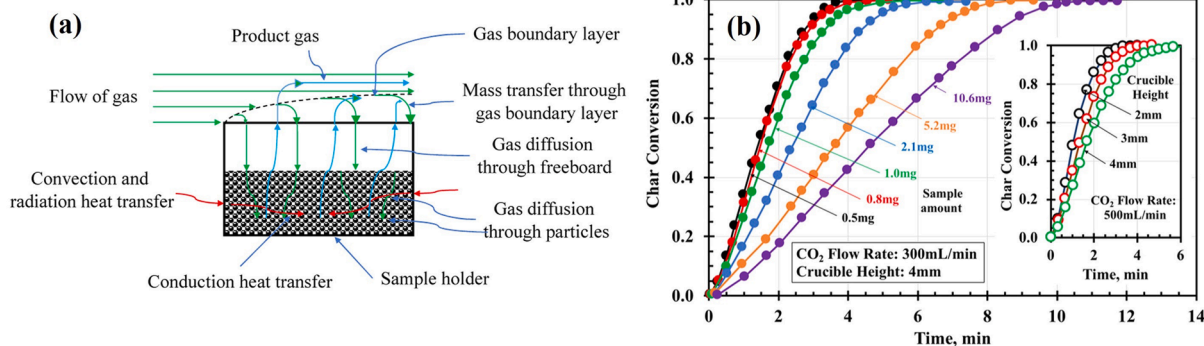


Fig. 2. Illustration of transport processes around and inside a sample holder and the experimental results showing the effect of mass transport on CO₂ gasification of char particles in a TGA. (a) illustration of transport processes; (b) effect of sample amount and crucible height on CO₂ gasification in a TGA [66].

reaction is operated under appropriate operating conditions [49,54,60, 68] (e.g., higher gas velocity and smaller particles). It is advisable that in experiments, one should carefully examine whether or not there exist external transport effects. This can be readily accomplished by some simple approaches, e.g., by observing the kinetic data corresponding to different sample loadings and varied gas velocities. Negligible external transport effects can be assumed if the kinetic data are not affected by these operating parameters.

3.3. Sample heating rate

Sample heating rate is a crucial operating parameter that affects the yields and compositions of products produced by biomass thermochemical reactions [33,43,69,70]. Fig. 3a shows that for biomass pyrolysis, increasing the heating rate increases both the yields of volatiles and tar but decreases the yield of chars [64]. As shown in Fig. 3b, when the heating rate is over 1000 °C/s, the char yield levels off [69]. Therefore, it is advised to carefully select reactor configuration and operating conditions by considering the characteristics of reaction kinetics and product preferences. For this purpose, we classified the reactors listed in Table 1 as follows in terms of the order of magnitude of the available heating rate.

- Heating rates of ~10 °C/s: This group of reactors includes TGAs and micro fixed bed reactors that are widely used in the study of

numerous reactions because of their vast availability and ease of operation. It is highly useful for investigations of slow reactions and the reactions that are controlled by mass transfer. Also, the advanced TGAs combining differential scanning calorimetry (DSC) or differential thermal analysis (DTA) can monitor changes in both mass and heat flow, thus greatly expanding the capability of TGAs in measuring the phase transitions like vaporization, melting, crystallization, glass transition, and solid-solid transition.

- Heating rate of 10²–10³ °C/s: The furnace-heating reactors (e.g., microtubular reactors, Py-GC/MS) can have the sample heating rate significantly increased by dropping sample particles loaded in a cup into the preheated reaction zone. In this way, the heating rate can be up to 10²–10³ °C/s, so the thermal exposure time before the sample reaches the reaction temperature can be reduced. This sample loading method has been used in microreactors and Py-GC/MS for measuring the evolution of volatiles from biomass pyrolysis [29,32, 33,36].
- Heating rate beyond 10³ °C/s: This category of reactors includes resistively heating reactors, unconventional heating reactors, and fluidized bed reactors. The heating rate at this order of magnitude is fast enough to characterize flash pyrolysis and combustion reactions. These reactions require sample particles to reach the preset temperature in a remarkably short time so that the sample exposure to the unwanted thermal conditions can be remarkably reduced. Fast heating can also minimize some side reactions during the

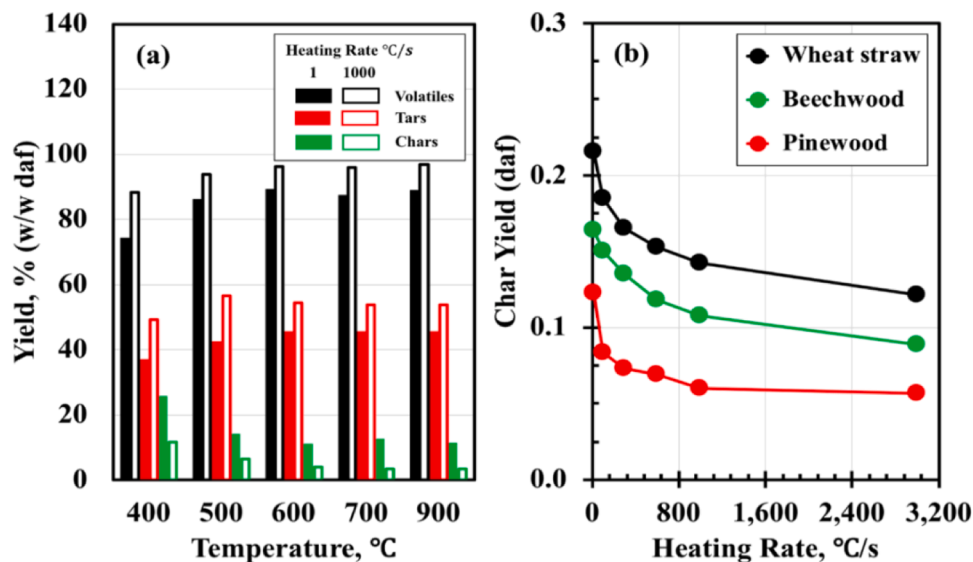


Fig. 3. Effect of heating rate on the yields of biomass materials pyrolyzed in wire mesh reactors. (a) holding time: 30 s [64]; (b) end temperature: 1000 °C & holding time: 1 s [69].

temperature elevation process. Since these fast reactions complete in seconds or even a fraction of a second [31], the heating rate needs to be thousands of degrees per second, and several reactor types can offer such high heating rates. The Curie point reactor offers very high heating rates, however, it lacks the flexibility of temperature control because of its limited choice of heating materials. For wire-heating reactors (i.e., wire mesh, heat grid, heat screen), the sample holding and placement variations would affect the temperature of the sample and thus the experimental results. The so-called induction-heating micro fluidized bed [41] requires a tube to lift the sample, which is held below the heating zone, to the reaction zone, thus increasing the complexity of operation. For MFBRA, the sample feeding to the bed is sufficiently fast (e.g., taking less than 0.1 s) as it is realized by the pulse injection method using compressed air [53]. When fine powders (e.g., $<100\ \mu\text{m}$ in size) are fed, the electrostatic interactions of particles, which may affect the sample loading and analysis results, should be considered.

In summary, the furnace heating reactors have low to moderate heating rates depending on how the sample particles are loaded, and the resistively heated reactors can provide significantly higher heating rates. However, when selecting thermal analytic reactors, another factor, i.e., the flexibility and controllability of the heating rate, may be worth taking into consideration. A reactor with a fast heating rate cannot adapt to reactions requiring slower heating. On the contrary, a reactor with a low heating rate is not suitable for reactions preferred for fast heating. In this regard, the advanced MFBRA offers a flexible choice allowing both fast heating or isothermal [6,71] and also lower heating or non-isothermal [44] operations. It depends on the heating of reaction sample by high-temperature bed-material particles in the state of fluidization. For isothermal operations, the bed material is kept at the desired operating temperature, then sample particles are quickly injected into the reactor by a compressed gas pulse. The injection and heating time of the sample particles can be less than 0.1 s. In non-isothermal operations, the sample particles are premixed with bed materials, loaded into the bed and then fluidized. Controlled by a heating program, the bed is heated at a specific heating rate. Despite the similarities in non-isothermal operations between MFBRA and TGA, MFBRA does differentiate itself from TGA in that it effectively eliminates the external mass transfer inhibition and therefore enables the approach of the intrinsic kinetics of reactions. This feature makes the micro fluidized bed reactor analysis adaptable for reaction analysis covering a wide range of

heating rates (e.g., slow / fast / flash pyrolysis).

3.4. Temperature and reactant distributions

Temperature and reactant distributions in the reaction zone also have great impacts on the accuracy of the reaction kinetic data. For fast reactions, a non-uniform temperature distribution may flaw the results even though the heating rate is high enough. Special attention should be paid to reactors with sample particles loaded in a cup or stacked between heating elements because potentially these reactors may suffer from such issues. Fig. 4 shows that for wire mesh reactors the temperature distributions across the region where sample particles are placed are not uniform [34,67]. The maximum temperature deviation can amount to several hundreds of degrees Celsius (Fig. 5). Noting that the average error caused by temperature measurement is only $1\text{--}5\ ^\circ\text{C}$ [34]. Therefore, both the heat transfer limitation between heat generation wires and particles and the non-even distribution of biomass particles on the heated grid cause the nonuniform temperature distribution. As a result of this nonuniform temperature distribution, the release of volatiles in biomass pyrolysis does not take place at the same rate in the area between the grids, and this greatly sacrifices the reliability of the test results.

Furthermore, for microtubular reactors [27] and drop-tube reactors [51,52], there are temperature transition sections before and after the stable temperature zone. This can become a concern for heat-sensitive

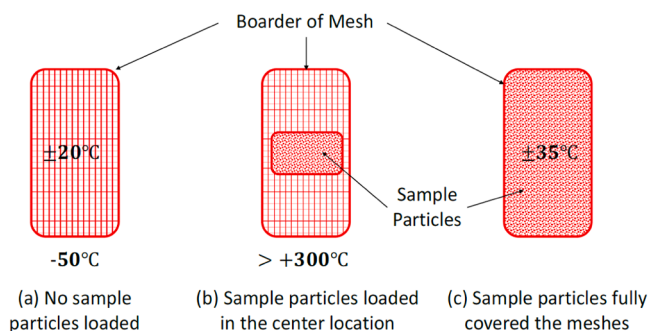


Fig. 5. Temperature distribution over mesh after a holding time of 1 s. The temperature at the center is $500\ ^\circ\text{C}$, and the numbers indicate the temperature differences from the center temperature [67].

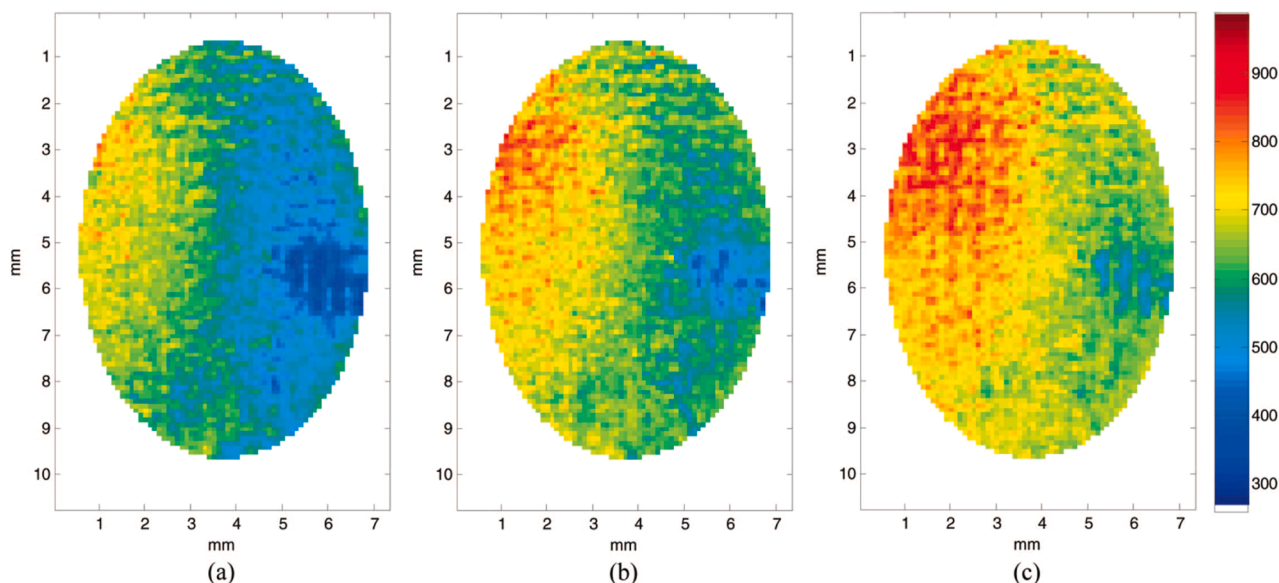


Fig. 4. Two-dimensional images of the measured temperature distributions of (a) $400\ ^\circ\text{C}$, (b) $500\ ^\circ\text{C}$, and (c) $600\ ^\circ\text{C}$ on the grid of a mesh reactor [34].

samples and fast reactions (e.g., fast and flash pyrolysis reactions). As shown in Fig. 6, despite a small variation in the temperature within a 40 mm length of the catalyst bed, the temperature in the entrance section varies in the range of a few hundreds of degrees Celsius. When sample particles fall through this entrance section before reaching the reaction zone of stable temperature, they are exposed to a varying thermal environment in which some physical and chemical changes may have occurred. Certainly, this will negatively impact the experimental results that are normally reported as the data for the specified stable temperatures.

For a micro fluidized bed, extensive mixing of bed materials creates a remarkably uniform temperature distribution within the bed. Therefore, when sample particles are injected quickly into the bed, they are not only heated promptly to the bed temperature but also distributed uniformly within the bed so that a differential isothermal operation can be realized [72].

3.5. Nascent char reactions

As stated previously, the gasification or combustion of char particles is the rate-controlling step of the global biomass gasification or combustion process. The experimental data has shown that char gasification or combustion takes approximately 70–90 % of the total fuel gasification or combustion time [6,73–75]. Therefore, investigating char gasification and combustion processes is of great significance for the design and operation of gasifiers and boilers. A brief review of the literature on char gasification and combustion has identified a few types of chars.

- **Slowly cooled char:** This is the most commonly used char by researchers, e.g. [6,76], which is prepared in a separate pyrolysis operation, slowly or naturally cooled, and stored before being used for the gasification tests. According to Wang et al. [6], the char prepared in this way has the smallest total surface area and the largest average pore diameter. Besides, during cooling and reheating secondary reactions may take place, leading to changes in the structural, microcrystalline, and physicochemical properties of char [6,7,73]. For both gasification [6] and combustion [7], the cold char showed the lowest reactivity and highest activation energy.
- **Rapidly cooled char:** This char is prepared by using a dual reactor system, in which the solid fuel is added and pyrolyzed in the first reactor under an inert gas atmosphere (e.g., Ar or N₂). When the pyrolysis is completed the produced hot char is quickly blown into the second reactor held at ambient temperature to be rapidly cooled [7]. Experiments have shown that the rapidly cooled char has an increased reactivity compared with the slowly cooled char, but still lower than that of the hot char particles depicted below [7].
- **Ex-situ hot char:** The char is prepared in the pyrolysis reactor, and then blown into the second reactor that is under preset gasification or combustion temperature. According to Fang et al. [7], the combustion rate of the ex-situ hot char is 1.1 to 1.2 times that of the quickly cooled char, and 1.5 to 1.6 times that of the slowly cooled char.

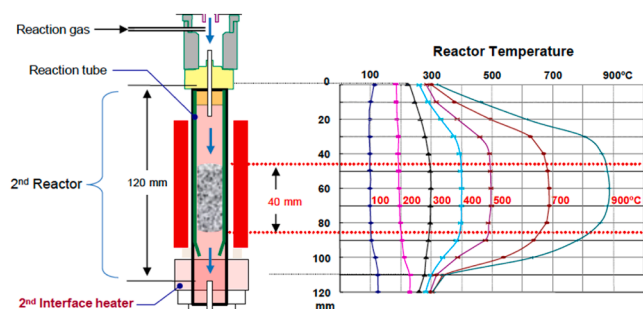


Fig. 6. Axial temperature profiles along the microreactor of drop tube [27].

- **In-situ hot char:** The so-called in-situ hot char is prepared and gasified or combusted at the same reactor temperature, but under a different atmosphere by switching gas from an inert gas (Ar) for pyrolysis to the oxidant CO₂ for gasification [77].
- **In-situ nascent char:** This char is produced by pyrolysis in situ at the same temperature and atmosphere as those of gasification or combustion [6]. This is what happens in actual gasifiers or combustors. The in-situ nascent char particles provide true reaction reactivity because they are not affected by any other artificial treatments.

As shown in Fig. 7, the reaction rates of gasification or combustion are highest for the in-situ nascent chars, followed by in-situ/ex-situ hot chars, rapidly cooled chars, and naturally cooled chars. The insert tables of Fig. 7 also show that the different char preparation environments have great impacts on the pore structural and chemical characteristics of char particles.

It is clear now that the correct char gasification performance can only be acquired by using in-situ nascent chars. This requires performing fuel pyrolysis and char gasification reactions at the same temperature and atmosphere in the same reactor without interruption. Additionally, the reactor system needs to have a precisely controlled reaction temperature with high uniformity, a near plug flow of gas with essentially eliminated gas backmixing, and a high-rate response of the gas analysis instrument. Among the reactors listed in Table 1, only MFBRA has been confirmed to meet these requirements, although the PHASR reactor has the potential but has not been practiced yet. Fig. 8b shows the production and gasification of the in-situ nascent char particles at the same temperature and atmosphere in the same micro fluidized bed reactor [6,66]. For comparison, the in-situ hot char production and gasification are shown in Fig. 8a. It is apparent that MFBRA equipped with pulse sample feeding and quick responding process MS is quite capable of distinguishing and determining the dynamics of sequentially occurring pyrolysis and gasification reactions.

3.6. Liquid feeding and atomization

To produce lighter hydrocarbon fuels, the tar produced by pyrolysis needs to be further refined through thermal cracking, reforming or other conversion routes [78–81]. In the case of gasification, the tar presence in the syngas is also required to be converted to hydrocarbon gasses because it causes operational issues, such as fouling the pipelines, filters, turbines, and engines. Early research works on tar conversions, such as steam reforming, dry reforming, thermal cracking, hydrocracking, or water-gas reactions were typically conducted by using either model compounds or condensates of tar collected from pyrolysis tests. In this way, the liquid sample would need to be reheated and vaporized during which some side reactions are likely to occur, such as cracking or polymerization.

Ideally, the characterization of tar conversion processes should be conducted in a reaction environment that closely mimics that of tar in real reactors, but this is a challenge for almost all of the common thermal analysis techniques. Loading a liquid sample before it is heated (e.g., TGA) or dropping it into a microreactor with a sample cup (e.g., μ -reactor or Py-GC/MS) does not guarantee the correct reaction kinetics to be developed. Use of a liquid injector or syringe pump, online feeding of liquid reactants is made possible for the Curie point reactors and MFBRA. Fig. 9 shows a schematic process diagram and photograph of the micro fluidized bed reactor system coupled with a syringe pump [82, 83]. Using this injector, several milliliters of liquid reactant samples can be sent to a micro fluidized bed reactor in less than 0.1 s, investigating the reactions including the thermal and/or catalytic cracking of realistic biomass tar and its model hydrocarbons [81,82,84,85].

3.7. Online sampling and characterization of solid particles

Pyrolysis gasses often need to be further transformed catalytically

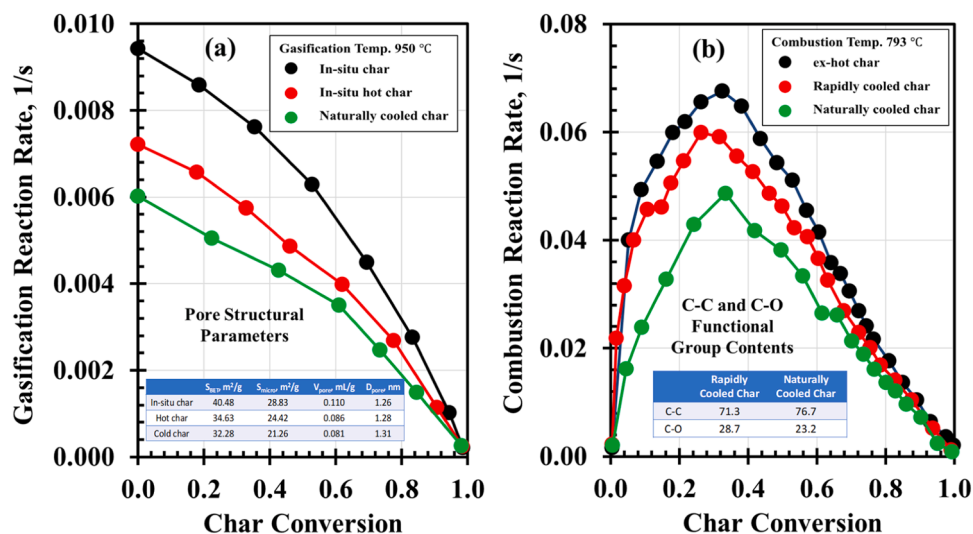


Fig. 7. Effects of char preparation methods on the char reaction rates. (a) char gasification by CO₂ [6]; (b) char combustion [7].

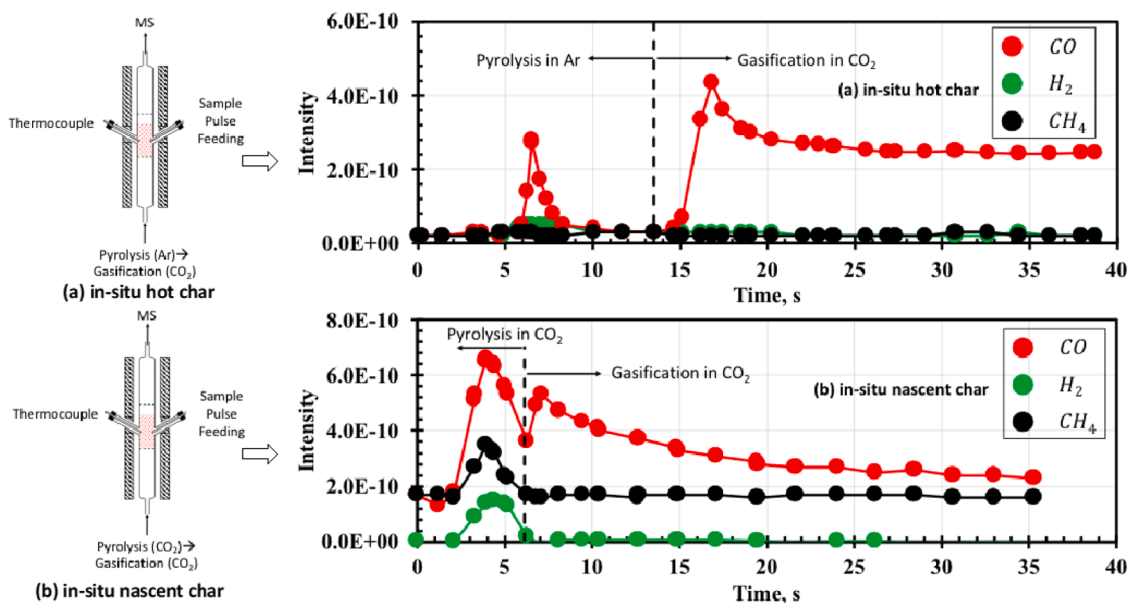


Fig. 8. Productions of (a) in-situ hot char and (b) in-situ nascent char and their gasification performances at 900 °C in a MFBR [6].

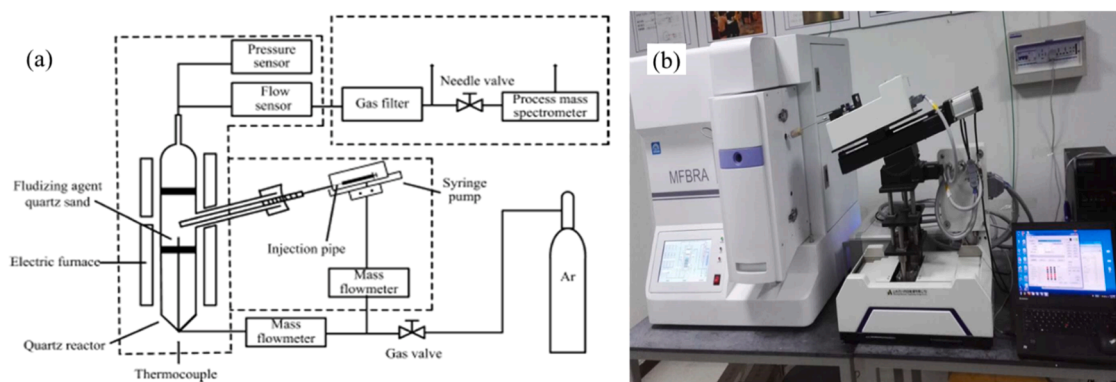


Fig. 9. A (a) schematic diagram and (b) a photograph of the micro fluidized bed reactor system with liquid sample injector [82].

into high-quality products. Depending on the target product, various catalyst formulations are usually tested with laboratory catalytic reactors to obtain the best catalyst formulations. In the search for the best catalyst formulation, the most challenging task is to determine the mechanism of the catalyst deactivation. To characterize catalysts, most of the research so far has relied on the method of post-experimental analysis. After each experiment is completed, the deactivated catalyst samples are analyzed, and the catalyst deactivation is explained by comparing with the characteristics of the fresh catalyst. By one test, it is impossible to get the dynamic process of catalyst deactivation in combination of the gas product variations. This post-experimental analysis method is not only time-consuming and costly but also likely to lead to uncertain or even misleading conclusions.

Therefore, it would be ideal if the characterization of the catalyst could be carried out in real-time during the reaction process. Fig. 10a shows a schematic diagram of the MFBRA equipped with the online sampling of particles in reaction. Based on this method, solid particles are sampled out of the bed during the reaction by a low-pressure suction inert gas stream into a sample collection bottle in a certain time interval. The particles sampled out are cooled down to room temperature rapidly and isolated from air by charging the sample bottle with an inert gas (e.g., N₂) at the end of sampling so that the particles can be kept at their original reaction state for subsequent characterizations. This provides a powerful diagnostic tool for characterization of reaction and thus process development and optimization, through directly correlating the gas product performance with changes in solid properties occurring in the reactor.

Fig. 10b shows the activity characterization results of online-sampled catalysts for the vapor-phase carbonylation of methanol by carbon monoxide over a kind of Ni/AC catalyst [86]. It shows that after 2 h on stream, the catalyst activity starts to decline, which corresponds to the increase in the oxygen content in the catalyst, while the contents of Ni and I approach stabilization. This indicates the catalytic performance is exclusively related to the quantity of oxygen-containing groups, a finding that would lead to a new development in this particular technology.

3.8. Change of reacting atmosphere during reactions

Being able to change or adjust reacting atmospheres smoothly and quickly during reactions is very useful for experimental investigations of many chemical reactions occurring in series, such as alternative oxidation and reduction of oxygen carriers (e.g., oxidation of metal and reduction of the metal oxides), and catalytic reaction (in which catalysts deactivate due to carbon deposition) and catalyst regeneration (e.g., coke oxidation or gasification). Having this capability would greatly improve the efficiency of reaction research. More importantly, it enables

the real behaviors of consecutive reactions occurring in different atmospheres to be acquired.

In principle, all the reactors listed in Table 1 can be operated in a gas switching manner to change the reacting atmosphere from one to another. However, to do it quickly and smoothly, several factors need to be met. First, near plug flow conditions need to prevail inside the reactor. It ensures that after gas switching, the gas back-mixing does not occur between the outgoing and incoming gas streams. Secondly, the total gas storage volume (including reactor and all pipelines from gas inlet to gas analyzer) needs to be small enough as compared to the gas volumetric flow rate. As a result, the average gas replacement time will be greatly shortened.

It is worth pointing out that the above-mentioned necessary conditions alone do not guarantee a fast switching of the reaction atmosphere. Because, for reactors where sample particles are packed or stacked tightly, the low rate of mass transfer may inhibit the switching rate of reaction atmosphere. For example, Fig. 11a shows an example of gas switching in a thermogravimetric analyzer [66]. It shows that completely replacing N₂ with CO₂ takes tens of minutes due to gas diffusion inhibitions in the TGA. In comparison, it takes only a few seconds for a complete gas replacement in a MFBRA, as shown in Fig. 11b [77]. Additionally, supplying reacting gas in pulses [27,39] has the potential to change reaction atmosphere, but this has not been practiced yet.

Partial or complete conversion of the reaction atmosphere to steam is a difficult task. However, it is often necessary and needed because many reactions use steam, such as steam gasification of carbonaceous materials, methane steam reforming, and water-gas shift reactions. Sometimes, these reactions also need to adjust the steam concentration or flow rate in the reaction processes to get better performance. Fig. 12a shows the most commonly used steam supply method [87–89]. This method uses a separate steam generator. The generated steam is premixed with the reaction gas before entering the reactor. This approach is suitable in principle for all the reactors listed in Table 1. However, this method has a potential issue when a quick change of the steam atmosphere is required. Normally, steam generators are not capable of following load changes quickly. Therefore, they may not respond to the demands for quick and large adjustments of steam supply. The method shown in Fig. 12b can effectively solve this problem [90, 91]. This advanced steam supply method applies to reactors (e.g., such as fixed-bed reactors and fluidized bed reactors) where a high-temperature zone with inert packing materials can be located at the bottom of the reactor for rapid evaporation of water to produce steam instantaneously. The liquid water is directed into the steam-generating part with a precise micro pump according to the amount of steam required. This water vapor supply method has the advantage of quick steam generation while maintaining a stable reactor operation, which

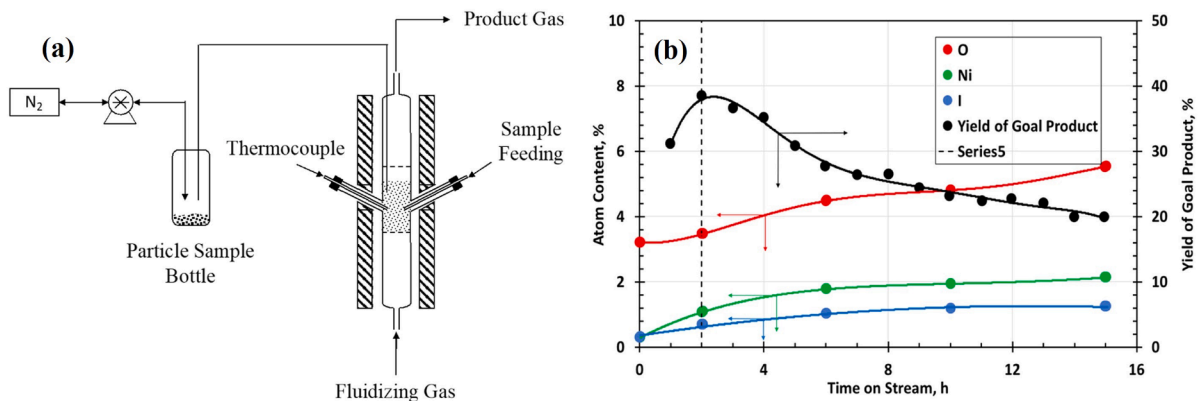


Fig. 10. Online catalyst sampling and activity characterization during the methanol vapor-phase carbonylation with carbon monoxide using Ni/AC catalyst [86]. (a) schematic of bed material sampling; (b) sampled catalyst characterization results.

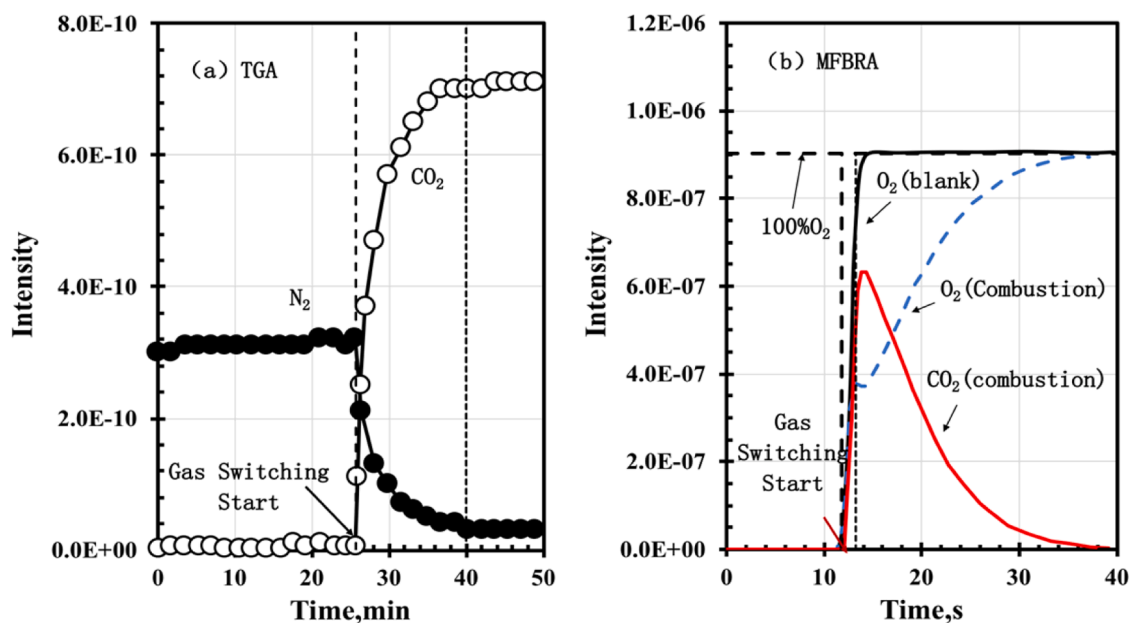


Fig. 11. Gas switching experiments conducted in (a) a TGA [66] and (b) a MFBRA [77].

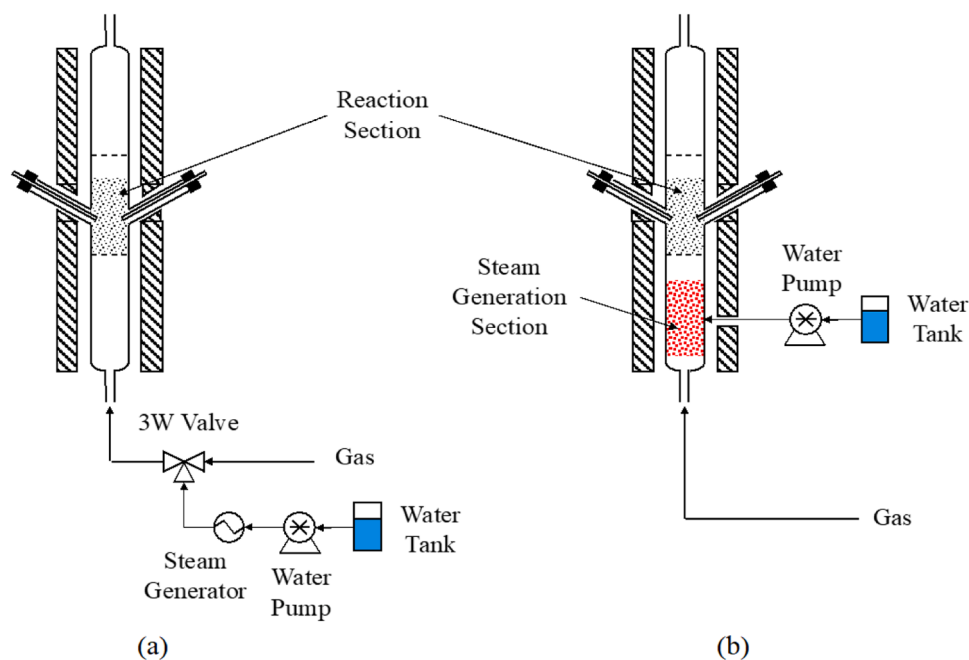


Fig. 12. Typical methods used to change the steam environment in reaction analysis [83].

has been successfully applied in several applications using the micro fluidized bed reaction analyzers [73,87,90,92-94].

4. Future research direction

As stated above, great progress has been made to advance the thermal analysis techniques to resolve the challenges existing for thermal conversion reactions of biomass fuels, but there are still some areas that deserve further attention and research in the future.

4.1. Detection and analysis of the full product spectra

Pyrolysis reactions are complex, and the products contain a wide array of gas and liquid products (i.e., tar). The tar consists of hundreds of

complex compounds, including aggregates of oxygenates, phenolic compounds and olefins, aromatic and polyaromatic hydrocarbons [95–98]. It is always desired, although very challenging, to be able to quantitatively determine all the chemical compounds, as well as their dynamical release behavior for gaining a better understanding of the pyrolysis process. In order to accomplish this goal, all the tar components have to be delivered to and quantified by analyzers. Various techniques including GC, MS, GC–MS, FTIR, nuclear magnetic resonance (NMR), molecular beam mass spectrometry (MBMS) and ultrahigh-resolution mass spectrometry have been used for the analysis of bio-oils [99]. However, most of them are still limited by the analyzable range of molecules. Recently, a time-of-flight mass spectrometer equipped with a soft photoionization source has been successfully applied to online analysis of primary tar produced from the fast pyrolysis

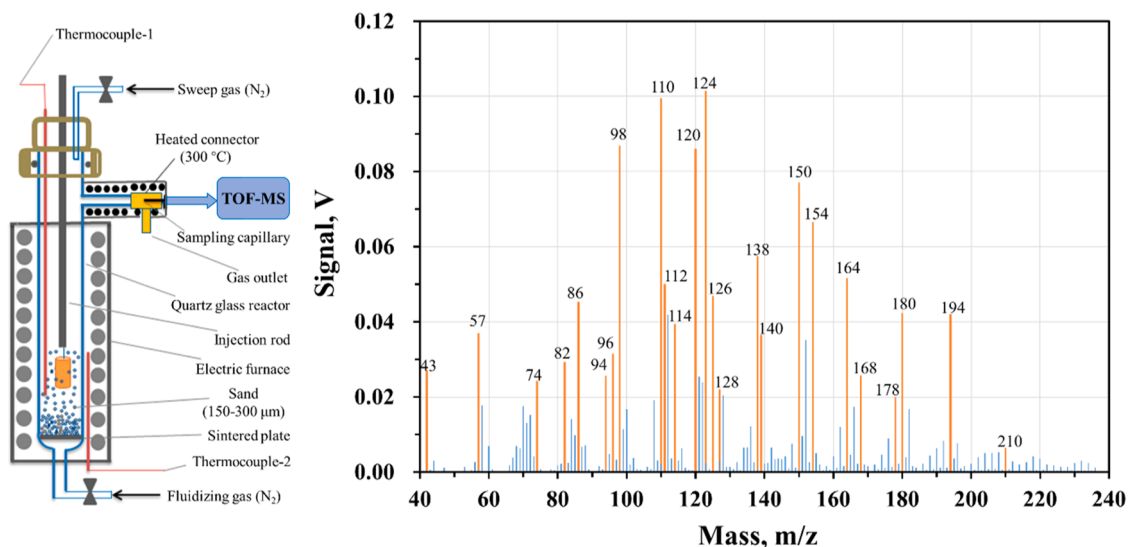


Fig. 13. A micro fluidized bed coupled with time-of-flight mass spectrometer and representative mass spectra from the fast pyrolysis of biomass [101].

of biomass in a micro fluidized bed reactor. However, not all of the detected mass spectra peaks (actually just 25 mass spectra peaks in Fig. 13) could be assigned to known molecular structures [100,101]. Therefore, the online detection and quantifying of the fuel product spectra for fast pyrolysis reactions and alike needs to be further developed. It is especially desirable to obtain the dynamic process of product formation through measuring the spectra of product at different reaction time.

4.2. Simultaneously monitoring changes in sample mass and gas products

For the techniques of reaction analysis based on measuring gas products, incorporating a gas analyzer such as an MS to a micro reactor can obtain the reaction kinetics of the product gases that are detectable by the analyzer. The derived kinetics is actually the “generation kinetics” of the detected gasses. As for MFBRA, the method is generally based on the concept of “relative conversion” [62]. For simple one-step and / or one-product reactions (such as combustion, and ore decomposition), this technique is well validated [54,101], but for complex reactions (e.g., biomass pyrolysis), it still needs to be improved to provide the global reaction kinetics.

Fluidized bed thermogravimetric analyzer (MFB-TGA) uses a precise balance to monitor the change in the bed mass and a fast-responding MS to measure the releases of gas products [48-50,102,103]. In our opinion, on the other hand, the MFB-TGA has several issues needed to be further addressed. First, it would be a tedious process to correct the effect of buoyancy force on the measured change in total bed mass, since the buoyancy force changes with bed temperature, fluidizing gas velocity and product gas composition. Secondly, it must use a high quantity of sample particles. Otherwise, the measured change in sample mass would be hardly distinguished from the signal noise of the system. Lastly, the use of a large quantity of sample particles also makes it impractical to adopt pulse injection, since it would have an unavoidable impact on the bed stability and homogeneity. Therefore, continuous research and development are highly anticipated in the future to resolve these issues for integrating thermogravimetric analysis to MFB.

4.3. Reactions under extreme conditions

It has been a challenge in the field of thermal analysis to quantitatively characterize reactions that take place under extreme conditions, such as high temperatures, high pressures, and reactions that are highly explosive, corrosive, strongly endothermic or exothermic and very fast (e.g.,

reaction completion time being in the order of milliseconds). In principle, the challenge comes from both reactor design and analytical instruments. So far, few thermal analytical instruments are available to meet these challenges. Table 2 lists two types of high-pressure analyzers, the HP-TGA and the CDS pyrolyzer, which have been applied to reaction analysis of gasification, pyrolysis, chemical looping combustion, etc. [104–110].

These analyzers are, however, still suffering from increased mass transfer inhibition problems due to their nature of design and sample placement method (based on stacked sample), because the gaseous-diffusion coefficient is inversely related to the pressure according to Fick’s law of diffusion. Consequently, the influence of mass transfer on the reaction kinetics becomes more pronounced at high pressures than at ambient pressure. It is thus reasonable to assume that the reaction kinetics would be underestimated in HP-TGA and CDS pyrolyzer. For this

Table 2

Typical thermal analytical instruments adapted to high-temperature and high-pressure conditions.

Instrument	Temperature range	Pressure range	Heating rate	Ref.
TherMax 500 (HP-TGA)	Up to 1000 °C	Up to 7.0 MPa (at 1000 °C)	0–25 °C/min	[111]
STA HP/1 (HP-TGA)	Up to 1000 °C	Up to 15.0 MPa (at 1000 °C)	Not specified	[112]
STA HP/2 (HP-TGA)	–170 °C up to 1800 °C	Up to 5.0 MPa (at 1800 °C)		
Discovery HP-TGA (HP-TGA)	Up to 1100 °C	Up to 8.0 MPa (at 1100 °C)	0–200 °C/min	[113]
Themys HP TGA (HP-TGA)	Up to 1200 °C	Up to 15.0 MPa	0–100 °C/min	[114]
HITECOM (HP-TGA)	Up to 1400 °C	Up to 4.0 MPa (at 1400 °C)	0–10 °C/min	[108, 115]
SPTGA (HP-TGA)	Up to 900 °C	Up to 3.0 MPa (at 900 °C)	0–20 °C/min	[116]
CDS 5200 HPR (CDS pyrolyzer)	Up to 1400 °C	Up to 3.4 MPa (at 900 °C)	0–20 °C/ms 0–999.9 °C/s 0–999.9 °C/min	[117]

reason, further research and development for an analysis technique with capabilities of intrinsic kinetics under extreme conditions are highly required, and some of the preliminary works are undergoing in the authors' group in this direction.

4.4. In situ monitoring and characterization of reaction processes

As stated previously, the thermal analysis technique applied to sampling of solid particles during the process of a reaction is now available [86]. However, the particle sampling is still intermittent, and the characterization of the gained particle sample is still offline. While this is very helpful, the opportunity exists for future developments of in-situ monitoring and characterization of the solid phase during reaction process. For instance, the integration of novel in-situ analytical means (e.g., in-situ XRD, in-situ XANES, etc.) with appropriate reactors presents an interesting research direction. In this way, the dynamic behaviors (e.g., surface and pore structure, chemical composition) of the reacting solids or catalysts can be monitored and characterized in real-time. Compared to the steady and offline characterizations, the new generation of dynamic in-situ characterization techniques will dramatically advance the thermal analysis techniques and contribute significantly to the related science and technology innovations.

5. Conclusion

Thermal analysis plays an important role in producing scientific knowledge and developing advanced thermochemical conversion technologies for better uses of carbonaceous materials including biomass. The article highlighted the challenges existing in thermal analysis for thermochemical conversion reactions of biomass including fuel pyrolysis and char reactions such as gasification and combustion. Heating, particularly quick heating of the sample is a critical demand for thermal analysis of biomass samples. Based on all particle methods heating samples, the typical thermal analytic reactors are classified into the types of furnace heating, resistively heating, and nonconventional inductive heating. Researchers are advised to be fully aware of the features and limitations of such heating techniques when selecting a thermal analytic reactor as well as an approach to meet their thermochemical reaction analysis needs.

In succession, the article critically reviewed the major advances so far achieved in resolving such challenges for thermal analysis of biomass conversion reactions. These include the new establishment of quick sample heating via hot particles and minimization of external diffusion inhibition in a micro fluidized bed reactor, formulation as well as delivery of time-dependent product formation dynamics via a near plug flow of gas throughout the reactor and system, production and further reaction of in-situ nascent hot char for the determination of realistic reaction performance and kinetics, online acquisition of particle samples during a gas-solid reaction for the simultaneous analysis of dynamic changes in both gas products and solid sample (or catalyst), and online instantaneous feed of liquid samples in micrograms into the micro reactor. All the advances have been well proved and practically applied. Lastly, several critical needs to further improve and expand the thermal analysis abilities are also presented.

Author declaration

We confirm that this manuscript has been read and approved by all authors named. We further confirm that the order of authors listed in the manuscript has been approved by all of us. We understand that the Corresponding Author is the sole contact for all the editorial process.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

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