

Application of Combined Catalyst/Sorbent on Hydrogen Generation from Biomass Gasification

J. A. Satrio, B. H. Shanks, and T. D. Wheelock

Department of Chemical Engineering & Center for Sustainable Environmental Technologies

Iowa State University, Ames, IA 50011

ABSTRACT

Air-blown gasification of biomass in fluidized bed reactors produces relatively low concentrations of hydrogen. The combination of a catalyst and calcium-based sorbent is being developed to increase the efficiency of converting producer gas from biomass gasification into hydrogen. The conversion process entails reforming the methane and tar, and converting carbon monoxide into hydrogen by the water-gas-shift reaction. The desired material is made in the form of small spherical pellets having a layered structure such that each pellet consists of a highly reactive lime core enclosed within a porous but strong protective shell made of alumina on which a nickel catalyst is loaded. The material serves two functions in catalyzing the reaction of hydrocarbons or carbon monoxide with steam to produce hydrogen while simultaneously absorbing carbon dioxide formed by the reaction. The *in-situ* removal of CO₂ shifts the equilibrium of the steam reforming reaction and/or water gas shift reaction to increase the hydrogen concentration and simultaneously decreases the concentration of carbon oxides in the producer gas stream.

The effects of other reaction conditions on the conversion of CH₄ and CO have also been investigated and will be presented. In addition, the results of the steam reforming of toluene in the presence of the combined catalyst/sorbent will be described since the compound is considered model for the tars produced by gasifying biomass. Finally, the results of several measures taken to improve the performance of the catalyst/sorbent will be discussed.

KEY WORDS

Producer gas, hydrogen, tar, hydrocarbons, steam reforming, water-gas shift, carbon dioxide sorbent.

INTRODUCTION

In the future hydrogen may be supplied to fuel cells on a large scale to generate electric power. The advancement of fuel cell technology for the clean and efficient production of electric power requires the concomitant advancement of hydrogen production technology so that it is produced inexpensively, efficiently, and reliably. The gasification of renewable materials, such as switch grass, provides a very promising means of obtaining hydrogen from renewable

resources. Air-blown gasification in fluidized bed reactors typically produces relatively low concentrations of hydrogen (9-17%). Other components are CO (14 - 24%), CO₂ (9-20%), CH₄ (1-7%), and tars (1-10 g/m³). More hydrogen can be produced by steam reforming tars and methane and converting CO via high and low temperature water-gas-shift reactions followed by scrubbing the gas to remove CO₂. All these steps traditionally are conducted separately with different catalysts at different temperatures, thus making the process complex and costly. A technology that can reduce the number of steps, thus making the production of hydrogen simpler, more efficient and less costly, will be very attractive.

Both the steam reforming and the water gas shift reaction can be limited by thermodynamic equilibrium as well as the rate of reaction. To overcome these limitations, a new material is proposed that combines a catalyst to increase the rate of reaction and a chemical sorbent for CO₂. Removing CO₂ by reaction with CaO to form CaCO₃ results in increased hydrogen production from the reforming and/or water gas shift reactions. This principle was demonstrated previously by conducting the water gas shift reaction in a fixed-bed reactor packed with dolomite particles (1) and by reforming methane in a similar reactor packed with a mixture of catalyst and CO₂-acceptor particles (2-4). While these demonstrations were valuable, they did not culminate in the development of a material that combines both a catalyst and a CO₂ acceptor in one durable pellet.

The integration of catalyst and sorbent into a single material potentially can make the process for converting hydrocarbons and carbon monoxide into hydrogen much simpler, more efficient, and less costly. Such a material is under development. This material, to be called core-in-shell catalyst/sorbent pellets, is in the form of spherical pellets in which a CaO core is surrounded by a porous shell that supports a catalyst for both the steam reforming and the water gas shift reactions. The schematic diagram of a pellet and the mechanism of the reactions involved when used to react hydrocarbons and carbon monoxide with water is shown in Figure 1.

The equilibrium modification by the CO₂ absorption makes it possible to conduct the water gas shift reaction at the higher temperature required for steam reforming of methane and with the same catalyst. Furthermore, since the CO₂ is absorbed, the reaction products are separated resulting in a product stream of nearly pure H₂ or a mixture of H₂ and N₂ in the case of air-blown gasification. The CaO sorbent is regenerated periodically, which can also produce a concentrated stream of CO₂ suitable for sequestration. The proof of concept of the core-in-shell sorbent pellets loaded with nickel catalyst recently has been demonstrated for steam reforming methane and propane in our laboratory by using thermogravimetric analysis (TGA) and fixed bed reactor (FBR) systems (6-7).

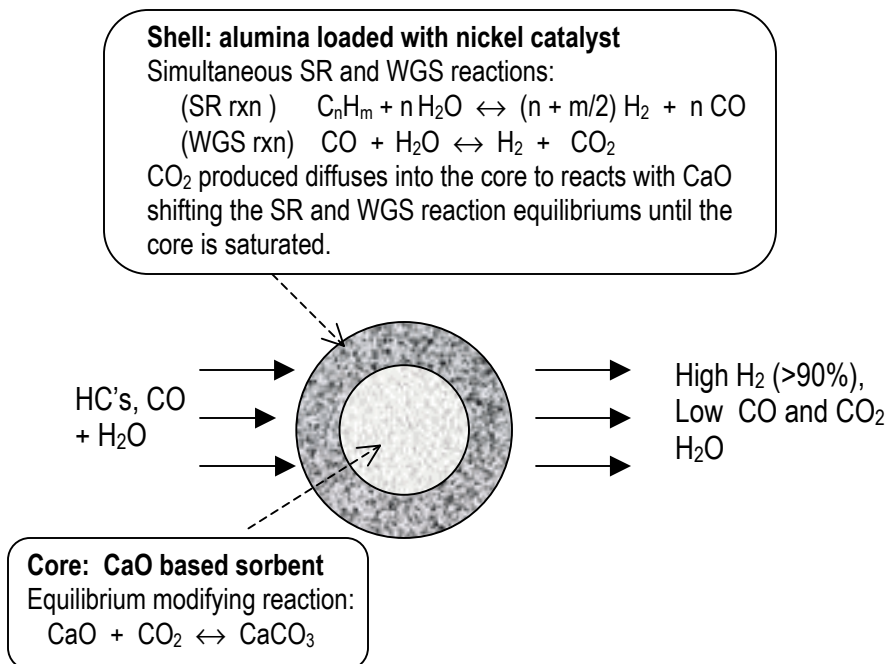


Figure 1. Schematic of core-in-shell catalyst/sorbent and main reactions involved in producing high purity H₂ from hydrocarbons and CO.

PERFORMANCE OF THE COMBINED CATALYST/SORBENT

Core-in-shell spherical pellets were prepared by using the procedure reported earlier (6). To evaluate the catalytic activity of the catalyst/sorbent pellets, several experiments were conducted using the Fixed Bed Reactor (FBR) system. A 1.27 cm (0.5 inch) diameter tubular reactor made of quartz was used. In a typical experiment 6.0 g of catalyst/sorbent pellets was placed in the reactor forming a 12 cm deep bed. During the reaction samples of the product gas were collected periodically and analyzed with a gas chromatograph for H₂, CO₂, CO, and CH₄. All the experiments were conducted at atmospheric pressure.

Hydrogen was produced from reforming of methane and toluene (typical model compound for tar) via methane and toluene steam reforming (SMR and STR) reactions, respectively, and for converting carbon monoxide to hydrogen via the water gas shift (WGS) reaction at various reaction temperature using different batches of catalyst/sorbent pellets. Table 1 shows the composition in the gaseous product streams from the SMR, WGS, STR, and the combination of STR and WGS reactions at 550-575°C. It can be seen that all the reactions showed very high concentration of H₂ (>90%) and significantly low CO and CO₂ concentrations in the gas product stream during the absorption period, i.e. when CO₂ produced was being absorbed by the sorbent. At the post-absorption period, the gas product compositions returned to 'normal' when CO₂ was no longer absorbed due to the saturation of the sorbent cores with CO₂. In general,

higher concentration of H₂ and lower CO's were obtained at lower reactor temperatures. Optimum results seemed to be obtained at reactor temperatures between 550 and 600°C for operation at atmospheric pressure.

The saturated sorbent was easily regenerated by simply heating the catalyst/sorbent pellet bed to 750°C or higher. The sorbent regeneration could be done even without having to stop the SR or WGS reaction. Once the sorbent cores were fully regenerated, the catalyst/sorbent pellets were ready for the next reaction/absorption cycle. Several batches of catalyst/sorbent pellets were used for multiple reaction/absorption and regeneration cycles. The catalyst/sorbent pellets were used for more than 100 hours of operation time without significant lose of their catalytic or absorption activities.

Table 1. Gas product composition from steam reforming reactions (methane and toluene) and water gas shift reaction at various temperatures with and without CO₂ absorption at atmospheric pressure. Carbon to steam mole ratio = 1 : 3.

Steam Methane Reforming (SMR) Reaction ¹					
Temperature	Period	H ₂ (%)	CO ₂	CO	CH ₄
575°C	CO ₂ absorption	95	1	1	3
	Post absorption	71	14	6	9
Water Gas Shift (WGS) Reaction ²					
550°C	Period	H ₂	CO ₂	CO	CH ₄
	CO ₂ absorption	96	3	1	0
	Post absorption	59	38	3	0
Steam Toluene Reforming (STR) Reaction ³					
550°C	Period	H ₂	CO ₂	CO	CH ₄
	CO ₂ absorption	96	1	3	0
	Post absorption	66	20	10	4
Combination of STR and WGS Reactions ⁴					
550°C	Period	H ₂	CO ₂	CO	CH ₄
	CO ₂ absorption	95	1	1	3
	Post absorption	63	23	6	8

1 Core-in-shell catalyst/sorbent specifications: sorbent core: mixture of dolime/limestone (ratio 1:1), shell material: 20% limestone and 80% alumina (γ -alumina: α -alumina = 20:80), calcined at 900°C for 3 hours before loaded with nickel nitrate; reducible nickel content: \pm 6 wt%. Flowrate of CH₄ : 36.4 mmol/h.

2 Core-in-shell catalyst/sorbent specifications: sorbent core: dolime, shell material: inner: 5% limestone and 95% alumina (γ -alumina: α -alumina = 30:70), outer, 5% limestone and 95% α -alumina; calcined at 900°C for 3 hours before loaded with nickel nitrate; reducible nickel content: \pm 3 wt%. Flowrate of CO: 36.4 mmol/h.

3,4 Core-in-shell catalyst/sorbent specifications: sorbent core: mixture of dolime/limestone (ratio 1:1), shell material: 5% limestone and 95% alumina (γ -alumina: α -alumina = 20:80), treated with 1.0 M lanthanum nitrate and calcined at 900°C before loaded with nickel nitrate; reducible nickel content: \pm 5 wt%. Flowrate of carbon (in CO or toluene): 36.4 mmol/h.

4 Toluene to CO mole ratio = 1:4. Flowrate of total carbon (in CO + toluene): 54.6 mmol/hr.

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