



# A novel technique for measuring the kinetics of high-temperature gasification of biomass char with steam

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## HIGHLIGHTS

- ▶ A novel system for measuring high temperature steam-char kinetics was developed.
- ▶ The kinetic rate was measured at 1000–1150 °C with various gas compositions.
- ▶ The rate as a function of conversion could be described by the random pore model.
- ▶ The initial kinetic rate followed a Langmuir–Hinshelwood type relationship.

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## ABSTRACT

Solar thermal gasification of biomass is a promising technology that allows for operation at high temperature without burning a large portion of the biomass feedstock. Additionally, the process allows for solar energy to be stored and transported in chemical form. In order to design efficient solar reactors, a kinetic rate expression for high-temperature steam gasification is needed. Various methods have been used to measure the steam gasification rate of coal and biomass char at temperatures up to 1000 °C. These conventional techniques often fail to collect accurate kinetic data at temperatures above 1000 °C due to heat and mass transfer resistance, and the time constants associated with the analysis system. In this paper we discuss a novel kinetics measurement technique based on a modified fixed bed and data collected solely from a gas flow meter. The technique was used to collect kinetic rate data for switchgrass char over a range of reaction conditions between 1000 °C and 1150 °C. An empirical expression to predict the kinetic rate as a function of the degree of conversion, temperature, steam concentration, and hydrogen concentration was developed. The random pore model was used to predict the reaction rate as a function of conversion, and the initial kinetic rate was fit using a Langmuir–Hinshelwood type expression.

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## 1. Introduction

Concerns about energy security and greenhouse gas emissions have driven a renewed interest in alternative sources of fuel. Gasification of carbonaceous material has been used for more than a century to produce synthesis gas, a mixture of CO, CO<sub>2</sub>, and H<sub>2</sub>. Synthesis gas can be burned directly for heat and electricity production, or used as a feedstock for the production of liquid fuels and commodity chemicals. One method to achieve the high temperatures needed for gasification is through the use of concentrated solar thermal energy. Using solar energy to supply the heat of reaction eliminates the need to burn a portion of the biomass and produces a higher quality synthesis gas [1–3].

Proper design of a solar thermal gasification reactor requires detailed knowledge of the kinetic rate under the varying conditions in

the reactor. Unfortunately, the kinetic rate of biomass gasification can vary widely and is dependent on the type of biomass, the mineral content, and the method of preparation [4,5]. Predicting accurate kinetic rates for a specific biomass source based on the available literature is difficult. For these reasons it is important to measure the kinetic rate of the intended biomass under the conditions expected in the reactor.

The kinetic investigation in this paper will focus on the steam-char reaction. Upon heating, biomass undergoes pyrolysis to produce synthesis gas, tar, and char, a material composed mostly of carbon and ash. In the second stage, char undergoes gasification with an oxidant such as oxygen or steam to produce more syngas. This reaction can be exothermic or endothermic depending on the oxidant used. A multitude of other reactions such as tar breakdown take place simultaneously, but the char gasification step is widely accepted to be rate limiting. It should be noted that this is an idealization and various products of pyrolysis may have an effect on the gasification rate [6].

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The conventional methods for measuring gasification rates can be roughly divided into two categories; rapid single-point measurements, and slow real-time measurements. Rapid measurement techniques utilize reactors with high rates of heat and mass transfer to react the biomass for a specified amount of time, usually on the order of 1 s to several minutes. The sample is then removed and the degree of conversion is calculated. Examples of this type of reactor include drop tubes [7–9] and wire mesh reactors [10]. While this method is effective in measuring reactions that take place over a short period of time, extensive analysis over a range of temperatures, gas concentrations and degrees of conversion is difficult due to the limitations associated with measuring only one extent of conversion per experiment.

Real time measurement systems such as thermogravimetric analysis (TGA) [11–13] and fixed beds [14–18] have been widely applied to coal and biomass gasification. These methods are traditionally employed for reactions taking place over 5 min to an hour. For reaction times less than 5 min, heat and mass transfer limitations may begin to dominate. Using TGA, care must be taken to avoid diffusional effects within the bed due to the nature of flow around the sample crucible [19]. These diffusional issues can largely be mitigated by using a thin layer of sample. Another concern is price; for many research groups the price of a TGA that is capable of operation at high temperatures and with an environment of 100% steam may be prohibitively expensive. With fixed beds, heat and mass transfer resistances can quickly begin to dominate at high temperature, and determining the reaction rate with high temporal resolution is difficult due to the time constants associated with the gas cleanup system and the analysis loop.

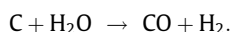
The authors have experimented with a fixed bed reactor utilizing non-dispersive infrared (NDIR) for real-time gas analysis. After much trial and error, the response time of the system was reduced to a point that allowed for the observation of reactions that complete in as little as 30 s. While this method provides a basis for approximating rapid reaction rates it is far from ideal. One modification includes increasing the gas flow through the analyzer to a level well above the manufacturer's recommendations. Additionally, aliasing of water vapor with the CO<sub>2</sub> signal is an issue that is very difficult to avoid. Common desiccants such as Drierite cannot be used, and complete removal with a cold bath is difficult under the restrictions of high flow and low reactor volume. For these reasons, it is of interest to develop an alternative to NDIR analysis that can be used to measure rapid gasification reactions.

The proposed method for measuring rapid gasification kinetics is based on a modified fixed bed designed to minimize the effects of heat and mass transfer. A very high reactant gas flow through the bed is used to decrease the external mass transfer limitations, and thermal media is included in the char bed to maintain the reaction temperature. The gasification rate is calculated solely from the total gas flow exiting the reactor, allowing for very fast response to changes in the reaction rate. Because the only piece of analytical equipment that is required is a flow meter, the total system cost is much lower than with traditional methods. In this paper we use the gas flow measurement technique to measure the steam-char reaction over a wide range of conditions and compare the results to select points measured with an NDIR analyzer.

## 2. Methods

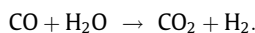
### 2.1. Gas flow measurement technique

The gas flow measurement technique is based on the molar flow rate of gaseous reaction products leaving the reactor. The steam-char gasification reaction can be represented as:



In this gasification reaction, two moles of gas are created for every one mole of carbon consumed. If the excess water is condensed, the reaction rate of carbon can be directly measured by measuring the molar flow rate out of the reactor.

In real world systems, water gas shift also occurs as follows:



If excess steam is removed before the flow meter as it is in most reactor systems, water gas shift complicates the measurement of the reaction rate because one mole of CO generates two moles of gas. In this case, three moles of gas are produced for every one mole of carbon, and the molar flow rate is not representative of the reaction rate. To counteract this effect the gas may be passed through a CO<sub>2</sub> scrubber that removes the CO<sub>2</sub> from the gas stream. If CO<sub>2</sub> is removed, two moles of gas are generated for every one mole of carbon regardless of the extent of water gas shift.

The gas flow measurement technique has a faster response time than systems that measure the concentration of product gases at the reactor outlet, but flow restrictions and reactor volume will affect the quality of the data and should be minimized. The response time of the gas flow measurement technique is faster because product gas that is generated inside the reactor causes an increase in the outlet flow before the gas reaches the exit of the reactor. If the flow path between the reactor and the flow meter had zero pressure drop, the response time would be nearly instantaneous, but if flow restrictions are introduced, the pressure in the reactor must rise slightly before the flow through the system will increase. Additionally, the volume of the tubing between the reactor and the condenser must be minimized to ensure that the steam is condensed shortly after contacting the char bed. When steam first reacts with the char in the bed, one molecule of steam reacts with the solid carbon to form two molecules of gas, resulting in a net change of one gas molecule in the system. It is not until the gas stream passes through the condenser where the steam molecule that reacted with the char would have been removed from the flow that the reaction results in a net generation of two gas molecules. These two effects combined may cause some smoothing of the data which would cause the measured kinetic rate to be lower than the actual kinetic rate.

### 2.2. Reactor design

The theory behind the proposed measurement system is relatively simple, but the implementation requires care to be taken in many areas of the reactor system. Gas residence time and flow restrictions must be minimized to ensure accurate readings of the gas generation rate. Heat and mass transfer resistance must be minimized to provide the most accurate measurement of the kinetic rate.

The reaction chamber is an 81 cm long alumina tube with a 2.54 cm O.D. and 1.9 cm I.D. suspended in a vertically oriented tube furnace. A diagram of the reactor system is shown in Fig. 1. Product gases exit the reactor through a 6.4 mm tube made of Inconel™ 600 that extends into the hot zone of the furnace and terminates 2 cm below a wire mesh. The wire mesh is held in place by supports welded to the side of the central tube. The central exhaust tube creates an undesirable dead zone between the inner Inconel™ and outer alumina tube, but sealing this area would be very difficult without the use of purge gas. On top of the mesh, zirconia beads are mixed with the biomass to provide extra thermal mass and limit the temperature drop in the bed when the reaction is initiated. An Inconel™ gas preheater is suspended above the reaction zone to adsorb radiant energy from the reactor walls and heat the incoming gas stream. Four K type thermocouples are located in the reaction bed; two at the bottom and two at a height of 3 cm. At each vertical position, one thermocouple is located in

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