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Non-Catalytic Co-Gasification of Sub-Bituminous Coal and Biomass

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NON-CATALYTIC CO-GASIFICATION OF SUB-BITUMINOUS COAL AND BIOMASS

By

Guevara Che Nyendu

A thesis submitted in partial fulfillment
of the requirements for the degree

of

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ABSTRACT

Non-Catalytic Co-Gasification of Sub-Bituminous Coal and Biomass

by

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Fluidization characteristics and co-gasification of pulverized sub-bituminous coal, hybrid poplar wood, corn stover, switchgrass, and their mixtures were investigated. Co-gasification studies were performed over temperature range from 700°C to 900°C in different media (N_2, CO_2, steam) using a bubbling fluidized bed reactor.

In fluidization experiments, pressure drop (ΔP) observed for coal-biomass mixtures was higher than those of single coal and biomass bed materials in the complete fluidization regime. There was no systematic trend observed for minimum fluidization velocity (U_{mf}) with increasing biomass content. However, porosity at minimum fluidization (ε_{mf}) increased with increasing biomass content. Channeling effects were observed in biomass bed materials and coal bed with 40 wt.% and 50 wt.% biomass content at low gas flowrates. The effect of coal pressure overshoot reduced with increasing biomass content.

Co-gasification of coal and corn stover mixtures showed minor interactions. Synergetic effects were observed with 10 wt.% corn stover. Coal mixed with corn stover formed agglomerates during co-gasification experiments and the effect was severe with increase in corn stover content and at 900°C. Syngas ($H_2 + CO$) concentrations obtained using CO_2 as co-gasification medium were higher (~78 vol.% at 700°C, ~87 vol.% at 800°C, ~93 vol.% at 900°C)

than those obtained with N_2 medium (~60 vol.% at 700°C, ~65 vol.% at 800°C, ~75 vol.% at 900°C).

Experiments involving co-gasification of coal with poplar showed no synergetic effects. Experimental yields were identical to predicted yield. However, synergetic effects were observed on H_2 production when steam was used as the co-gasification medium. Additionally, the presence of steam increased H_2/CO ratio up to 2.5 with 10 wt.% hybrid poplar content. Overall, char and tar yields decreased with increasing temperature and increasing biomass content, which led to increase in product gas.

(130 pages)

PUBLIC ABSTRACT

Non-Catalytic Co-Gasification of Sub-Bituminous Coal and Biomass

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Utilization of coal as a low-cost domestic energy source is becoming a subject of utmost importance due to fluctuating crude oil prices. However, coal use emits pollutants such as nitrous oxides (NO_x), sulfur oxides (SO_x), carbon dioxide (CO_2), and particulates that have negative environmental impact and significant issues on health. To minimize the harmful effects of coal use, renewable and sustainable biological or green materials called biomass are processed with coal to produce synthetic gas (syngas) that can be processed into clean energy fuels and value-added products.

Currently, coal is converted using combustion technology; however, novel techniques such as co-gasification (thermochemical process) convert coal under conditions that reduce pollutant emissions. However, very limited information exists on the behavior of coal and biomass mixtures during thermal conversion, which could be due to large variations in the physical and chemical properties of various biomass.

This study investigated the effect of co-gasifying biomass feedstocks (hybrid poplar wood and corn stover) with sub-bituminous coal on product yields and gaseous compounds. Results showed that hybrid poplar wood can be successfully gasified with coal. However, use of corn stover needs further processing consideration as it produced agglomerates (ash sticking effect) that had negative impact on the co-gasification process.

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Finally, I appreciate my family for their patience and support and my thanks to my colleagues who have made my time in the lab a great experience on both professional and personal levels.

Guevara C. Nyendu

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CHAPTER 1

LITERATURE REVIEW

1. Research Motivation

It is widely acknowledged that fossil fuels, especially coals are not eco-friendly and petroleum resources are being depleted. Growing energy demand, instability of fuel prices, and problems with pollution caused by petroleum crude; in addition to declining reserves has received tremendous global concern. Exhaustion of petroleum resources is expected to have destructive impact on human life, economy, and overall global stabilization. Also, climate change as a result of using petroleum is expected to have multitude of potential impacts that vary in intensity and effect according to region and sector (EEA, 2008; Rannow et al., 2010), primarily on agriculture and health. These concerns have stimulated the search for alternative sources to supplement petroleum. Presently, fuels and chemicals are predominantly derived from fossil resources such as coal and petroleum (Demirbas, 2008). However, due to increasing concern of petroleum depletion and fluctuating prices, greater attention is being directed towards coal use.

In 2011, petroleum was the most consumed fuel in the United States (EIA, 2012). Figure 1.1 shows the United States energy consumption (quadrillion Btu) by source from year 1950 to 2011. The potential of rapidly replenishing petroleum crude after exhaustion is minimal and therefore, labeled as nonrenewable and unsustainable. Also, it was established that we have reach peak oil (maximum possible global oil production rate (Kerschner et al., 2013)), which is corroborated with the concept of Energy Return on Energy Input (EROEI) (Heun and de Wit, 2012).
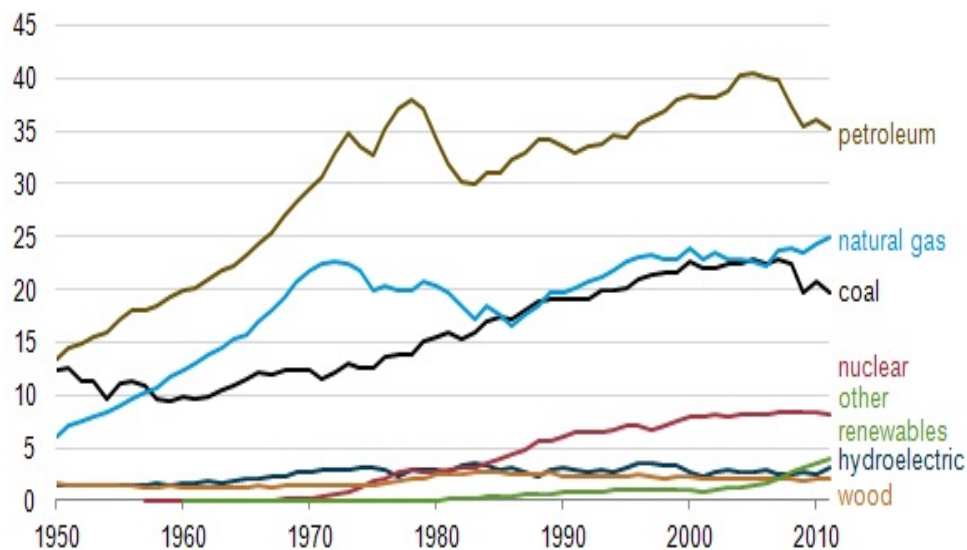
Figure 1.1 U.S. primary energy consumption (quadrillion Btu) estimates by source (EIA, 2012).

Despite the drawbacks with petroleum, demand for energy is increasing and will have to be absorbed by other sources of energy. For that matter, there is now considerable interest, and research funds allocated to develop new sources of renewable energy (Bolinger et al., 2005) and new technologies to convert existing fossil fuels (coal and natural gas) to clean energy. The anticipated outcomes for alternative energies are; provision of energy security, clean energy, competition with crude oil prices, and stimulation of local job creation.

Biofuels especially bioethanol produced from corn and sugarcane that is widely used as transportation fuel is a major breakthrough in the biorenewable fuel industry. Unfortunately, coal is an important source of pollution and a large contributor to global warming (Kunstler, 2005; Xie et al., 2006). To promote clean coal-energy, biomass (an organic materials of recent biological origin (Brown, 2003)) a potentially underutilized renewable and sustainable feedstock (Baxter, 2005) is combined with coal and processed via technologies such as gasification to produce fuels and synthesis gas (syngas).

Syngas is primarily a mixture of hydrogen and carbon monoxide gas that can further be transformed into substitutes for petroleum-based products (Kumar et al., 2009) or converted to

heat for homes, energy for gas turbines, and fuel cells for electricity generation (Weiland et al., 2012). Based on the numerous advantages, co-gasification technology is considered a promising hydrocarbon alternative. In addition, co-gasification of coal and biomass fuel is a considered as a link between fossil fuels and renewable fuels aimed at reducing pollution and greenhouse gas emissions.

Gasification has been used commercially around the world for more than 50 years by chemical, refining, and fertilizer industries, and for more than 35 years by electric power industries (GTC, 2008). Presently, gasification is the most preferred thermochemical routes for coal conversion because it accommodates low-value feedstocks and the product gas can be synthesized into hydrocarbons (Kumar et al., 2009). As of 2014, there are more than 269 operating gasification plants worldwide with 677 gasifiers (GTC, 2014). Nowadays, coal and other carbon sources are converted into either pure hydrogen or syngas for efficient and clean power using Integrated Gasification Combined Cycle (IGCC) technology (Song, 2010).

Pyrolysis technology, another thermochemical route for coal, biomass, and coal-biomass conversion is also gaining attention as an important method for converting carbonaceous feedstocks into useful products. Nevertheless, pyrolysis or co-pyrolysis is aimed at converting organic materials into liquids in the absence of oxygen at moderate temperatures (Brown, 2011).

2. Key drivers for gasification technology

The emergence and effect of global climate-change has attracted environmental policies that creates awareness that utilization of greenhouse-gas-emitting fossil fuels constitute a threat to our present way of life and posterity (Charles et al., 2007). As a result, government regulations on fuel standards and incentives have spurred industries and academic institutions to improve upon existing technologies and to develop advanced technologies for producing clean energy. A typical example is the US Energy Policy Act of 2005, that has provided large incentives to gasification project in the power industry and industrial sector (Higman and van der Burgt, 2008c). The

Europeans have regulations that promote the development of clean coal-biomass energy (Hernández et al., 2010).

Combustion of coal, which is currently, the dominant technology used in the industry for electricity production generates greenhouse gases such as carbon dioxide (CO_2), methane (CH_4), nitrous oxides (NO_x), and sulfuric oxides (SO_x) that cause acid rains. These pollutant and many others are enlisted as priority pollutants by US Environmental Agency (Bell et al., 2011e). Also, gases produced from combustion processes cannot be further burned to produce energy; however, product gases obtained from gasification can be burned to produce energy, or chemically converted to other valuable products (Bell et al., 2011a).

With the compelling challenge to find ways to meet the growing energy demand, three major energy areas (Song, 2006, 2010) needs to be addressed:

1) to supply more clean fuel to meet the increasing demands for liquid and gaseous fuels and electricity.

2) to increase the efficiency of energy utilization for fuels and electricity generation, and

3) to eliminate pollutants and disconnect the link between energy utilization and greenhouse gas emissions in the end-use systems.

3. Objectives

Current developments with coal and biomass co-gasification technology show that energy production and chemical manufacturing from gasification facilities will continue to rise and may dominate convectional combustion technology. Furthermore, it is believed that coal will become the dominant world energy source because of its relative abundance compared to the declining reserves of both petroleum and natural gas (Xu et al., 2004). Up until now, the chemistry of coal gasification is a well-established technology however the chemistry of coal-biomass co-gasification has not been widely studied (Brar et al., 2012). For that reason, information on coal and biomass reactivity during co-gasification is limited.

Therefore, the overall objective of this study is to investigate the effect of biomass feedstocks (corn stover, hybrid poplar, and switchgrass) on sub-bituminous coal gasification using fluidized-bed reactor. The specific objectives include:

1) to investigate the fluidization characteristics of coal and biomass mixtures.

2) to perform bench-scale non-catalytic co-gasification of coal and biomass mixtures at atmospheric conditions and investigate the effects of biomass concentration, steam, nitrogen gas (N_2), carbon dioxide (CO_2), and temperatures (700°C, 800°C, 900°C) on product yields and product gas compounds.

4. Gasification

Gasification is a thermochemical process that converts organic material into combustible gas under reducing conditions to produce gas mixture of carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2), methane (CH_4), low molecular weight hydrocarbons, nitrogen (N_2) (Bain and Broer, 2011) and trace compounds like hydrogen sulfide (H_2S) and ammonia (NH_3) (Liu et al., 2010). The expected cumulative growth of gasification capacity by 2018 is shown in Figure 1.2.

5. Types of gasifiers

There are two major techniques of coal gasification based on the source location of coal feedstock. These are surface and underground gasification. Surface gasification involves mining and transporting coal to a gasifier for processing whereas in underground gasification energy is generated from deeply buried coal by sending reactant gases underground where the coal is located (Bell et al., 2011b). Various types of gasifiers are used for surface gasification and these are broadly categorized according to the method of heating and method of transport (Bain and Broer, 2011).
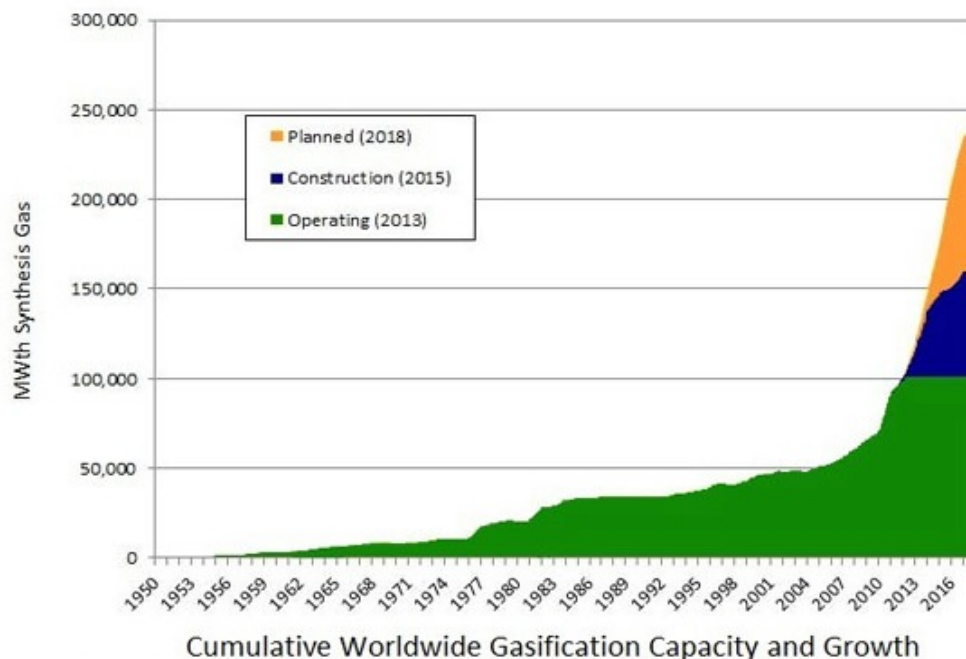
Figure 1.2 Expected gasification capacity by year 2018 (GTC, 2014).

Examples of gasifiers based on method of heating include: air-blown gasifier, steam/oxygen-blown gasifier, and indirectly heated gasifier. Gasifiers classified according to transport method are: fixed bed gasifier, entrained-flow gasifier, circulating fluidized bed gasifier, and bubbling fluidized bed gasifier (Bain and Broer, 2011). Among the different types of gasifiers, entrained-flow gasifier has the largest treatment capacity and the smallest environmental impact (Liu et al., 2010). Therefore, entrained-flow processes occupy most of the commercial market from leading companies like Shell, General Electric Company, ConocoPhillips, and Gas Schwarze Pumpe (Liu et al., 2010).

Moreover, fluidized-bed technology (a subject of this study) has been widely used over many decades for fluid catalytic cracking (FCC) (Srivastava and Sundaresan, 2002). Fluidized bed gasifier is a major attraction in the gasification industry because they have more advantages than any other solid handling equipment (Isemin et al., 2010). Fluidized bed gasifiers are flexible, has high heat and mass transfer between gas and solid particles due to proper turbulent mixing

resulting in a uniformly distributed temperature throughout the reactor. The principal applications of fluidization technology are energy conversion (gasification, pyrolysis, combustion), petrochemical processes (Fischer–Tropsch Synthesis, fluid catalytic cracking), mineral processing (calcination of alumina), chemical and pharmaceutical (decomposition of sulfate), and physical processing (drying) (Basu, 2006b).

6. Gasification feedstock

Although any carbonaceous material can be gasified, coal and recently biomass are the dominant input feedstock for gasification processes and the importance of these two feedstocks as energy source continue to increase. As of 2013 (Figure 1.3), coal is the second largest source of energy production in the United States whereas biomass is the fifth largest. Gasification process can broadly be classified as conventional gasification and co-gasification. In conventional gasification, one type of feedstock is processed for example: coal or biomass (wood). In contrast, co-gasification employs the use of more than one type of feedstock where two different feeds (coal and biomass) are blended and processed. Co-gasification emerged as a result of promoting the use of renewable fuels.

6.1 Coal as a fuel

In the past, coal was the primary solid fuel for gasification. Energy generated from coal gasification was used to power steam turbines. In 2011, coal was reported as the fastest form of energy outside renewables (WCA, 2014). Coal provides 30.1% of global primary energy needs (WCA, 2014). According to U.S. Energy Information Administration (EIA, 2014c), the demonstrated reserve base (DRB) for coal was estimated to contain 481 billion short tons as of January 1, 2013. Despite the abundance of coal reserves, not all of the coal resource is readily available for power demands because of economics, restrictions to mining, and coal quality issues.
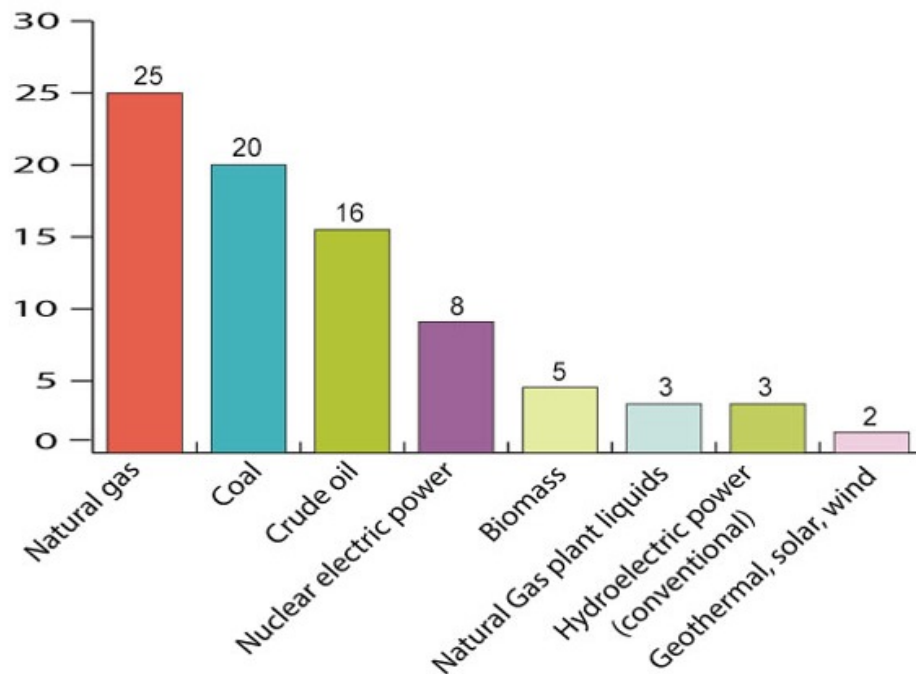
Figure 1.3 U.S. primary energy production (quadrillion Btu) by major source, 2013 (EIA, 2014d).

Coal is formed through a process called coalification. Coalification process involves the biochemical and physiochemical transformation of plant matter into peat and then to coal under heat and pressure (Flores, 2013). Coals have more than 50% by weight and more than 70% by volume of carbonaceous material including inherent moisture (Speight, 2005). The degree of coalification known as rank is used to classify coal. There are four major ranks of coal and this is categorized according to the heating value, fixed carbon, volatile matter content, and caking properties (EIA, 2014b). The rank of coal from highest to lowest according to carbon and energy content are: anthracite, bituminous, subbituminous, and lignite (EIA, 2014a). In general, coal reactivity increase with decreasing rank (Speight, 2013) because volatile matter content decreases with increasing rank. Bituminous and sub-bituminous coals are the primary commercial coal with small amount of anthracite available (Bell et al., 2011d).

The structure and chemical properties of coal depends mainly on various macerals (vitrinite, fusinite, exinite, etc.) and the content of functional groups (Gavalas, 1982). Among the

various macerals, vitrinite is dominant; more than 70% in most coals (Gavalas, 1982). In general, coal structure consists of polymer network of aromatic clusters connected by aliphatic bridges with methyl, ethyl, and carboxylic groups as side chains (Liu et al., 2010). Coal also contain varying amounts of carbon, hydrogen, nitrogen, oxygen, and sulfur as well as trace elements, including mineral matter (ASTM, 2004; Gluskoter, 1975; Speight, 1994, 2005; Van Krevelen, 1961). When coal is combusted, impurities such as nitrogen and sulfur combine with oxygen to form weak forms of nitric and sulfuric acid as acid rain, which can cause acidification of water bodies (lakes, rivers, and wetlands) that can affect aquatic life and crop growth.

6.2 Biomass as a fuel

Biomass or biorenewable resources are organic materials of recent biological origin (Brown, 2003). Biomass is a low-cost renewable feedstock containing low ash and sulfur content and does not increase the level of carbon dioxide in the atmosphere and subsequent greenhouse effect (provided that consumption does not exceed annual production) (Reed and Das, 1988). The availability of biomass is estimated at 220 billion oven-dry tons per year (Hall and Rao, 1999; Vaezi and Kumar, 2014) and accounts for about 10% of world energy (Roberts et al., 2015).

Biomass sources can be classified as: 1) forest products; these include wood, logging residue, trees, 2) biorenewable wastes; such as agricultural residue, municipal solid waste, crop residue, 3) dedicated energy crops; these are crops grown purposely for energy other than for food and feed. They include; short rotation woody crops, herbaceous woody crops, forage crops, oilseed crops, grasses, 4) aquatic plants such as algae, water hyacinth, water weed, 5) food crops, which include grains and oil crops, and 6) sugar crops such as sugar cane, molasses, sorghum, and sugar beets (Ayhan, 2009). Generally, conventional biomass used for gasification are pine (André et al., 2005; Pinto et al., 2002, 2003; Vélez et al., 2009), olive oil wastes (André et al., 2005; García-Ibañez et al., 2004; Vélez et al., 2009), wood (Aznar et al., 2006; Kurkela et al.; Vélez et al., 2009), and rice husk (Jiang et al., 2003; Vélez et al., 2009).

7. Gasification media

Gasification processes generally occur under reducing atmosphere. External medium (agent) or oxidant such as air, carbon dioxide, steam, hydrogen (Wang et al., 2008), and plasma (NETL, 2014) are used to aid conversion of carbonaceous solids into gaseous products. Generally, mixtures of gasification agents such as steam-carbon dioxide and steam-hydrogen are used. The type of gasification is associated to the kind of medium used. Therefore, air gasification, carbon dioxide gasification, hydrogasification, steam gasification, and plasma gasification uses air, CO_2, H_2, steam, and plasma medium respectively. In some gasifiers, oxygen is partially used as a reactive agent and inert gases such as argon and nitrogen are used to dilute the reactive gasification agents.

7.1 Steam gasification

Steam is produced from water using steam generators (boilers) operating at a certain temperature and pressure. External heat source is required when pure steam is used for gasification. Steam is used to increase the hydrogen concentration of product gas derived from thermochemical process (Everson et al., 2006) and it is non-hazardous.

7.2 Air gasification

The cheapest and simplest gasification medium is air (Bell et al., 2011a). The quality of product gas obtained strongly depends on the equivalent ratio (Basu, 2006a). Equivalent ratio is the ratio of actual air fuel ratio to the stoichiometric air fuel ratio (Basu, 2006a). In air gasification, product gas composition, operating temperature, product gas yield, and carbon conversion can be influenced by equivalent ratio (Cao et al., 2006; Guo et al., 2009; Mansaray et al., 1999).

7.3 Carbon dioxide gasification

CO_2 is one of the most significant and major greenhouse gases (Bhattacharyya et al., 2012). There are both natural and human sources of CO_2 emissions. The three main sources of emissions are: stationary, mobile, and natural (Zaidi, 2010). Human activities are the major contributor to greenhouse gases emission and in the United States; the largest source emerges from burning fossil fuels for electricity, heat, and transportation (EPA, 2014; IPCC, 2007).

To reduce CO_2 emissions and pollution, several strategies are presently practiced. These strategies include: CO_2 capture and storage (Bouzalakos and Mercedes, 2010; Davison, 2007; Steeneveldt et al., 2006), CO_2 use as input feed: algae nutrient (Benemann et al., 2003; Ramaraj et al., 2014), and, conversion of CO_2 into value-added products by dry reforming (Alenazey, 2014 Er-rbib et al., 2012).

7.4 Hydrogasification

Hydrogasification is the conversion of carbonaceous materials to methane using hydrogen as gasification agent. This type of gasification has low carbon conversions, product yields and slower reaction rates without catalysts (NETL, 2014) except at high pressures (Rezaiyan and Cheremisinoff, 2005).

7.5 Plasma gasification

Plasma is a highly ionized gas stream generated at high temperature that is capable of electrical conductivity (Janajreh et al., 2013). Plasma gasification is an advanced technology demonstrated as one of the most effective and environmentally friendly methods for solid waste treatment and energy utilization (Moustakas et al., 2005). Product gas from plasma gasification is mainly composed of H_2 and CO, which can be utilized directly as fuel in power plants for electricity generation or synthetic fuels (Byun et al., 2011).

8. Gasification mechanism

Coal gasification is a complex chemical process (Liu et al., 2010) that operates at pressures of 30 bar or higher temperatures above 1300°C (Higman and van der Burgt, 2008d). For example, fluidized bed gasifiers operate at about 1000°C and entrained flow gasifiers operate at 1400 to 1500°C (Bell et al., 2011c). Apart from operating pressure safety concerns, high temperature gasification reduces overall efficiency, restricts the use of catalysts (Higman and van der Burgt, 2008d), limits material of construction, and complicates reactor design. As a result, there are on-going gasification studies using catalysts with the aim of reducing gasification temperatures (Elbaba et al., 2011; Li et al., 2010; Tomita et al., 1983; Xiao et al., 2011).

Conversely, biomass generally has high volatile content and low char content compared to coal, which makes biomass a highly reactive feedstock (Van Loo and Koppejan, 2008). Also, biomass, apart from being renewable, is widely distributed and available in large quantities and contain low sulfur levels. The chemistry of co-gasification of coal and biomass is a complex process; however Figure 1.4 shows a simplified outline of co-gasification process.

The major process of gasification mechanism irrespective of feedstock type involves drying, pyrolysis, gas-solid reactions, and gas-phase reactions (Bain and Broer, 2011). Several factors including feedstock composition, feedstock preparation and particle size, temperature, heating rate, residence time, and pressure can influence gasification reaction pathway and product formation (Rezaiyan and Cheremisinoff, 2005). Figure 1.5 (Brown, 2003) illustrates thermal kinetics of gasification process that occurs in a gasifier.

Primary stage   Secondary stage   Tertiary stage   Syngas utilization
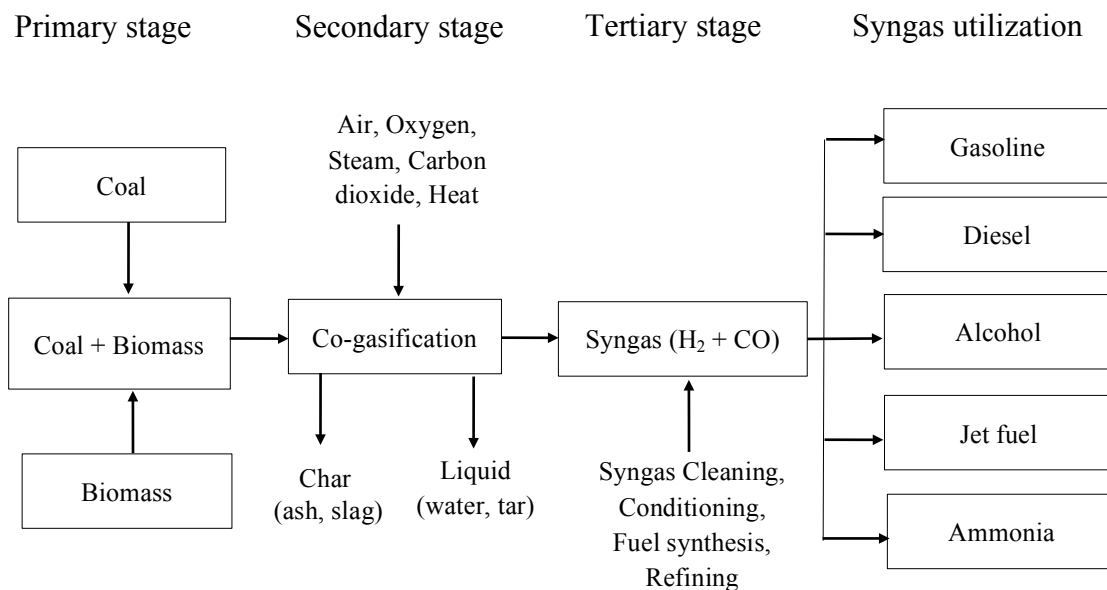
Figure 1.4 Stages of coal and biomass co-gasification.

Heating and Drying   Pyrolysis   Gas-Soild Reactions   Gas-phase Reactions

$CO + H_2O \rightarrow CO_2 + H_2$

$CO + 3H_2 \rightarrow CH_4 + H_2O$
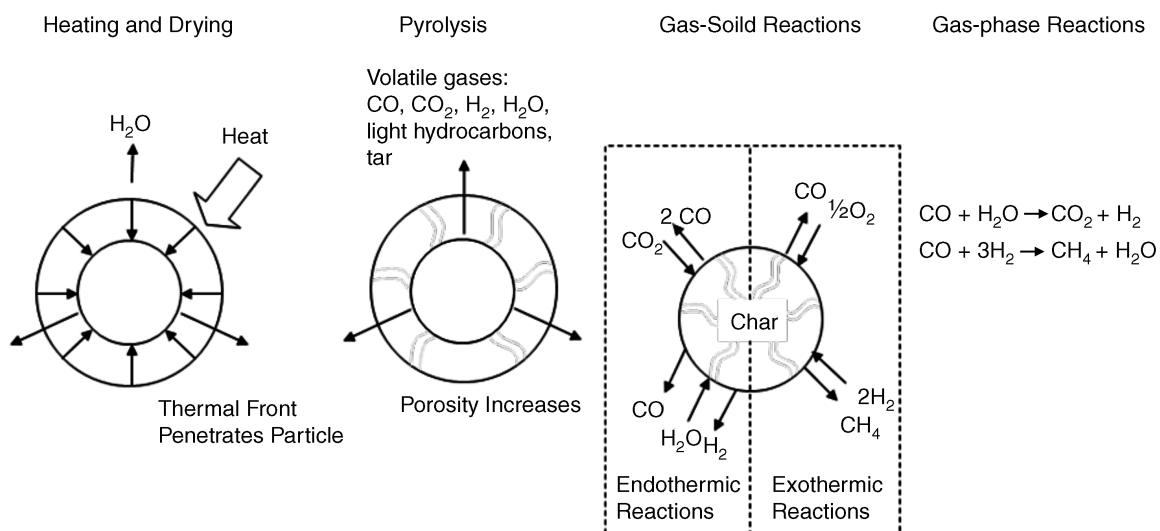
Figure 1.5 The process of thermal gasification (adapted from Brown, 2003).

8.1 Heating and drying

"The process of heating and drying begins on the surface of feed particle and progresses towards the center" (Bain and Broer, 2011). As feed (coal, biomass, or coal-biomass mixtures, etc.) enters the gasifier at a set reaction temperature, water evaporates until the feed becomes dry. Heating and drying reaction are endothermic process because heat energy is absorbed from the gasifier. Loosely bound water in the feed is gradually driven off as heat transferred to the feed particles increase and become irreversibly removed at temperatures from 100°C to 150°C. The speed at which heating takes place has an influence on the subsequent steps of the gasification process (Higman and van der Burgt, 2008a).

$$Feed + Heat \longrightarrow Dry\ feed + Water\ (H_2O)$$

8.2 Pyrolysis

Pyrolysis is the rapid thermal decomposition of carbonaceous material in the absence of oxygen (Brown, 2003). The process begins slowly with exothermic dehydration reactions that form porous carbonaceous solid residue (char) and releases volatile gases (Diebold and Bridgwater, 1997). Char is the ungasified solid residual consisting of organic and inorganic materials (ash) that do not volatized at pyrolysis temperatures. The main volatiles from the decomposition reaction include: 1) produced water, 2) permanent gases (gases that do not condense upon cooling) such as CO, H_2, CO_2, methane, and other light hydrocarbons, 3) tarry vapors (gases that condense upon cooling) (Bain and Broer, 2011). Tar compounds are formed when volatile matter condenses at room temperature and pressure (Liu et al., 2010).

$$Dry\ feed + Heat \longrightarrow Char + Volatiles\ (produced\ H_2O + tar + gases)$$

8.3 Gas-solid reactions

The next phase in the gasification process after pyrolysis is gas-solid reaction or char gasification reaction that converts char into gaseous products. The char at this phase reacts mainly with the gasification medium (steam, CO_2, H_2, etc.). Gas-solid reactions are series of endothermic and exothermic process. This reaction phase is the slowest, rate-controlling process in a gasifier that involves series of complex physiochemical processes (Liu et al., 2010). Gas-solid reactions are heterogeneous and they govern the overall conversion rate (Higman and van der Burgt, 2008b). Water released during the drying phase as steam can react with char to yield gaseous products. The main gas-solid reactions (Brown, 2003) are presented below:

$C + 0.5O_2 \longleftrightarrow CO$ (Carbon-oxygen reaction)

$C + CO_2 \longleftrightarrow 2CO$ (Boudouard reaction)

$C + H_2O \longleftrightarrow H_2 + CO$ (Water-gas or steam reaction)

$C + 2H_2 \longleftrightarrow CH_4$ (Hydrogenation reaction)

8.3.1   Gas-phase reactions

Gas-phase reactions in the gasification process determine the final composition of gaseous products and it is strongly dependent on the amount and type of gasification medium (Brown, 2003). The predominant gas-phase reactions are represented by:

$CO + H_2O \longleftrightarrow H_2 + CO_2$ (Water-gas shift reaction)

$CO + 3H_2 \longleftrightarrow CH_4 + H_2O$ (Methanation reaction)
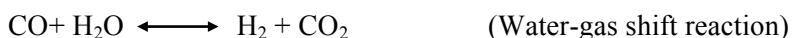
9. Syngas utilization

Product gas obtained from gasification is a versatile raw material that can be used to produce transportation fuels, heat, power, and chemicals. Gaseous product consists of H_2, CO_2, CO, hydrocarbons (for example CH_4), and other impurities such as H_2S, and NH_3. Higher

concentrations of H_2, or syngas (mixture of H_2 and CO) are mostly desired. However, syngas properties largely depend on the gasifier type, operating conditions (temperature and residence time), and nature of feedstock, which differs significantly for various types of gasifiers (Mondal et al., 2011).

Usually, syngas is often cleaned-up before conversion into useful products because the raw gas that exits a gasifier contains unwanted impurities such as organic hydrocarbons (including tar), HCl, alkali metals, particulates, NH_3, HCN, H_2S, and other sulfur and nitrogen containing compounds (Dayton et al., 2011). Following the cleaning stage, syngas is conditioned and synthesized using processes such as Fischer-Tropsch (Schulz et al., 1991), catalytic conversion (Gupta et al., 2011), and fermentation (Liu et al., 2014; Skidmore et al., 2013).

Hydrogen, a product from gasification is environmentally friendly and has multiple uses in the food industry, chemical industry, and transportation (fuel cells systems) industries (Song, 2010). Similarly, syngas has many applications such as transportation fuels, building block for chemical industry, and clean electricity generation (Stiegel, 2005). Specific products that can be obtained from syngas include: dimethyl ether, liquid hydrocarbon, methanol, ethanol, ammonia, Fischer Tropsch gasoline, and Fischer Tropsch diesel.

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CHAPTER 2

FLUIDIZATION BEHAVIOR OF BINARY MIXTURES OF PULVERIZED SUB-

BITUMINOUS COAL AND VARIOUS BIOMASS

1. Abstract

While co-processing of coal with biomass offers a more efficient and cleaner way of energy production, there have been few reports on fluidization behavior of coal and biomass mixtures using fluidized-bed reactors. In this study, fluidization characteristics for pulverized sub-bituminous coal mixed with hybrid poplar, switchgrass, and corn stover were investigated in a 5 cm (2 in) laboratory-scale fluidized-bed reactor. At low biomass content, the mixture completely fluidized. The ε_{mf} values increased with increase in biomass content whereas U_{mf} values did not show any specific trend. The ε_{mf} for all mixtures ranged from 0.75–0.84 and U_{mf} for coal mixed with hybrid poplar, switchgrass, and corn stover ranged from 2.1–4.9 cm/s, 1.6–7.0 cm/s, and 4.9–5.2 cm/s, respectively. Pressure drop for coal-biomass mixtures was higher than pressure drop for single coal or biomass bed materials when the bed was completely fluidized. The magnitude of pressure drop was dependent on the type and ratio of biomass mixed with the coal. Both biomass and coal bed materials showed hysteresis and pressure overshoot. The pressure overshoot was reduced when coal and biomass mixtures were used.

2. Introduction

Fluidization occurs when solid particles are made to behave like a fluid in a reactor by suspension in liquid or gas (McCabe et al., 2001). The basic concept underlying fluidization is contact between solid and fluid therefore the fluidization behavior of solid particles becomes prominent to the design of fluidized-bed unit, equipment selection, and scale-up. In gas-solid fluidized beds, the most important issue from chemical reaction perspective is the behavior of solid particles in suspension. The process becomes more complex for mixtures of heterogeneous

bed materials because of mixing and segregation issues (Formisani et al., 2008). Generally, fluidized beds are characterized by high heat and mass transfer between gas and solid particles (Gidaspow, 1994) because of turbulent mixing resulting in a uniformly distributed temperature throughout the reactor.

Usually, fluidized bed materials (e.g. catalysts or inert materials such as sand) are used as heat transfer medium. Even though fluidization technologies have numerous applications, there are still problems associated with irregularities of solid particles such as size, density, porosity, and shape (Escudié et al., 2006; Ramakers et al., 2004; Sau et al., 2007; Zhang et al., 2008). However, the most notable issues with binary mixture fluidization are mixing and segregation (Huilin et al., 2003). For biomass, the flow characteristics of particles are highly unpredictable because of large variations in particulate properties (Cui and Grace, 2007).

Since utilization of binary mixtures for fluidization processes has potential to accommodate biorenewable resources, several work has been devoted to fluidization of binary particulate mixtures (Čársky et al., 1987; Chen and Keairns, 1975; Formisani et al., 2001, 2004, 2006, 2008; Marzocchella et al., 2000; Olivieri et al., 2004) and various experimental studies have been performed and empirical models developed. Some studies focused on the mechanism of mixing and segregation (Baeyens and Geldart, 1986; Bai et al., 1996; Formisani et al., 2001; Nienow et al., 1978; Rincon et al., 1994; Rowe and Nienow, 1972; Tanimoto et al., 1980; Thonglimp et al., 1984; Zhang et al., 2008) whereas others focused on the dynamics of mixing and segregation (Chiba et al., 1986; Formisani et al., 2001, 2008; Marzocchella et al., 2000; Nienow and Naimer, 1980; Noda et al., 1986; Olivieri et al., 2004).

Other experimental studies were carried out in bubbling fluidized-bed units with focus on segregation behavior and determination of minimum fluidization velocities (Cheung et al., 1974; Chiba et al., 1979; Huilin et al., 2003; Nienow et al., 1987). Further, models for maximum pressure drop, minimum fluidization velocity of mono-solids and binary mixtures in various types of fluidized-bed units have been reported (Biswal et al., 1985, 1984; Leu and Wu, 2000; Olazar et

al., 1993; Peng and Fan, 1997; Sau et al., 2007, 2008). Works on fluidization of binary mixtures of sand and different biomass (GTC, 2008; Karmakar et al., 2012; Ramakers et al., 2004; Rao and Bheemarasetti, 2001) and coal mixed with straw pellet (Isemin et al., 2010) has been reported in literature.

Unfortunately, in most cases, it is very difficult to extrapolate existing fluidization empirical data and models to every binary coal-biomass fluidization system probably because of variations of biomass properties.

The aim of this study was to investigate the fluidization behavior of sub-bituminous coal, poplar, corn stover, switchgrass and their mixtures in a fluidized-bed reactor. Furthermore, data obtained from numerical simulations using Computational Fluid Dynamics (CFD) and Multiphase Flow with Interphase eXchanges (MFIX) from research project collaborators (Estejab and Battaglia, 2013) were compared to experimental data from this work. Initial results showed that simulated and experimental data are in very good agreement (Estejab and Battaglia, 2013). The overall goal for the on-going project: *Investigation of Coal-biomass Catalytic Gasification using Experiments, Reaction Kinetics and Computational Fluid Dynamics* is to develop a general model that can be applied to fluidized-bed coal-biomass gasification systems on industrial scale.

3. Materials and Method

3.1 Experimental materials

Fluidized-bed materials used in this study include pulverized sub-bituminous coal, hybrid poplar wood, switchgrass, and corn stover. Lignocellulosic biomass were provided by Idaho National Laboratory (INL)/Battelle Energy Alliance (BEA), LLC (Idaho Falls, Idaho, USA) and coal was obtained from Powder River Basin (North Antelope Rochelle Mine, Wyoming, USA). The physical properties of coal and biomass materials are listed in Table 2.1. Pulverized coal was used

Table 2.1 Physical properties of test materials.

Material	Mean diameter, d_m (μm)	Bulk density, ρ_b (g/cm^3)	Particle density, ρ_s (g/cm^3)	Sphericity, ψ	Porosity, Φ (1- $\rho b/\rho s$)	Geldart group
Hybrid poplar	152.65 ±1.21	0.16 ±0.02	0.35 ±0.05	0.59 ±0.05	0.86	A
Switchgrass	144.77 ±0.70	0.19 ±0.01	0.32 ±0.04	0.65 ±0.04	0.83	A
Corn stover	417.77 ±1.64	0.21 ±0.01	0.37 ±0.01	0.62 ±0.05	0.83	B
Coal	61.62 ±0.51	0.49 ±0.01	1.38 ±0.01	0.95 ±0.02	0.64	A
Sand	251.39 ±0.17	1.51 ±0.04	2.62 ±0.01	0.93 ±0.01	0.42	B

as received however the biomass samples were ground to pass through a 1-mm sieve using a Thomas-Wiley® mill (Model # 3375-E15).

3.2 Particle characterization of test materials

Particle size distributions were determined using Ro-Tap® Model E test sieve shaker (W. S. Tyler Mentor, Ohio, USA). The sieve sizes ranged from 850 μm to 45 μm. After sieving, the materials retained on each sieve were weighed and recorded. Mean diameter of particles was determined using sieve analysis data.

For sphericity measurements, computerized image analysis technique was used to obtained geometrical dimensions of coal and biomass particles. The solid particles were evenly spread on a microscope slide and analyzed using a Leica DM750 microscope (Leica Microsystems Ltd., Switzerland) equipped with a digital camera. Images were analyzed using a Leica Application Suite (LAS) EZ. The equivalent diameter was obtained for coal and sand particles, which were more spherical in shape and the length and width dimensions, were measured for the more rectangular-shaped biomass particles. The sphericity (ψ) of particles were estimated from the

equation: $\psi = 4\pi a/p^2$ (Phanphanich and Mani, 2011), where a = projected area of particle and p = perimeter of particle.

The bulk densities of coal and biomass samples were determined using the ratio of mass to the volume occupied by the material. Samples were gently poured into a measuring cylinder and allowed to settle freely. The mass of solids and volume contained were measured and the bulk density calculated. Biomass particle densities (basic density) were calculated using the ratio of oven-dry mass of solid particles per volume of solid particles when green. Coal particle density was determined using methanol.

3.3 Fluidization of solid particles

Fluidization experiment was carried out in a borosilicate glass laboratory-scale bubbling fluidized-bed reactor equipped with a 100-μm fritted glass gas distributor. Figure 2.1 shows a schematic diagram of experimental apparatus. The experimental set-up consisted of gas source, fluidized-bed reactor, and U-tube manometer filled with distilled water, and a cyclone with dust collector. The reactor is 5 cm (2 in) in diameter and 30 cm (12 in) height above the gas distributor including a freeboard zone. The freeboard is an expanded zone provided to reduce particle entrainment.

All experiments were performed at room temperature and atmospheric pressure, with a total solid mass of 30 g for individual coal, biomass, and their mixtures. The biomass content mixed with coal prior to fluidization were 0%, 10%, 20%, 30%, 40%, and 50%. The behaviors of coal and individual biomass materials during fluidization and defluidization were studied before performing fluidization experiment for coal-biomass mixtures. For the purpose of modeling and as a reference, the fluidization characteristic for silica sand (100 g) was also determined.

Minimum fluidization was determined for individual coal, poplar wood, and their mixtures following the method used by (Li et al., 2003). The pressure drop across the gas
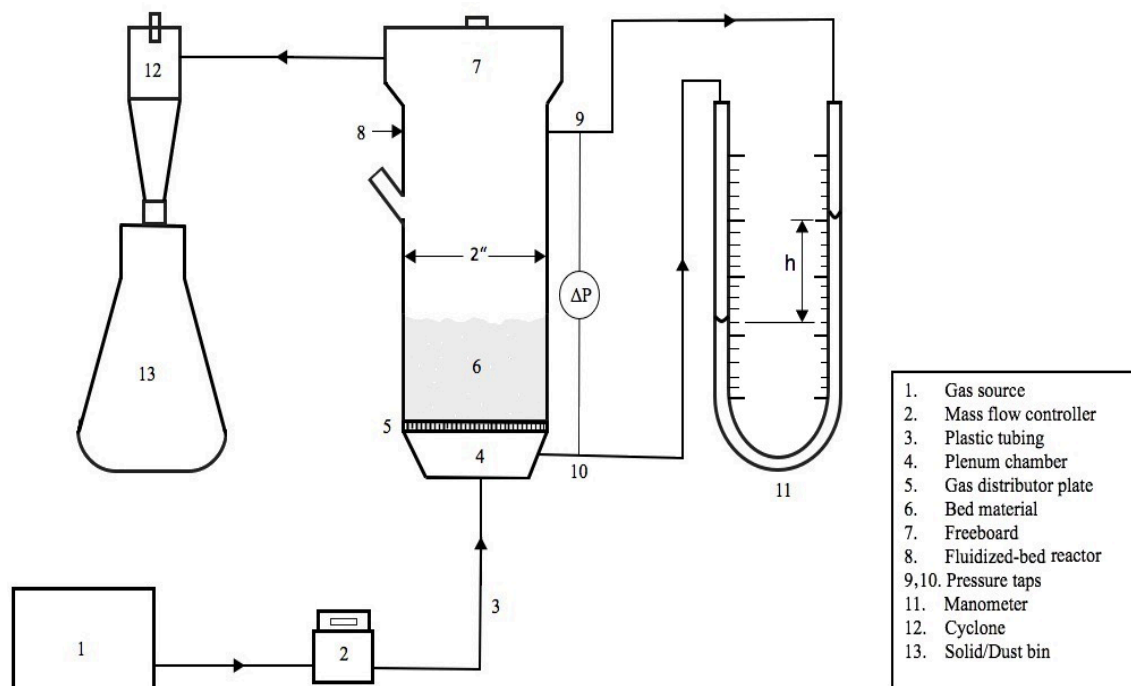
Figure 2.1 Schematic diagram of fluidized-bed setup.

distributor was first determined at all flow rates used when the reactor was empty. This is to correct for pressure drop measurements. Further on, coal and biomass mixtures were thoroughly mixed, unloaded and allowed to fall freely into the fluidization column. Prior to fluidization measurements, the bed was fluidized with gas without any particle transport and the gas was turned off to allow the bed materials to settle. The initial height of the bed was recorded. Following this step, nitrogen was introduced below the distributor plate progressively at a rate of 2 L/min to 14 L/min using an Aalborg mass flow controller (Model GFC 37, Orangeburg, New York, USA) with a range of 0 - 30 L/min and accuracy ±1.5% of full scale. The pressure drop was measured using a manometer filled with distilled water (accuracy of ±0.25).

For defluidization cycle, the gas flow rate was reduced step-by-step at a rate of 2 L/min until the bed settled back to a packed state. For both fluidization and defluidization experiments, the pressure drop measured by the liquid manometer was recorded when the bed reached a stable

state at each flow rate. The initial and final bed heights were recorded and visual observations were made. Solid particles that were transported with the gas stream exiting the freeboard were captured using a cyclone. Each fluidization and defluidization experiment was repeated three times.

Pressure drop across the bed materials was calculated using the empirical formula $\Delta P = \rho_w g h$, where ΔP is the pressure drop, ρ_w is the density of water in manometer, g is gravitational acceleration, and h is the difference in height of water in manometer. Superficial gas velocities were calculated from flow rate recorded by mass flow meter and the area of the fluidizing column. The average bed porosity at minimum fluidization velocity (ε_{mf}) was estimated from the equation, $\varepsilon_{mf = 1- (m_s/\rho_s h_{mf} A_c)}$ where m_s = mass of fluidized solid particles, ρ_s = particle density, h_{mf} = bed height at minimum fluidization, A_c = cross-sectional area of reactor. The particle density of the mixtures was calculated as the sum of individual test materials based on the mass fraction and density.

4. Results and Discussion

4.1 Properties of bed materials

Knowledge about binary mixture fluidization is a critical step towards reaction condition optimization to ensure proper gas-solid contact and increased heat and mass transfer in fluidized bed gasifiers. In this study, the fluidization behavior for coal mixed with different biomass proportions was experimentally determined. Particle size distributions for test materials ranged from 45 - 425 µm and 180 - 425 µm for silica sand.

Particles were categorized according to Geldart's classification based on diameter (Hideki and Yoshinobu, 2006) as follows, pulverized coal: 62 µm (A type), poplar: 153 µm (A type), switchgrass: 145 µm (A type), corn stover: 418 µm (B type) and, sand: 251 µm (B type). Particle density for coal was 1.38 g/cm³, poplar (0.35 g/cm³), switchgrass (0.32 g/cm³), corn stover (0.37 g/cm³), and sand (2.62 g/cm³). Uniform particle size for binary mixtures is ideal

however, particle size reduction is intensive and expensive (Bitra et al., 2009; Mani et al., 2004), and can lead to slugging, non-uniform fluidization, and particle entrainment in cylindrical fluidized beds (Sau et al., 2008).

4.2 Fluidization and defluidization of single bed materials

Pressure fluctuations in fluidized-bed systems play a crucial role in understanding the flow behavior and hydrodynamics of particles (Fan et al., 1983; Leu and Wu, 1992, 2000; Svoboda et al., 1983). In this study, fluidization characteristic was described using pressure drop (ΔP) measured across bed materials and corresponding gas velocities. From Figure 2.2 to Figure 2.5, it can be seen that the individual bed materials (coal and biomass) particles exhibited hysteresis effect.

Hysteresis phenomenon occurs when pressure drop or bed height during fluidization and defluidization gives a different path or are dependent on gas velocity (Heck and Onken, 1987; Peng and Fan, 1995; Zhu et al., 2005). The pressure drop across the coal bed (Figure 2.2) increased with increase in superficial velocity until a maximum of 107 Pa (phase A-B). The bed at this phase behaves like a fixed-bed of which pressure drop is directly proportional to the superficial velocity. Then at the point of incipient fluidization (point B), the ΔP decreased gradually to point C then stabilized at 72 Pa. Partial fluidization occurred at phase B-C where the bed materials start to loosen up and complete fluidization occurred at phase C-D. At complete fluidization, pressure drop remained constant and the solid particles were suspended in the fluidizing gas stream.

The velocity corresponding to the maximum pressure drop (point B) was used as the minimum fluidization velocity (U_{mf}) (Sau et al., 2008). The point of intersection of bed pressure drop versus fluidizing velocity curves for fixed-bed and fluid-bed regime also gives U_{mf} (Kuipers et al., 1991). For defluidization cycle, the ΔP decreased and remained almost constant at 59 Pa
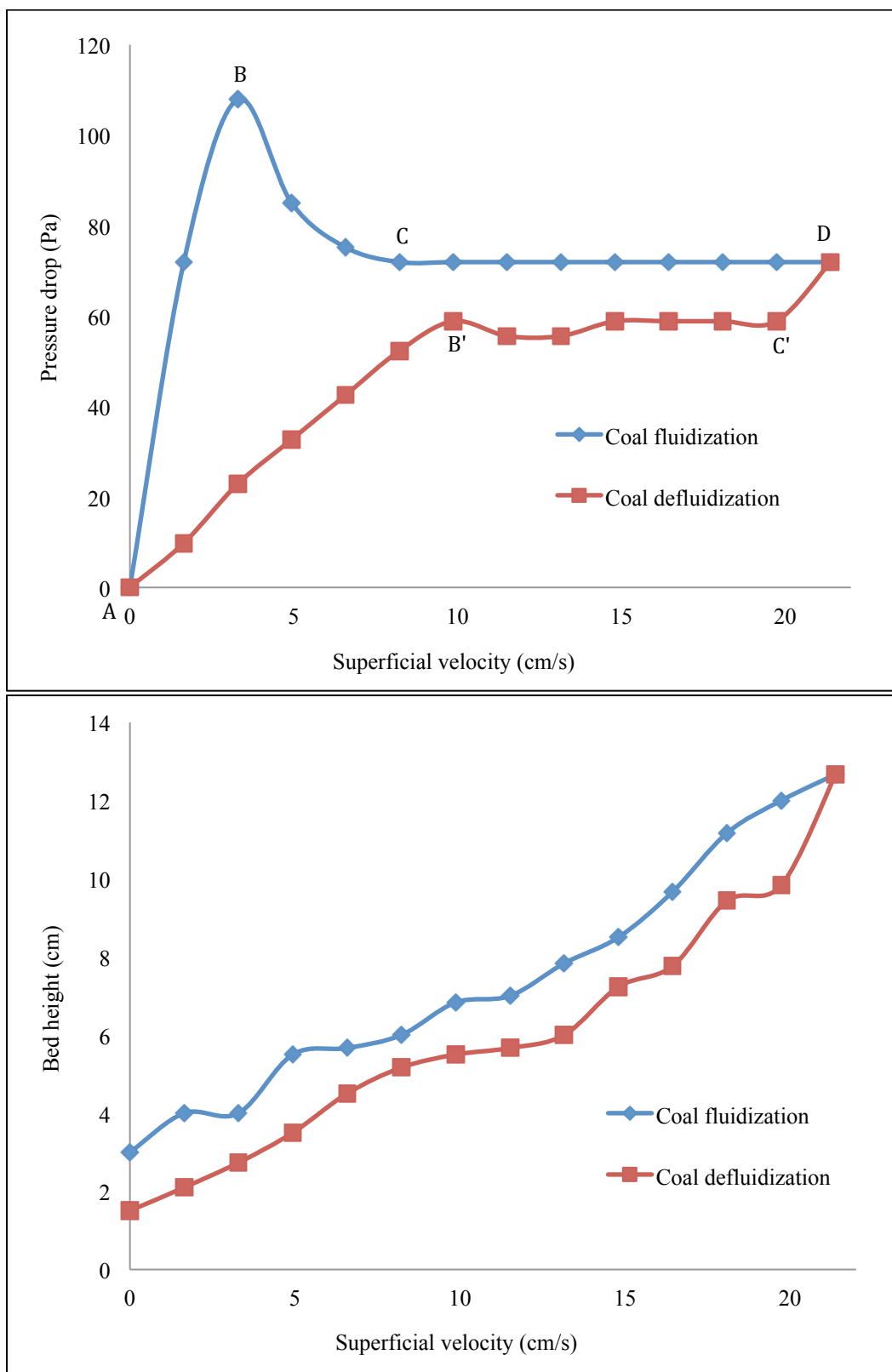
Figure 2.2 Fluidization and defluidization characteristics of sub-bituminous coal.
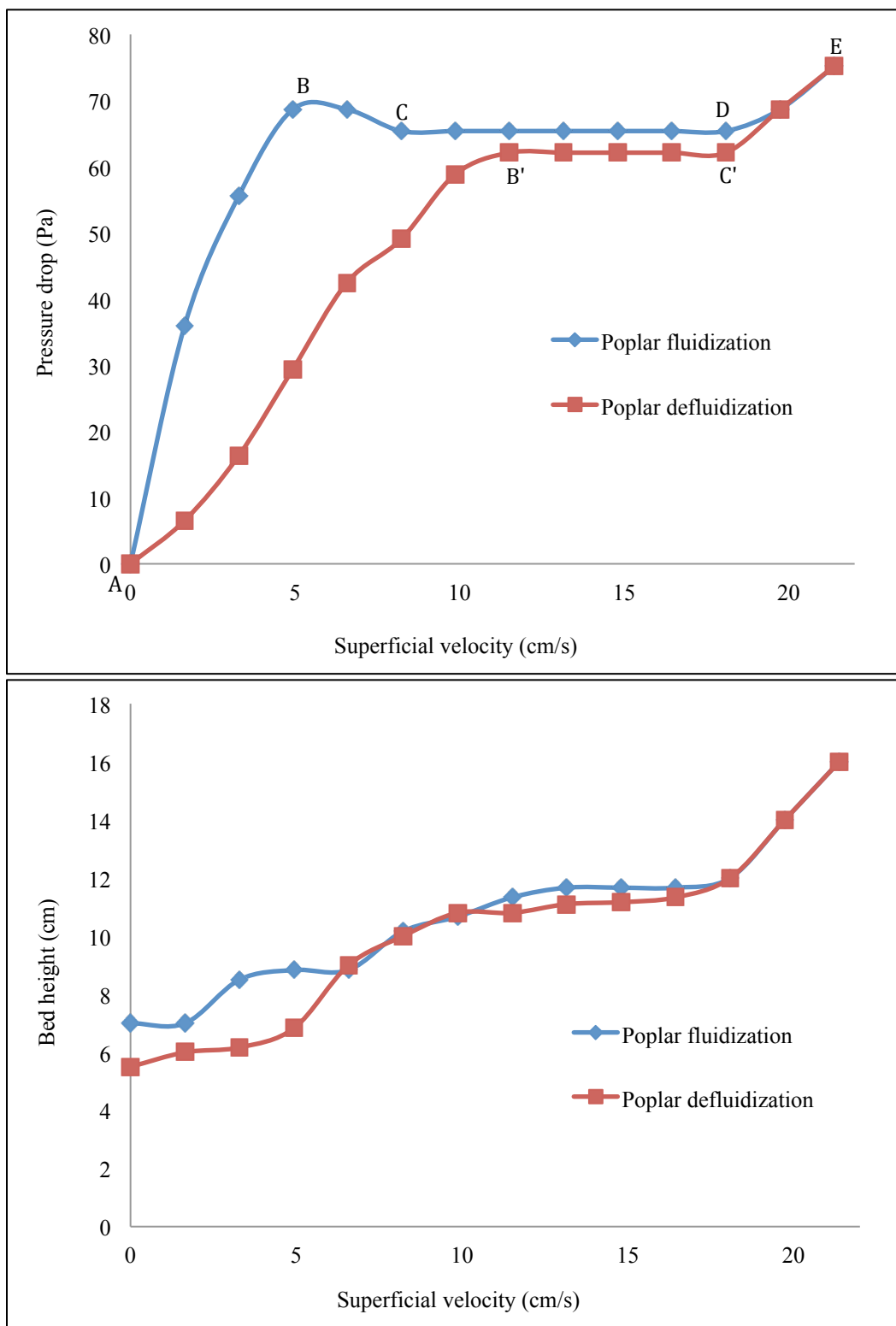
Figure 2.3 Fluidization and defluidization characteristics of hybrid poplar.
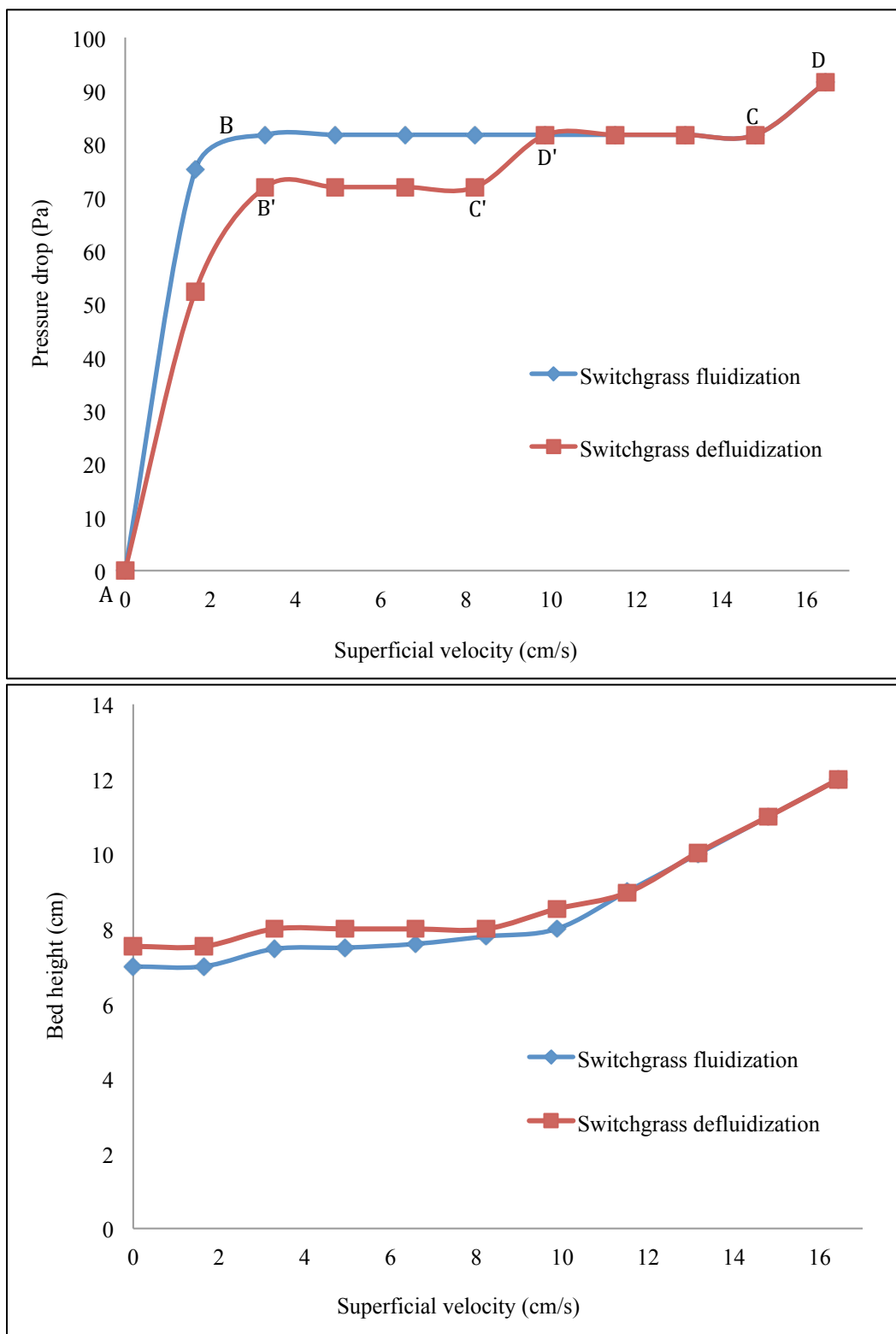
Figure 2.4 Fluidization and defluidization characteristics of switchgrass.
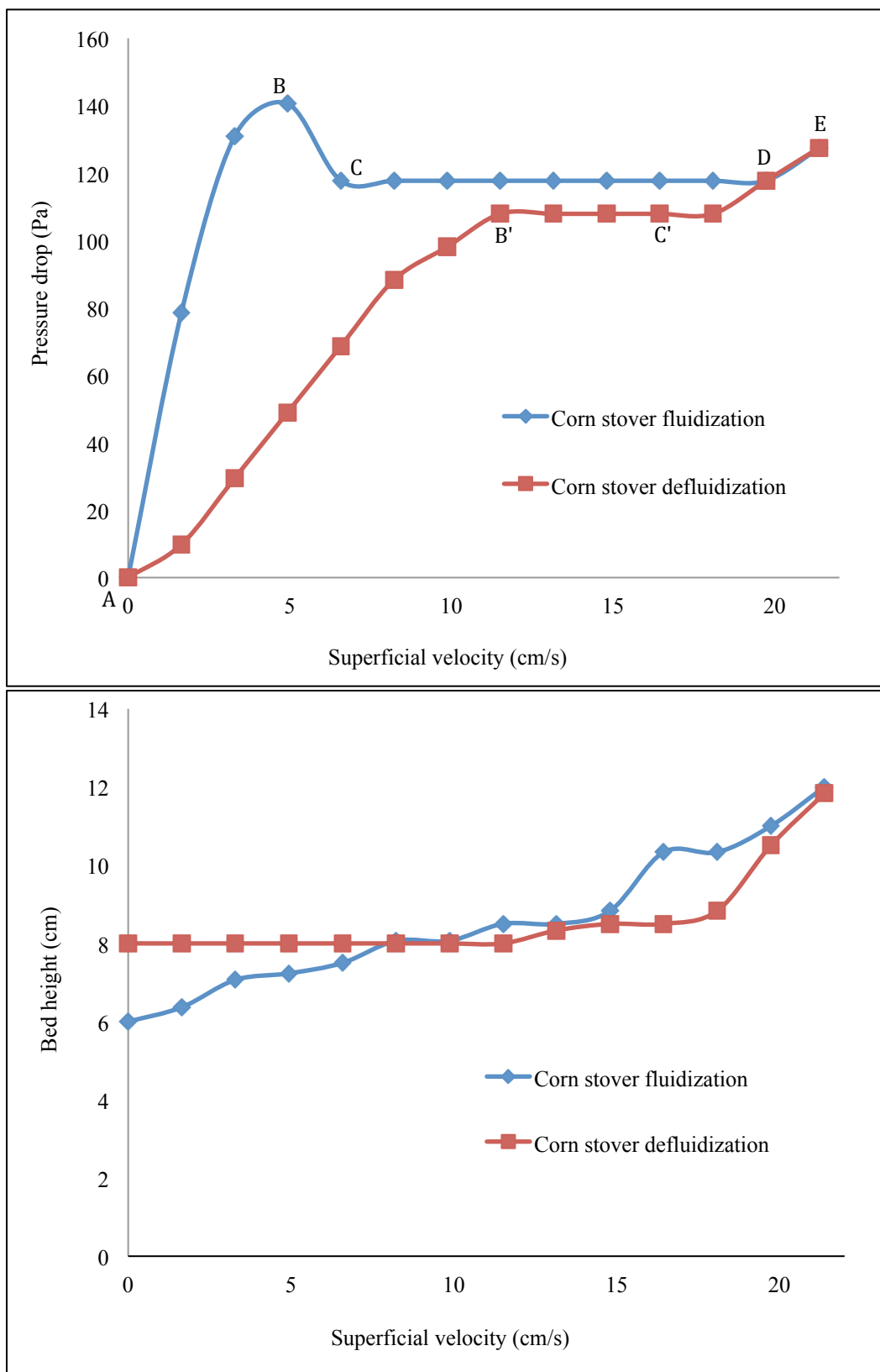
Figure 2.5 Fluidization and defluidization characteristics of corn stover.

(phase C'-B'). Pressure drop fluctuations can cause significant effect in fluidized bed reactors. Also the corresponding bed heights versus superficial velocities confirmed the effect of hysteresis. The hysteresis effect in fluidized beds can be attributed to: a) interparticle cohesive forces, b) particle-sidewall friction, and c) small fluidized-bed diameter (Jackson, 1998; Loezos et al., 2002; Srivastava and Sundaresan, 2002; Tsinontides and Jackson, 1993; Weber and Hrenya, 2007). These factors cause pressure overshoot resulting from yield stress generated between inter-particle and particle-wall interactions during fluidization (Tsinontides and Jackson, 1993). Pressure overshoot was observed in pulverized coal (Figure 2.2), poplar (Figure 2.3), and corn stover (Figure 2.5) bed materials. Pressure overshoot and hysteresis effect are typical of Geldart A particles (Tsinontides and Jackson, 1993; Weber and Hrenya, 2007). Interestingly, no pressure overshoot was observed with switchgrass (Figure 2.4).

Kwauk (1998) suggested that hysteresis can be caused by particle transport in dense phase and jetting in dilute phase in fluidized-beds. Typically, fine particles are transported out of the reactor when the superficial velocity of gas through the bed exceeds the terminal velocity (Kunii and Levenspiel, 1991). This phenomenon is strongly affected by onset of bubbles breakage at bed surface and can also occur at low velocities (Kunii and Levenspiel, 1991). Because of the irregular particle sizes of biomass used, fine particle entrainment was observed which led to about 2 g (6.7 %) of fines transported into cyclone dust collector. Larger particles were transported out of the reactor at velocities beyond complete fluidization regime with increase in pressure drop (phase D-E in Figure 2.3, phase C-D in Figure 2.4, and phase D-E in Figure 2.5). At complete fluidization, the pressure drops for the single test materials followed the order: hybrid poplar < sub-bituminous coal < switchgrass < corn stover.

Fluidization of poplar and switchgrass particles showed characteristic similar to Geldart C particles. With increasing gas flow rate, the bed materials tend to channel (Figure 2.6 to Figure 2.9) at the sidewall of the reactor and center of bed. As a result, there was poor and unstable fluidization up to a certain gas velocity. The formation of channels could be due to irregular
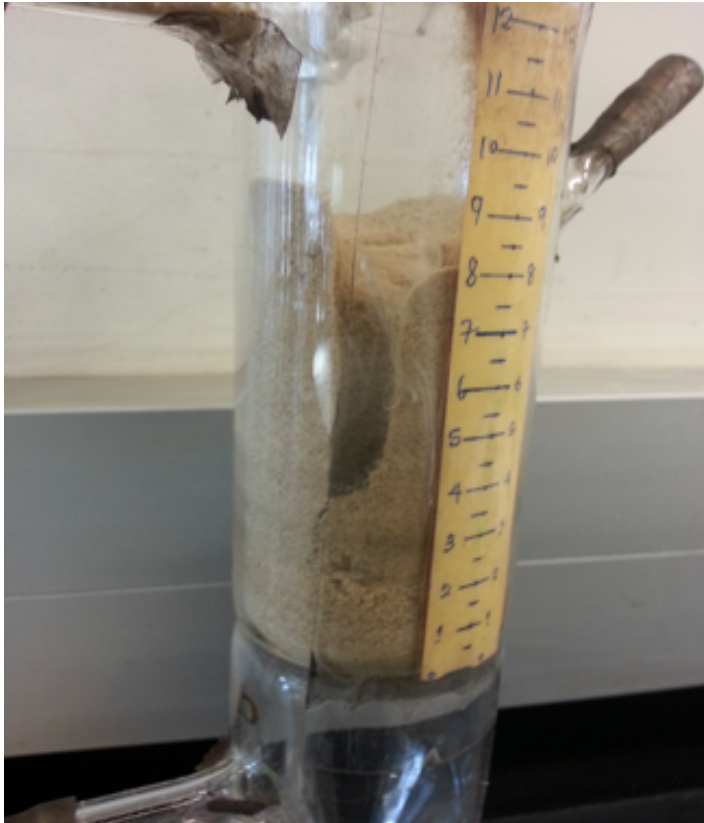
Figure 2.6 Channel in hybrid poplar bed (side view).

Figure 2.7 Channels in hybrid poplar bed (top view).
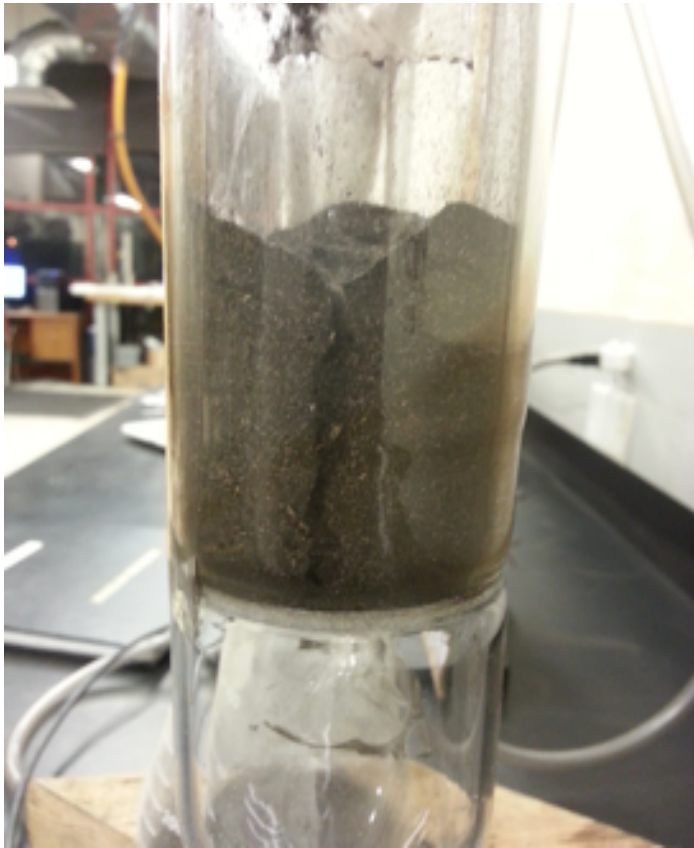
Figure 2.8 Channel effect in coal-poplar (50:50) bed.

Figure 2.9 Channel in switchgrass bed.

shape of the biomass materials (Table 2.1) resulting in the formation of non-uniform mesh. Clarke et al. (2005) studied the fluidization of moist sawdust and glass spheres and observed that sawdust alone showed considerable channeling and poor fluidization properties. Channeling can present challenges such as decreased mass and heat transfer (Wang et al., 2003) and significant pressure drop fluctuations across bed (Kunii and Levenspiel, 1991; Wang and Fan, 2013). The effect of channeling in fluidization systems can present difficulties in the design and scale-up to larger units. The behavior of silica sand fluidization is shown in Figure 2.10. Pressure drop for sand particles increased from zero to 454 Pa at 6.5 cm/s and thereafter remained constant at 454 Pa with increasing superficial velocity.
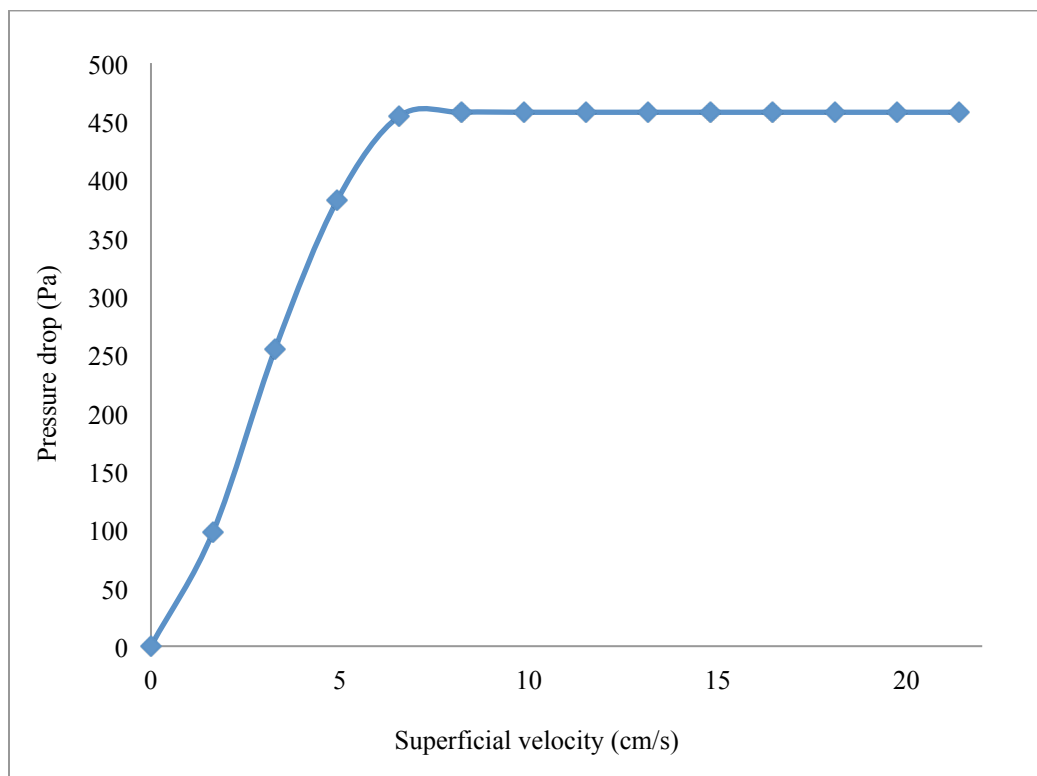
Figure 2.10 Fluidization characteristic of silica sand.

4.3 Fluidization behavior of coal and biomass mixtures

Experimental data on minimum fluidization velocity (U_{mf}), porosity at minimum fluidization velocity (ε_{mf}), maximum pressure drop (ΔP_{max}), and initial and final bed heights are given in Table 2.2. The ε_{mf} values for coal and biomass mixtures increased with increasing biomass content. Maximum pressure drop (ΔP_{max}) data did not show any trend except for coal-poplar mixture where the ΔP_{max} increased from 78 Pa with 10% poplar to a maximum of 141 Pa (20% poplar) then decreased to 78 Pa with 50% poplar composition.

Fluidization characteristics for binary mixtures are shown in Figure 2.11 (coal-poplar), Figure 2.12 (coal-switchgrass), and Figure 2.13 (coal-corn stover). Coal with 10% - 30% poplar and switchgrass composition did not show signs of channeling however the effect of channeling was observed with 40% and 50% biomass content (Figure 2.8). At complete fluidization, pressure drop (ΔP) for coal-biomass mixtures were higher than ΔP for single coal and biomass. A simple reason is put forward to explain this event: biomass particles are irregular in shape and easily interlace and interlock to form a mesh that trap fine coal particles. The entrapment of smaller particle in the mesh causes the bed mass to become heavier requiring a higher pressure to break the mesh for full fluidization to occur. The mechanistic behavior of particle interlocking was reported by other researchers (Pattipati and Wen, 1981; Reina et al., 2000).

In the complete fluid regime, ΔP for 20%, 30%, and 40% coal-poplar mixtures (Figure 2.11), were considerably higher than corresponding ΔP for 10% and 50% poplar composition. Figure 2.12 shows a completely different trend for 30%, 40%, and 50% switchgrass composition. Their fluidization curves changed significantly with increasing superficial velocity, however the ΔP for 40% composition reached a maximum value of 130 Pa at 8.0 cm/s superficial velocity before stabilizing.

In case of coal-corn stover fluidization (Figure 2.13), the ΔP for 30% and 40% corn stover composition were constant at 128 Pa whereas ΔP for 10%, 20% and 50% mixtures were

Table 2.2 Experimental fluidization results for mixtures of coal-biomass bed materials.

Material	Biomass (%)	U_{mf} (cm/s)	ε_{mf}	ΔP_{max} (Pa)	Bed Height (cm)	
					Initial	Final
Silica sand	0	6.6	0.42	457.80	3.0 ±0.0	3.0 ±0.0
Coal	0	3.2	0.64	107.91	3.5 ±0.3	1.5 ±0.2
Poplar	100	4.9	0.86	68.67	7.5 ±0.1	5.5 ±0.4
Coal-poplar	10	2.1	0.75	78.48	3.5 ±0.1	3.4 ±0.2
Coal-poplar	20	4.1	0.78	140.61	4.1 ±0.1	3.9 ±0.1
Coal-poplar	30	2.5	0.80	117.72	4.3 ±0.1	5.9 ±0.1
Coal-poplar	40	3.4	0.81	114.45	4.4 ±0.2	6.1 ±0.1
Coal-poplar	50	4.9	0.82	78.48	5.0 ±0.1	6.4 ±0.1
Switchgrass	100	2.0	0.83	81.75	7.0 ±0.2	7.5 ±0.1
Coal-switchgrass	10	3.6	0.75	117.72	3.9 ±0.1	4.1 ±0.1
Coal-switchgrass	20	2.0	0.80	117.72	4.3 ±0.1	5.3 ±0.5
Coal-switchgrass	30	6.4	0.80	120.99	4.6 ±0.1	5.7 ±0.3
Coal-switchgrass	40	7.0	0.81	137.34	4.4 ±0.1	6.0 ± 0.2
Coal-switchgrass	50	6.4	0.83	101.37	4.8 ±0.2	6.4 ±0.2
Coal-corn stover	100	4.4	0.83	140.61	6.0 ±0.2	8.0 ±0.2
Coal-corn stover	10	5.2	0.79	117.72	3.7 ±0.2	3.9 ±0.1
Coal-corn stover	20	4.9	0.82	117.72	4.0 ±0.0	4.4 ±0.1
Coal-corn stover	30	4.9	0.84	127.53	4.5 ±0.1	4.8 ±0.3
Coal-corn stover	40	4.9	0.84	127.53	4.6 ±0.2	5.5 ±0.4
Coal-corn stover	50	4.9	0.84	117.72	5.1 ±0.1	5.7 ±0.3

U_{mf} – minimum fluidization velocity, ε_{mf} – porosity at minimum fluidization, ΔP_{max} – maximum pressure drop
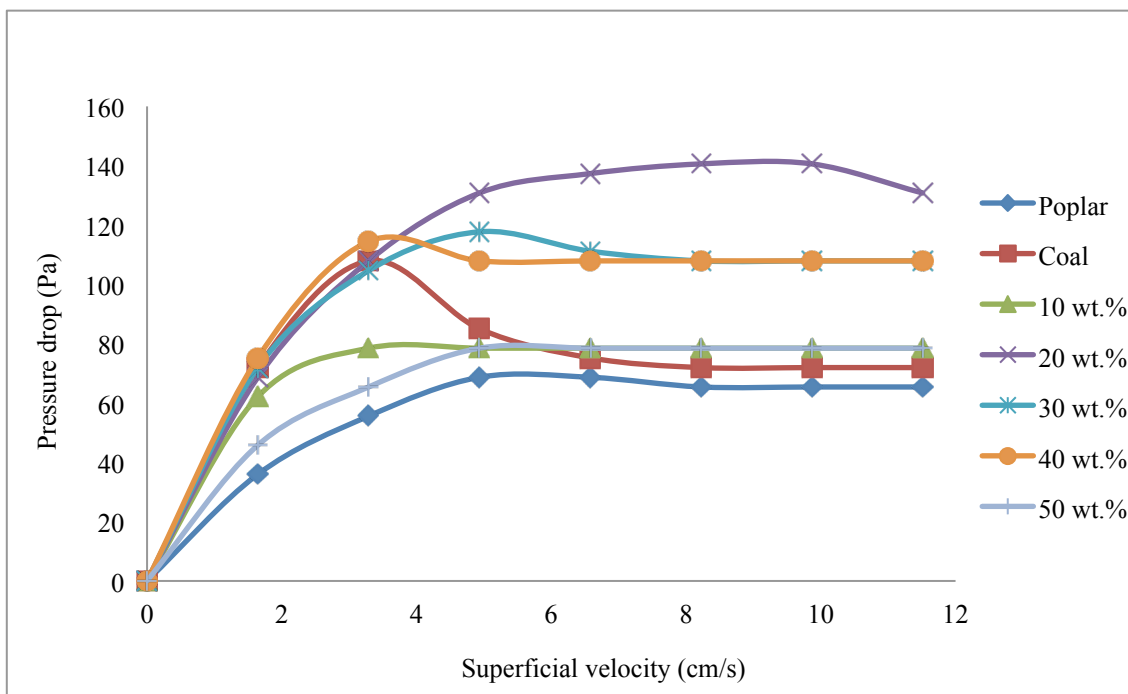
Figure 2.11 Fluidization characteristics of sub-bituminous coal mixed with 0-50 wt.% hybrid poplar.
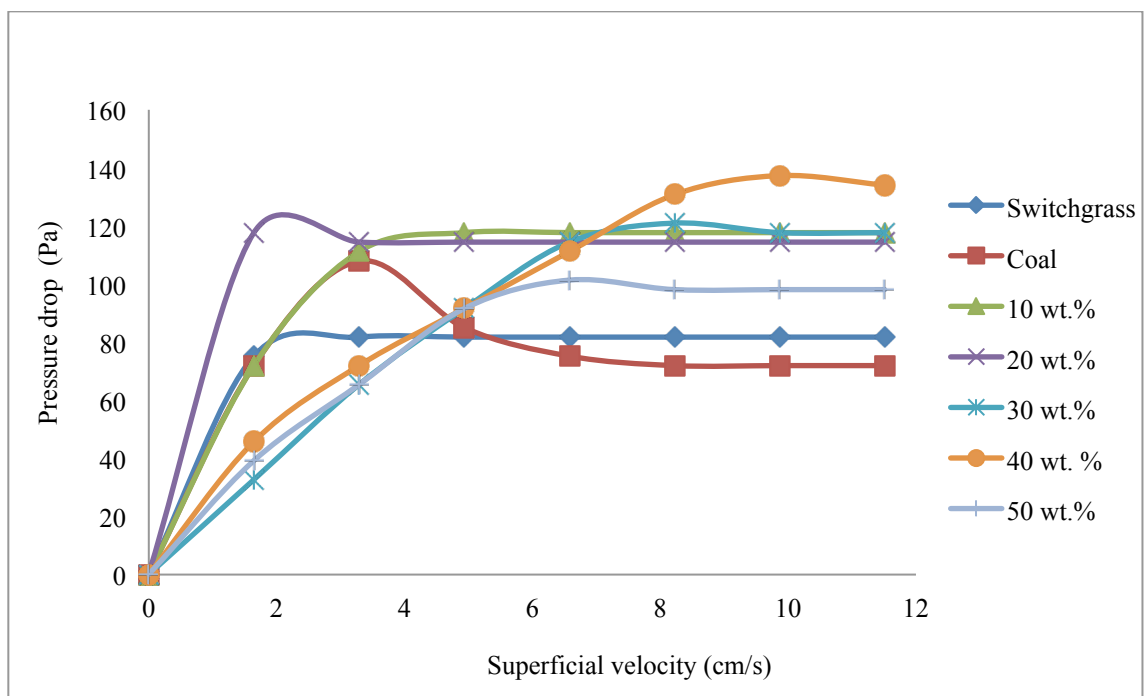
Figure 2.12 Fluidization characteristics of sub-bituminous coal mixed with 0-50 wt.% switchgrass.
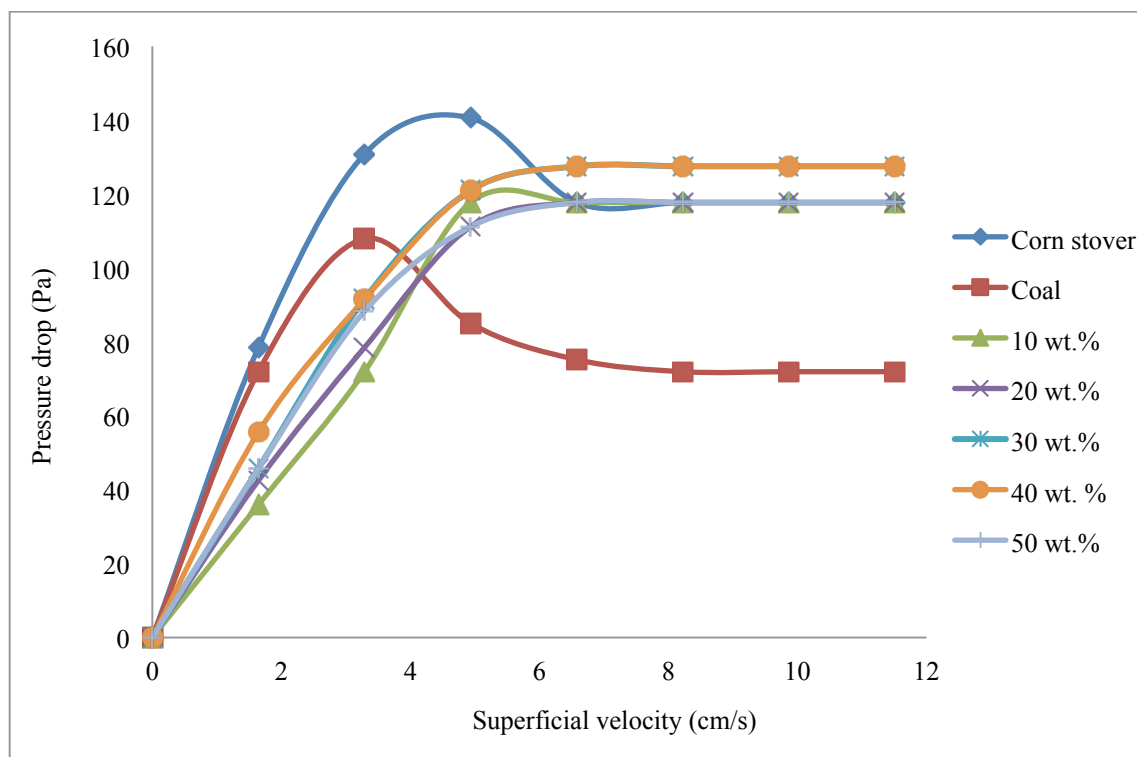
Figure 2.13 Fluidization characteristics of sub-bituminous coal mixed with 0-50 wt.% corn stover.

similar to ΔP of corn stover alone. This could be due to differences in particle size between coal and corn stover. Furthermore, there appeared to be interaction between coal and various biomass mixtures. The pressure overshoot observed with coal and biomass mixtures were minimal compared to the pressure overshoot observed for single bed materials.

The influence of biomass ratios on U_{mf} values shown in Table 2.2 suggests that the U_{mf} for coal-biomass mixtures vary depending on biomass type and composition. No specific trend was observed with increase in biomass content. With the exception of coal-corn stover mixtures (Figure 2.13), the transition behavior of the binary bed materials for coal-poplar (Figure 2.11) and coal-switchgrass (Figure 2.12) varied greatly from fixed-bed phase to complete fluidization

phase. The lack of trend in U_{mf} data for these binary materials could be due to the concentration and distribution of solid particles in the fixed-bed (Formisani et al., 2008). In all cases of coal-biomass study, the binary mixture mixed partially with increasing gas flow rate. However there was complete mixing at complete fluidization. Formisani et al., 2008 observed that binary mixture fluidization and bubbling are simultaneous processes rather than sequential which leads to component segregation before the entire bed of particulate is fully fluidized. Thus, the U_{mf} for binary mixtures vary significantly with particle distribution in a fixed-bed.

From Table 2.2, coal with 10% poplar composition gave the lowest U_{mf} value (2.1 cm/s) and highest U_{mf} value (4.9 cm/s) with 50% poplar content. For coal-switchgrass mixtures, 20% switchgrass composition gave the smallest U_{mf} of 2.0 cm/s whereas 40% switchgrass composition gave the largest U_{mf} of 7.0 cm/s. In exception of 10% corn stover concentration (U_{mf} = 5.2 cm/s), the U_{mf} values for coal-corn stover mixtures remained constant at 4.9 cm/s.

5. Conclusions

Based on the experimental investigation of this study, the following conclusions were drawn:

(1) Single coal and biomass test materials exhibited significant hysteresis and pressure overshoot. Bed height versus superficial velocity plots showed evidence of hysteresis.

(2) The pressure drops for coal-biomass mixtures were higher than the pressure drops for single coal and biomass bed materials in the complete fluidization regime.

(3) The U_{mf} values for coal-biomass mixtures showed no trend with biomass content, however the ε_{mf} values increased with increase in biomass content.

(4) For 40 wt.% and 50 wt.% hybrid poplar and switchgrass content in coal, there was channeling at low gas flowrates.

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CHAPTER 3

CO-GASIFICATION OF SUB-BITUMINOUS COAL WITH CORN STOVER USING A

FLUIDIZED BED

1. **Abstract**

Co-gasification of sub-bituminous coal and corn stover was studied in a bench-scale bubbling fluidized bed gasifier using N_2 and CO_2 as fluidizing gases. This study was designed to investigate the potential of using corn stover, a renewable waste material as feedstock for low-temperature coal gasification. Results showed that the char reactivity and tar cracking of coal and corn stover mixtures increased with increasing temperature, which led to increase in product gases. Minor interactions were observed between coal and corn stover reactivity at 700°C with low biomass content. Coal and corn stover mixtures formed agglomerates of different sizes and shapes at 800°C and 900°C. The agglomeration effect increased with increase in corn stover content at magnitudes that can limit operations of coal gasification using fluidized bed. H_2 yields were more pronounced at 900°C (41 vol.%) in N_2 gasification medium and 25 vol.% at 700°C in CO_2 medium with 10 wt.% biomass. Overall, syngas (H_2 + CO) concentration was dominant in the product gases especially in CO_2 gasification medium.

2. **Introduction**

In recent years, the effect of global warming caused by greenhouse gases resulting in climate change (Kokic et al., 2014) has received tremendous attention. Coal-fired power plants have been identified as major source of environmental pollution (Kahn, 2009). These concerns have stimulated the search for alternative methods of producing clean energy from coal.

Coal, a cheap energy source is commonly utilized for electricity generation and heating homes. In 2013, coal is the largest source (39%) for electricity generation in the United States following by natural gas (27%), nuclear (19%), renewables (6%), petroleum (1%) and other

minor gases (< 1%) (EIA, 2014b). According to estimates, 257 billion short tons (1 short ton = 2,000 pounds) of recoverable coal exist in the United States (EIA, 2014a). Despite existing coal reserves, coal is still considered one of the dirtiest forms of energy (Emami-Taba et al., 2013).

About 238 million dry tons of corn stover are generated in the United States each year (Sokhansanj et al., 2002). Large quantities and relatively low cost of production make corn stover a potential domestic energy feedstock. In addition, using corn stover as lignocellulosic biomass feedstock material is advantageous because it has no direct impact on food production.

Several studies have been carried out with coal and biomass using fluidized-beds (Aigner et al., 2011; Mastellone et al., 2010; McLendon et al., 2004; Sjöström et al., 1999). Many of these works concluded differently. The fundamental reason being that biomass comes in varieties and their physical and chemical properties differ greatly and this may explain the different findings.

Aigner et al. (2011) co-gasified coal and Austrian wood pellets in a dual fluidized-bed gasifier. They found that the product gas composition correlated linearly with coal/wood ratios. They also observed that H_2 concentrations increased with decreasing wood ratio whereas CO decreased. Mastellone et al. (2010) studied co-gasification of pelletized mixtures of coal, wood, and plastic wastes in a bubbling fluidized-bed. Their results showed that the ternary mixture showed reduction in both tar production and specific energy of the syngas produced. McLendon et al. (2004) and Sjöström et al. (1999) co-gasified coal and biomass in a pressurized fluidized-bed gasifier. McLendon et al. (2004) did not observe any discernible synergies between sub-bituminous coal and biomass mixtures; however, Sjöström et al. (1999) saw increased reactivity in gasification process using mixtures of the two feedstocks.

At present, numerous biomass feedstocks have been co-gasified with coal however there are very limited reports on coal-corn stover gasification. Therefore this work was aimed at investigating the effect of corn stover blends with sub-bituminous coal on product distribution and product gas compounds at low co-gasification temperatures.

3. Experimental

3.1 Coal and biomass sample

The chemical composition and calorific value of coal and corn stover biomass are presented in Table 3.1. Pulverized sub-bituminous coal from Powder River Basin (North Antelope Rochelle Mine, Wyoming, USA) was used in the experiment. Corn stover biomass was obtained from Idaho National Laboratory (INL) (Battelle Energy Alliance, LLC, Idaho Falls, USA). The biomass was ground using a Thomas-Wiley® mill (Model # 3375-E15) to pass through a 1-mm

Table 3.1 Properties of sub-bituminous coal and corn stover.

	Coal	Corn stover
Proximate analysis (wt.%)		
Moisture	22	5.14 ±0.03
Ash	4.94	8.51 ±0.44
Fixed Carbon	38.01	14.6 ±0.10
Volatiles	33.36	71.75 ±1.08
Ultimate analysis (wt.%)		
Carbon	53.72	43.07 ±0.50
Hydrogen	6.22	5.77 ±0.15
Nitrogen	0.78	1.26 ±0.25
Sulfur	0.23	0.04 ±0.01
Oxygen[a]	34.11	41.35
HHV (MJ/kg)	21.12	17.21 ±0.13

Oxygen[a] was determined by difference

sieve. Ultimate analysis was performed with organic elemental analyzer (Model: Flash 2000, Thermo Scientific). Moisture content of coal was determined according to ASTM D-3173 (1996).

Ash and moisture content of biomass were carried out according to ASTM E1755 (2010) and ASTM E1756 (2010) standards, respectively.

3.2 Apparatus and experimental procedure

Co-gasification experiments were performed in a bench-scale bubbling fluidized-bed designed to operate under a wide range of operating conditions at atmospheric pressure. Silica sand was used as bed material. Nitrogen (N_2) and a bone-dry carbon dioxide (CO_2) gas were used as fluidizing gases. Figure 3.1 shows a schematic diagram of experimental fluidized-bed unit. The fluidized bed gasifier is 5 cm (2 in) in diameter and 50 cm (20 in) in height including a 14 cm (5.5 in) preheating zone. The preheating zone was packed with Berl saddles. A temperature well, starting just above the distributor plate provide for insertion of thermocouples (K-type, Omega Engineering, Inc., Stamford, CT, USA) to monitor reactor temperatures.

A 100-µm porous metal distributor plate above the preheater zone ensured uniform distribution of fluidizing gas. The reactor was externally heated using three-zone electric furnace (Model: 2334-22-3ZV, Thermcraft Inc. Winston-Salem, North Carolina). The gasification reactor was heated to reaction temperature and the bed material was fluidized with fluidizing gas. Temperatures investigated were 700°C, 800°C, and 900°C. When the bed reached a stable temperature, feed was introduced into the reactor at a rate of 200 g/h using a volumetric twin-screw feeder (Model: K2VT20, K-tron, Pitman, New Jersey, USA).

Sub-bituminous coal and biomass were prepared in the proportion of 100:0, 90:10, 80:20, 70:30, 60:40, and 50:50 (weight basis) respectively. The feed was moved by a K-tron screw feeder (Model: K2VT20, K-tron, Pitman, New Jersey, USA) into the entrainment zone where feed was swept into the reactor using high-velocity co-gasification gas. Feeding rate, gas flow
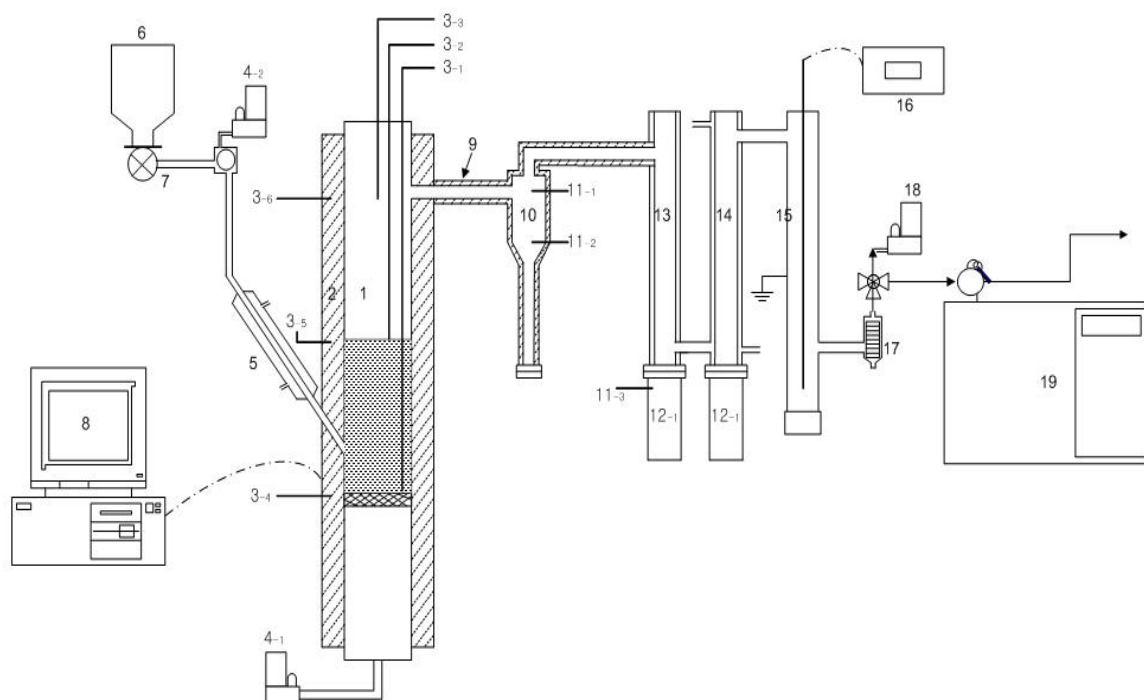
Figure 3.1 Experimental set-up of bench-scale fluidized bed unit.

1-fluidized bed reactor, 2-furnance, 3; 11-thermocouple, 4-mass flow controller, 5-jacketed air-cooled feeder tube, 6-hopper, 7-twin screw feeder, 8-computer, 9-heating tape, 10-high temperature filter, 12-reservoir, 13; 14-condenser, 15-electrostatic precipitator (ESP), 16-AC power supply, 17-coalescing filter, 18-wet gas meter, 19-gas chromatography.

Table 3.2 Operating conditions of fluidized bed reactor.

Parameter	Notes
Experimental time	60 min
Feed rate	200 g/h
Reactor temperature	700°C, 800°C, 900°C
Reactor diameter	5 cm (2 in)
Reactor height /including preheating zone	50 cm (20 in) / 14 cm (5.5 in)
Bed material	Silica sand (100 g)
Fluidizing medium	N_2, CO_2
Residence time	3 s
Superficial velocity	2 x minimum fluidization velocity

rate, and bed temperature were kept constant throughout the experiment. Operating conditions and parameters are given in Table 3.2. The vapor (condensable and non-condensable) exiting the reactor passed through a high-temperature filter (Mott Corporation) to separate char and any entrained bed material. The cleaned vapor was then directed via two series of ethylene glycol-cooled condensers kept below 10°C. Vapors that condense were collected as liquid fractions. Non-condensable vapor exiting the condensers were further passed through an electrostatic precipitator (ESP) maintained at 18-20 kV. The ESP ionizes and captures aerosols that escape the condenser.

The product gas leaving the ESP was passed through a coalescing filter and the total gas was measured with a Top-Trak™ mass flow meter before analysis with an online micro gas chromatography (micro-GC) (Varian 490, Agilent Technologies). The micro-GC was equipped with two columns (10-m PoraPLOT U column and 10-m Molsieve 5Å column). The product gas

was analyzed for hydrocarbons (C_2-C_4) and CO_2 gases with PPU column whereas CH_4 and permanent gases (H_2, N_2, CO) were analyzed using Molsieve 5Å column.

3.3 Yield calculation and mass balance

Overall material balance was determined by weighing each gasification unit before and after experiment. Co-gasification product yields were calculated on dry basis using the method described by Westerhof et al. (2007) below:

$$\text{Yield}_{dry} \ (\%) \ =$$

$$\frac{(\text{kg of product formed})}{[\text{kg of feed (as received) consumed} \times (1 - \text{feed moisture content})]}$$

Therefore, total mass =

$$\sum[\text{Char } + \text{ gasification liquid (organics } + \text{ total water) } + \text{ gas}]$$

Synergetic effects were checked for by comparing experimental product yields (Expt.) to predicted product yields (Pred.). Predicted product yields were based on yields of individual coal and biomass product and experimental yields are those obtained from co-gasifying coal-biomass mixtures. Predicted product yields were calculated using the equation below.

$$Y_x \ (\%) = \ \left(\frac{R}{100}\right) \times Y_{biomass} + \frac{(1-R)}{100} \times Y_{coal}$$

where

Y_x = predicted product yield for mixture of biomass and coal

R = blend of biomass in percentage

$Y_{biomass}$ = product yield from gasifying biomass (R = 100%)

Y_{coal} = product yield from gasifying coal (R = 0%)

Synergy or synergetic effect as used in this study refers to interaction of coal and biomass to produce a combined effect on product gas greater than the sum of their (coal and biomass) separate effects and a combined effect on char and tar lower than the sum of their separate effects. This implies that yields for product gas and gas compounds obtained from co-gasification experiment (Expt.) should be greater than corresponding predicted yields (Pred.) within experimental error. Likewise, char and tar product yields should be lower than corresponding predicted yields.

4. Results and Discussion

Co-gasification results on sub-bituminous coal and corn stover mixtures are presented on char yield, liquid (tar and water) yield, product gas yield, and product gas composition. All experiments were conducted in triplicates. Mean values were calculated with standard deviations, unless otherwise stated.

4.1 Effect of co-gasification temperature

The product yields obtained from corn stover gasification in N_2 and CO_2 gasification medium are shown in Table 3.3. Char yields obtained using CO_2 gasification medium were about twice as high as char yields from N_2 medium. In contrast, tar yields observed in CO_2 medium were lower than in N_2 medium. In general, the yields of char and tar decreased with increasing temperature with corresponding increase in product gas yields. Corn stover product gas yield in nitrogen medium increased from 51 wt.% (all product yields are dry wt.%) at 700°C to 82 wt.% at 900°C and in CO_2 medium, gas yield increased from 48 wt.% at 700°C to 63 wt.% at 900°C. High temperatures promoted gasification of char and tar molecules which led to increased product gas.

The effects of temperature on char, tar and product gas yields were similar for coal gasification and coal-corn stover co-gasification in N_2 medium (Table 3.4) and CO_2 medium (Table 3.5). It can be seen that there is tremendous degree of variations between the product

yields between single coal and corn stover feedstocks. This is expected because the volatile content for corn stover (Table 3.1) is higher than coal. The effect of temperature on the distribution of product yields for 0-50 wt.% corn stover in coal are shown in Figure 3.2 to Figure 3.5 (N_2 medium) and Figure 3.6 to Figure 3.9 (CO_2 medium).

4.2 Effect of corn stover biomass

An appreciable reactivity between coal and corn stover was expected due to the level of minerals present in both feedstocks. However, the presence of these minerals when corn stover (~9% ash) was mixed with coal (~5% ash) promoted the formation of agglomerates (ash sticking effect) of different sizes and shapes. Agglomerates formation were severe at 800°C and 900°C. Photographs of agglomerates of silica sand before and after coal-corn stover co-gasification experiment are shown in Figure 3.10. Agglomeration phenomenon occurs when alkali species in the ash of feedstock interact with fluidized bed material (silica sand) under high temperature conditions to form low-melting point eutectics (Shiyuan et al., 2010). The alkali species are mainly due to oxides (Na_2O, K_2O, CaO) (Gao et al., 2009), which are catalytically active (Kern et al., 2013).

In this study, large chunks of eutectics were collected from the reactor after each experiment and the magnitude of formation increased with increasing corn stover content. Mostly, it required some effort to remove the eutectics as it adhered to the surface of the reactor. Formation of agglomerates may have caused loss of fluidization (Lin and Wey, 2004) resulting in poor heat and mass transfer (Parveen et al., 2013) during co-gasification experiments. As a result, lower product gas yields were obtained from experiment (Expt.) compared to predicted (Pred.) product gas yields (Table 3.4 and Table 3.5).

Agglomeration phenomenon can occur even when the temperature is below ash fusion point (Basu and Sarka, 1983). The presence of K, Na, and Ca compounds lower ash melting temperatures (Bell et al., 2011). Lin et al. (2003) observed defluidization caused by

agglomeration when they processed straw in a laboratory-scale fluidized-bed. They also reported that temperature had a significant influence on formation of agglomerates that led to defluidization. They concluded that increase in temperature increased the ash melt and reduced the viscosity of ash melt. In a gasification study, Fryda et al. (2008) observed that giant reed (*Arundo donax* L.) and sweet sorghum had defluidization temperatures of ~790°C and ~810°C respectively.

Despite formation of agglomerates, coal reactivity increased with increase in corn stover content. As presented in Table 3.4 and Table 3.5, char yields for coal-corn stover mixtures were lower than those of single coal. The experimental product yields were additive compared to predicted values. In Table 3.5, char yields with 10 – 20 wt.% corn stover were 3% to 10% lower than predicted char yields indicating minor synergetic effects. The effect of synergy occurred at 700°C and 800°C. However, synergetic effects diminished with increasing biomass content and temperature. Similar observations of decreasing interaction between coal and biomass with

Table 3.3 Product yield (dry wt.%) for corn stover gasification.

Temp. (°C)	Char	Water	Tar	Gas
Nitrogen (gasification medium)				
700	11.37 ±1.21	19.01 ±0.92	16.77 ±1.01	50.84 ±1.65
800	6.80 ±0.97	20.22 ±1.05	5.44 ±0.89	66.00 ±1.02
900	4.49 ±1.12	10.65 ±0.76	1.70 ±0.11	81.99 ±0.99
Carbon dioxide (gasification medium)				
700	18.20 ±1.34	25.32 ±0.56	6.48 ±1.13	48.35 ±0.65
800	12.37 ±1.65	24.02 ±1.19	4.08 ±0.28	57.91 ±1.09
900	9.83 ±0.52	25.08 ±0.62	1.00 ±0.31	63.37 ±1.75
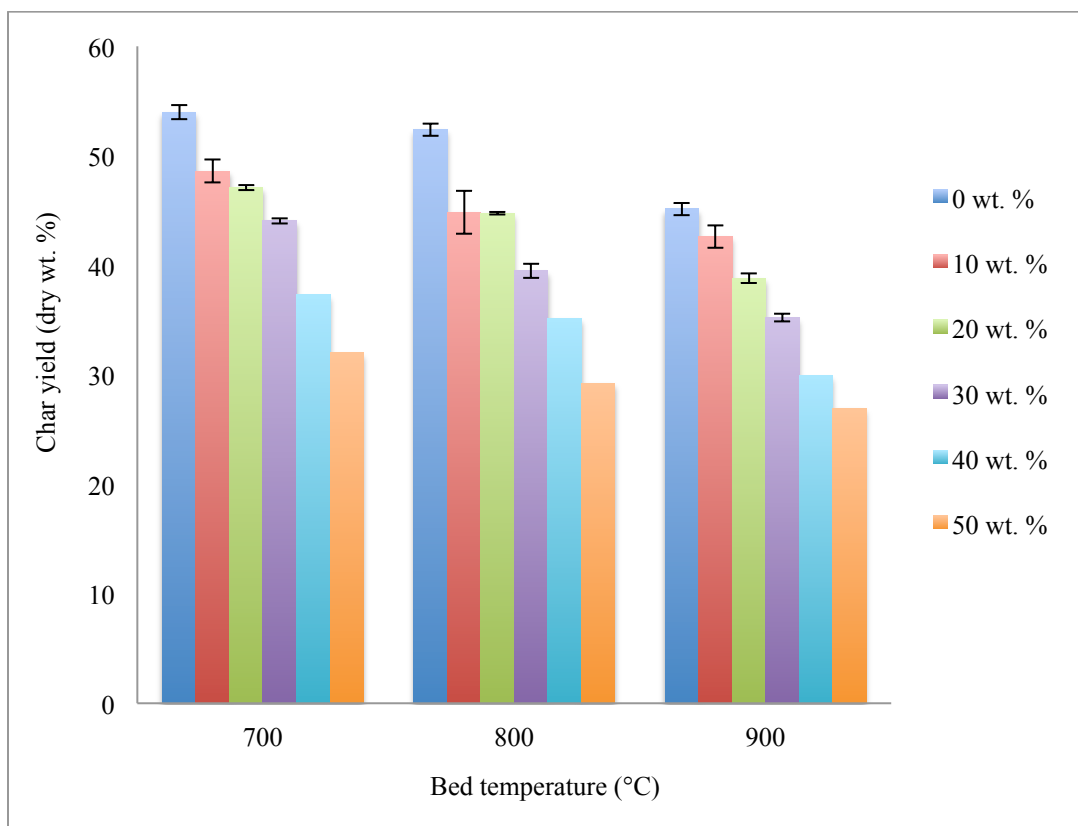
Figure 3.2 Effect of bed temperature and corn stover content on char yield in N_2.
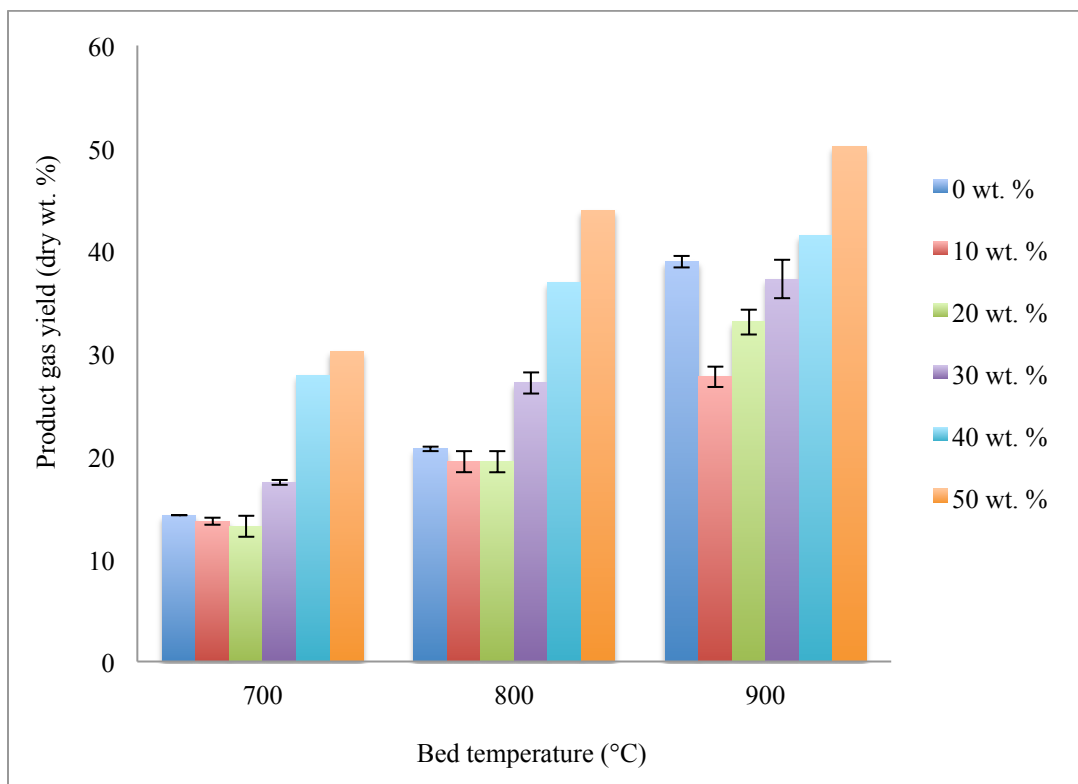
Figure 3.3 Effect of bed temperature and corn stover content on product gas yield in N_2.
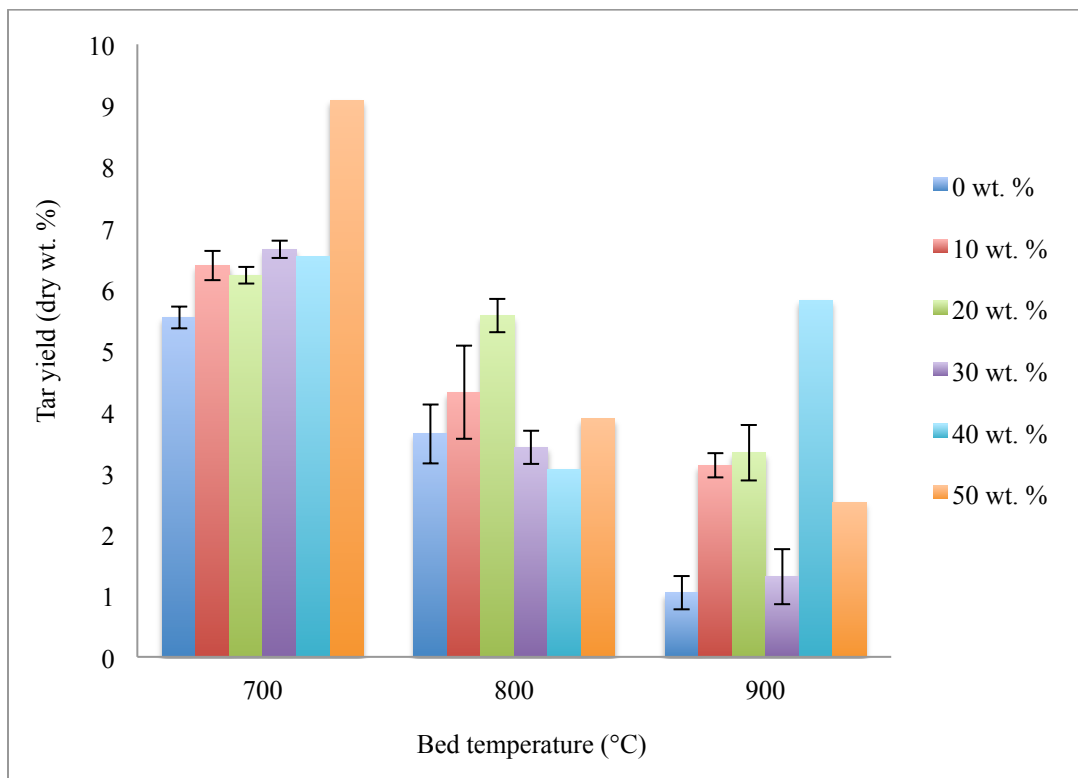
Figure 3.4 Effect of bed temperature and corn stover content on tar yield in N_2.
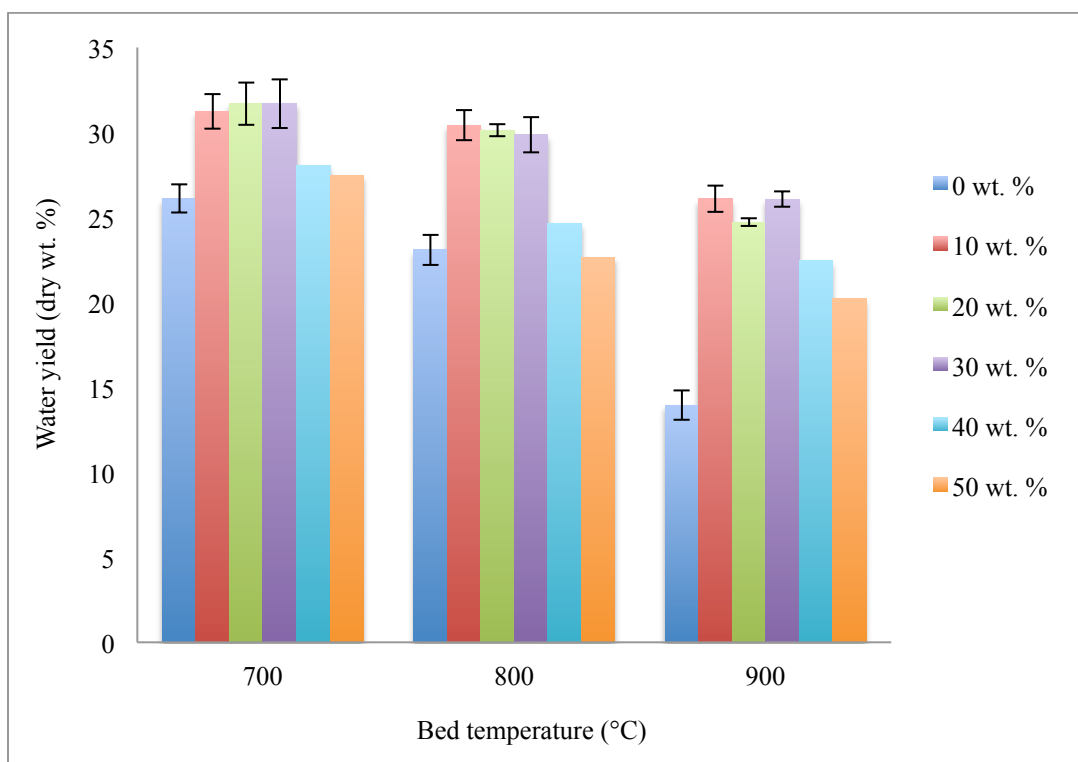
Figure 3.5 Effect of bed temperature and corn stover content on water yield in N_2.
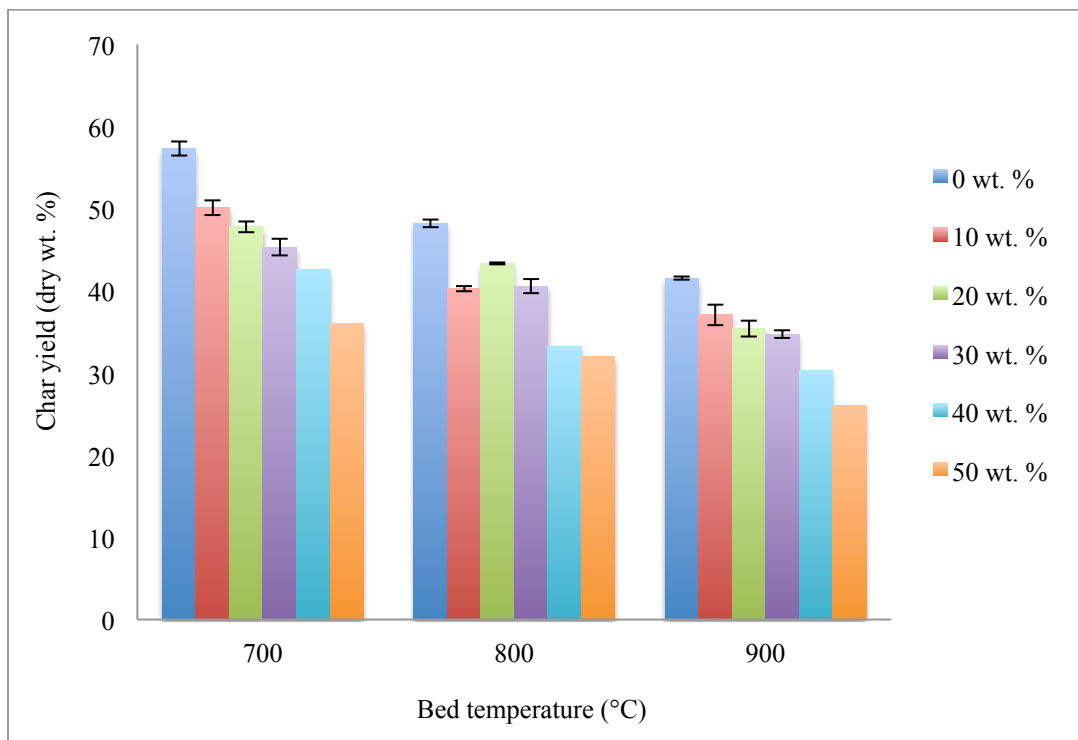
Figure 3.6 Effect of bed temperature and corn stover content on char yield in CO_2.
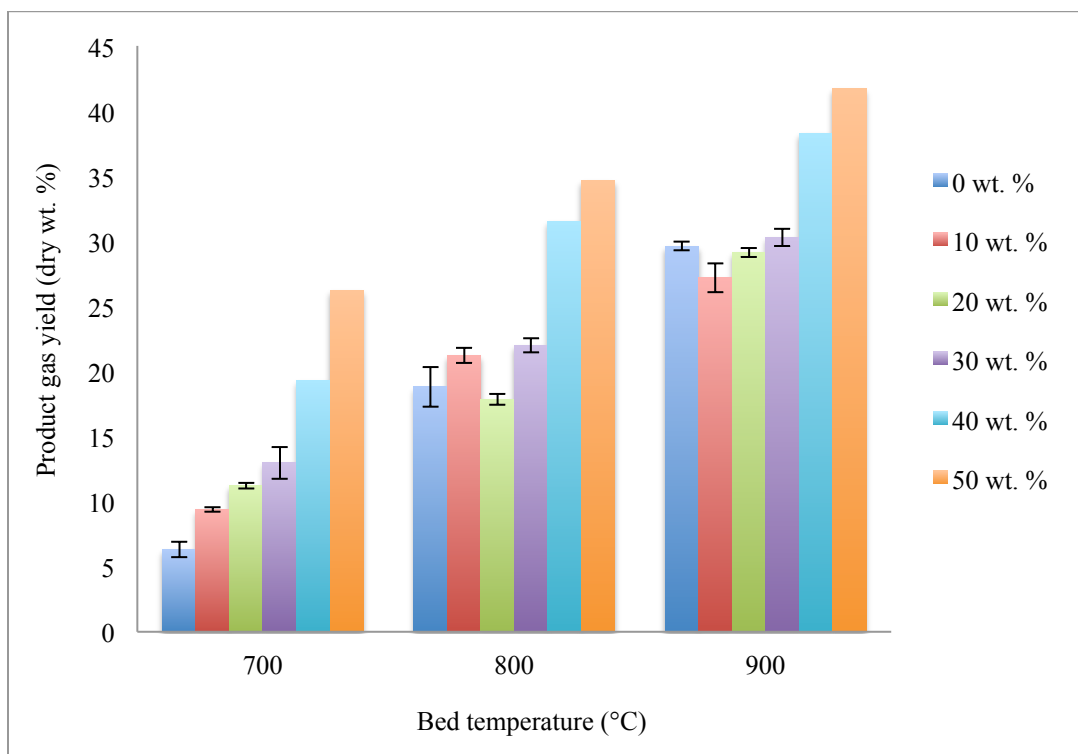
Figure 3.7 Effect of bed temperature and corn stover content on product gas yield in CO_2.
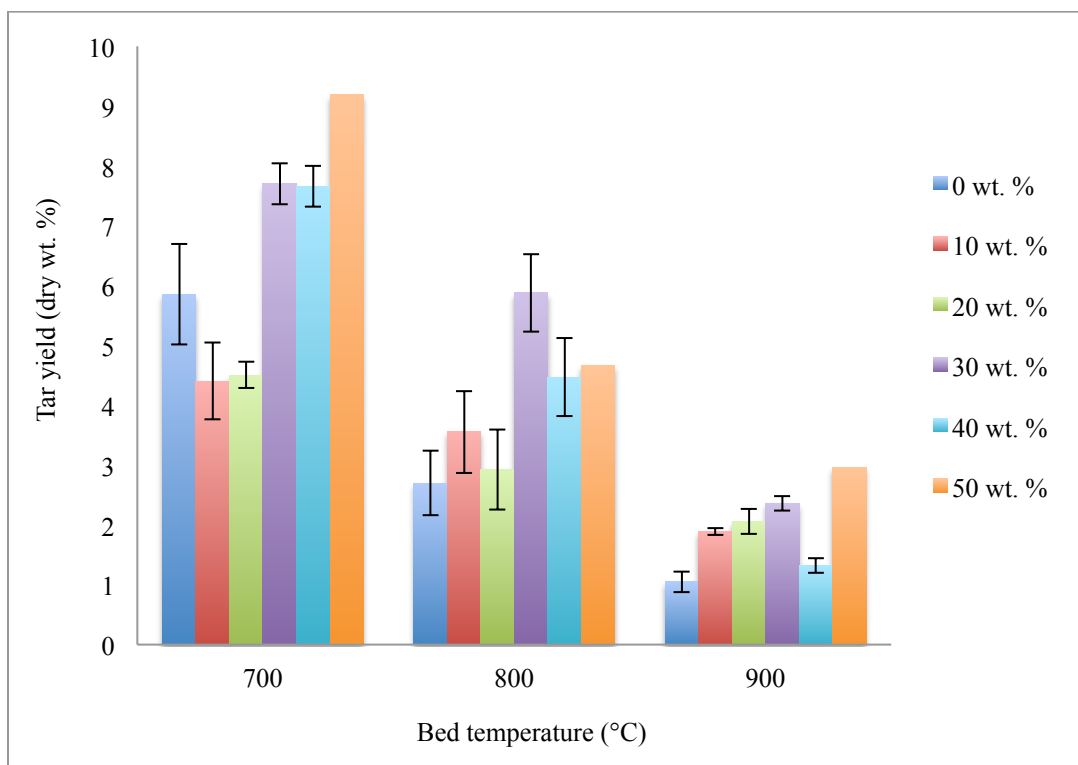
Figure 3.8 Effect of bed temperature and corn stover content on tar yield in CO_2.
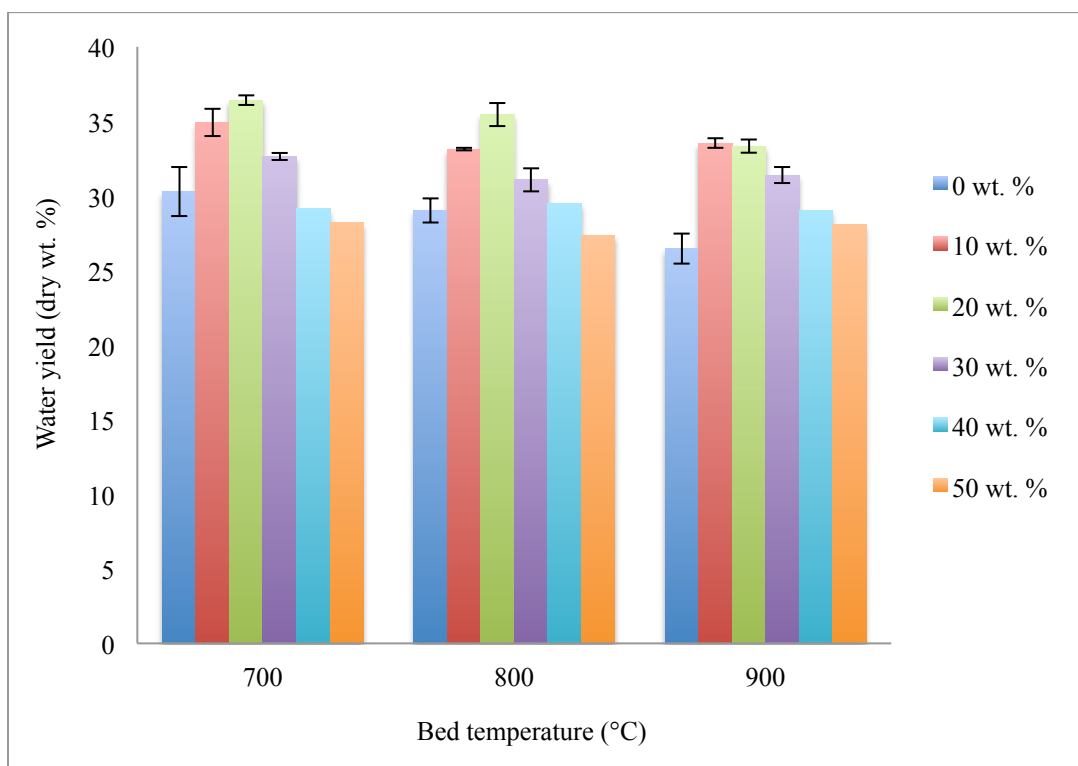
Figure 3.9 Effect of bed temperature and corn stover content on water yield in CO_2.

Table 3.4 Product yield (dry wt.%) for sub-bituminous coal and corn stover mixtures co-gasification in N_2.

Biomass (wt.%)	Temp. (°C)	Char		Water		Tar		Gas	
		Expt.	Pred.	Expt.	Pred.	Expt.	Pred.	Expt.	Pred.
0	700	53.98 ±0.65		26.10 ±0.83		5.54 ±0.18		14.25 ±0.01	
	800	52.38 ±0.58		23.09 ±0.88		3.64 ±0.48		20.72 ±0.23	
	900	45.14 ±0.57		13.96 ±0.87		1.04 ±0.27		38.96 ±0.57	
10	700	48.61 ±1.04	49.72	31.24 ±1.02	25.39	6.39 ±0.24	6.66	13.66 ±0.34	17.91
	800	44.84 ±1.98	47.83	30.43 ±0.89	22.80	4.32 ±0.76	3.82	19.47 ±1.03	25.25
	900	42.62 ±1.02	41.08	26.09 ±0.77	13.63	3.13 ±0.20	1.11	27.74 ±1.00	43.26
20	700	47.11 ±0.24	45.46	31.69 ±1.25	24.68	6.23 ±0.24	7.79	13.17 ±1.02	21.15
	800	44.75 ±0.11	43.27	30.13 ±0.35	22.52	5.57 ±0.13	4.00	19.47 ±1.04	29.78
	900	38.81 ±0.45	37.01	24.73 ±0.23	13.30	3.33 ±0.35	1.17	33.07 ±1.22	47.56
30	700	44.06 ±0.24	41.19	31.69 ±1.43	23.98	6.65 ±0.14	8.91	17.44 ±0.23	25.23
	800	39.48 ±0.64	38.71	29.86 ±1.03	22.23	3.42 ±0.27	4.18	27.13 ±1.03	34.30
	900	35.22 ±0.35	32.95	26.08 ±0.45	12.97	1.31 ±0.45	1.24	37.24 ±1.87	51.87
40	700	37.30	36.93	28.04	23.27	6.53	10.03	27.89	28.89
	800	35.12	34.15	24.66	21.94	3.06	4.36	36.92	38.83
	900	29.91	28.88	22.45	12.64	5.82	1.31	41.50	56.17
50	700	32.00	32.67	27.48	22.56	9.09	11.16	30.24	32.55
	800	29.24	29.59	22.63	21.66	3.89	4.54	43.95	43.36
	900	26.90	24.82	20.25	12.31	2.52	1.37	50.16	60.47

Table 3.5 Product yield (dry wt.%) for sub-bituminous coal and corn stover mixtures co-gasification in CO_2.

Biomass (wt.%)	Temp. (°C)	Char Expt.	Pred.	Water Expt.	Pred.	Tar Expt.	Pred.	Gas Expt.	Pred.
0	700	57.30 ±0.87		30.29 ±1.64		5.86 ±0.84		6.30 ±0.59	
	800	48.20 ±0.46		29.03 ±0.81		2.70 ±0.54		18.80 ±1.52	
	900	41.56 ±0.20		26.46 ±1.00		1.05 ±0.17		29.62 ±0.32	
10	700	50.12 ±0.91	53.39	34.93 ±0.32	29.80	4.41 ±0.64	5.92	9.39 ±0.19	10.51
	800	40.24 ±0.32	44.62	33.14 ±0.91	28.53	3.56 ±0.69	2.84	21.24 ±0.59	22.72
	900	37.09 ±1.27	38.39	33.54 ±0.08	26.32	1.89 ±0.06	1.05	27.49 ±1.24	33.00
20	700	47.80 ±0.66	49.48	36.41 ±0.32	29.30	4.51 ±0.22	5.98	11.23 ±0.22	14.71
	800	43.31 ±0.12	41.04	35.46 ±0.78	28.03	2.93 ±0.67	2.98	17.85 ±0.41	26.63
	900	35.42 ±0.98	35.21	33.35 ±0.45	26.18	2.06 ±0.21	1.04	29.12 ±0.34	36.37
30	700	45.32 ±1.02	45.32	32.64 ±0.23	28.80	7.70 ±0.34	6.04	12.98 ±1.23	18.92
	800	40.56 ±0.85	37.45	31.08 ±0.79	27.52	5.88 ±0.65	3.11	22.00 ±0.54	30.54
	900	34.71 ±0.46	32.04	31.39 ±0.54	26.05	2.36 ±0.12	1.04	30.30 ±0.67	39.75
40	700	42.59	41.66	29.16	28.30	7.66	6.11	19.28	23.12
	800	33.24	33.87	29.49	27.02	4.47	3.25	31.55	34.45
	900	30.35	28.87	29.02	25.91	1.32	1.03	38.28	43.12
50	700	36.02	37.75	28.21	27.80	9.19	6.17	26.23	27.33
	800	32.02	30.29	27.34	26.52	4.67	3.39	34.67	38.36
	900	26.10	25.69	28.08	25.77	2.96	1.03	41.74	46.49
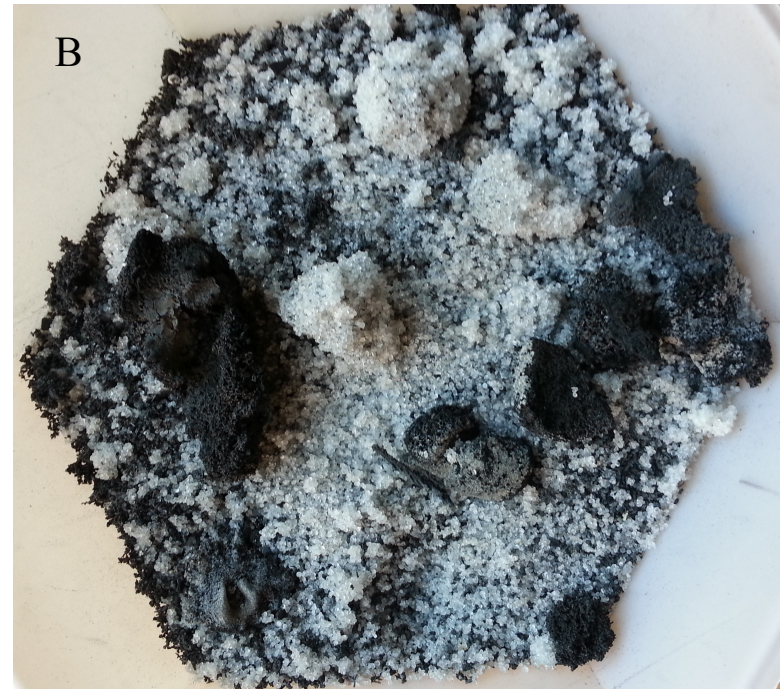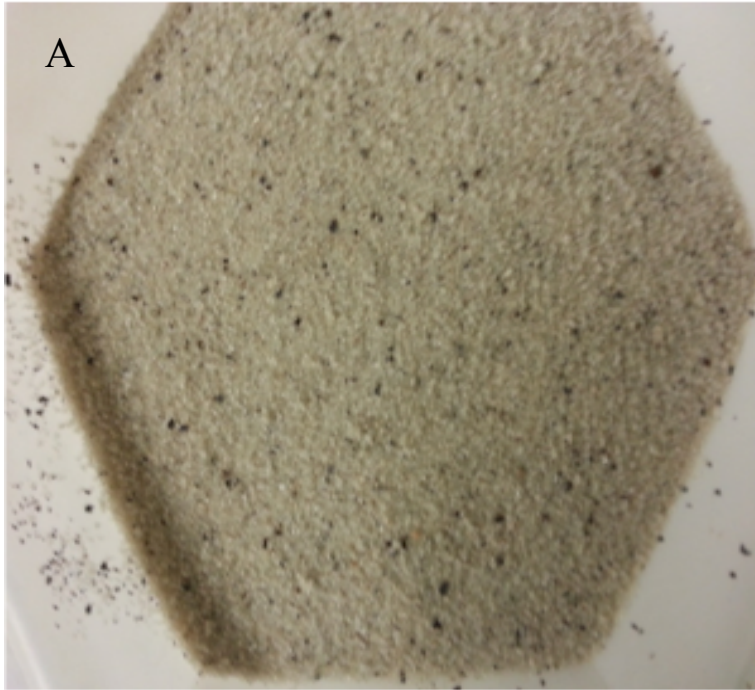
Figure 3.10 Photographs of agglomerates from co-gasification of sub-bituminous coal with 20 wt.% corn stover content at 900°C. Pictures: (A) silica sand before experiment and (B) agglomerates of silica sand and char after experiment.

increasing temperature was reported by Zhang et al. (2007), Gao et al. (2009), and Hernández et al. (2010) in separate studies on coal and biomass co-pyrolysis and co-gasification. It is suggested that, active sites responsible for interactions leading to synergies are lost when temperature increases (Hernández et al., 2010).

Furthermore, liquid yields obtained from co-gasification experiments were higher than expected, as compared to predicted liquid yields. In addition, increase in corn stover proportion in coal led to increase in tar yields.

4.3 Gaseous product composition

Final conversion of carbonaceous feed via thermochemical process into desired products is controlled by char reactivity (Everson et al., 2006; Gao et al., 2009). The major product gas compounds quantified from co-gasification experiments were: H_2, CO, CO_2, and CH_4. Light molecular weight hydrocarbons (C_2-C_4) were present but at low concentrations. Table 3.6 shows the yield of corn stover product gas. H_2 and CO were the major compounds produced and their yields increased with increasing temperature. Comparisons between experimental and predicted product gas compounds from coal and corn stover mixtures are presented in Table 3.7 and Table 3.8. Clearly, there are obvious signs of interaction between coal and corn stover co-gasification on product gas formation. The experimental product gas compounds are either additive or lower than predicted yields except for CO yields in N_2 medium where experimental values are significantly higher at 700°C to 800°C.

The mechanism of coal and biomass interaction leading to synergy has been reported (Krerkkaiwan et al., 2013; Zhang et al., 2007). The phenomenon of synergy was theorized as transfer of OH and H radicals from biomass to coal during co-gasification reactions. In this study, up to 36 wt.% of liquid (water) yields was obtained from co-gasification experiments compared to 30 wt.% for predicted water yields. The product gas comprised mainly of syngas (H_2 and CO) as shown in Figure 3.11 to Figure 3.13 (N_2 medium) and Figure 3.14 to Figure 3.16 (CO_2

medium). The concentration of syngas obtained using CO_2 as gasification medium were higher (~78 vol.% at 700°C, ~87 vol.% at 800°C, ~93 vol.% at 900°C) than those obtained with N_2 medium (~60 vol.% at 700°C, ~65 vol.% at 800°C, ~75 vol.% at 900°C) as shown in Figure 3.17 to Figure 3.19. While syngas concentrations appeared independent of corn stover content using N_2 gas at all operating temperatures, concentrations of syngas decreased slightly with increasing biomass content when CO_2 was used.

The effects of temperature and biomass concentration on the major gas compounds are presented in Figure 3.20 to Figure 3.23 (N_2 medium) and Figure 3.24 to Figure 3.27 (CO_2 medium). In N_2 medium, the yield of H_2 (Figure 3.20) was higher at 900°C (41 vol.% with 10 wt.% corn stover) but decreased with increasing biomass content (33 vol.% with 50 wt.% corn stover).

Table 3.6 Yield (vol.%) of product gas compounds for corn stover gasification.

Temp. (°C)	H_2	CO	CH_4	CO_2	$C_2 - C_4$
		Nitrogen (gasification medium)			
700	19.36 ±1.01	48.66 ±1.02	10.92 ±0.87	17.13 ±1.00	0.40 ±0.11
800	24.03 ±0.98	48.38 ±1.51	11.73 ±0.11	14.62 ±0.58	0.50 ±0.01
900	28.48 ±1.18	51.44 ±2.16	10.54 ±1.01	9.21 ±0.67	0.55 ±0.01
		Carbon dioxide (gasification medium)			
700	13.84 ±0.03	54.57 ±0.94	10.52 ±0.30	19.91 ±0.04	1.16 ±0.65
800	16.60 ±0.02	65.72 ±0.64	10.70 ±0.04	6.10 ±0.43	0.88 ±0.02
900	11.14 ±0.08	75.95 ±1.37	9.23 ±0.40	3.44 ±0.14	0.24 ±0.03

Table 3.7 Yield (vol.%) of product gas compounds for sub-bituminous coal and corn stover mixtures in N_2.

Biomass (wt.%)	Temp. (°C)	H_2		CO		CH_4		CO_2		C_2 - C_4	
		Expt.	Pred.	Expt.	Pred.	Expt.	Pred.	Expt.	Pred.	Expt.	Pred.
	700	39.63 ±1.03		18.58 ±1.51		11.57 ±1.03		27.92 ±1.43		2.31 ±0.45	
0	800	43.12 ±0.97		20.79 ±2.11		9.13 ±0.43		26.37 ±1.98		0.58 ±0.26	
	900	48.53 ±1.95		31.80 ±1.84		6.81 ±1.08		12.84 ±1.66		0.02 ±0.00	
	700	24.25 ±2.01	37.60	31.23 ±1.94	21.59	13.62 ±0.92	11.50	27.45 ±2.32	26.84	3.44 ±0.65	2.47
10	800	32.75 ±1.35	41.22	31.58 ±1.52	23.55	12.29 ±1.08	9.39	21.86 ±1.82	25.19	1.51 ±0.13	0.65
	900	41.00 ±2.28	46.53	31.00 ±0.79	33.77	9.69 ±1.13	7.18	18.08 ±1.01	12.47	0.23 ±0.04	0.05
	700	24.96 ±0.53	35.57	35.16 ±1.33	24.59	12.24 ±2.47	11.44	24.59 ±1.87	25.76	3.06 ±0.73	2.64
20	800	30.14 ±1.01	39.31	36.31 ±2.45	26.31	13.53 ±0.44	9.65	18.51 ±2.06	24.02	1.51 ±0.33	0.72
	900	37.02 ±0.78	44.52	35.89 ±1.08	35.73	10.99 ±0.53	7.55	15.75 ±0.25	12.11	0.35 ±0.02	0.08
	700	25.25 ±1.11	33.55	36.48 ±2.25	27.60	11.40 ±0.01	11.37	24.45 ±2.04	24.68	2.42 ±0.17	2.80
30	800	29.93 ±0.43	37.40	34.40 ±2.46	29.07	12.73 ±0.62	9.91	21.50 ±2.19	22.84	1.44 ±0.19	0.78
	900	35.79 ±2.64	42.52	34.99 ±0.32	37.69	11.60 ±0.43	7.93	17.12 ±0.98	11.75	0.50 ±0.04	0.11
	700	26.47	31.52	35.96	30.61	10.04	11.31	24.78	23.60	2.76	2.96
40	800	33.13	35.49	34.70	31.83	11.02	10.17	20.06	21.67	1.09	0.85
	900	34.49	40.51	40.23	39.66	10.28	8.30	14.70	11.39	0.30	0.14
	700	24.49	29.49	37.10	33.62	9.38	11.24	25.78	22.52	3.25	3.12
50	800	27.91	33.58	38.87	34.58	11.84	10.43	19.87	20.49	1.51	0.91
	900	33.40	38.51	39.21	41.62	11.63	8.67	15.47	11.02	0.28	0.18

Table 3.8 Yield (vol.%) of product gas compounds for sub-bituminous coal and corn stover mixtures in CO_2.

Biomass (wt.%)	Temp. (°C)	H_2 Expt.	Pred.	CO Expt.	Pred.	CH_4 Expt.	Pred.	CO_2 Expt.	Pred.	C_2 - C_4 Expt.	Pred.
	700	30.52 ±1.46		51.84 ±2.33		12.77 ±0.42		3.13 ±1.27		1.73 ±0.25	
0	800	28.07 ±1.59		61.16 ±2.18		7.76 ±0.81		2.78 ±0.57		0.22 ±0.05	
	900	23.52 ±1.13		69.12 ±0.79		5.85 ±0.17		1.50 ±0.01		0.01 ±0.00	
	700	25.31 ±0.78	28.85	51.23 ±2.39	52.11	12.90 ±0.83	12.55	8.87 ±1.44	4.81	1.69 ±0.09	1.68
10	800	21.29 ±1.72	26.93	65.44 ±2.93	61.62	8.78 ±0.57	8.06	4.07 ±0.52	3.12	0.43 ±0.12	0.28
	900	20.84 ±2.39	22.29	71.86 ±2.69	69.80	6.02 ±0.08	6.18	1.26 ±0.22	1.70	0.02 ±0.00	0.03
	700	24.30 ±1.40	27.19	53.42 ±2.27	52.39	9.58 ±2.95	12.32	11.18 ±0.93	6.49	1.52 ±0.13	1.62
20	800	20.02 ±1.84	25.78	53.16 ±3.02	62.07	12.00 ±0.45	8.35	13.26 ±0.75	3.45	1.57 ±0.02	0.35
	900	19.25 ±2.11	21.05	67.28 ±2.11	70.49	6.89 ±1.05	6.52	6.35 ±0.77	1.89	0.22 ±0.01	0.05
	700	19.25 ±2.02	25.52	53.99 ±2.72	52.66	12.52 ±0.21	12.10	12.08 ±0.14	8.16	2.16 ±0.03	1.56
30	800	19.33 ±1.98	24.63	61.36 ±2.88	62.53	11.03 ±1.01	8.64	7.31 ±1.22	3.78	0.97 ±0.01	0.42
	900	20.53 ±2.74	19.81	63.95 ±2.97	71.17	8.50 ±0.74	6.86	6.86 ±0.29	2.08	0.17 ±0.01	0.08
	700	18.60	23.85	51.81	52.93	13.14	11.87	13.69	9.84	2.75	1.50
40	800	19.61	23.48	56.94	62.99	12.54	8.94	9.96	4.11	0.95	0.48
	900	20.17	18.57	62.68	71.85	10.79	7.20	6.19	2.28	0.17	0.10
	700	18.21	22.18	51.21	53.20	12.97	11.64	15.07	11.52	2.53	1.45
50	800	18.25	22.34	59.44	63.44	11.86	9.23	9.59	4.44	0.87	0.55
	900	18.82	17.33	65.50	72.54	11.10	7.54	4.42	2.47	0.16	0.12

Figure 3.11 Effect of corn stover content on the yield of product gas compounds for sub-

bituminous coal and corn stover co-gasification in N_2 at 700°C.

Figure 3.12 Effect of corn stover content on the yield of product gas compounds for sub-

bituminous coal and corn stover co-gasification in N_2 at 800°C.
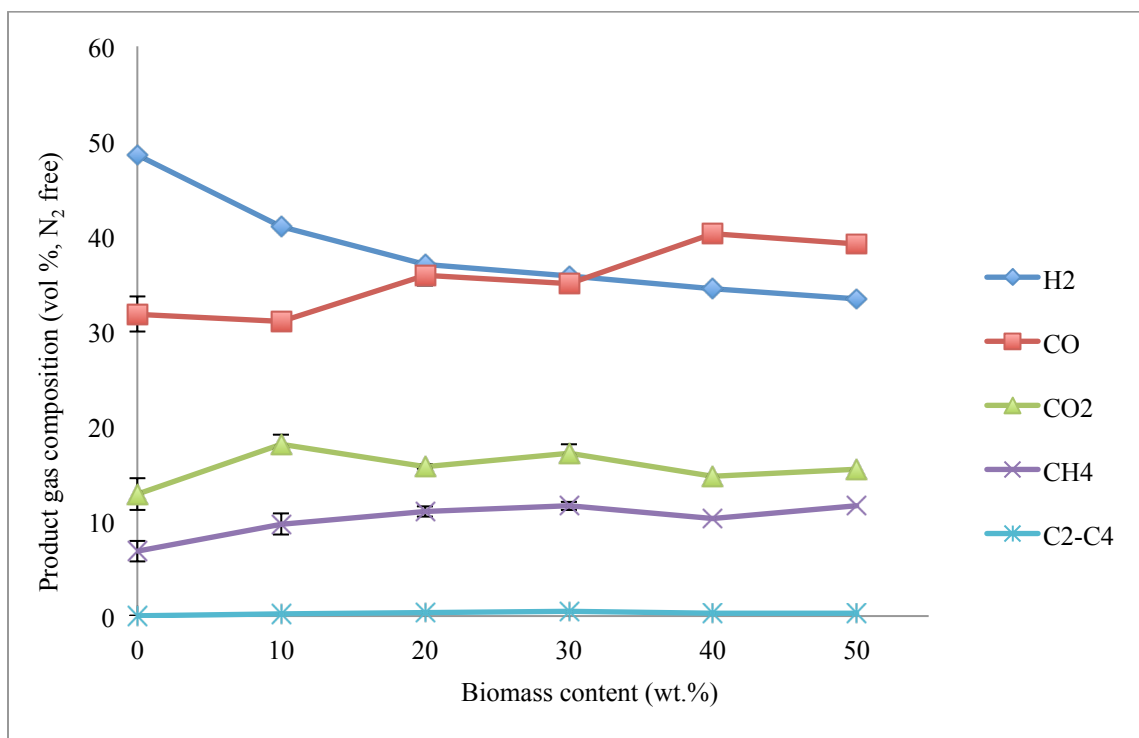
Figure 3.13 Effect of corn stover content on the yield of product gas compounds for sub-bituminous coal and corn stover co-gasification in N_2 at 900°C.
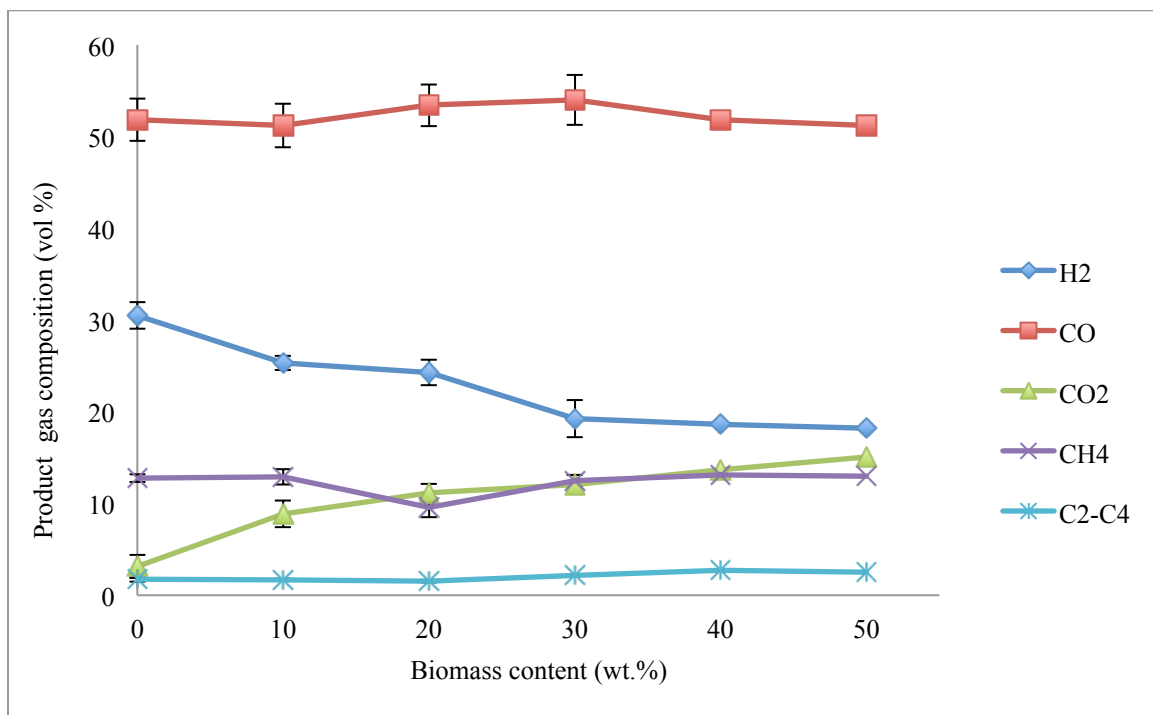
Figure 3.14 Effect of corn stover content on the yield of product gas compounds in for sub-bituminous coal and corn stover co-gasification CO_2 at 700°C.
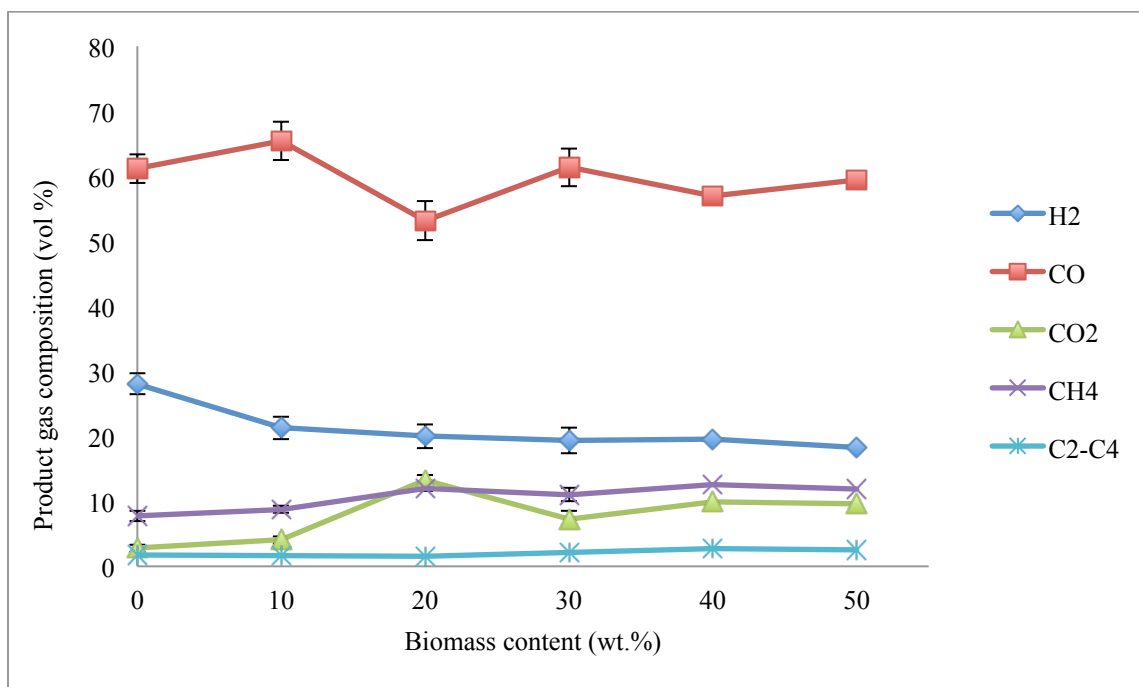
Figure 3.15 Effect of corn stover content on the yield of product gas compounds in for sub-bituminous coal and corn stover co-gasification CO_2 at 800°C.

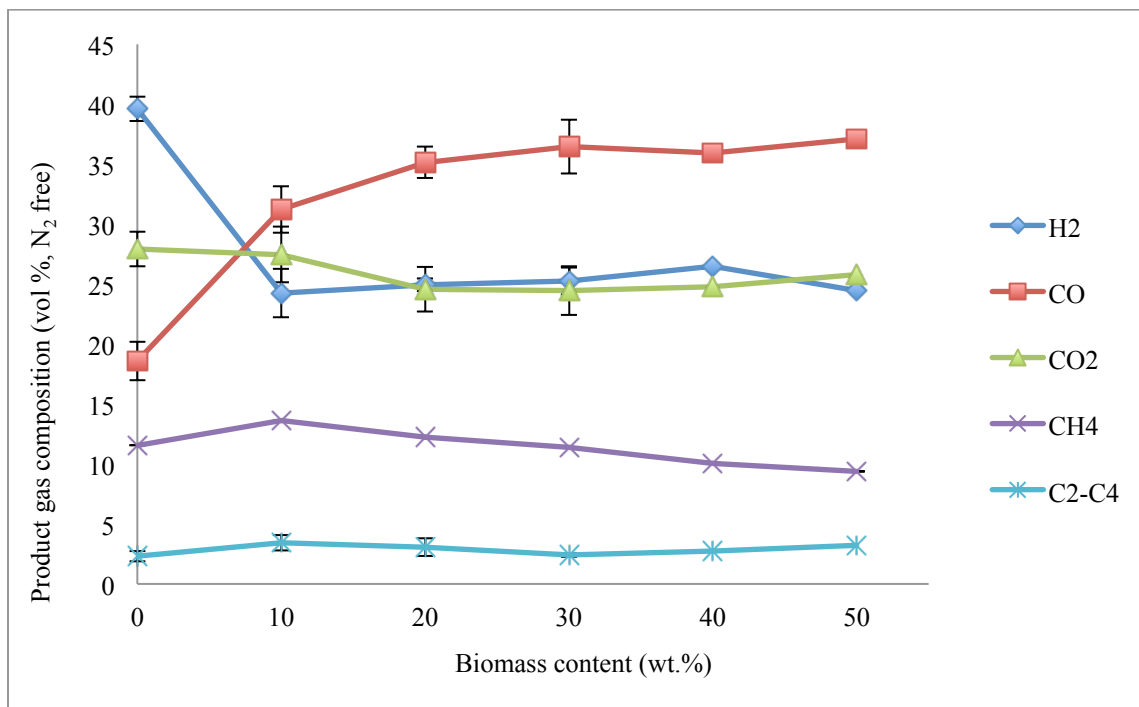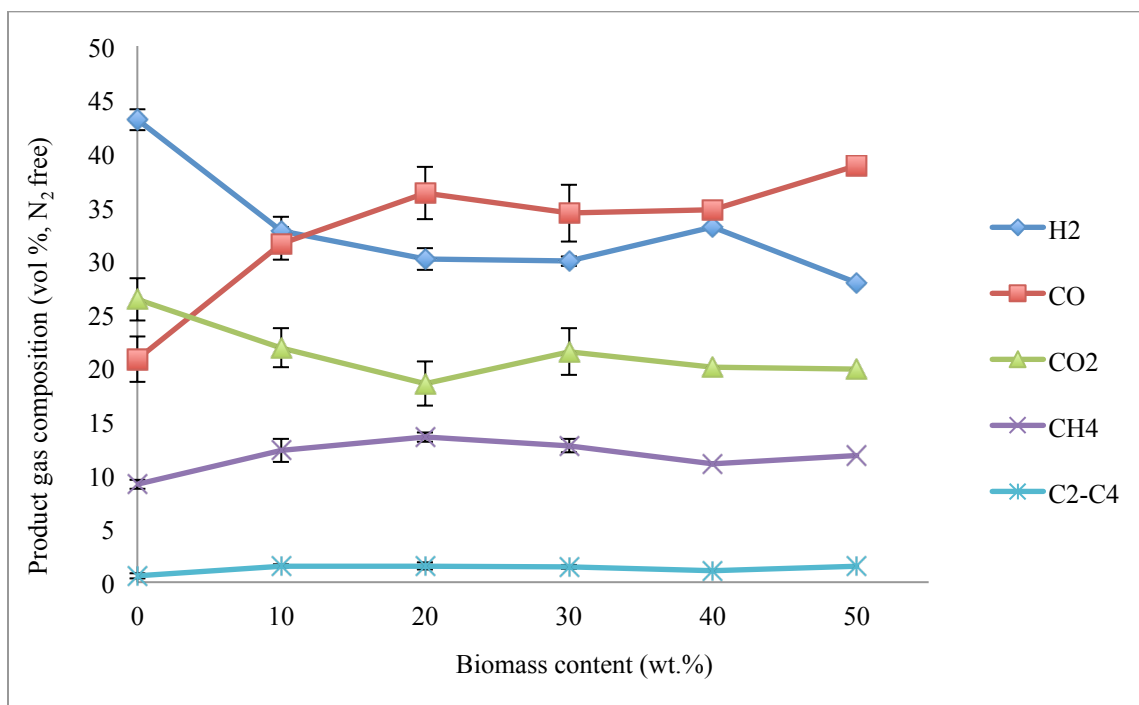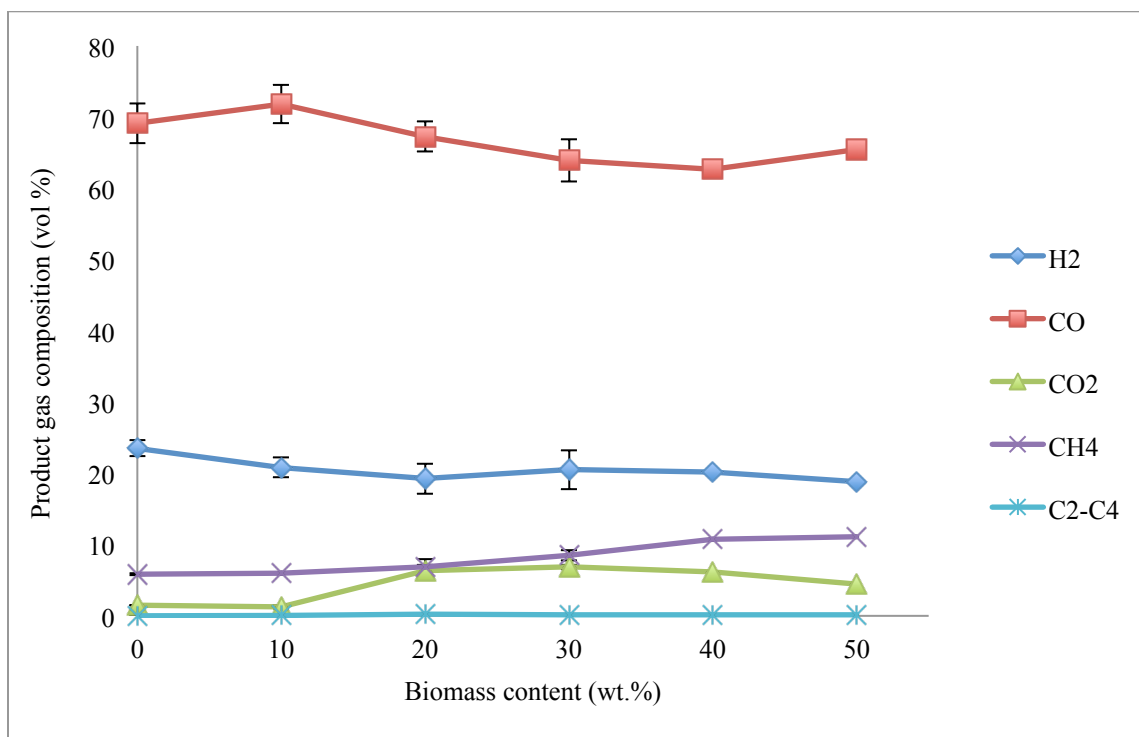

Figure 3.16 Effect of corn stover content on the yield of product gas compounds in for sub-bituminous coal and corn stover co-gasification CO_2 at 900°C.
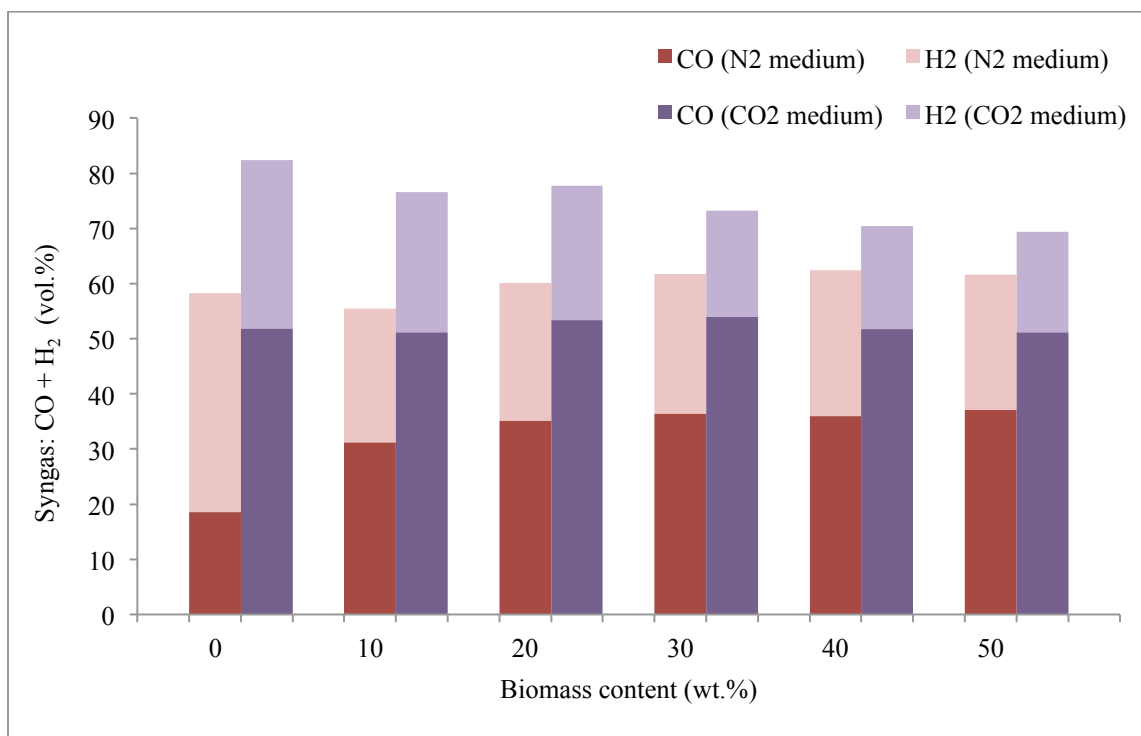
Figure 3.17 Effect of corn stover content and gasification gases on syngas yield at 700°C.
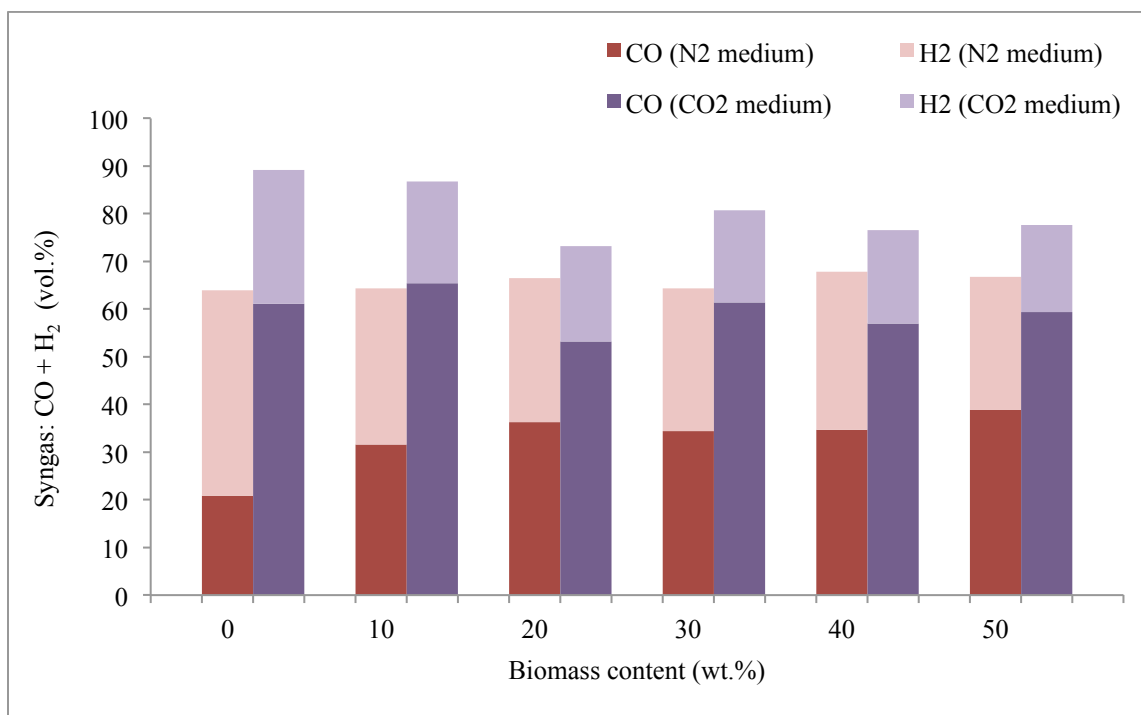
Figure 3.18 Effect of corn stover content and gasification gases on syngas yield at 800°C.
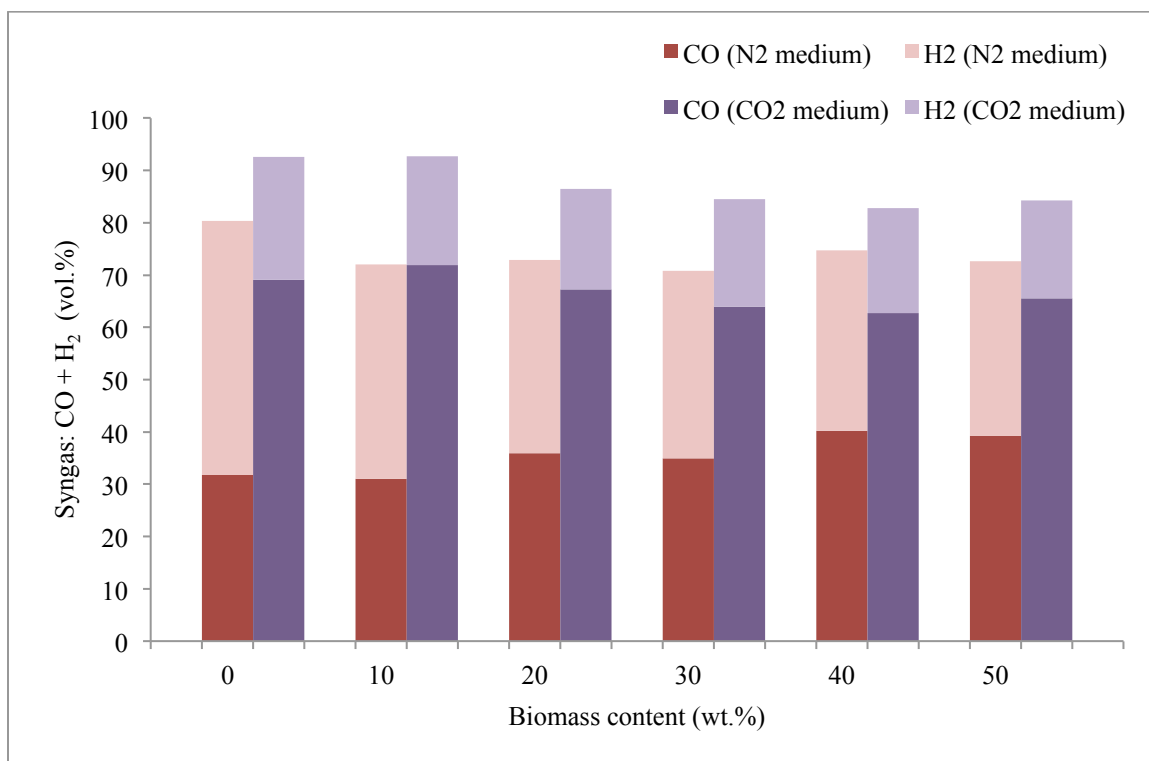
Figure 3.19 Effect of corn stover content and gasification gases on syngas yield at 900°C.
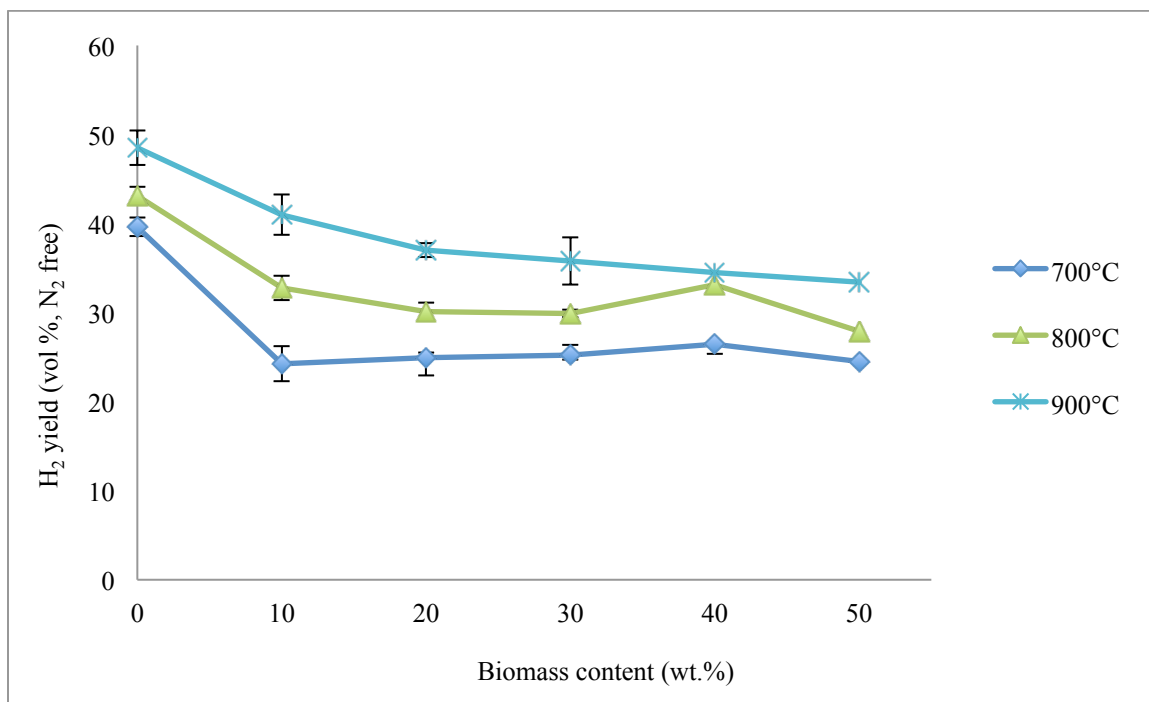
Figure 3.20 Effect of bed temperature and corn stover content on H_2 yield for sub-bituminous

coal and corn stover co-gasification in N_2.
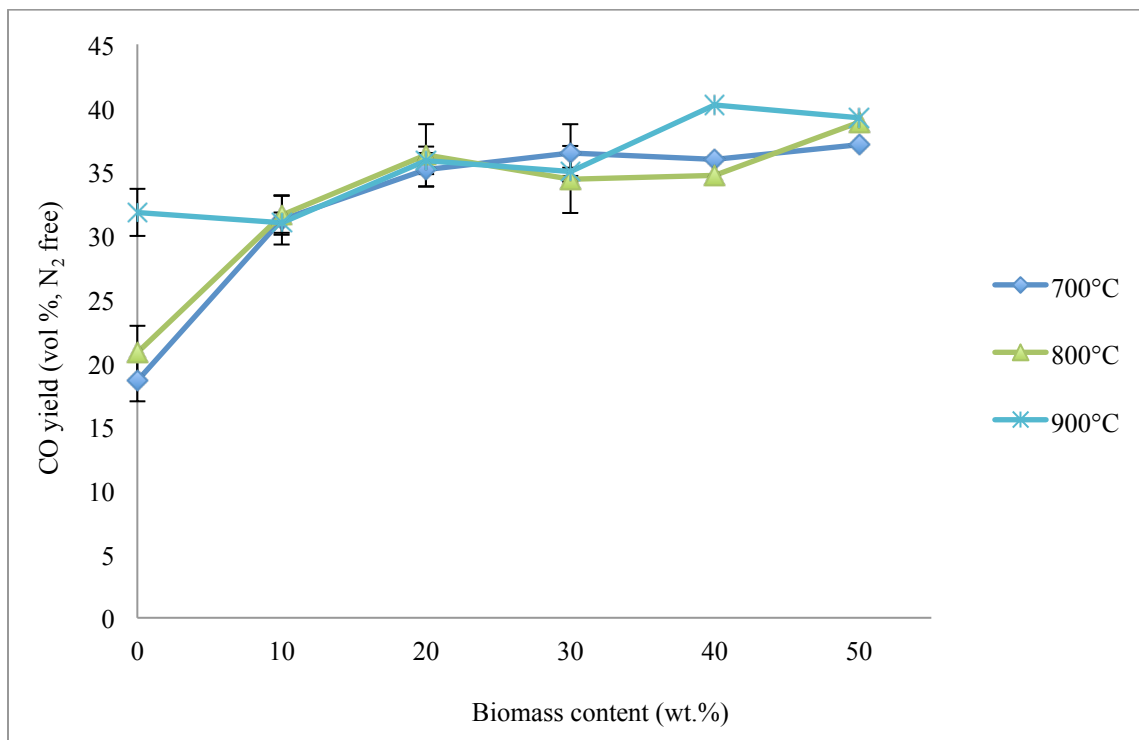
Figure 3.21 Effect of bed temperature and corn stover content on CO yield for sub-bituminous coal and corn stover co-gasification in N_2.
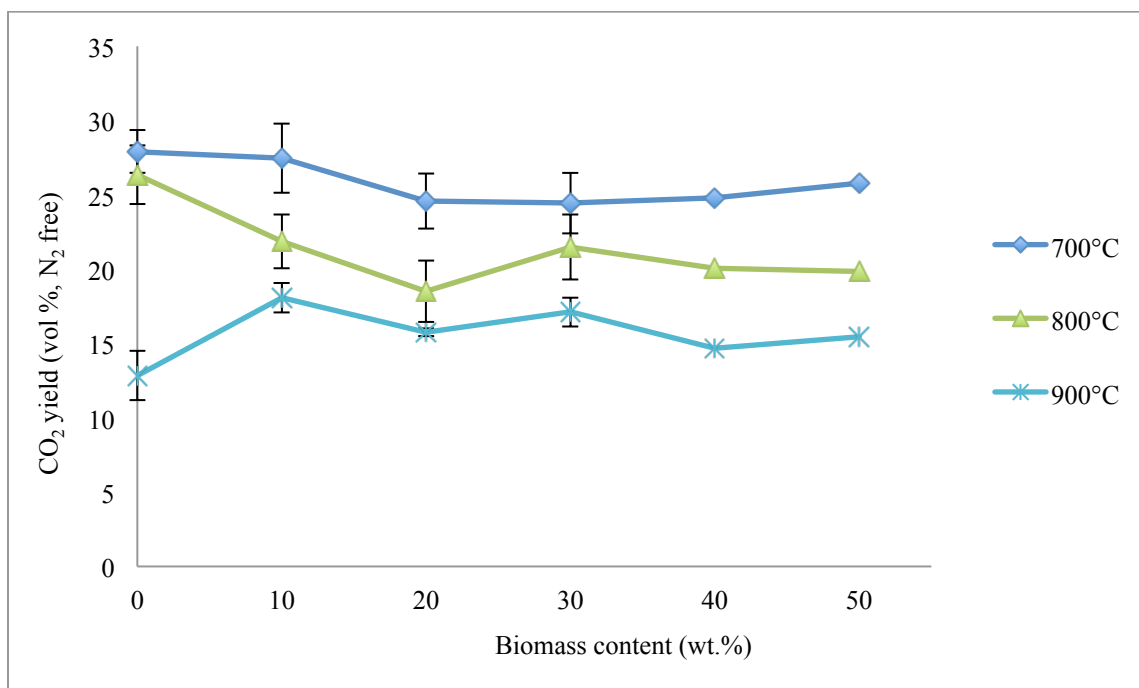
Figure 3.22 Effect of bed temperature and corn stover content on CO_2 yield for sub-bituminous coal and corn stover co-gasification in N_2.
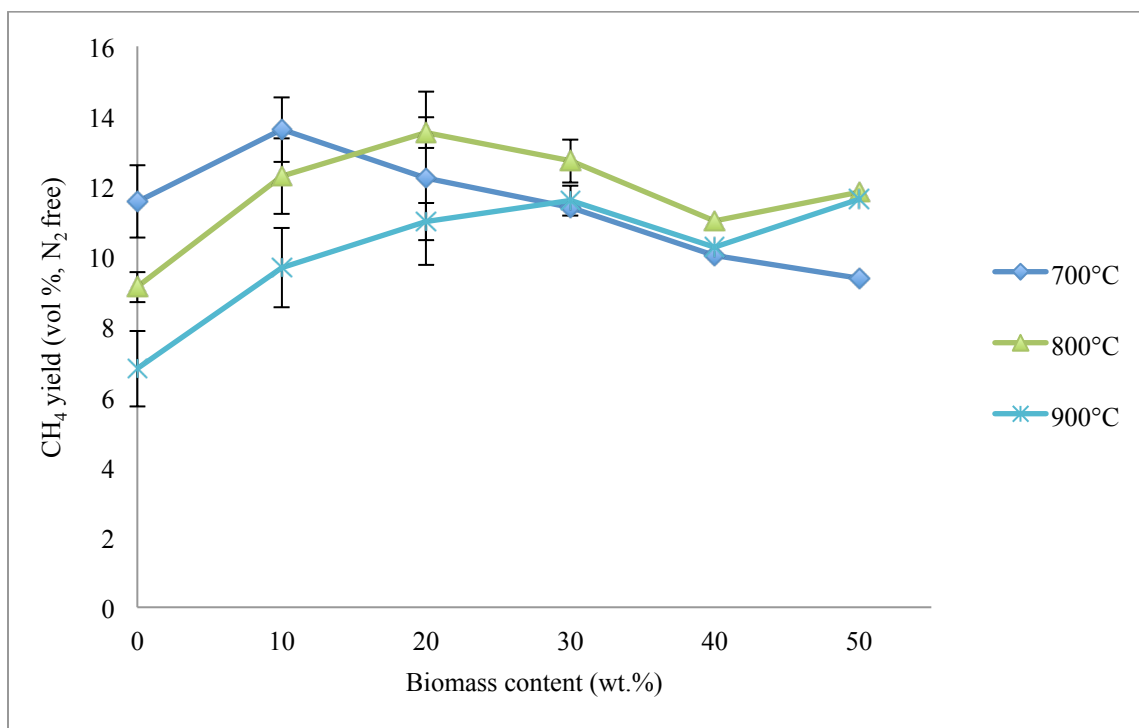
Figure 3.23 Effect of bed temperature and corn stover content on CH_4 yield for sub-bituminous coal and corn stover co-gasification in N_2.
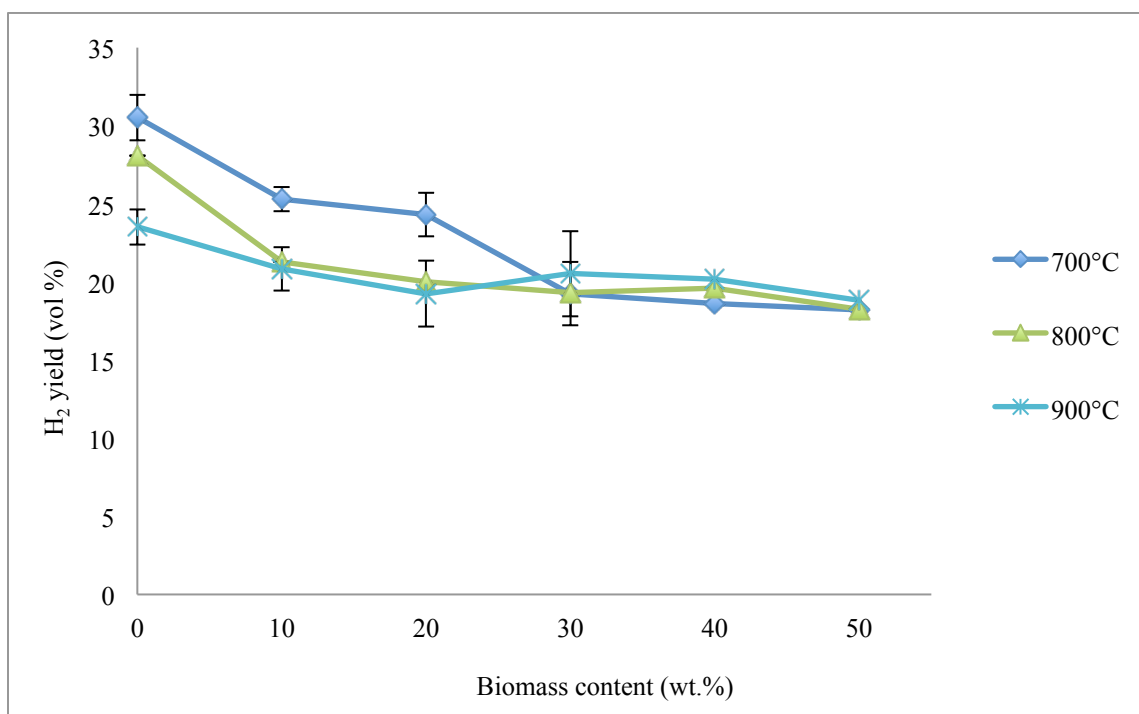
Figure 3.24 Effect of bed temperature and corn stover content on H_2 yield for sub-bituminous coal and corn stover co-gasification in CO_2.
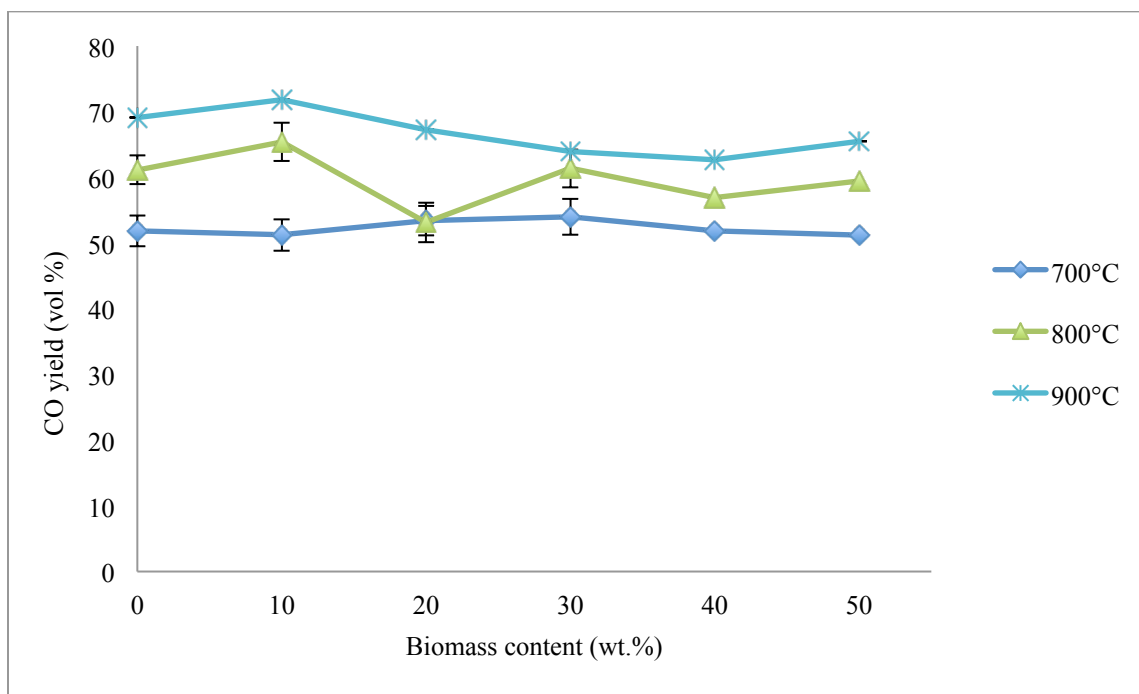
Figure 3.25 Effect of bed temperature and corn stover content on CO yield for sub-bituminous coal and corn stover co-gasification in CO_2.
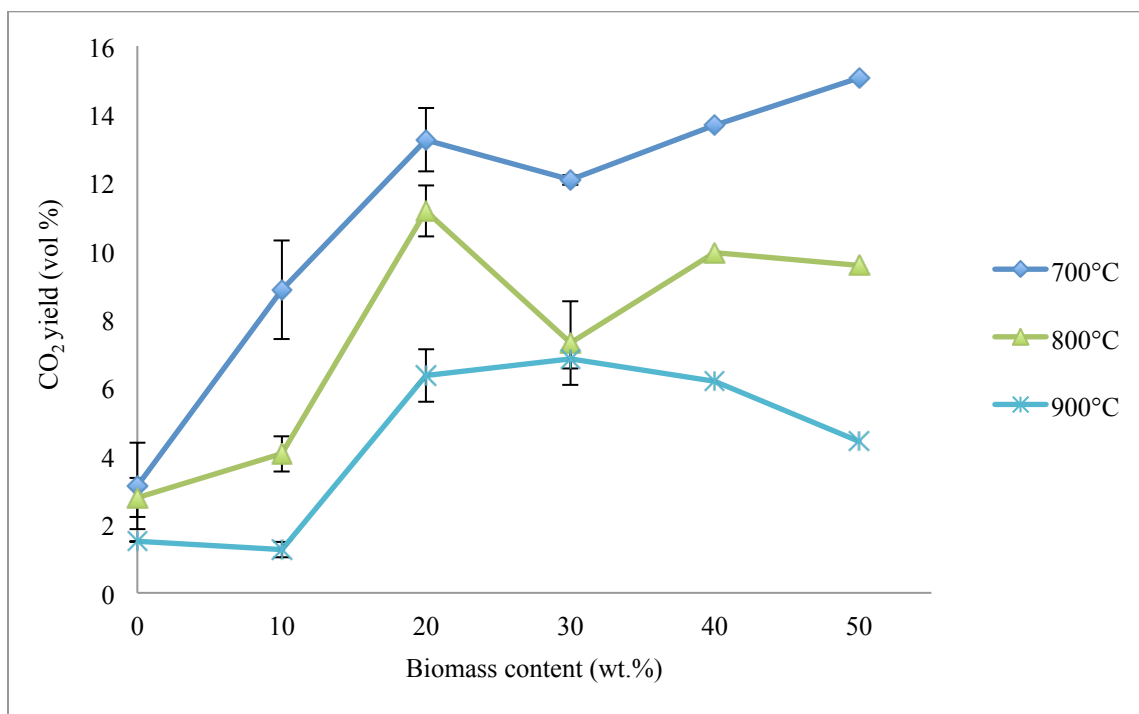
Figure 3.26 Effect of bed temperature and corn stover content on CO_2 yield for sub-bituminous coal and corn stover co-gasification in CO_2.
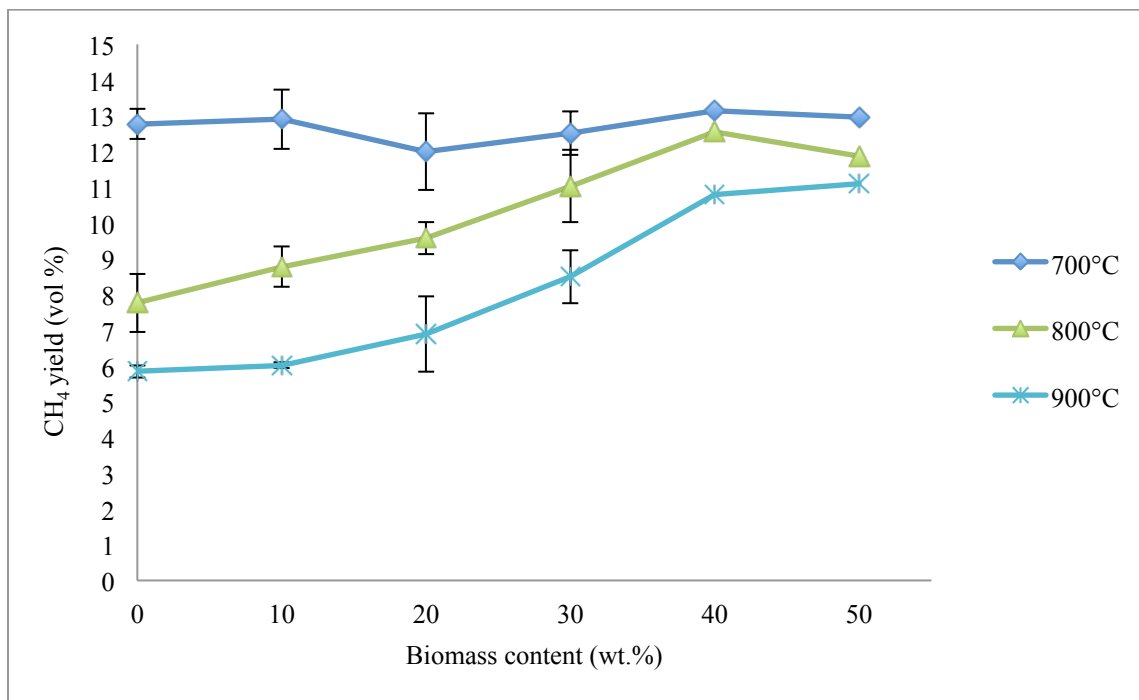
Figure 3.27 Effect of bed temperature and corn stover content on H_2 yield for sub-bituminous coal and corn stover co-gasification in CO_2.

CO yields (Figure 3.21) appeared to increase with increasing corn stover content however no systematic trend was observed. CO_2 and CH_4 yields (Figure 3.22 and Figure 3.23) decreased with increasing biomass content. In CO_2 medium, H_2 yields (Figure 3.24) were higher at 700°C with 10-20 wt.% biomass content (25 vol.%). Similarly, H_2 concentrations decreased with increase in corn stover content (19 vol.% with 50 wt.% corn stover). Higher concentrations of CO (Figure 3.25) were obtained at 900°C, whereas CO_2 (Figure 3.26), and CH_4 (Figure 3.27) dominated at 700°C.

5. Conclusions

From the results of this study, the following conclusions were drawn:

1. Char and tar yields decreased with increasing temperature. Char yield for coal-corn stover mixtures were lower than those of single coal. Conversion into gaseous products increased with increase in corn stover content.

2. Co-gasification of coal with corn stover led to formation of agglomerates. This is undesirable because agglomeration effect causes technical difficulties, instability of fluidization, reactor blockage, corrosion, and loss of efficiency.

3. Synergetic effects in co-gasification of coal-corn stover char were observed with 10-20 wt.% biomass at 700°C and 800°C. The signs of synergy however diminished with increasing temperature and biomass.

4. Volume of syngas yields was higher in CO_2 co-gasification medium compared to syngas yields obtained from N_2 medium.

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CHAPTER 4

CO-GASIFICATION OF SUB-BITUMINOUS COAL WITH HYBRID POPLAR WOOD IN

VARIOUS GASES

1. Abstract

Co-gasification of coal with biomass into energy and useful products is a promising technology especially for coal-based Integrated Gasification Combined Cycle (IGCC) power plants. Therefore this study was designed to investigate co-gasification behavior of sub-bituminous coal and hybrid poplar wood mixtures using different gases (N_2, CO_2, steam) at low temperatures in a fluidized bed. Results showed additive behavior between coal and poplar co-gasification in N_2 and CO_2 medium indicating lack of synergetic effects. It appeared the two feedstocks underwent thermal degradation independently which could be attributed to different temperature of devolatilization for coal and biomass. However, signs of synergy were observed on H_2 production using steam. Further, product gases were composed mainly of syngas. Experiments suggest that high syngas yields can be obtained using CO_2 as co-gasification medium but with poor H_2/CO ratio (≤ 0.6). Nevertheless, H_2/CO ratios increased up to 2.5 with 10 wt.% poplar content when steam was used. H_2 yields decreased with increase in hybrid poplar content whereas CO concentrations remained constant or increased with increase in biomass content. In spite of lack of major synergies between coal and poplar, co-gasifying the two feedstocks should be considered a key to a sustainable natural resource management.

2. Introduction

In the United States, coal energy fuels about half of the electricity generation (EIA, 2011; Grubert, 2012) and it is abundant and cheap (EIA, 2014). Therefore coal is considered as an energy resource for the future (Sami et al., 2001). However, coal combustion provides oxygen-

rich atmosphere that favor emission of carbon dioxide, nitrous oxides, and sulfur oxides (Emami-Taba et al., 2013; Li et al., 2008; Quaark et al., 1999).

To deal with pollution problems associated with coal use, co-gasification of coal with biomass is actively being researched towards provision of sustainable, renewable, and clean energy (Hartmann and Kaltschmitt, 1999; Hein and Bemtgen, 1998; Spliethoff and Hein, 1998). Besides, CO_2 generated from gasification process can be captured and stored permanently or utilized for Enhanced Oil Recovery (EOR) (Ferguson et al., 2009; Herzog and Golomb, 2004; Todd and Grand, 1993), or converted catalytically into methanol or dimethyl ether (Jun et al., 1998).

Among several biomass feedstocks, hybrid poplar wood is among the fast-growing short-rotation lignocellulosic energy crops in North America that yields between 8 000 and 22 000 kg-dry weight of wood per hectare per year (Felix et al., 2008).

During the past few years, a number of studies (Alzate et al., 2009; Collot et al., 1999; Kajitani et al., 2009; Lapuerta et al., 2008; Li et al., 2010; McLendon et al., 2004; Pan et al., 2000; Sjöström et al., 1999; Xiao et al., 2013; Zhang et al., 2007) focused on coal-biomass synergy, char reactivity, and product gas composition using fluidized beds. Despite these works, coal-biomass use is still in the developmental stage and information on their combined reactivity is insufficient (Kumabe et al., 2007; Pinto et al., 2003). For example, the expected synergetic interaction between coal and biomass may likely show variations due to thermal reactivity, chemical, or physical properties on solid, liquid and gaseous products (Haykiri-Acma and Yaman, 2010; Weiland et al., 2012).

Many investigators have extensively studied co-gasification and co-pyrolysis in various gasifiers. Xu et al. (2011) studied the reaction kinetics of various ratios of coal and biomass mixtures using steam. They observed that coal and biomass showed different gasification characteristics and the overall reaction rates decreased with increasing coal-to-biomass ratio. Kumabe et al. (2007) studied the effect of biomass variation on coal products using a downdraft

fixed-bed gasifier in air and steam medium. They found that gas production increased with biomass content whereas char and tar yields decreased. Also they observed that H_2 composition of the fuel gas decreased and CO_2 increased with increase in biomass content but CO was unaffected.

Hernández et al. (2010) co-gasify biomass wastes (grape marc) and coal-coke blends in an air-blown entrained flow gasifier and observed some signs of synergy at low fuel/air ratios and low reaction temperatures. Fermoso et al. (2010) observed interactions between biomass blended with coal and petroleum coke on fuel gas production using a fixed-bed reactor and steam/oxygen as a gasifying agents at an elevated pressure. Several other studies (Alzate et al., 2009; Li et al., 2010; Pan et al., 2000; Pinto et al., 2003) focused on steam as a gasification medium for coal and biomass co-gasification. They concluded from their work that the presence of steam helped improved syngas composition.

This study was therefore designed to investigate low-temperature co-gasification of sub-bituminous coal and hybrid poplar wood using nitrogen (N_2) gas, carbon dioxide (CO_2) gas, and steam as fluidizing medium in a bubbling fluidized bed reactor.

3. Methods

3.1 Raw materials

Hybrid poplar biomass used in the study was provided by Idaho National Laboratory (INL)/Battelle Energy Alliance (BEA), LLC (Idaho Falls, Idaho, USA). Particle size of poplar was reduced to pass through a 1-mm sieve using Thomas-Wiley mill (Model # 3375-E15). Pulverized sub-bituminous coal was obtained from Powder River Basin (North Antelope Rochelle Mine, Wyoming, USA). Analyses of materials are provided in Table 4.1.

Table 4.1 Analysis of samples.

	Coal	Hybrid poplar
Proximate analysis (wt.%)		
Moisture	22	6.55 ±0.08
Ash	4.94	0.43 ±0.01
Fixed Carbon	38.01	11.85 ±0.15
Volatiles[a]	33.36	81.17 ±1.07
Ultimate analysis (wt.%)		
Carbon	53.72	46.33 ±0.13
Hydrogen	6.22	6.04 ±0.05
Nitrogen	0.78	0.10 ±0.0
Sulfur	0.23	0.00
Oxygen[b]	34.11	47.1
HHV (MJ/kg)	21.12	18.6 ±0.04

Oxygen[a] was determined by difference

3.2 Experimental setup and procedure

A schematic diagram of fluidized bed gasifier is shown in Figure 4.1. The fluidized bed gasifier setup consists of a reactor: 5 cm (2 in) in diameter and 50 cm (20 in) in height including a 14 cm (5.5 in) preheating zone below the gas distributor, a volumetric twin-screw feeder (Model: K2VT20, K-tron, Pitman, New Jersey, USA), 20-µm high-temperature-filter (HTF), two condensers placed in series, electrostatic precipitator (18-20 kV), a coalescing filter, and an online micro-GC (Model: Varian 490, Agilent Technologies). The micro-GC was equipped with two columns (10-m PoraPLOT U column and 10-m Molsieve 5 Å column). A 100-µm porous metal distributor plate was used for uniform distribution of fluidizing gases.
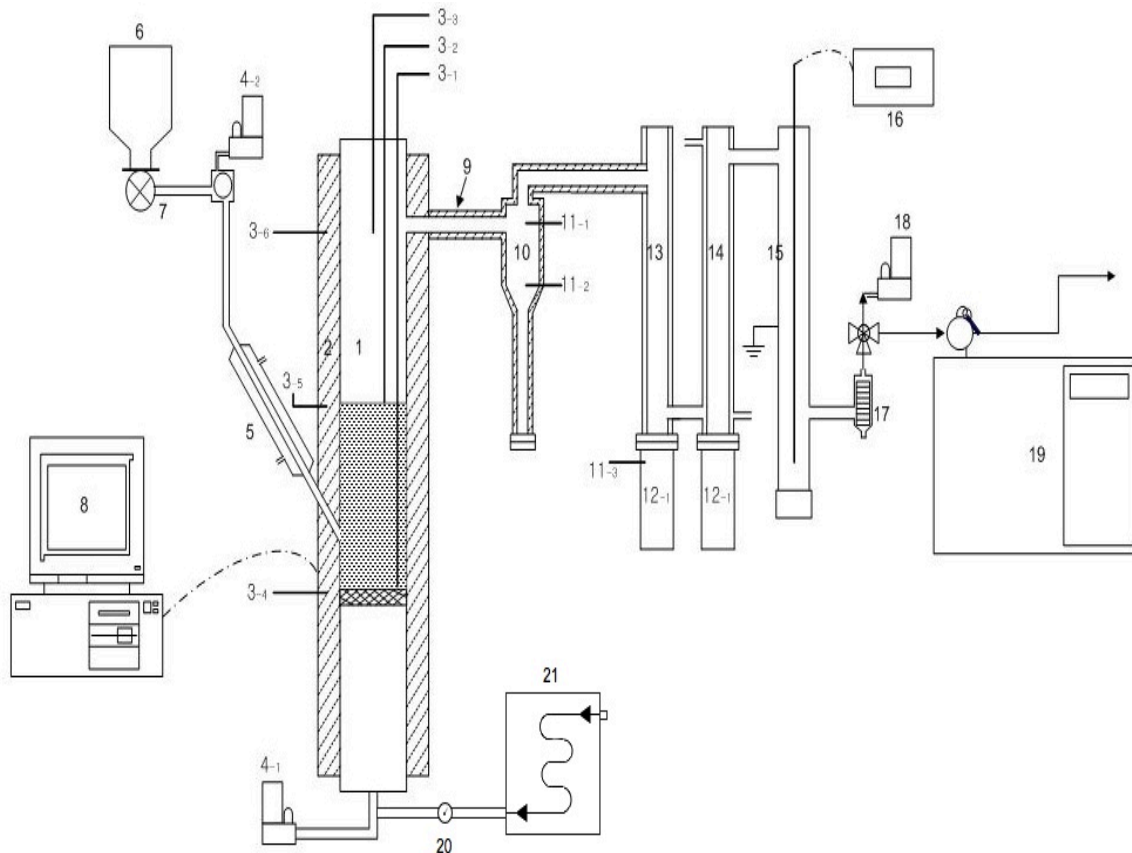
Figure 4.1 Schematic diagram of fluidized bed reactor and auxiliary components.

1-fluidized bed reactor, 2-furnance, 3; 11-thermocouple, 4-mass flow controller, 5-jacketed air-cooled feeder tube, 6-hopper, 7-twin screw feeder, 8-computer, 9-heating tape, 10-cyclone, 12-reservoir, 13; 14-condenser, 15-electrostatic precipitator (ESP), 16-AC power supply, 17-coalescing filter, 18-wet gas meter, 19-gas chromatography, 20- steam regulator, 21- boiler.

Co-gasification experiments were conducted with silica sand as bed material using N_2 gas, bone-dry CO_2 gas, and steam as fluidizing medium under atmospheric pressure. Saturate steam was generated using a Sussman Electric Boiler (model MBA9, Sussman - Automatic Corporation, Long Island City, New York, USA). Hybrid poplar biomass was blended with coal in the proportion of 0%, 10%, 20%, 30%, 40%, and 50% (weight basis). Operating temperatures used were 700°C, 800°C, and 900°C. Coal-biomass feed rate was controlled using a twin-screw volumetric feeder and the feed material was swept into the gasification zone with fluidizing gas.

Bed temperature, which is critical to gasification reaction, was monitored using a K-type thermocouple (Omega Engineering, Inc., Stamford, Connecticut, USA).

For steam experiments, silica sand was used as bed material. When the fluidized bed stabilized at the target temperature, saturated steam at 115°C was introduced into the reactor via preheating zone containing Berl saddles. The amount of steam and steam flow rate required to ensure fluidization of silica sand was determined by collecting condensate by metering steam into the reactor when empty. Steam was regulated using a stainless steel high-flow metering valve (Model: SS-4L2-MH, Swagelok®, Salt Lake, Utah, USA). Nitrogen gas was used to entrained feed into the reaction zone. Experimental conditions are presented in Table 4.2.

After thermal devolatilization of the feed mixture, product gas was cleaned from char and tar using high-temperature filter, condensers, electrostatic precipitator, and coalescing filter placed in series. The cleaned gas was analyzed with an online 490-micro GC equipped with two columns: Molsieve column (carrier gas: argon, column temperature: 55°C) and PoraPLOT U

Table 4.2 Operating conditions of fluidized bed reactor.

Parameter	Notes
Experimental time	60 min
Feed rate	200 g/h
Reactor temperature	700°C, 800°C, 900°C
Reactor diameter	5 cm (2 in)
Reactor height /including preheating zone	50 cm (20 in) /14 cm (5.5 in)
Bed material	Silica sand (100 g)
Fluidizing medium	N_2, CO_2, Steam
Residence time	3 s
Superficial velocity	2 x minimum fluidization velocity
Steam/feed (dry) ratio	2
Steam/nitrogen ratio	1.9

column (carrier gas: helium, column temperature: 100°C). Concentrations of product gas compounds were recorded at intervals of 5 minutes. All experiments lasted for 60 minutes.

4. Results and Discussion

In the experiments, sub-bituminous coal and hybrid poplar wood (poplar) were initially gasified using N_2, bone-dry CO_2, and steam before conducting co-gasification of mixtures of coal and poplar. Experimental data (Expt.) obtained from experiments were compared to predicted (calculated) data for signs of interaction and synergetic effects. Unless otherwise stated, all experiments were repeated at least three times and mean values were calculated with standard deviations.

4.1 Effect of hybrid poplar wood content and fluidizing medium on product yields

Table 4.3 present product yields obtained from gasifying poplar alone. Yield of product gas compounds are shown in Table 4.4. From Table 4.3, the yield of product gases obtained using N_2 and CO_2 fluidizing gases were similar but higher than product gas obtained using steam. Because conversion of feed involves endothermic reaction, the presence of steam may have reduced char reactivity. Liquid yields obtained from poplar gasification experiments reach about 22% dry wt. Product gas comprised mainly of CO (Table 4.4). The concentrations of H_2 and CO_2 can be seen to vary depending on operating temperature and gasification medium.

The main product yields from co-gasification experiments are shown in Table 4.5 (N_2 medium), Table 4.6 (CO_2 medium), and Table 4.7 (steam medium). It can be seen that experimental product yields (Expt.) were identical to predicted yields (Pred.). Further, the experimental product gas yields were not all in conformity with the predicted product gas yields. Lack of synergetic effect suggests that the two feedstocks behaved independently during thermal conversion. Kajitani et al. (2009) co-gasified bituminous coals and cedar bark and their mixtures using N_2 gas and CO_2 gas at temperatures up to 1400°C. They found no synergetic effect between

Table 4.3 Product yield (dry wt.%) for hybrid poplar wood gasification.

Temp. (°C)	Char	Water	Tar	Gas
Nitrogen (gasification medium)				
700	1.86 ±0.71	21.23 ±1.83	5.31 ±1.11	69.86 ±0.85
800	1.17 ±0.68	16.76 ±1.98	2.70 ±0.88	77.32 ±1.19
900	0.67 ±0.09	11.56 ±1.09	0.28 ±0.10	85.46 ±0.79
Carbon dioxide (gasification medium)				
700	5.63 ±0.18	18.99 ±0.59	7.69 ±0.95	67.64 ±0.04
800	2.14 ±0.13	14.54 ±0.96	2.90 ±0.54	79.68 ±1.95
900	0.65 ±0.29	13.66 ±0.52	1.05 ±0.25	84.40 ±0.75
Steam (gasification medium)				
700	11.40	22.54	5.70	59.61
800	3.21	18.91	3.85	69.94
900	0.77	16.69	1.5	78.04

Table 4.4 Yield (vol.%) of product gas compounds for hybrid poplar wood gasification.

Temp. (°C)	H_2	CO	CH_4	CO_2	C_2 - C_4
Nitrogen (gasification medium)					
700	18.81 ±0.40	47.97 ±1.08	9.85 ±1.04	22.33 ±3.35	1.05 ±0.06
800	22.46 ±1.03	47.42 ±1.19	13.11 ±1.24	16.28 ±2.21	0.74 ±0.25
900	27.19 ±0.65	50.93 ±2.02	10.93 ±0.16	10.88 ±2.42	0.07 ±0.01
Carbon dioxide (gasification medium)					
700	14.07 ±0.01	58.91 ±0.21	13.45 ±0.25	11.66 ±0.24	1.91 ±0.15
800	15.00 ±1.01	61.78 ±1.28	14.13 ±0.09	7.59 ±0.84	1.49 ±0.03
900	13.27 ±1.23	73.88 ±0.49	11.10 ±0.22	1.52 ±0.55	0.23 ±0.01
Steam (gasification medium)					
700	17.91	50.64	11.81	18.05	1.59
800	22.47	49.44	12.97	14.13	1.00
900	35.80	35.11	10.08	18.78	0.22

Table 4.5 Product yield (dry wt.%) for sub-bituminous coal and hybrid poplar wood mixtures co-gasification in N_2.

Biomass (wt.%)	Temp. (°C)	Char		Water		Tar		Gas	
		Expt.	Pred.	Expt.	Pred.	Expt.	Pred.	Expt.	Pred.
	700	53.98 ±0.65		26.10 ±0.83		5.54 ±0.18		14.25 ±0.88	
0	800	52.38 ±0.58		23.09 ±0.88		3.64 ±0.48		20.72 ±0.23	
	900	45.14 ±0.57		13.96 ±0.87		1.04 ±0.27		38.96 ±0.57	
	700	51.14 ±1.03	48.77	24.00 ±1.21	25.62	4.85 ±0.01	5.52	19.93 ±0.13	19.81
10	800	47.50 ±1.98	47.26	24.68 ±1.50	22.46	2.69 ±0.16	3.55	22.73 ±0.95	26.38
	900	40.16 ±0.86	40.70	15.42 ±0.98	13.72	1.60 ±0.18	0.97	42.69 ±0.23	43.61
	700	44.98 ±0.78	43.55	26.11 ±0.92	25.13	2.51 ±0.28	5.49	25.60 ±0.97	25.37
20	800	42.14 ±0.83	42.14	19.68 ±0.76	21.82	2.01 ±0.05	3.45	35.33 ±0.40	32.04
	900	36.42 ±1.01	36.25	17.26 ±0.78	13.48	1.23 ±0.17	0.89	43.34 ±1.02	48.26
	700	39.42 ±0.23	38.34	24.19 ±1.03	24.64	6.52 ±0.54	5.47	29.79 ±0.78	30.93
30	800	34.09 ±1.52	37.02	23.08 ±0.86	21.19	4.03 ±0.23	3.36	38.77 ±0.69	37.70
	900	31.53 ±0.43	31.80	20.18 ±1.01	13.24	2.11 ±0.43	0.81	46.01 ±0.25	52.91
	700	32.60 ±1.11	33.13	26.22 ±0.76	24.15	7.40 ±0.02	5.45	33.11 ±0.65	36.49
40	800	30.62 ±0.45	31.90	22.93 ±1.11	20.56	4.42 ±0.84	3.27	41.81 ±0.74	43.36
	900	26.15 ±1.03	27.35	19.99 ±0.13	13.00	2.14 ±0.23	0.74	51.30 ±0.56	57.56
	700	28.91 ±0.23	27.92	23.24 ±0.93	23.67	7.64 ±0.08	5.43	40.00 ±0.25	42.05
50	800	27.83 ±1.05	26.78	19.27 ±0.67	19.92	4.29 ±0.03	3.17	47.40 ±0.65	49.02
	900	21.84 ±0.96	22.91	15.73 ±1.03	12.76	2.80 ±0.12	0.66	59.14 ±1.20	62.21

Table 4.6. Product yield (dry weight.%) for sub-bituminous coal and hybrid poplar wood mixtures co-gasification in CO_2.

Biomass (wt.%)	Temp. (°C)	Char Expt.	Char Pred.	Water Expt.	Water Pred.	Tar Expt.	Tar Pred.	Gas Expt.	Gas Pred.
	700	57.30 ±0.87		30.29 ±1.64		5.86 ±0.84		6.30 ±0.59	
0	800	48.20 ±0.46		29.03 ±0.81		2.70 ±0.54		18.80 ±1.52	
	900	41.56 ±0.20		26.46 ±1.00		1.05 ±0.17		29.62 ±0.32	
	700	51.07 ±0.25	52.14	33.02 ±0.77	29.16	4.84 ±0.42	6.04	10.51 ±0.25	12.44
10	800	45.94 ±0.01	43.60	32.88 ±0.25	27.58	5.32 ±0.04	2.72	15.41 ±0.28	24.89
	900	39.53 ±1.80	37.47	29.96 ±2.00	25.18	2.86 ±0.09	1.05	27.45 ±1.36	35.10
	700	43.07 ±0.28	46.97	32.45 ±0.18	28.03	6.97 ±0.62	6.22	17.34 ±0.04	18.57
20	800	41.14 ±0.49	38.99	33.51 ±0.04	26.13	5.28 ±0.03	2.74	19.34 ±0.22	30.98
	900	37.15 ±1.01	33.38	28.30 ±0.11	23.90	2.29 ±0.10	1.05	30.49 ±0.46	40.58
	700	42.74 ±1.04	41.80	30.39 ±1.32	26.90	6.86 ±0.34	6.41	19.81 ±0.23	24.70
30	800	36.21 ±0.18	34.38	30.00 ±0.45	24.68	5.69 ±0.27	2.76	28.00 ±0.16	37.07
	900	31.36 ±0.73	29.29	29.68 ±0.19	22.62	2.72 ±0.23	1.05	35.58 ±0.25	46.05
	700	35.50 ±1.19	36.63	27.74 ±1.23	25.77	8.80 ±0.99	6.59	27.36 ±1.23	30.84
40	800	29.78 ±0.75	29.78	26.21 ±0.24	23.23	5.29 ±0.23	2.78	37.45 ±0.24	43.15
	900	26.02 ±0.85	25.20	25.01 ±0.32	21.34	2.75 ±0.45	1.05	46.03 ±0.95	51.53
	700	32.17 ±0.04	31.47	26.40 ±0.34	24.64	8.30 ±0.34	4.38	33.1 ±0.92	36.97
50	800	24.16 ±0.63	25.17	22.41 ±1.01	21.78	4.93 ±0.12	2.80	48.40 ±1.04	49.24
	900	22.09 ±0.56	21.11	21.18 ±0.02	20.06	2.92 ±0.22	1.05	52.83 ±1.02	57.01

Table 4.7. Product yield (dry wt.%) for sub-bituminous coal and hybrid poplar wood mixtures co-gasification in steam.

Biomass (wt.%)	Temp. (°C)	Char Expt.	Char Pred.	Water Expt.	Water Pred.	Tar Expt.	Tar Pred.	Gas Expt.	Gas Pred.
	700	53.65		25.36		5.00		14.91	
0	800	50.21		21.65		4.47		22.07	
	900	42.06		15.05		1.47		39.75	
	700	47.60	49.43	22.89	25.08	3.72	5.07	22.10	19.38
10	800	42.49	45.51	21.76	21.38	3.12	4.41	29.64	26.86
	900	37.98	37.93	14.23	15.21	1.25	1.47	45.10	43.58
	700	43.23	45.20	21.32	24.80	4.01	5.14	27.14	23.85
20	800	39.21	40.81	21.14	21.10	2.11	4.35	33.38	31.64
	900	33.46	33.80	14.89	15.38	1.42	1.48	48.41	47.41
	700	39.46	40.98	23.86	24.51	5.88	5.21	30.32	28.32
30	800	34.38	36.11	23.37	20.83	2.81	4.28	35.08	36.43
	900	31.60	29.67	13.43	15.54	1.76	1.48	52.08	51.24
	700	33.45	36.75	27.11	24.23	6.60	5.28	32.86	32.79
40	800	30.12	31.41	22.31	20.55	3.39	4.22	41.98	41.22
	900	27.49	25.54	14.98	15.71	2.30	1.48	54.49	55.07
	700	28.22	32.53	22.43	23.95	7.50	5.35	37.74	37.26
50	800	25.65	26.71	21.54	20.28	3.75	4.16	46.18	46.01
	900	23.09	21.42	15.01	15.87	2.97	1.49	58.14	58.90

coal and biomass. Other studies have also reported the absence of synergy between coal and biomass under thermochemical conversion (Biagini et al., 2002; Gil et al., 2010; Idris et al., 2010; Kirtania and Bhattacharya, 2013; Li et al., 2014; Pan et al., 1996; Sadhukhan et al., 2008; Vamvuka et al., 2003; Vuthaluru, 2004; Zhu et al., 2008).

Although no synergy was observed between coal and poplar co-gasification, char and tar yields decreased as temperature increased; which led to increase in product gas. The product gas yields were higher compared to single coal product gas yields and char yields were lower than single coal char yields. The distributions of product yields are illustrated in Figure 4.2 to Figure 4.5 (N_2 medium), Figure 4.6 to Figure 4.9 (CO_2 medium), and Figure 4.10 to Figure 4.13 (steam medium). Tar yields increased with increasing poplar content (from 30 wt.% and above) as shown in Figure 4.4, Figure 4.8, and Figure 4.12 and water yields obtained were higher (Figure 4.5, Figure 4.9, and Figure 4.13).
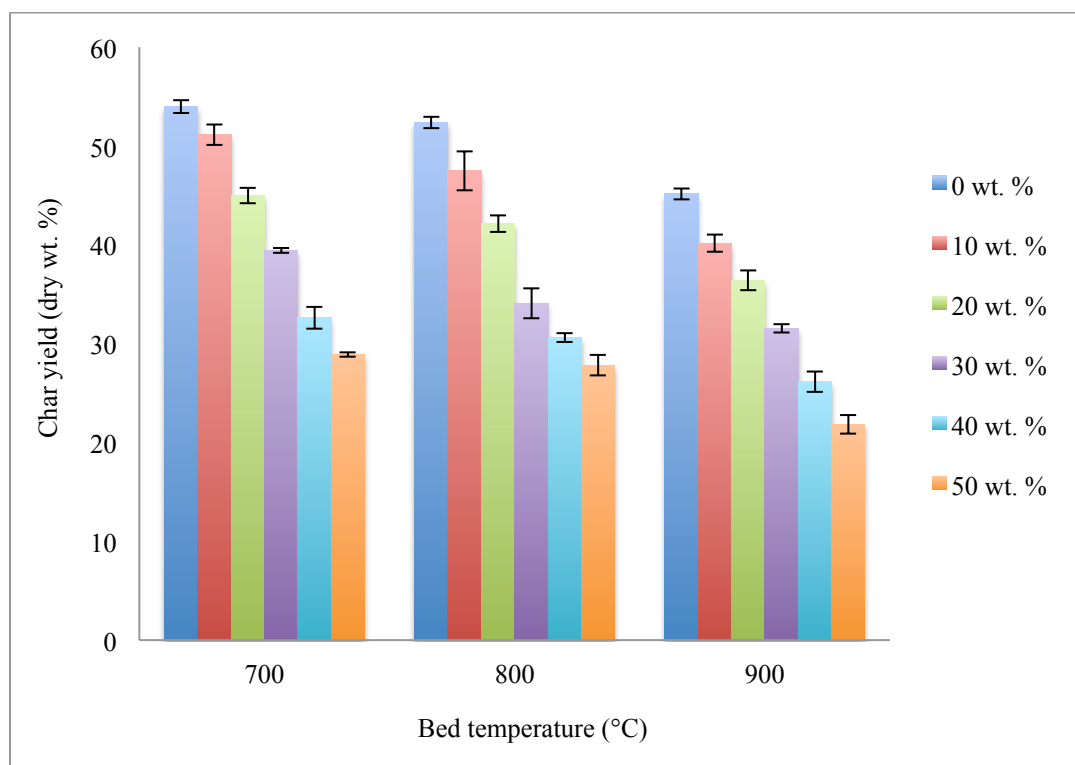

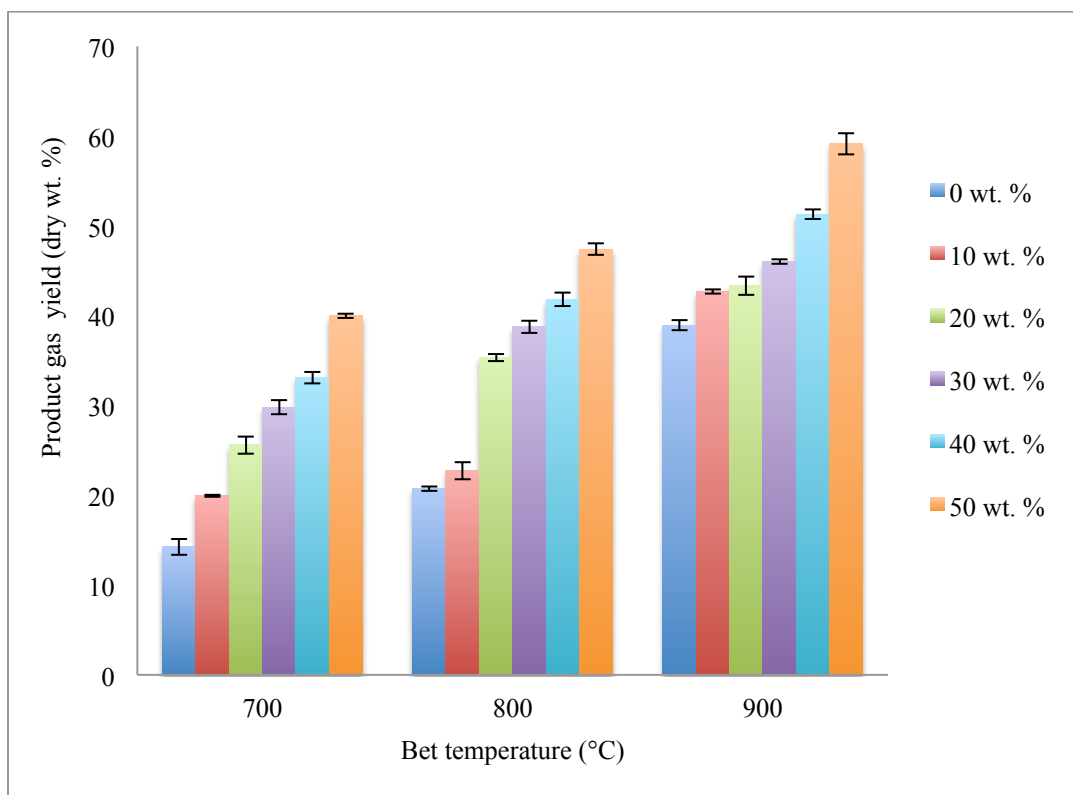Figure 4.2 Effect of bed temperature and hybrid poplar content on char yield in N_2.

Figure 4.3 Effect of bed temperature and hybrid poplar content on product gas yield in N_2.
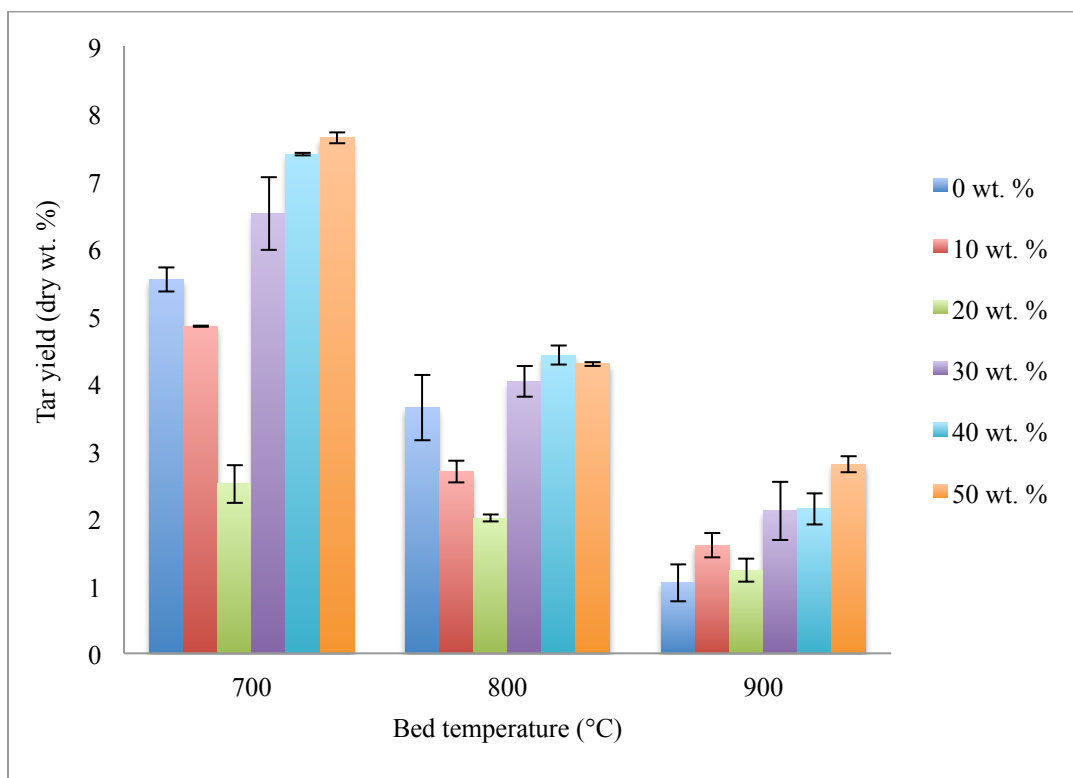

Figure 4.4 Effect of bed temperature and hybrid poplar content on tar yield in N_2.
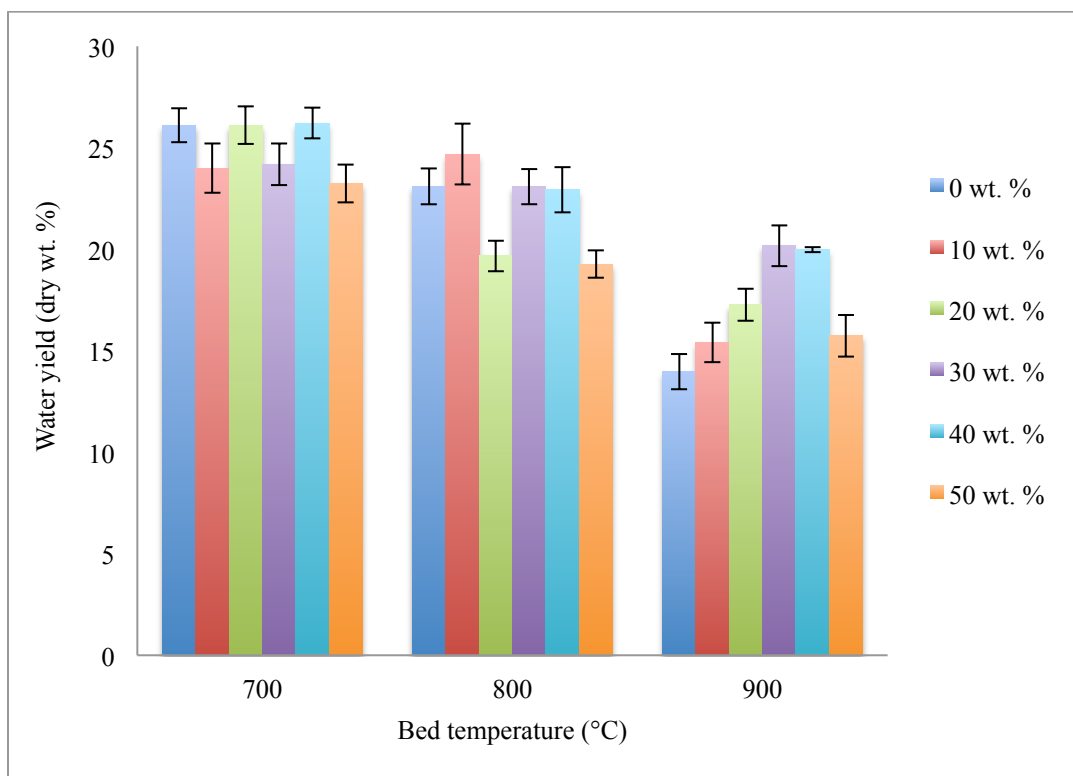
Figure 4.5 Effect of bed temperature and hybrid poplar content on water yield in N_2.
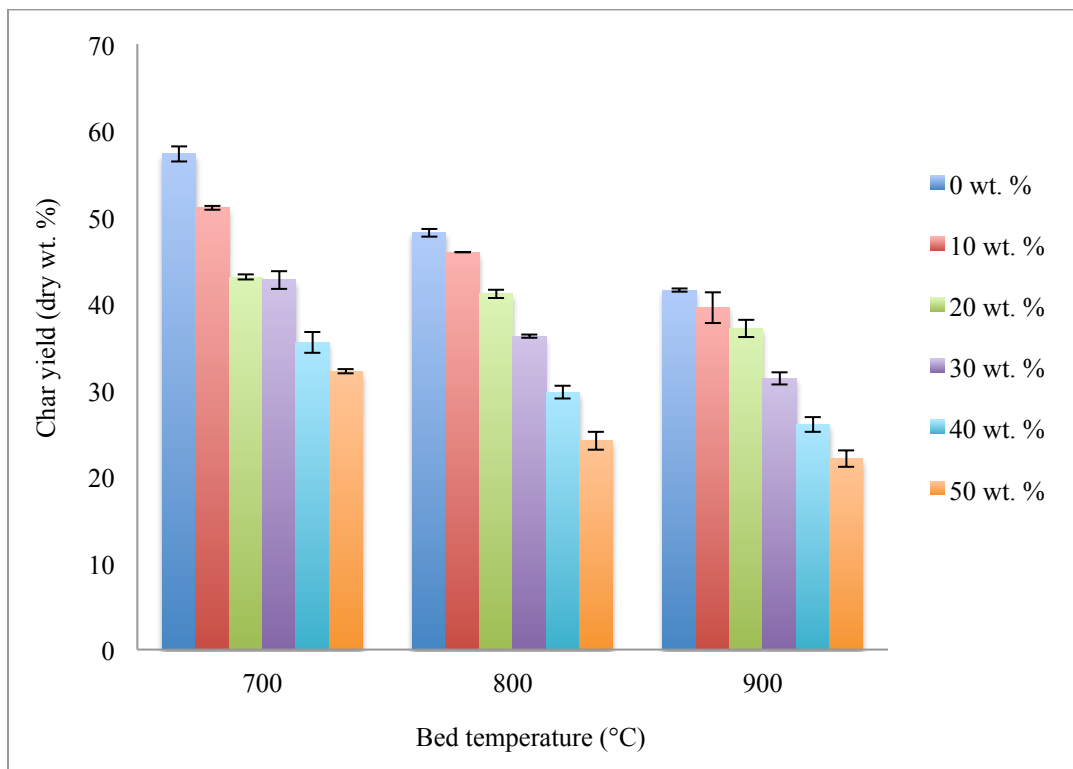

Figure 4.6 Effect of bed temperature and hybrid poplar content on char yield in N_2.
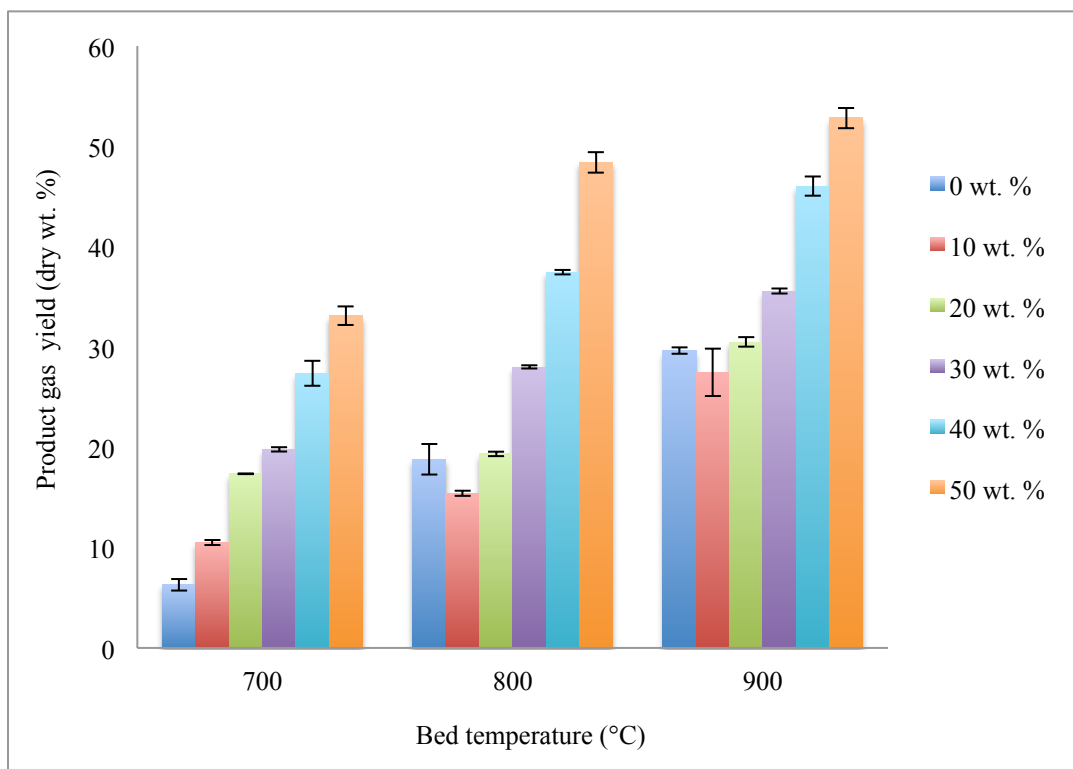
Figure 4.7 Effect of bed temperature and hybrid poplar content on product gas yield in CO_2.

Figure 4.8 Effect of bed temperature and hybrid poplar content on tar yield in CO_2.

Figure 4.9 Effect of bed temperature and hybrid poplar content on water yield in CO_2.

Figure 4.10 Effect of bed temperature and hybrid poplar content on char yield in steam.

Figure 4.11 Effect of bed temperature and hybrid poplar content on product gas yield in steam.
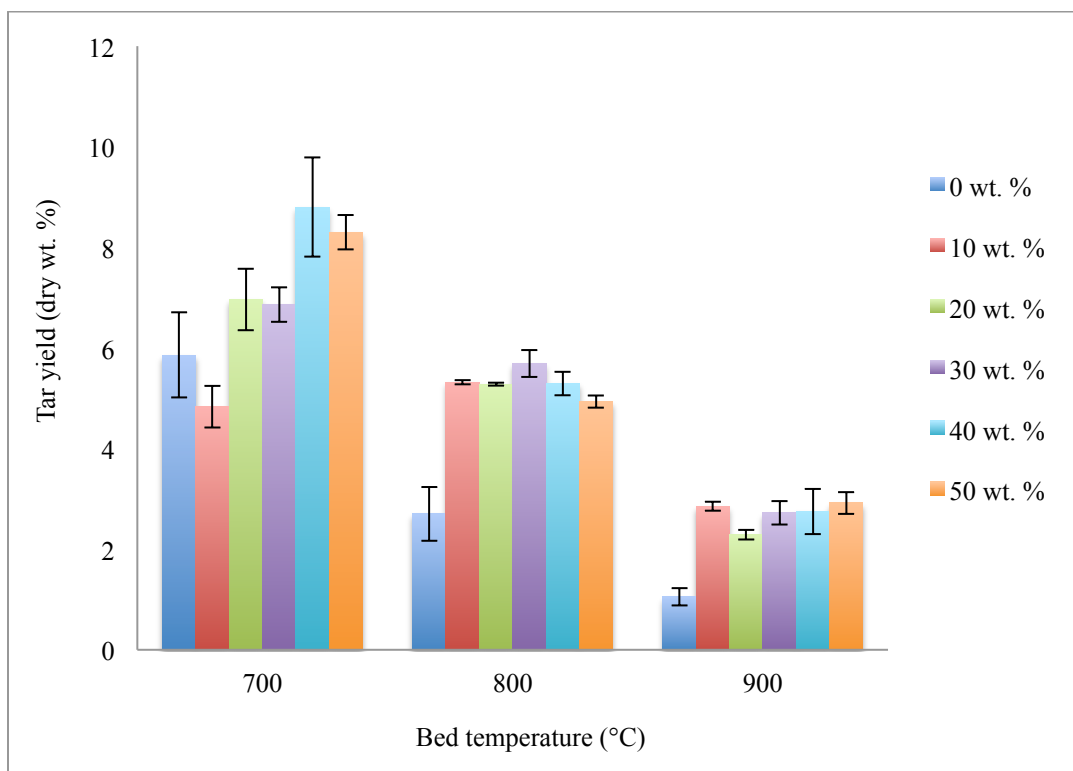

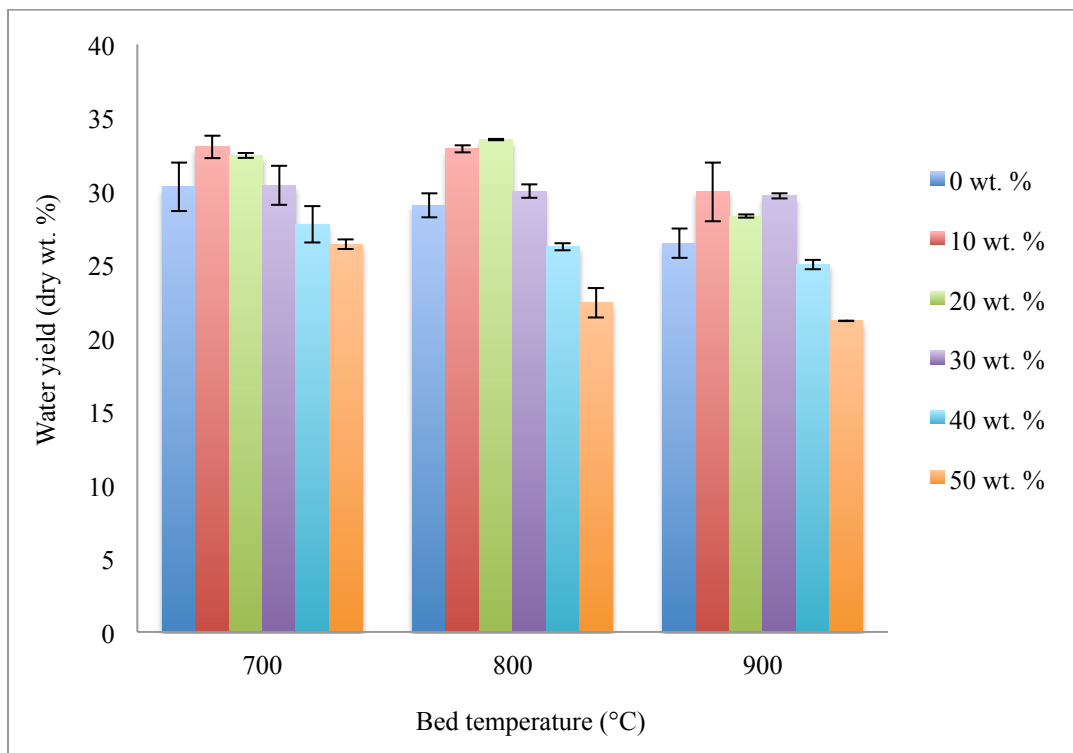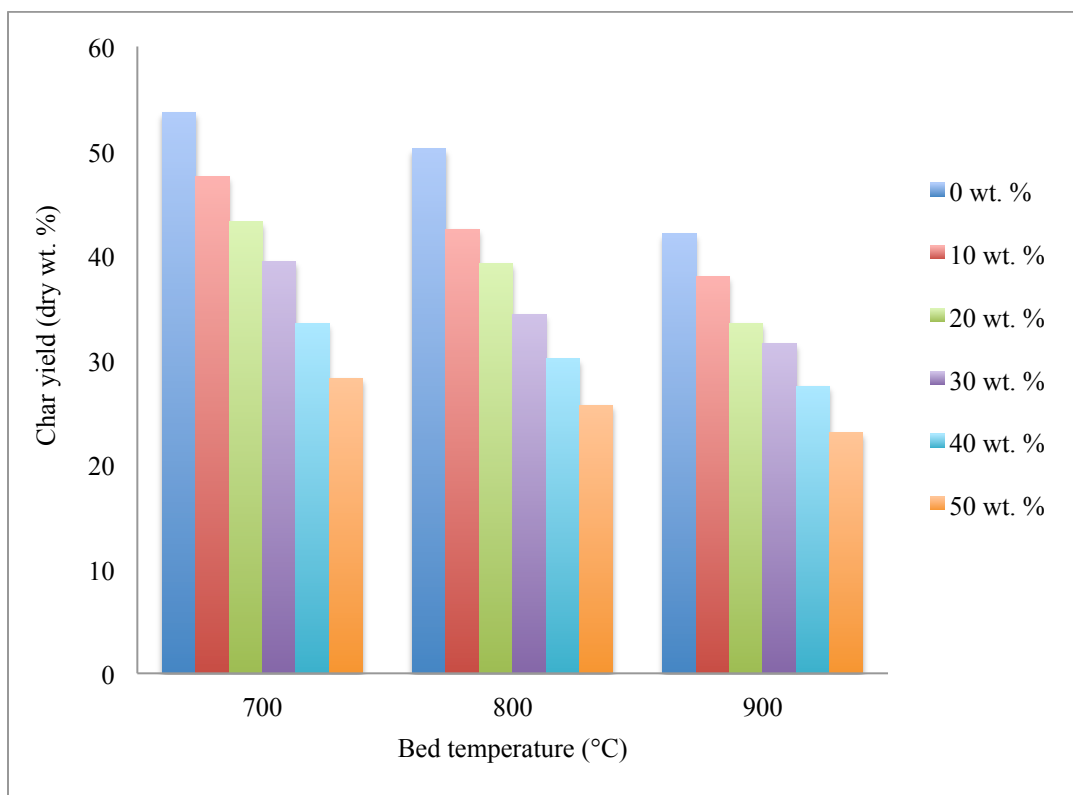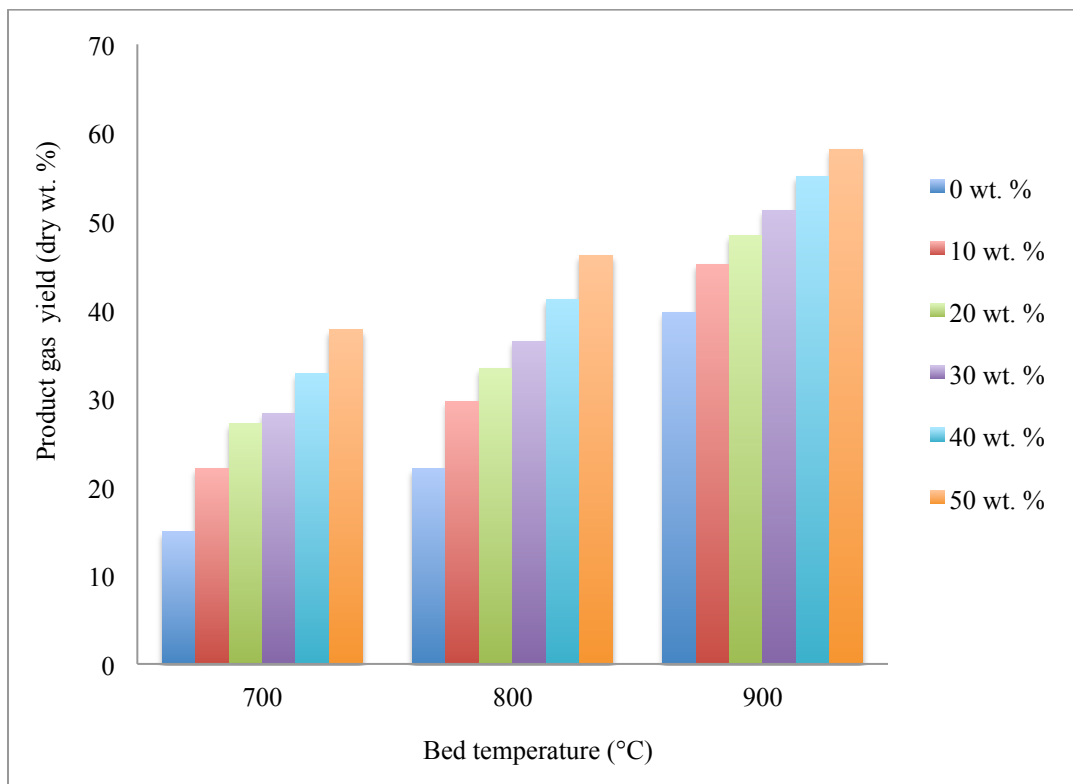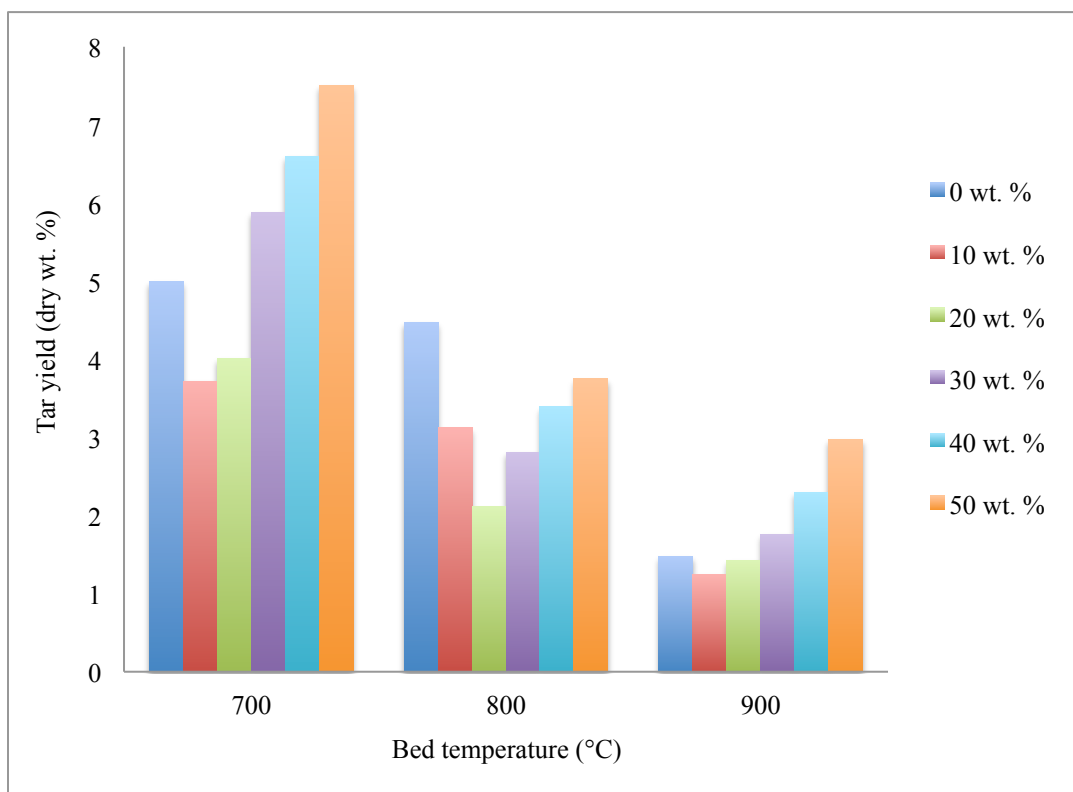Figure 4.12 Effect of bed temperature and hybrid poplar content on tar yield in steam.
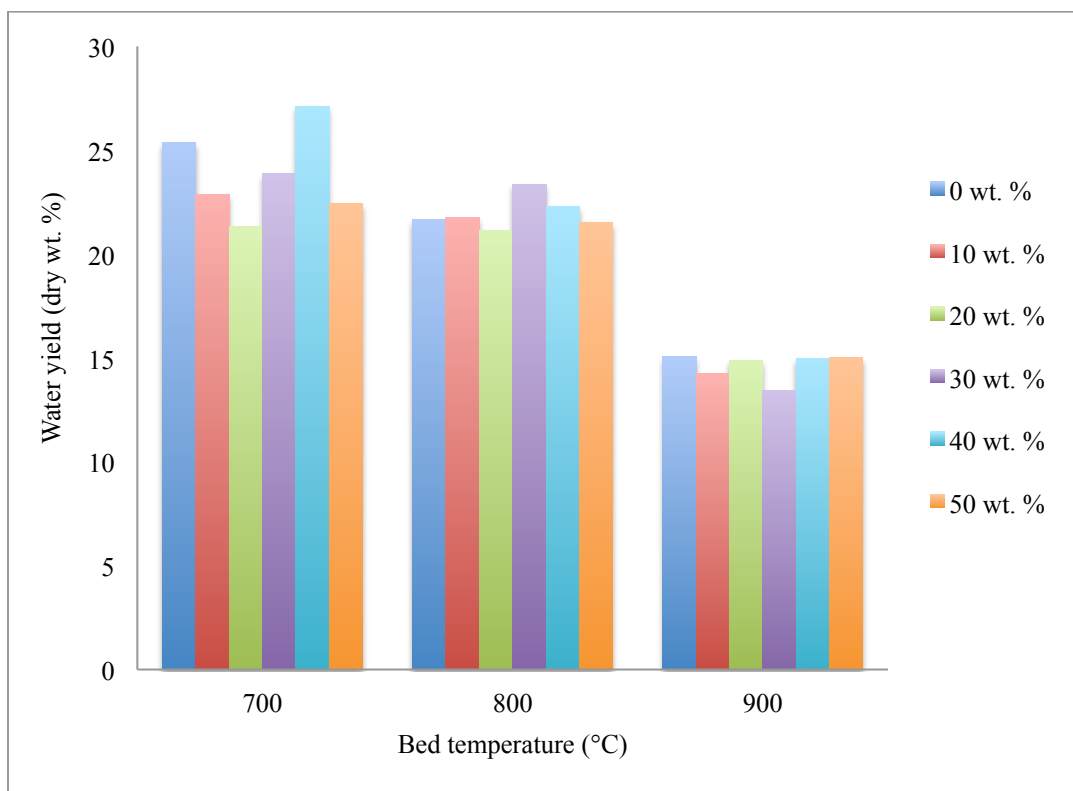
Figure 4.13 Effect of bed temperature and hybrid poplar content on water yield in steam.

4.2 Effect of hybrid poplar wood ratio and fluidizing medium on product gas compounds

Product gas composition and their yields obtained are presented in Table 4.8 (N_2 medium) and Table 4.9 (CO_2 medium). There is fair agreement between the yields of experimental product gas compounds (Expt.) and predicted values (Pred.) with N_2 gas as shown in Table 4.8. Likewise differences between experimental yields and predicted yields within experimental error given in Table 4.9 are not enough to conclude synergetic effects between coal and poplar co-gasification using CO_2. Collot et al. (1999) observed similar trends on coal and biomass mixtures co-pyrolysis and co-gasification in He and CO_2 medium using a fluidized-bed. They found that neither intimate contact between the two feedstocks nor their relative segregation led to synergetic effects between the volatile yields. Lack of synergy between gas species for coal and biomass during thermochemical conversion was reported by other authors (Meesri and Moghtaderi, 2002; Moghtaderi et al., 2004).

Table 4.10 shows product gas compounds obtained using steam as gasification medium. H_2 yields obtained from experiment were higher than predicted H_2 yields. This was due to water-gas shift reaction ($C + H_2O \longrightarrow H_2 + CO$) that led to higher H_2 and CO yields for coal-hybrid poplar mixtures. The effect of synergy occurred mainly at 700°C. H_2 yields obtained from experiment were 21%, 19%, and 14% higher than predicted H_2 yields at 700°C, 800°C, and 900°C respectively with 10 wt.% poplar content. With 20 wt.% poplar, experimental H_2 yields were about 16%, 17%, and 9% higher compared to predicted yields at 700°C, 800°C, and 900°C respectively. Howaniec et al. (2011) observed synergetic effects between coal and biomass in terms of high volumes of H_2 production when coal and biomass were co-gasified in a fixed bed reactor at 700°C, 800°C, and 900°C under atmospheric pressure. They attributed the observed synergy to catalytic effect of K_2O in coal-biomass ash.

A typical temperature profile measured during steam co-gasification experiment is shown in Figure 4.14. Plots in Figure 4.15 to Figure 4.17 show the effect of gasification medium on syngas ($H_2 + CO$) production. Concentration of syngas were higher in CO_2 medium compared to both N_2 and steam media. Quantity of syngas is important however; the quality (ratio of H_2 to CO) is crucial to end-use application. For example, stoichiometric ratio of H_2/CO of about 2 is desirable for methanol synthesis and for methane production, H_2/CO of about 3 is required (Liu et al., 2010). In this study, H_2/CO ratios (Figure 4.18 to Figure 4.20) were greatly influenced by temperature, poplar content, and gasification media. Co-gasification using steam gave the highest H_2/CO ratios at 900°C (Figure 4.20). However, increase in biomass content decreased H_2/CO ratios at all temperature levels.

Figure 4.21 to Figure 4.23 show the distribution of product gas compounds obtained using N_2 as gasification medium. The concentrations of H_2 and CO form a larger proportion of the product gas. Nevertheless, the concentration of H_2 decreased with increase in hybrid poplar content whereas CO increased. The reduction of H_2 could be due to water forming reactions ($H_2 + CO_2 \longrightarrow H_2O + CO$) at equilibrium. In CO_2 medium, Boudouard reaction ($C + CO \longrightarrow 2CO$)

Table 4.8. Yield (vol.%) of product gas compounds for sub-bituminous coal and hybrid poplar wood mixtures in N_2.

Biomass (wt.%)	Temp. (°C)	H_2 Expt.	H_2 Pred.	CO Expt.	CO Pred.	CH_4 Expt.	CH_4 Pred.	CO_2 Expt.	CO_2 Pred.	C_2 - C_4 Expt.	C_2 - C_4 Pred.
0	700	39.63 ± 2.01		18.58 ±1.73		11.57 ±1.07		27.92 ±0.76		2.31 ±0.20	
	800	43.12 ±1.64		20.79 ±1.08		9.13 ±0.71		26.37 ±2.10		0.58 ±0.06	
	900	48.53 ±1.29		31.80 ±2.67		6.81±0.09		12.84 ±1.04		0.02 ±0.01	
10	700	30.66 ±0.13	37.54	30.69 ±2.12	21.52	11.11 ±1.51	11.40	24.32 ±2.76	27.36	3.21 ±1.71	2.19
	800	38.46 ±2.05	41.06	28.98 ±1.89	23.45	12.39 ±1.45	9.53	19.37 ±0.22	25.36	2.83 ±0.24	0.60
	900	43.82 ±1.58	46.40	25.31 ±2.96	33.72	9.29 ±0.24	7.22	18.75 ±1.12	12.64	0.79 ±0.09	0.02
20	700	29.34 ±1.98	35.46	31.96 ±2.68	24.46	11.72 ±0.15	11.22	25.09 ±2.16	26.80	1.89 ±0.28	2.06
	800	34.23 ±0.30	38.99	35.21 ±2.91	26.12	11.76 ±0.65	9.93	16.93 ±0.52	24.35	1.87 ±0.07	0.61
	900	39.17 ±1.53	44.26	34.23 ±0.12	35.63	10.76 ±0.10	7.63	15.54 ±1.19	12.45	0.30 ±0.05	0.03
30	700	29.42 ±1.32	33.38	33.01 ±1.21	27.39	11.05 ±1.06	11.05	23.74 ±1.77	26.24	2.78 ±0.78	1.93
	800	34.47 ±1.01	36.92	35.45 ±1.67	28.78	12.68 ±1.00	10.33	16.19 ±2.36	23.34	1.21 ±0.11	0.63
	900	38.33 ±1.43	42.13	32.59 ±2.02	37.54	11.28 ±0.98	8.05	17.50 ±1.03	12.25	0.30 ±0.18	0.03
40	700	26.41 ±0.78	31.30	34.90 ±1.65	30.33	12.08 ±0.63	10.88	24.35 ±2.98	25.68	2.25 ±1.03	1.81
	800	30.32 ±1.23	34.86	40.30 ±2.31	31.44	12.04 ±1.01	10.72	16.07 ±2.34	22.33	1.27 ±0.88	0.65
	900	34.70 ±2.11	39.99	40.13 ±2.10	39.45	11.33 ±0.28	8.46	13.59 ±1.03	12.06	0.25 ±0.07	0.04
50	700	23.30 ±1.23	29.22	44.64 ±2.31	33.27	9.78 ±2.15	10.71	19.07 ±1.43	25.12	3.22 ±1.21	1.68
	800	27.39 ±0.99	32.79	43.64 ±2.11	34.10	12.06 ±0.96	11.12	15.56 ±0.46	21.32	1.35 ±0.50	0.66
	900	33.48 ±1.76	37.86	43.45 ±2.53	41.37	10.58 ±1.11	8.87	12.12 ±1.53	11.86	0.22 ±0.03	0.04

Table 4.9. Yield (vol.%) of product gas compounds for sub-bituminous coal and hybrid poplar wood mixtures co-gasification in CO_2.

Biomass (wt.%)	Temp. (°C)	H_2 Expt.	H_2 Pred.	CO Expt.	CO Pred.	CH_4 Expt.	CH_4 Pred.	CO_2 Expt.	CO_2 Pred.	$C_2 - C_4$ Expt.	$C_2 - C_4$ Pred.
0	700	30.52 ±1.46		51.84 ±0.03		12.77 ±0.42		3.13 ±1.27		1.73 ±0.25	
	800	28.07 ±0.95		61.16 ±2.18		7.76 ±0.81		2.78 ±0.57		0.22 ±0.05	
	900	23.52 ±1.13		69.12 ±2.79		5.85 ±0.17		1.50 ±0.01		0.01 ±0.00	
10	700	23.39 ±1.84	28.88	53.71 ±0.90	52.55	14.32 ±0.63	12.84	6.89 ±0.42	3.98	1.68 ±0.06	1.75
	800	21.32 ±0.44	26.77	62.73 ±1.98	61.22	11.68 ±0.74	8.40	3.51 ±0.37	3.27	0.74 ±0.09	0.34
	900	21.75 ±1.65	22.50	68.30 ±2.98	69.60	8.09 ±0.53	6.37	1.80 ±0.09	1.51	0.06 ±0.01	0.03
20	700	19.63 ±0.78	27.23	52.18 ±2.01	53.25	13.71 ±1.21	12.91	12.94 ±0.94	4.84	1.55 ±0.16	1.77
	800	21.65 ±0.71	25.46	61.21 ±1.97	61.29	11.65 ±0.86	9.04	4.91 ±0.31	3.75	0.59 ±0.11	0.47
	900	22.33 ±0.34	21.47	67.58 ±2.18	70.07	8.97 ±0.19	6.90	0.92 ±0.63	1.51	0.19 ±0.22	0.05
30	700	18.19 ±0.15	25.59	51.03 ±2.22	53.96	13.93 ±1.01	12.97	13.97 ±0.25	5.69	2.88 ±0.15	1.79
	800	19.71 ±0.20	24.15	57.59 ±2.03	61.35	11.95 ±0.45	9.68	9.80 ±1.02	4.23	0.94 ±0.23	0.60
	900	20.78 ±0.11	20.45	65.00 ±2.18	70.55	9.36 ±1.65	7.42	4.69 ±0.83	1.51	0.18 ±0.01	0.07
40	700	16.05 ±0.43	23.94	52.33 ±1.66	54.67	12.02 ±1.11	13.04	17.04 ±1.05	6.54	2.55 ±0.21	1.80
	800	17.27 ±0.07	22.84	59.75 ±1.88	61.41	10.48 ±1.05	10.32	11.64 ±0.26	4.71	0.86 ±0.34	0.73
	900	19.50 ±0.10	19.42	67.65 ±2.99	71.02	9.76 ±0.68	7.95	2.98 ±0.14	1.51	0.12 ±1.11	0.09
50	700	14.43 ±0.12	22.30	54.69 ±0.94	55.38	11.12 ±0.74	13.11	18.18 ±1.22	7.40	2.58 ±0.14	1.82
	800	15.75 ±0.32	21.54	63.14 ±1.99	61.47	9.34 ±0.32	10.95	11.13 ±1.09	5.19	0.65 ±0.20	0.85
	900	17.63 ±1.01	18.40	68.86 ±2.11	71.50	9.72 ±1.14	8.47	3.64 ±1.11	1.51	0.15 ±0.03	0.12

Table 4.10. Yield (vol.%) of product gas compounds for sub-bituminous coal and poplar wood mixtures co-gasification in steam.

Biomass (wt.%)	Temp. (°C)	H_2		CO		CH_4		CO_2		$C_2 - C_4$	
		Expt.	Pred.	Expt.	Pred.	Expt.	Pred.	Expt.	Pred.	Expt.	Pred.
0	700	18.31		27.90		16.10		31.98		5.70	
	800	32.28		25.37		14.83		25.13		2.39	
	900	42.67		27.27		10.61		18.95		0.49	
10	700	22.13	18.27	31.91	30.17	13.97	15.68	28.27	30.59	3.71	5.29
	800	37.16	31.30	24.09	27.77	11.84	14.65	25.51	24.03	1.41	2.25
	900	47.86	41.99	18.97	28.05	8.26	10.56	24.68	18.93	0.23	0.47
20	700	21.08	18.23	39.44	32.45	12.97	15.25	23.32	29.19	3.20	4.88
	800	35.52	30.32	31.41	30.18	12.86	14.46	19.30	22.93	0.91	2.11
	900	44.82	41.30	28.07	28.84	10.23	10.51	16.73	18.92	0.16	0.44
30	700	22.06	18.19	40.25	34.72	12.93	14.82	21.79	27.80	2.98	4.47
	800	30.04	29.33	35.67	32.59	12.51	14.27	20.34	21.83	1.44	1.97
	900	39.67	40.61	28.91	29.62	10.21	10.45	20.91	18.90	0.30	0.41
40	700	21.51	18.15	43.19	36.99	11.74	14.39	21.01	26.41	2.56	4.06
	800	31.55	28.35	36.08	34.99	11.54	14.09	19.72	20.73	1.11	1.84
	900	41.46	39.93	28.90	30.41	9.19	10.40	20.29	18.88	0.16	0.39
50	700	21.37	18.11	40.34	39.27	12.67	13.96	23.43	25.02	2.19	3.65
	800	29.86	27.37	36.85	37.40	12.68	13.90	19.67	19.63	0.94	1.70
	900	37.30	39.24	33.05	31.19	10.81	10.35	18.54	18.87	0.30	0.36

dominated co-gasification reactions, which resulted in high yields of CO (Figure 4.24 to Figure 4.26) at all temperature levels. The yield of CO however appeared independent, as the concentrations remained fairly constant with increasing poplar content. CO yields remained at 53 vol.% at 700°C, 60 vol.% at 800°C, and 70 vol.% at 900°C.

In steam gasification medium, CO concentrations increased with increasing poplar content at 700°C (Figure 4.27) whereas H_2 and CO_2 decreased. At 800°C (Figure 4.28) H_2 concentrations dominated with 10-20 wt.% poplar content. As temperature increased to 900°C (Figure 4.29) the volumes of H_2 produced were highest however, the concentrations decreased gradually with increase in biomass content.

The effect of temperature on product gas compounds is shown in Figure 4.30 to Figure 4.33 (N_2 medium), Figure 4.34 to Figure 4.37 (CO_2 medium), and Figure 4.38 to Figure 4.41 (steam medium). In N_2 medium, H_2 yields dominated at 900°C (Figure 4.30) whereas CO_2 yields dominated at 700°C (Figure 4.32). In CO_2 medium, high CO concentrations were produced at 900°C (Figure 4.35) whereas CO_2 and CH_4 concentrations dominated at 700°C (Figure 4.36 and Figure 4.37, respectively). For steam co-gasification medium, H_2 concentrations were maximum at 900°C (Figure 4.38) whereas CO and CO_2 yields were highest at 700°C (Figure 4.39 and Figure 4.40, respectively).
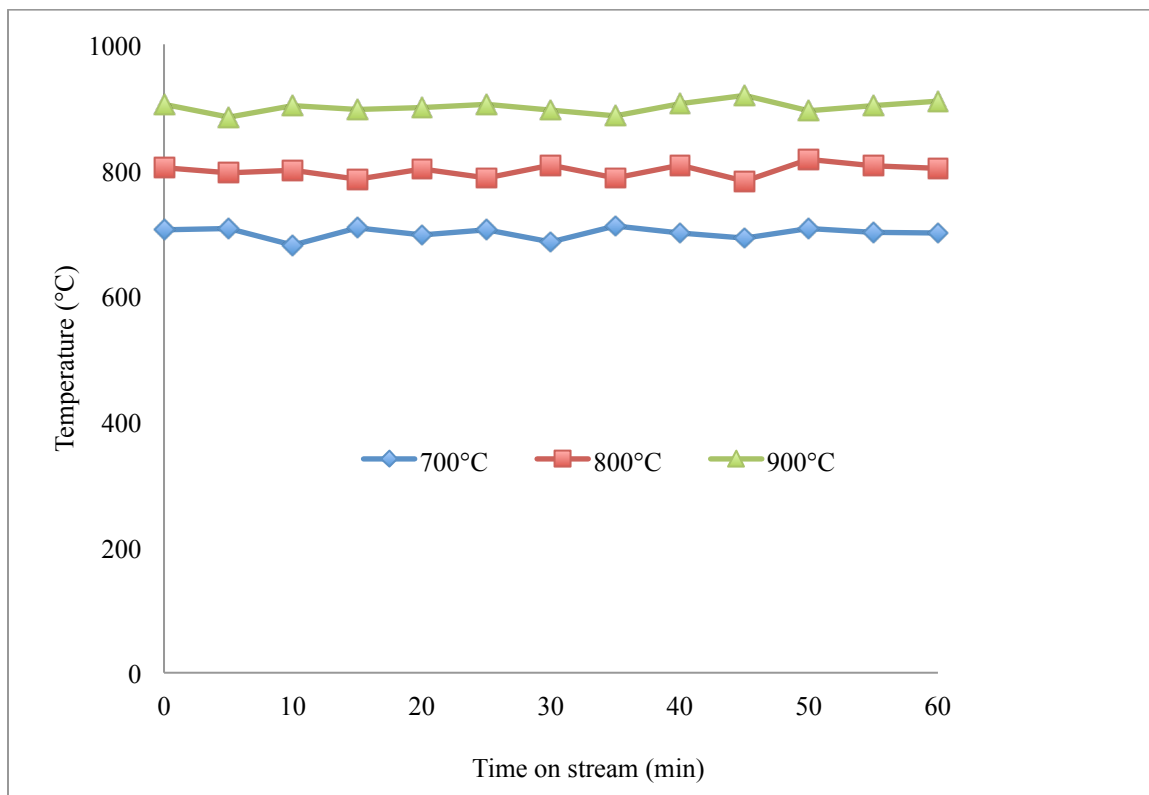
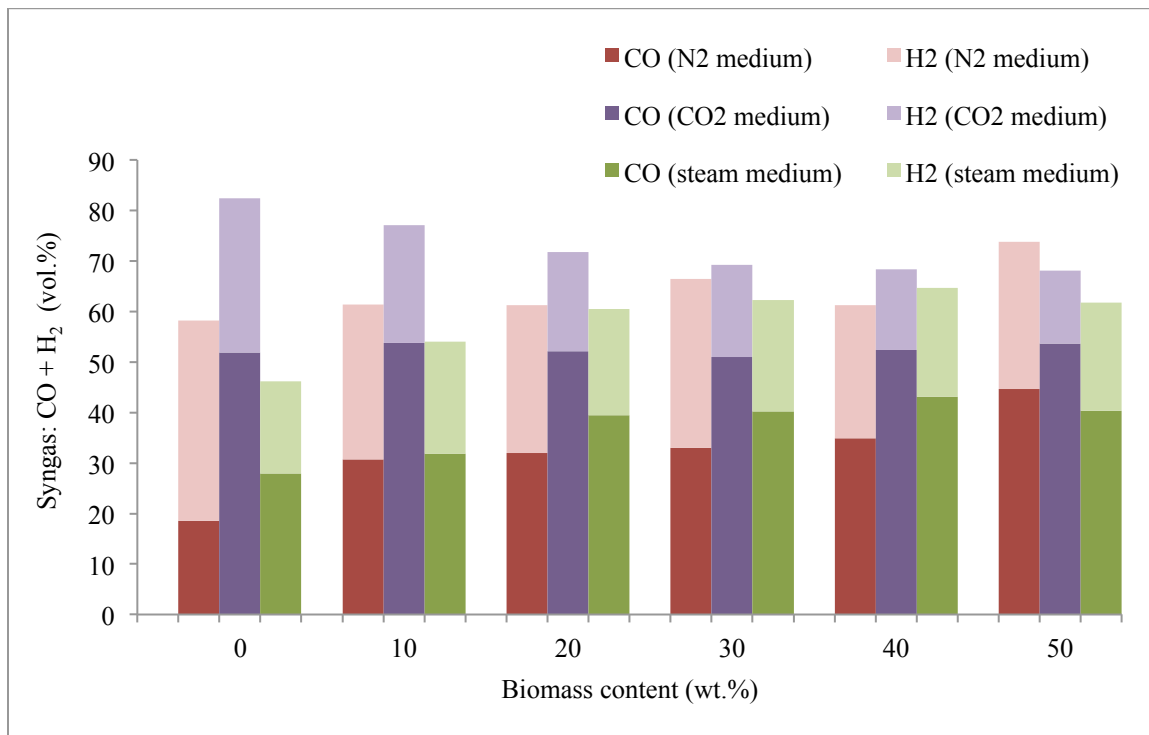Figure 4.14 Typical temperature profile for steam co-gasification.

Figure 4.15 Effect of hybrid poplar content and gasification gases on syngas yield at 700°C.
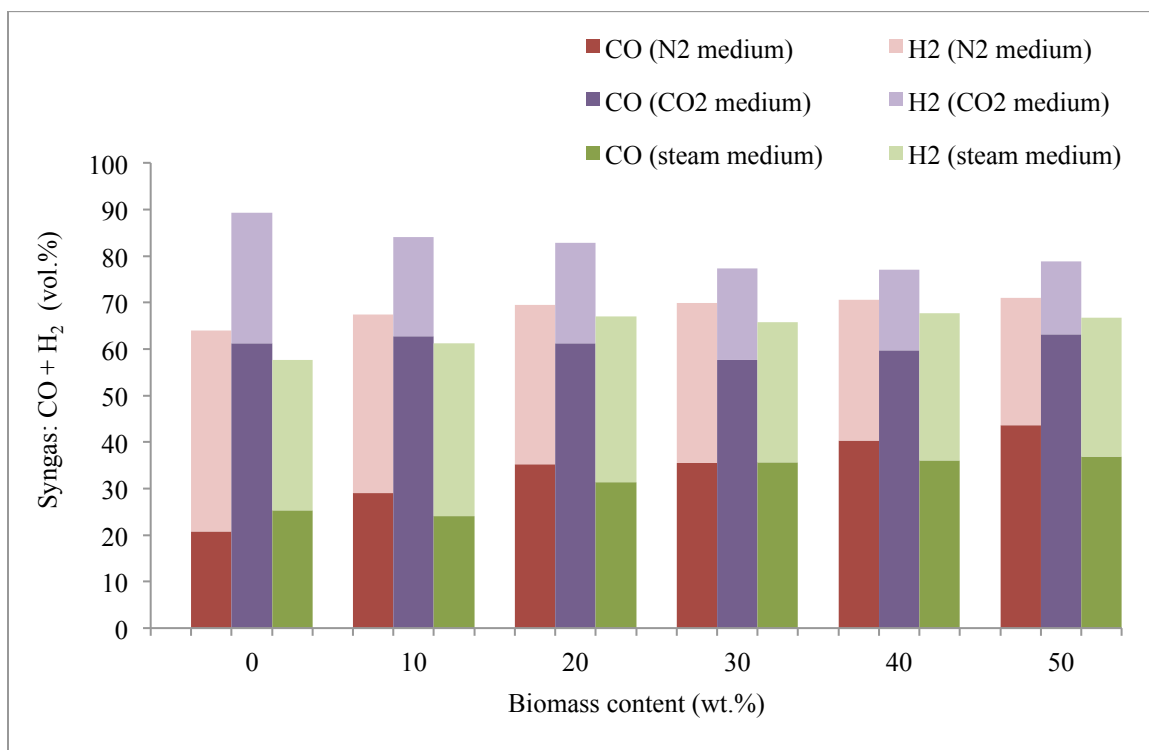
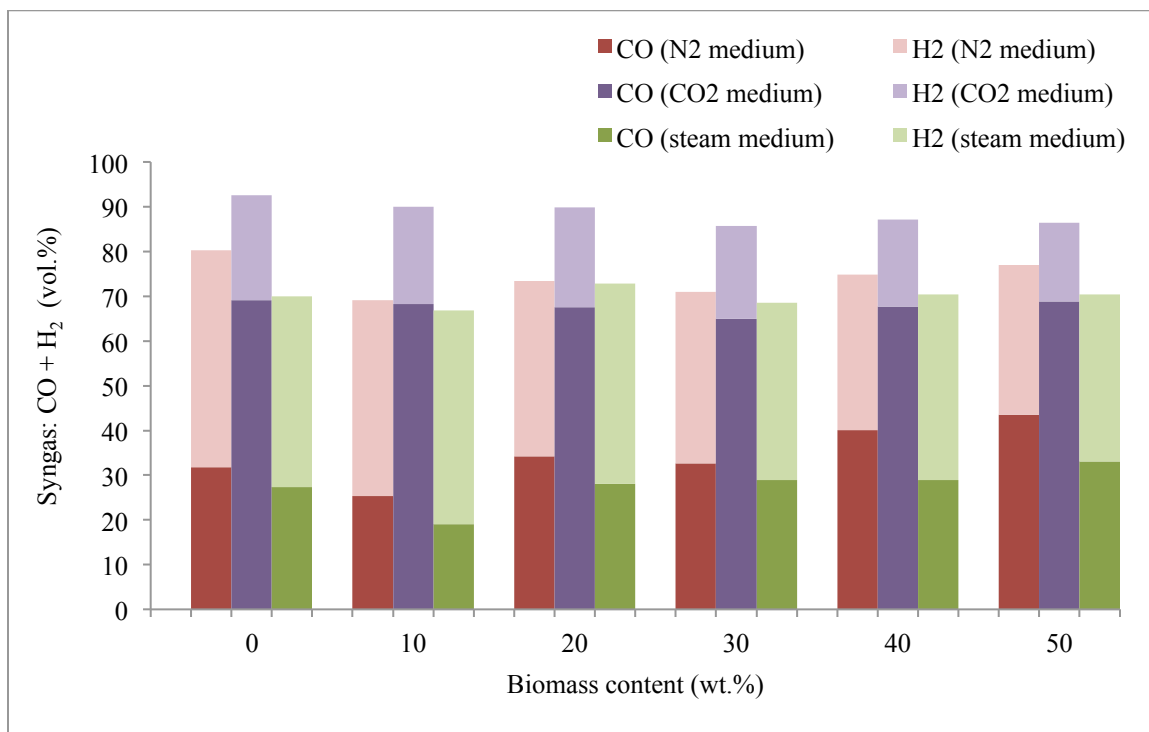Figure 4.16 Effect of hybrid poplar content and gasification gases on syngas yield at 800°C.

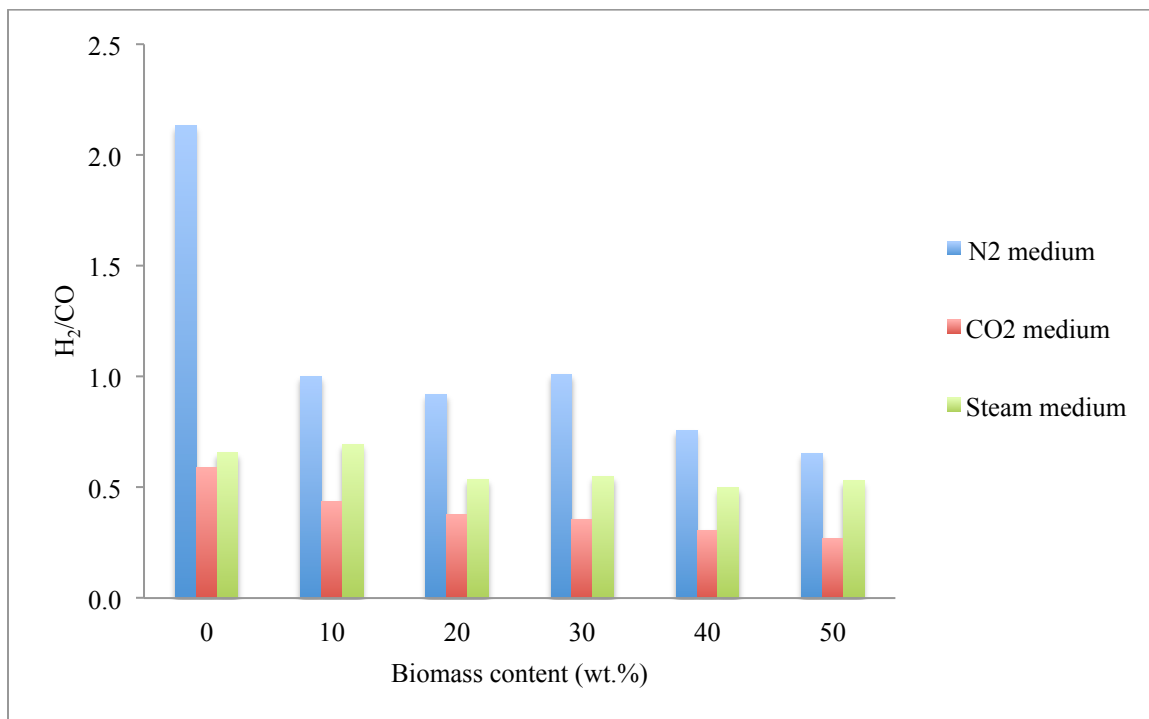Figure 4.17 Effect of hybrid poplar content and gasification gases on syngas yield at 900°C.

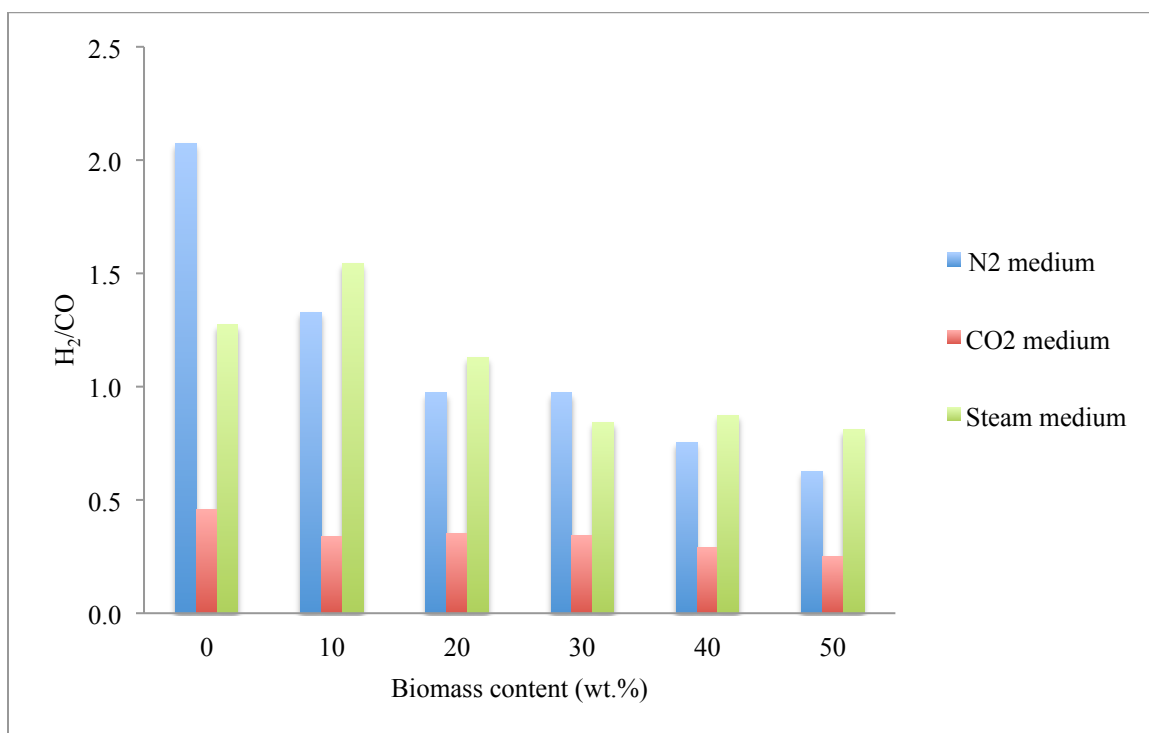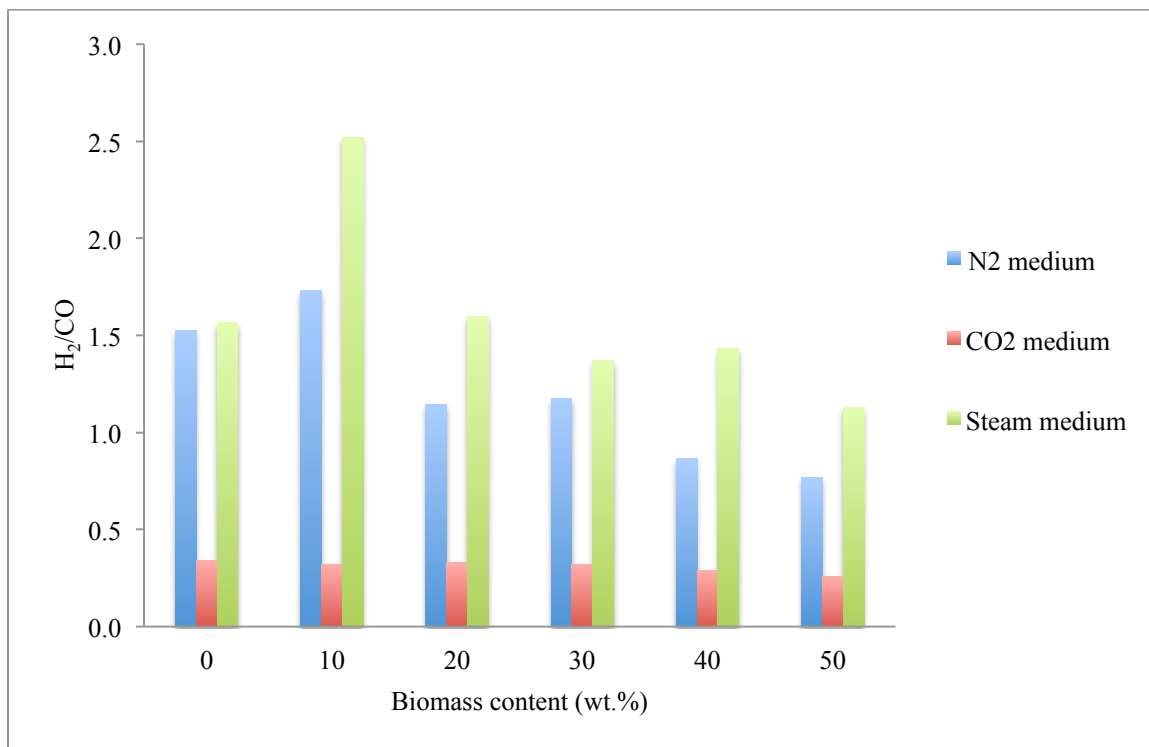Figure 4.18 Effect of hybrid poplar content and gasification gases on H_2/CO ratio at 700°C.

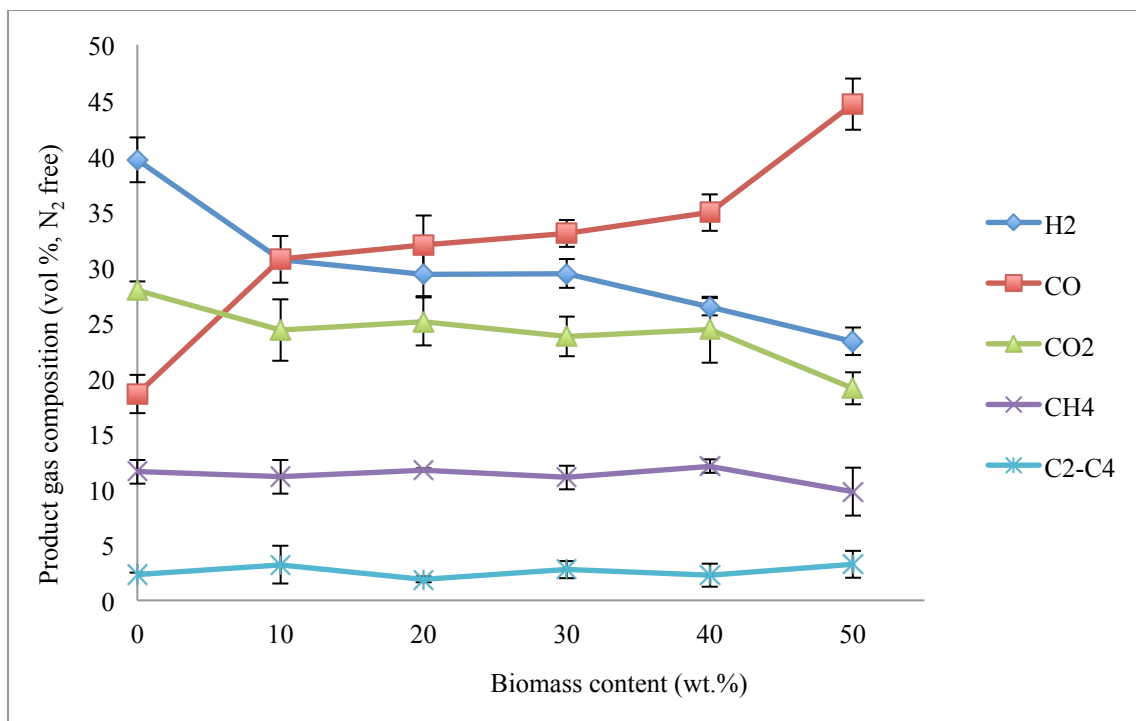Figure 4.19 Effect of hybrid poplar content and gasification gases on H_2/CO ratio at 800°C.

Figure 4.20 Effect of hybrid poplar content and gasification gases on H_2/CO ratio at 900°C.

Figure 4.21 Effect of hybrid poplar content on the yield of product gas compounds for sub-

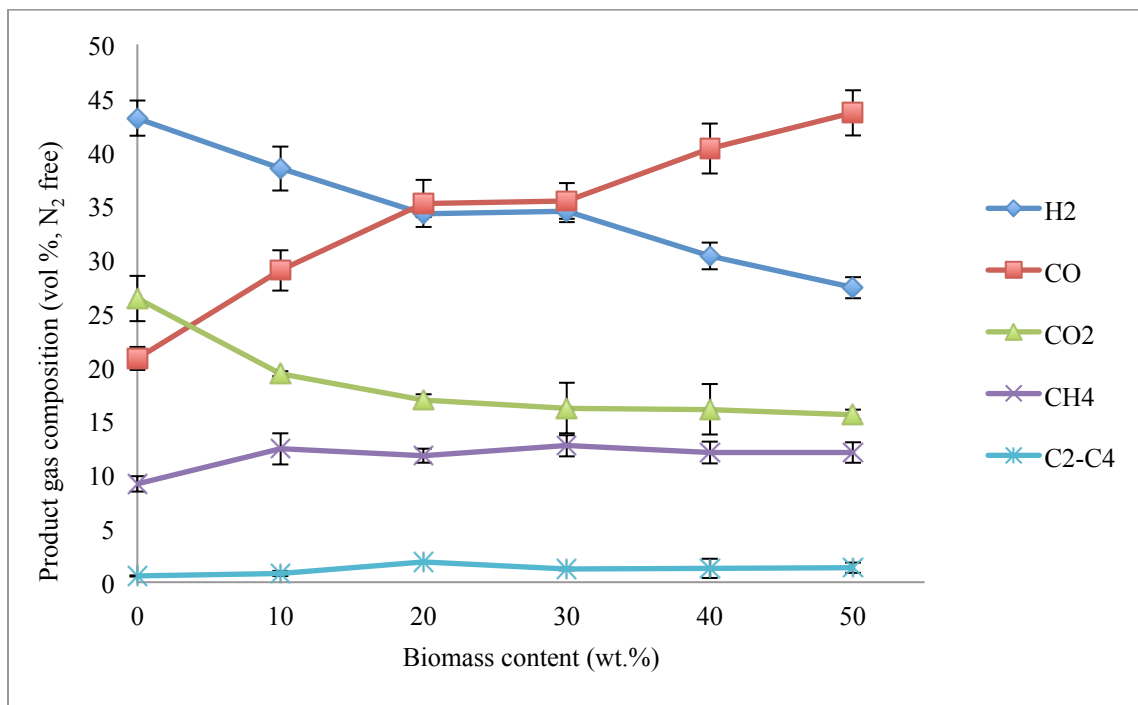bituminous coal and hybrid poplar co-gasification in N_2 at 700°C.

Figure 4.22 Effect of hybrid poplar content on the yield of product gas compounds for sub-

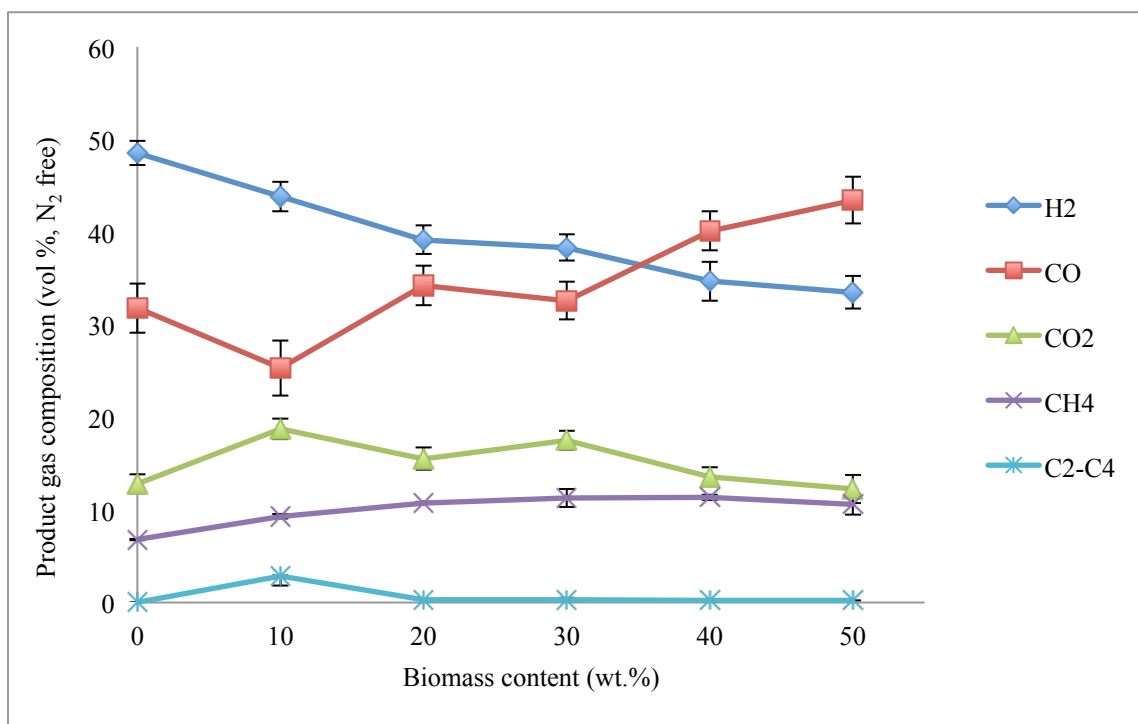bituminous coal and hybrid poplar co-gasification in N_2 at 800°C.

Figure 4.23 Effect of hybrid poplar content on the yield of product gas compounds for sub-

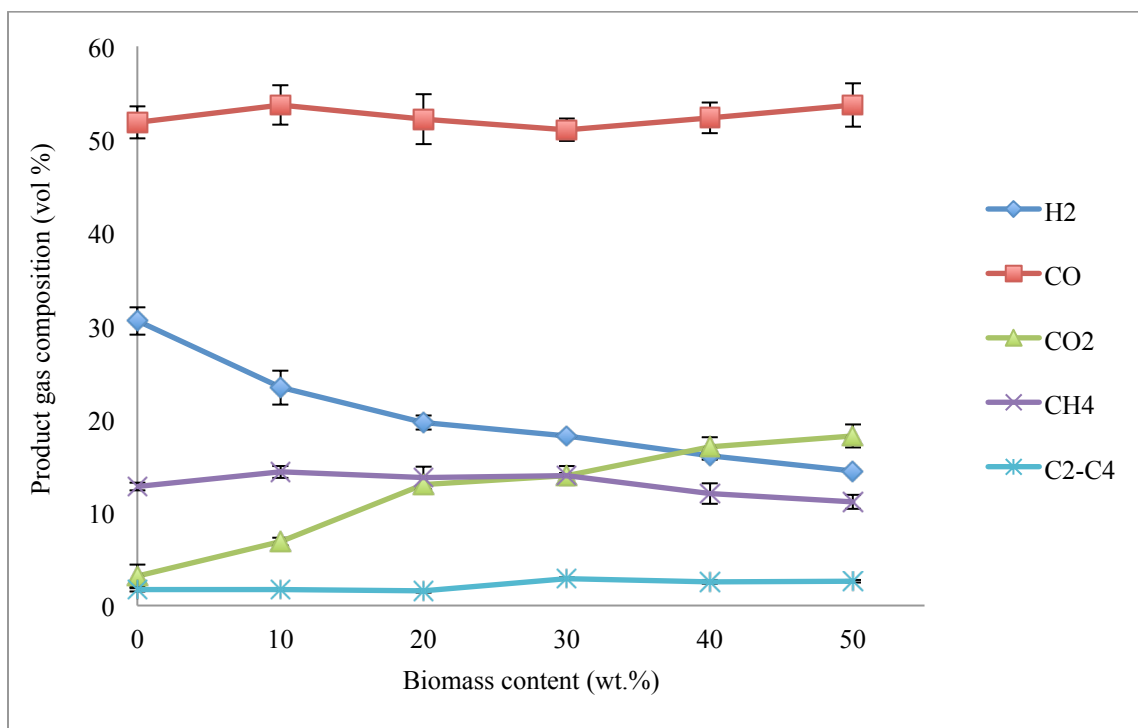bituminous coal and hybrid poplar co-gasification in N_2 at 900°C.

Figure 4.24 Effect of hybrid poplar content on the yield of product gas compounds for sub-bituminous coal and hybrid poplar co-gasification in CO_2 at 700°C.

Figure 4.25 Effect of hybrid poplar content on the yield of product gas compounds for sub-bituminous coal and hybrid poplar co-gasification in CO_2 at 800°C.
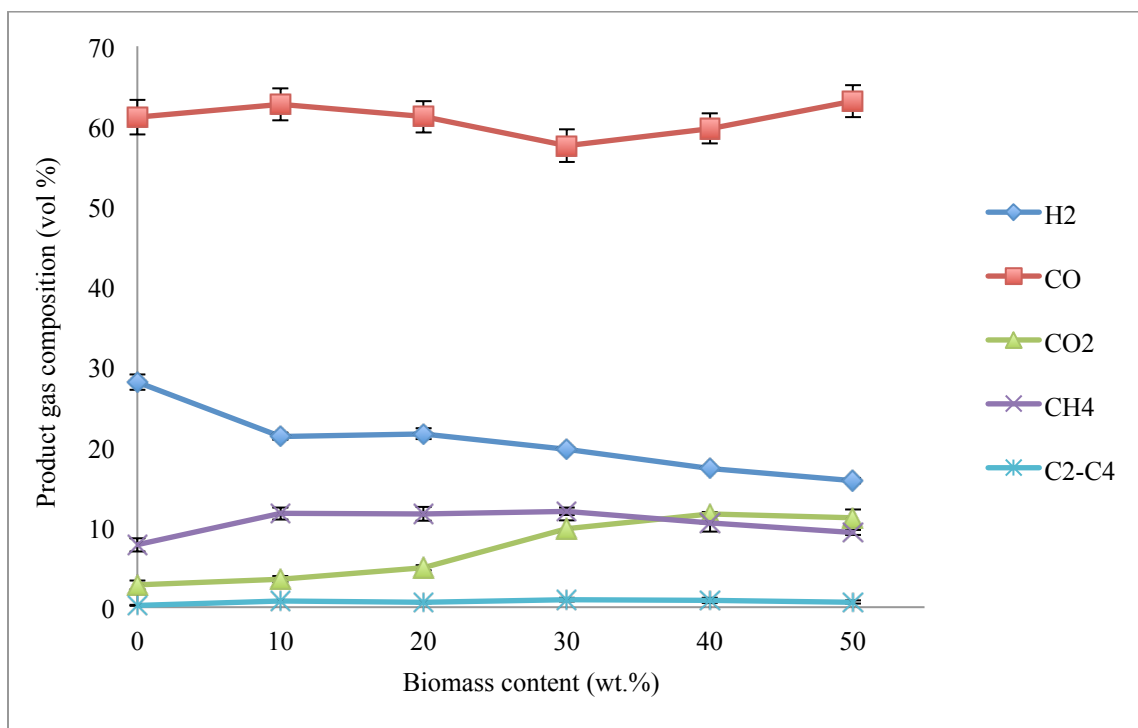
Figure 4.26 Effect of hybrid poplar content on the yield of product gas compounds for sub-bituminous coal and hybrid poplar co-gasification in CO_2 at 900°C.

Figure 4.27 Effect of hybrid poplar content on the yield of product gas compounds for sub-bituminous coal and hybrid poplar co-gasification in steam at 700°C.
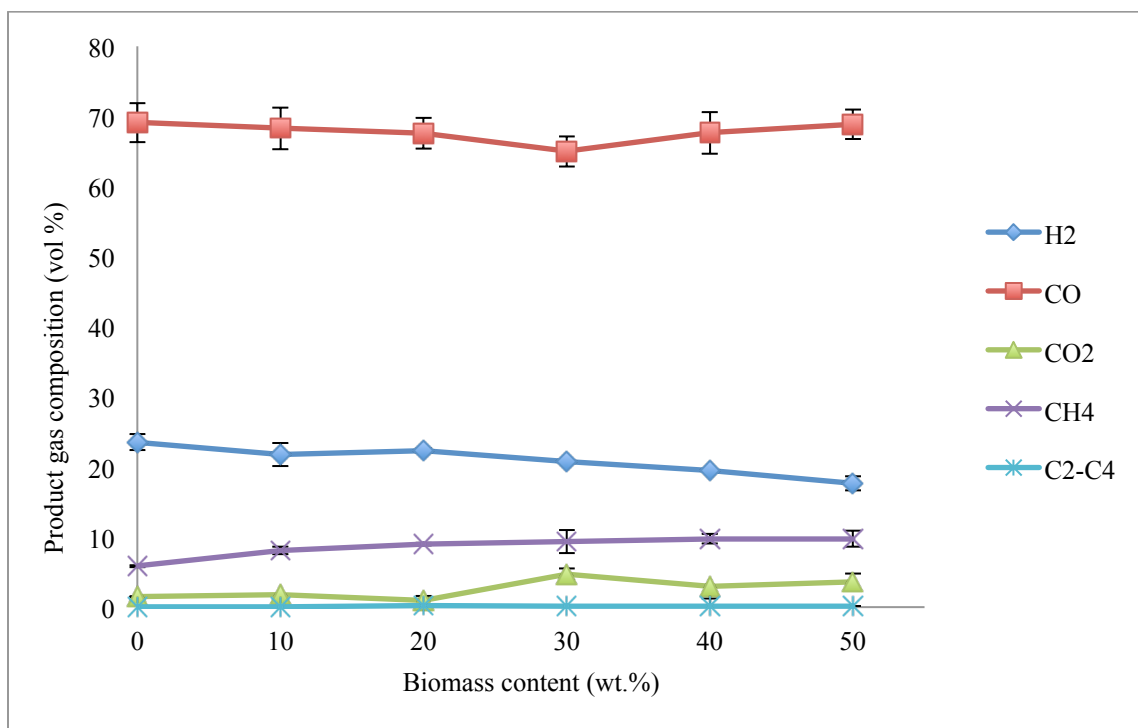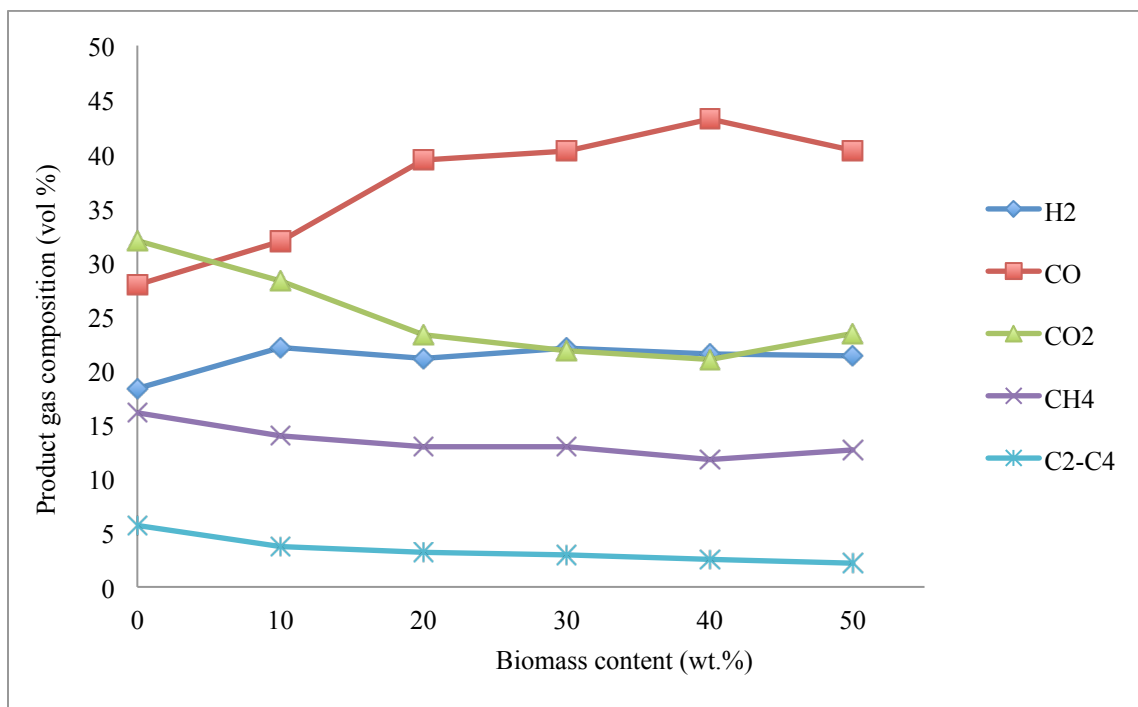
Figure 4.28 Effect of hybrid poplar content on the yield of product gas compounds for sub-

bituminous coal and hybrid poplar co-gasification in steam at 800°C.
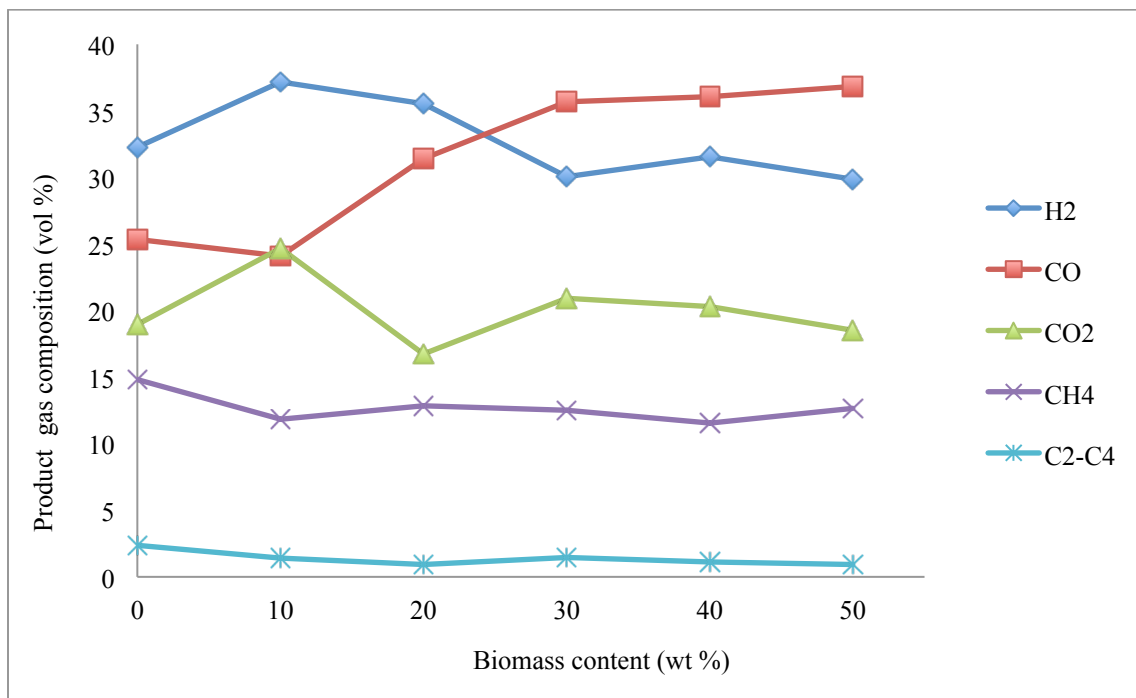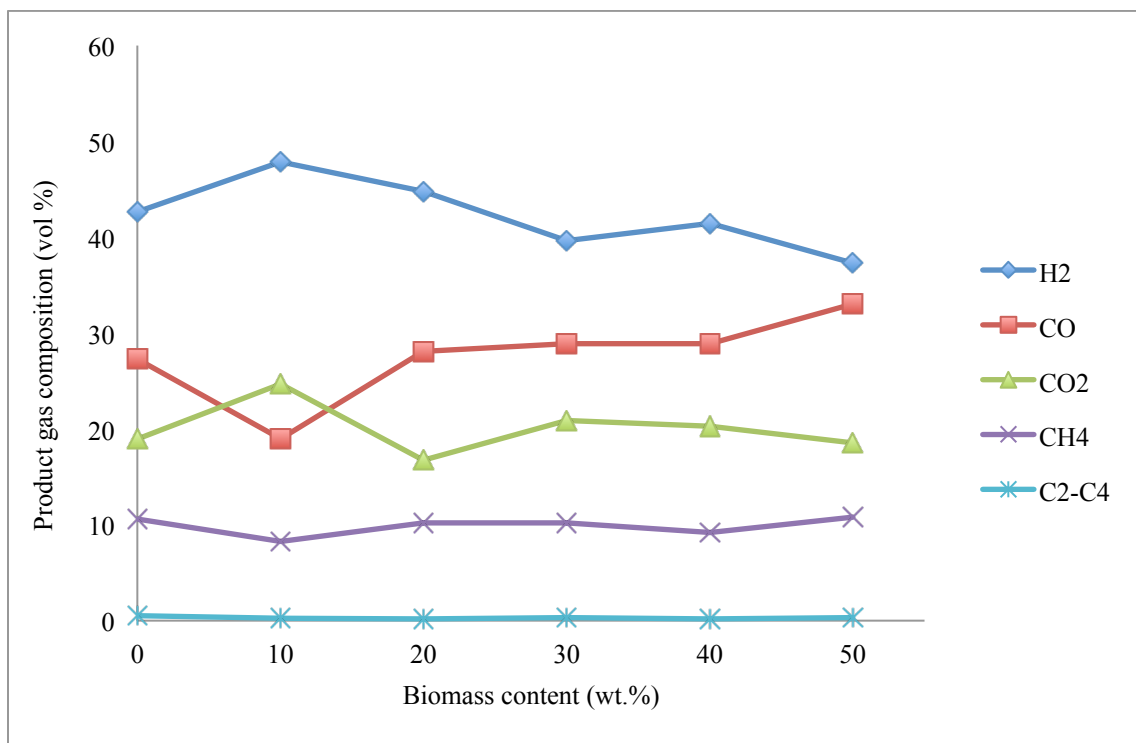

Figure 4.29 Effect of hybrid poplar content on the yield of product gas compounds for sub-

bituminous coal and hybrid poplar co-gasification in steam at 900°C.

Figure 4.30 Effect of bed temperature and hybrid poplar content on H_2 yield for sub-bituminous coal and hybrid poplar co-gasification in N_2.

Figure 4.31 Effect of bed temperature and hybrid poplar content on CO yield for sub-bituminous coal and hybrid poplar co-gasification in N_2.

Figure 4.32 Effect of bed temperature and hybrid poplar content on CO_2 yield for sub-bituminous coal and hybrid poplar co-gasification in N_2.

Figure 4.33 Effect of bed temperature and hybrid poplar content on CH_4 yield for sub-bituminous coal and hybrid poplar co-gasification in N_2.
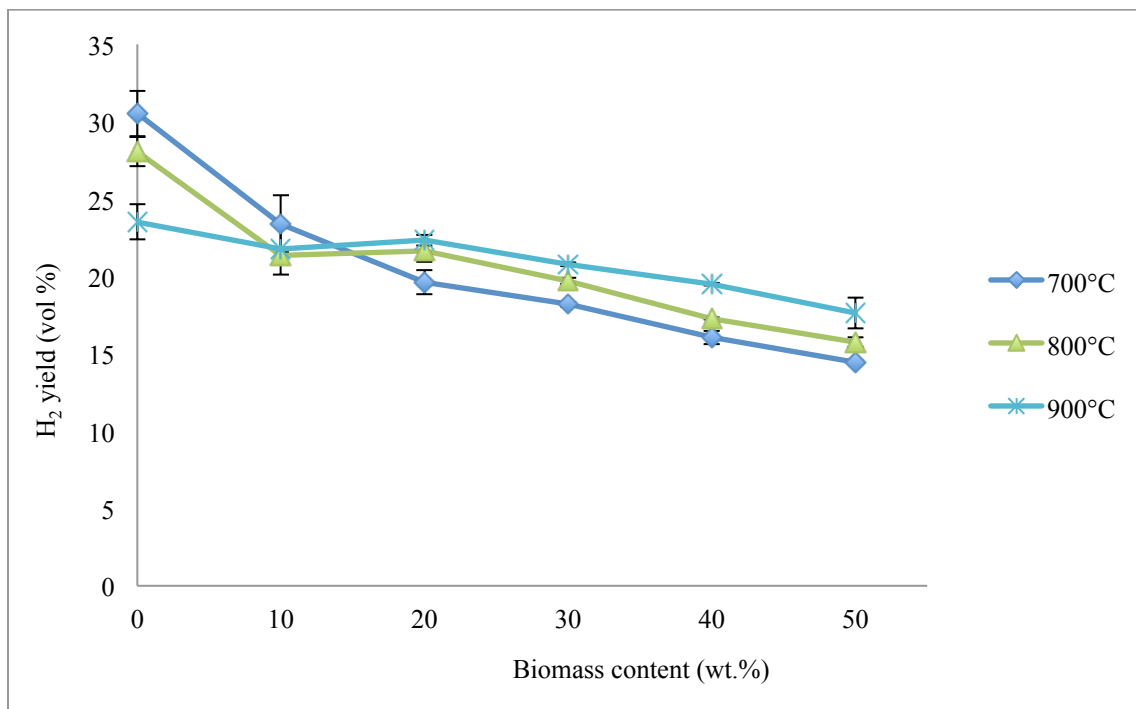
Figure 4.34 Effect of bed temperature and hybrid poplar content on H_2 yield for sub-bituminous coal and hybrid poplar co-gasification in CO_2.
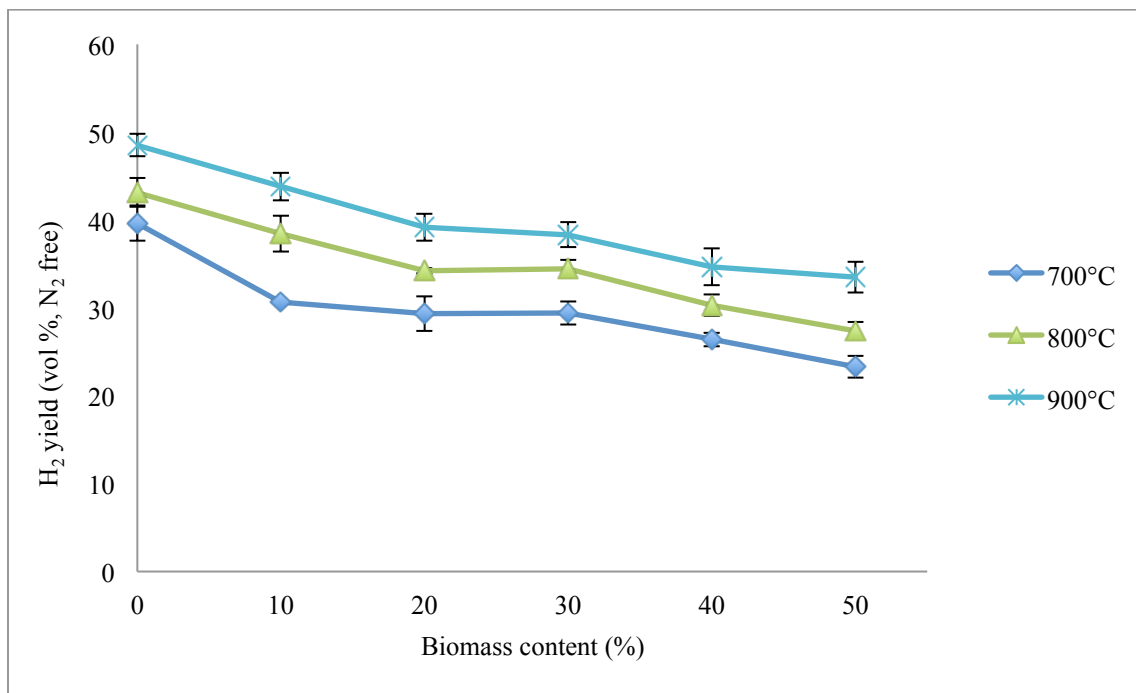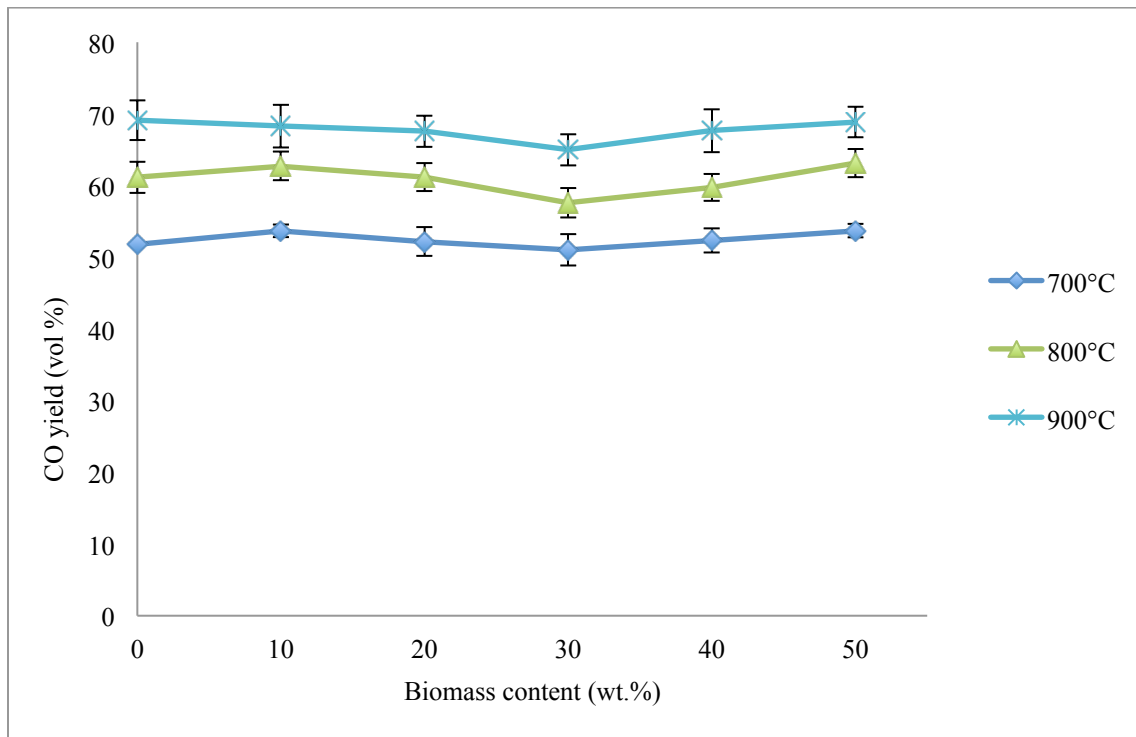

Figure 4.35 Effect of bed temperature and hybrid poplar content on CO yield for sub-bituminous coal and hybrid poplar co-gasification in CO_2.
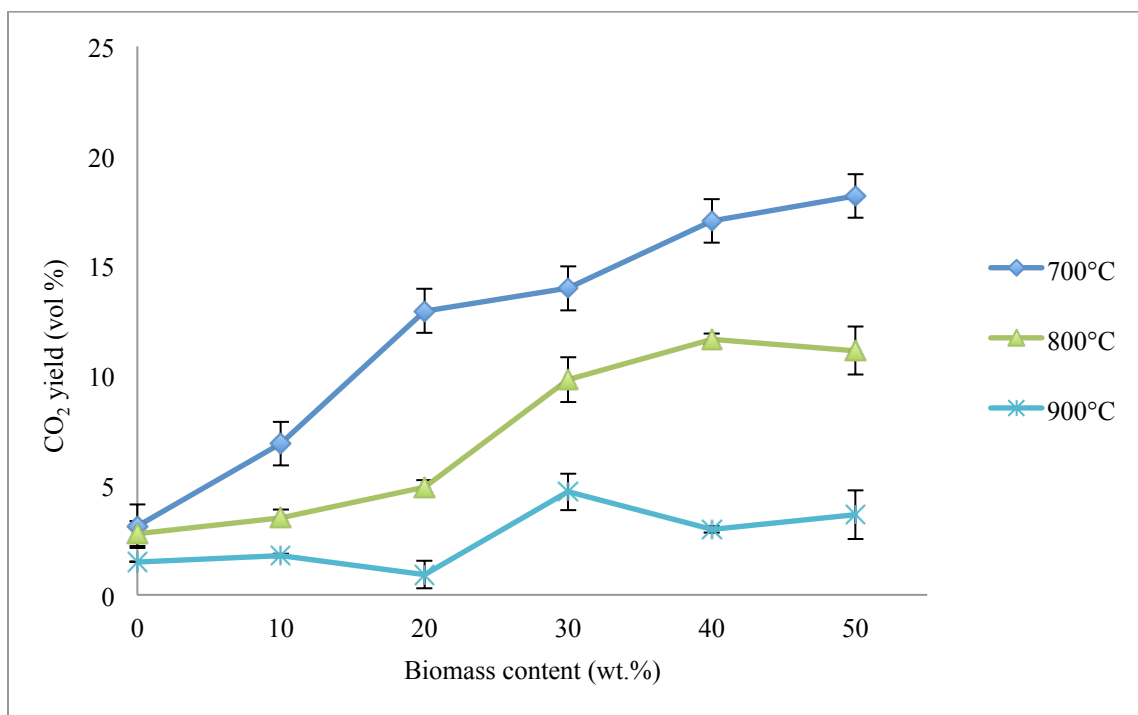
Figure 4.36 Effect of bed temperature and hybrid poplar content on CO_2 yield for sub-bituminous coal and hybrid poplar co-gasification in CO_2.
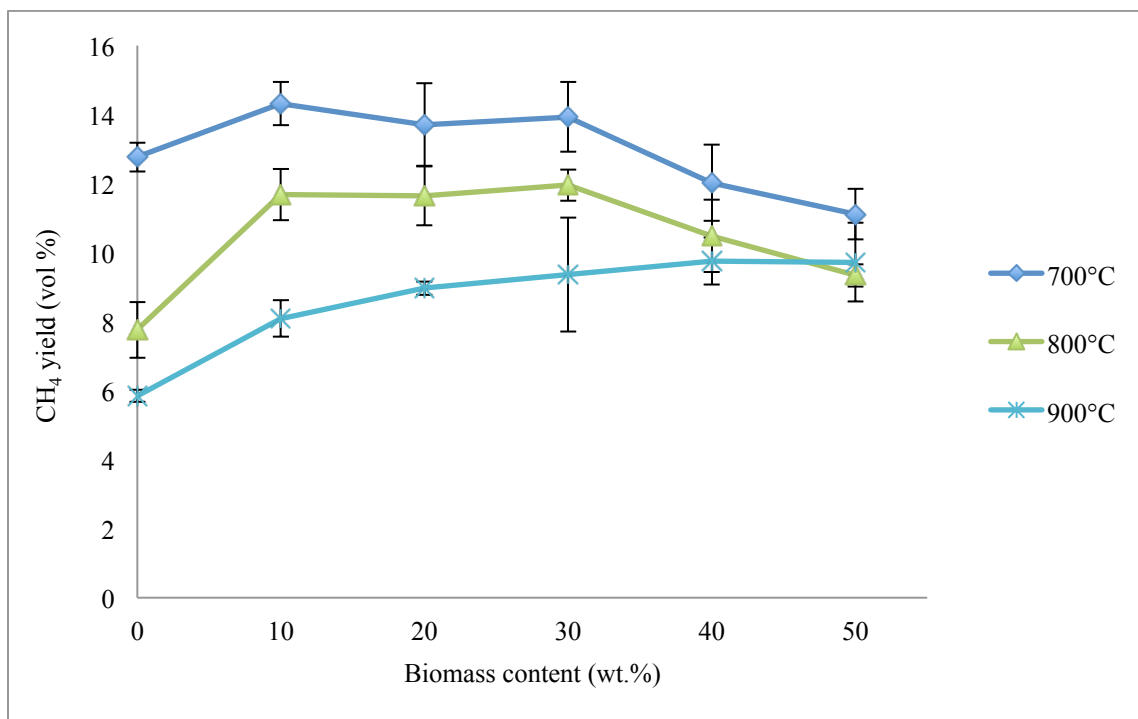
Figure 4.37 Effect of bed temperature and hybrid poplar content on CH_4 yield for sub-bituminous coal and hybrid poplar co-gasification in CO_2.
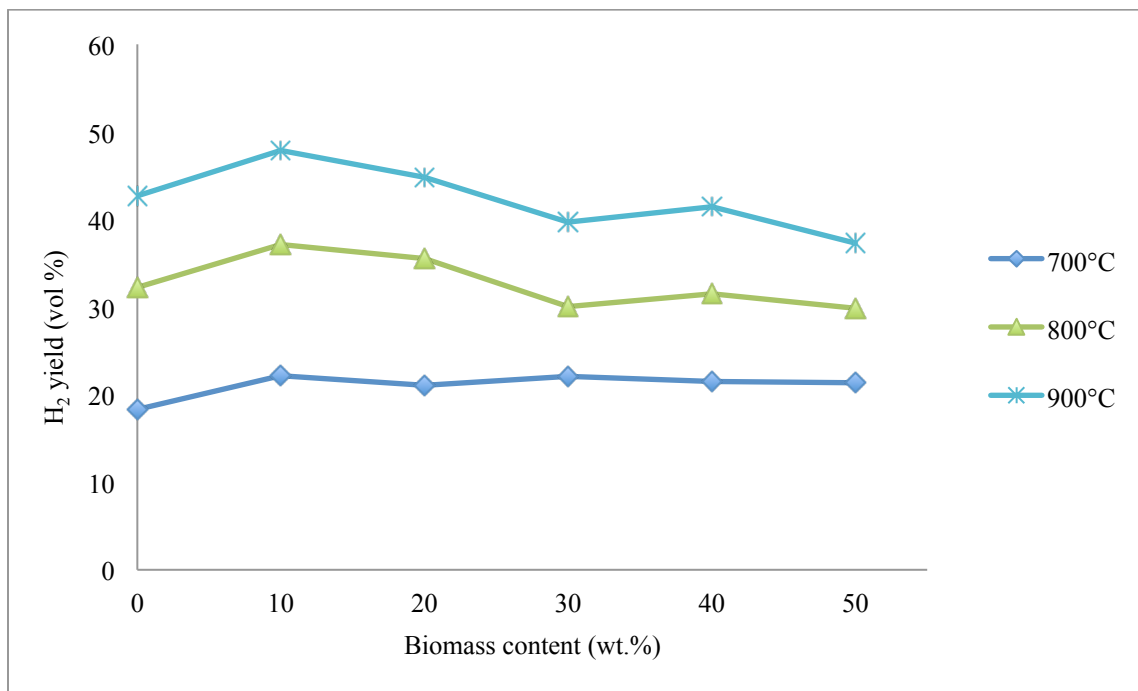
Figure 4.38 Effect of bed temperature and hybrid poplar content on H_2 yield for sub-bituminous coal and hybrid poplar co-gasification in steam.
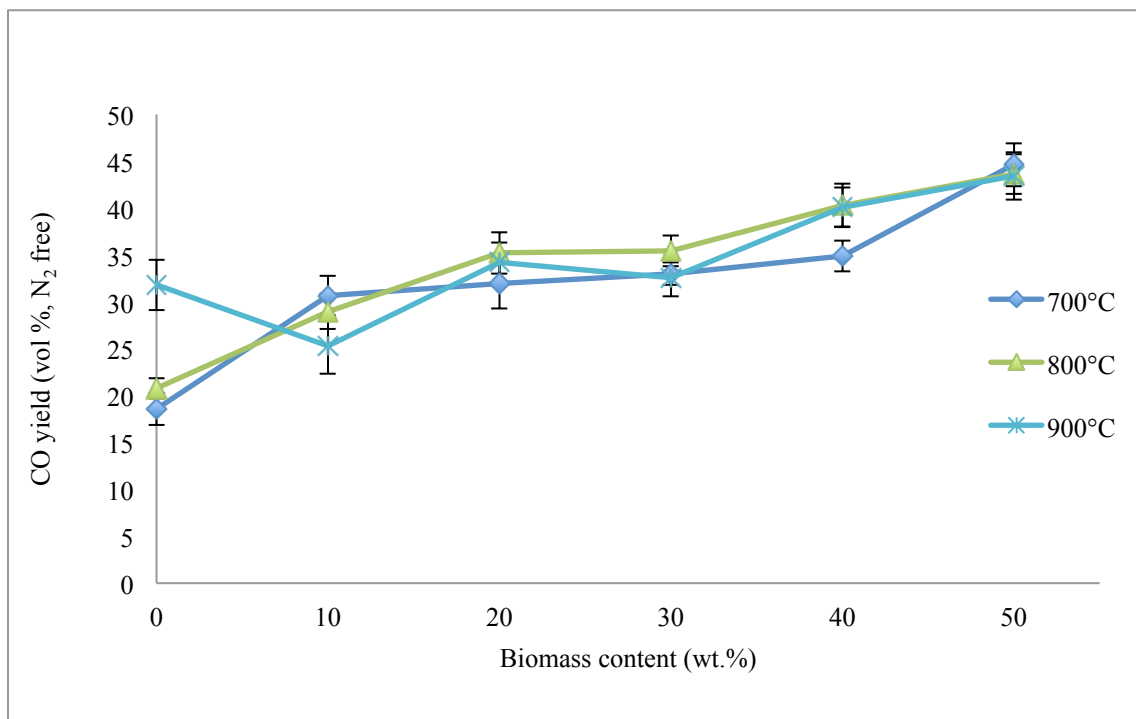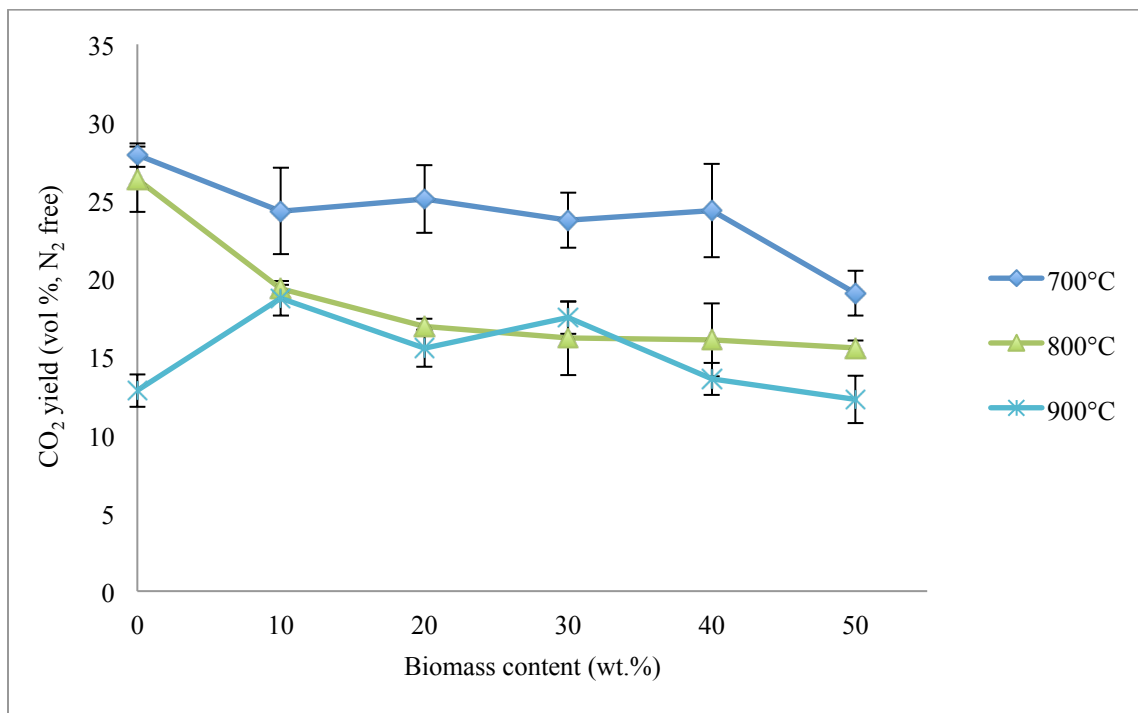

Figure 4.39 Effect of bed temperature and hybrid poplar content on CO yield for sub-bituminous coal and hybrid poplar co-gasification in steam.
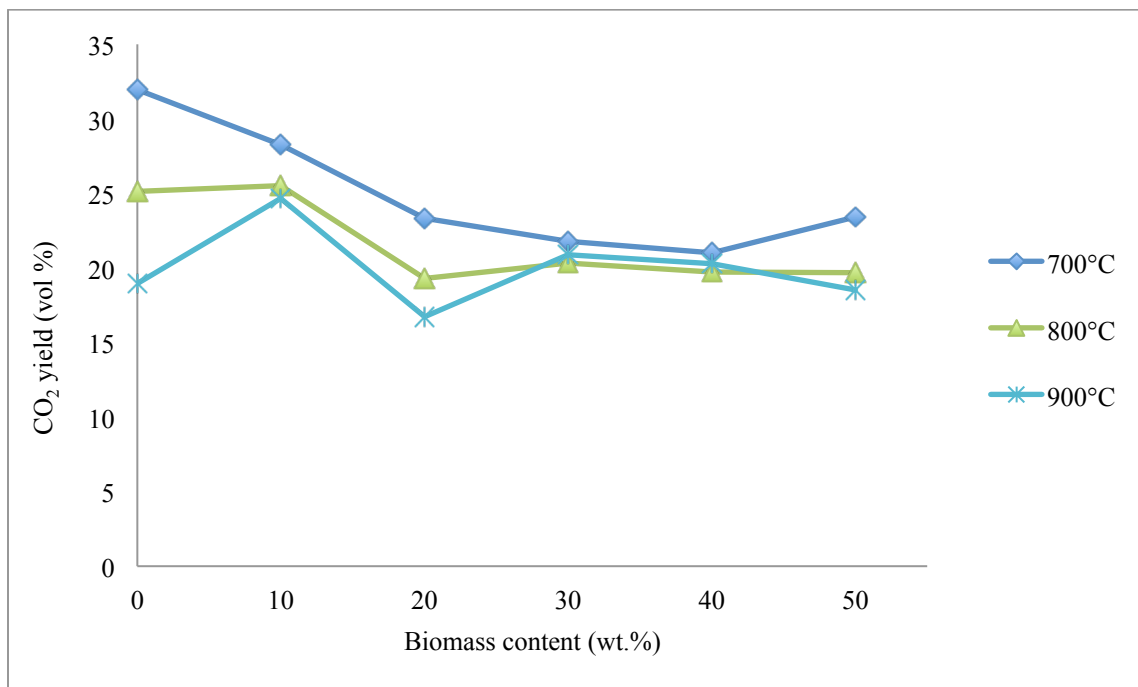
Figure 4.40 Effect of bed temperature and hybrid poplar content on CO_2 yield for sub-bituminous coal and hybrid poplar co-gasification in steam.
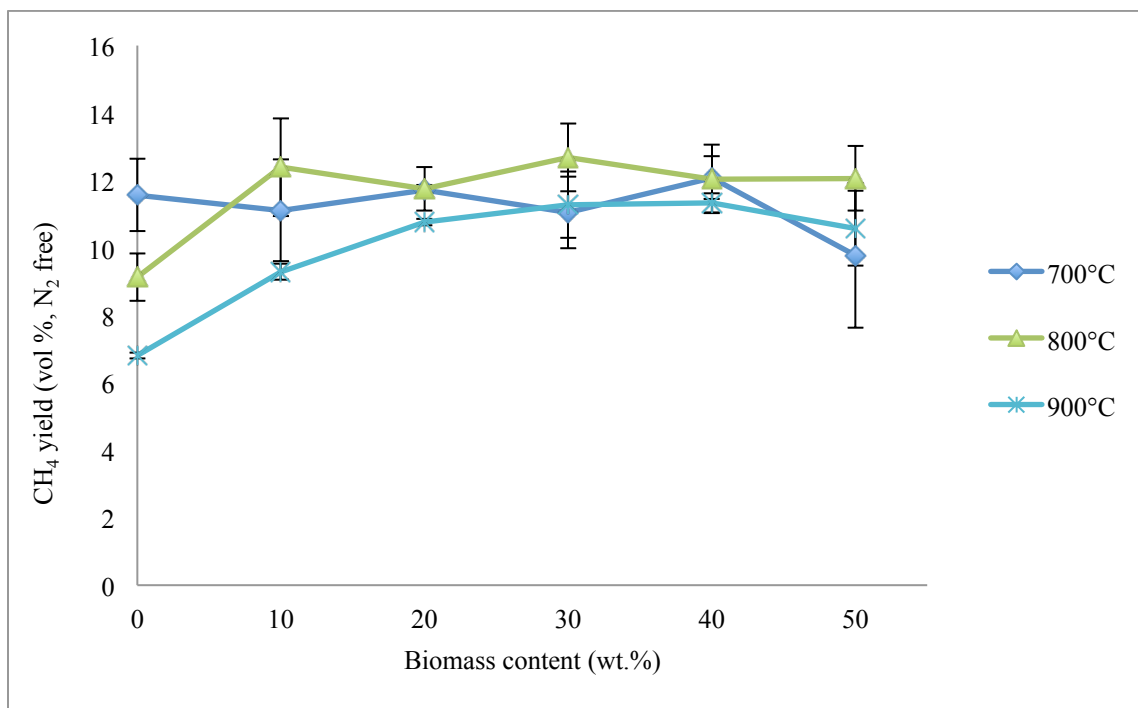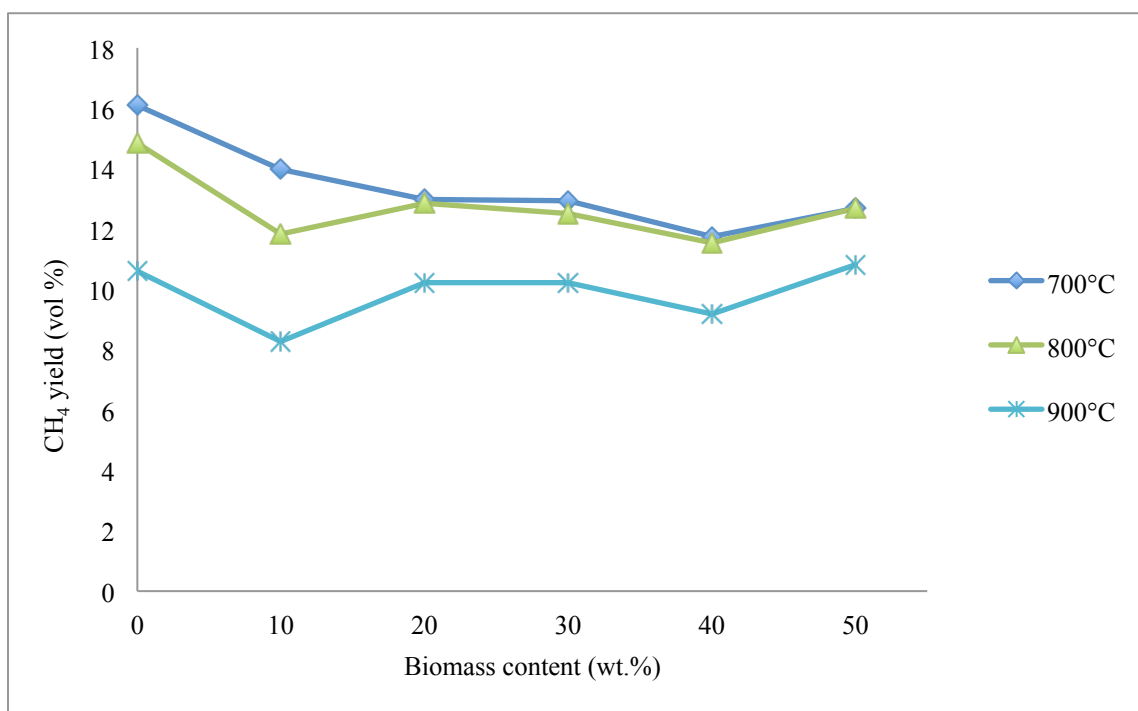

Figure 4.41 Effect of bed temperature and hybrid poplar content on CH_4 yield for sub-bituminous coal and hybrid poplar co-gasification in steam.
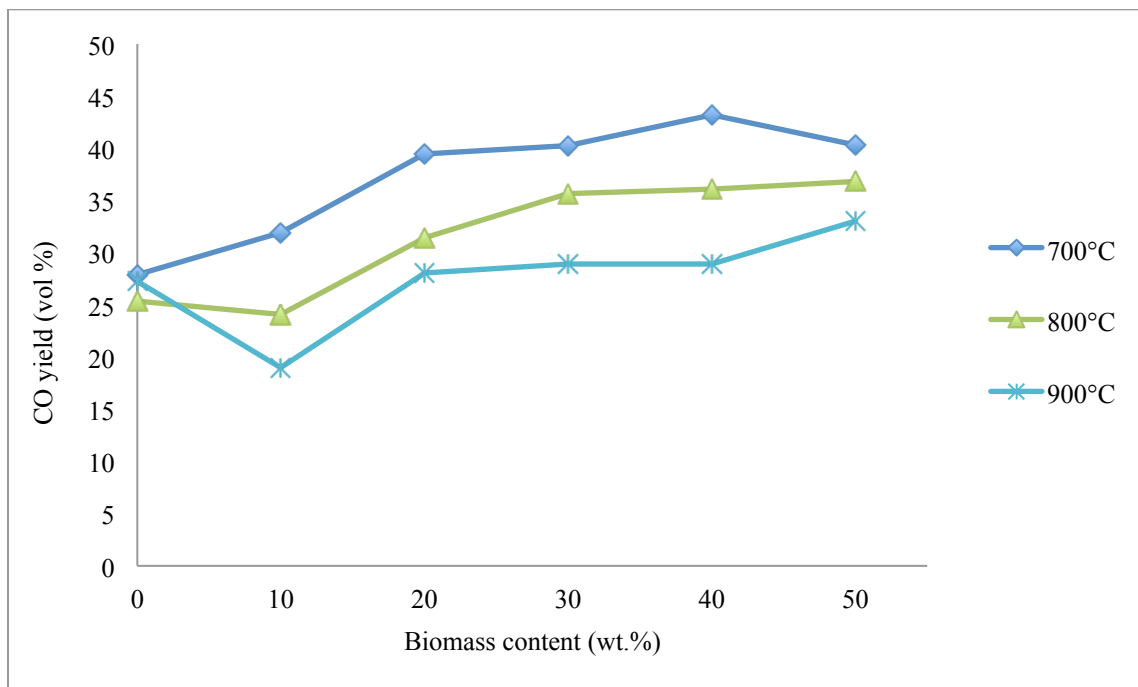
5. Conclusions

The following conclusions were drawn based on the results:

1. Product (char, tar, and gas) yields and product gas compounds showed agreement with predicted yields indicating lack of synergetic effects between coal and hybrid poplar wood. However, some synergetic effects were observed with steam on product gas compounds that led to greater volumes of H_2 than predicted yields at 700°C mostly with 10 wt.% and 20 wt.% poplar content.

2. High syngas proportions were obtained using CO_2 as gasification medium but with poor H_2/CO ratios. However, H_2/CO ratios were greatly enhanced at 900°C with steam as co–gasification medium.

3. H_2 yields decreased with increase in poplar content. Concentrations of CO remained constant at all temperatures in CO_2 gasification medium.

4. The reactivity of char increased with increase in poplar content resulting in higher product gas yields. Tar yields increased with increase in poplar content (30 wt.% and above).

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CHAPTER 5

RECOMMENDATIONS

1. Sub-bituminous coal was resistant to thermal cracking at co-gasification temperatures studied using silica sand as fluidized bed material. This led to high char yields. Therefore development of a suitable catalyst is crucial to enhance coal-biomass char conversion into product gas and to selectively produce syngas with desirable H_2 and CO concentrations.

2. Water product obtained from co-gasification experiments should be studied as a source of steam on co-gasification reactions.

3. Experiments have shown that CO_2 gas as co-gasification medium produced more syngas but with poor H_2/CO ratios whereas H_2/CO ratios were improved for coal-biomass mixtures using steam especially at 800°C and 900°C. Therefore the effect of combining steam and CO_2 as co-gasification medium should be studied.

4. Effect of biomass content and gasification medium on pollutants (NOx and SOx) emission from sub-bituminous coal gasification should bed studied.

APPENDIX

RED MUD AS A CATALYST FOR SUB-BITUMINOUS COAL AND BIOMASS CO-GASIFICATION

1. Introduction

Red mud is an industrial waste generated during the production of alumina from the Bayer process and contains mainly oxides of iron, aluminum, titanium, silicon, calcium, and sodium (Álvarez et al., 1999). The potential of red mud as a catalyst is related to the intrinsic properties such as iron content in the form of ferric oxide (Fe_2O_3), high surface area, sintering resistant, resistance to poising, low cost (Sushil and Batra, 2008) and high alkalinity with pH ranging from 10 to 12 (Pradhan et al., 1998). There are some reports on red mud catalytic effects (Pratt and Christoverson, 1982; Mastral et al., 1993; Álvarez et al., 1999; Dulger Irdem et al., 2014). Till date, there is little or no information available on red mud use as a gasification and co-gasification catalyst. However, some researchers studied red mud as a desulfurization sorbent for gasification processes (Zhao et al., 2010; Sahu et al., 2011).

2. Materials and Method

Experiments in progress are aimed at screening red mud for catalytic properties on coal and corn stover co-gasification. Trial studies were conducted using regenerated red mud (≤ 125 μm) as bed material in a bubbling fluidized-bed operated at atmospheric pressure at 700°C, 800°C, and 900°C. The bed material was fluidized with nitrogen gas. Coal and corn stover feed were gasified separately and their product and product gas compound yields were used to compute predicted yields (Pred.). Experimental yields (Exp.) were compared with predicted yields for synergetic effects. Experimental yields are yields obtained when coal was co-gasified with 10 wt.% corn stover.

3.   Results

Table 1. Effect of red mud on product yield (dry wt.%) for sub-bituminous coal and corn stover co-gasification.

Biomass (wt.%)	Temp. (°C)	Char Exp.	Pred.	Water Exp.	Pred.	Tar Exp.	Pred.	Gas Exp.	Pred.
	700	50.07		31.67		3.26		16.50	
0	800	47.31		30.91		2.75		22.66	
	900	43.03		21.29		1.49		40.66	
	700	47.15	46.73	29.90	30.88	3.58	3.48	17.66	18.92
10	800	43.35	43.62	31.39	31.39	2.71	2.70	24.65	24.01
	900	42.21	39.03	20.02	20.52	1.40	1.47	29.40	38.98

Table 2. Effect of silica sand on product yield (dry wt.%) for sub-bituminous coal and corn stover co-gasification.

Biomass (wt.%)	Temp. (°C)	Char Expt.	Pred.	Water Expt.	Pred.	Tar Expt.	Pred.	Gas Expt.	Pred.
	700	53.98 ±0.65		26.10 ±0.83		5.54 ±0.18		14.25 ±0.01	
0	800	52.38 ±0.58		23.09 ±0.88		3.64 ±0.48		20.72 ±0.23	
	900	45.14 ±0.57		13.96 ±0.87		1.04 ±0.27		38.96 ±0.57	
	700	48.61 ±1.04	49.72	31.24 ±1.02	25.39	6.39 ±0.24	6.66	13.66 ±0.34	17.91
10	800	44.84 ±1.98	47.83	30.43 ±0.89	22.80	4.32 ±0.76	3.82	19.47 ±1.03	25.25
	900	42.62 ±1.02	41.08	26.09 ±0.77	13.63	3.13 ±0.20	1.11	27.74 ±1.00	43.26

Table 3. Effect of red mud on product gas compounds (vol.%) for sub-bituminous coal and corn stover co-gasification.

Biomass (wt.%)	Temp. (°C)	H_2		CO		CH_4		CO_2		$C_2 - C_4$	
		Expt.	Pred.	Expt.	Pred.	Expt.	Pred.	Expt.	Pred.	Expt.	Pred.
	700	41.73		14.47		10.72		31.21		1.87	
0	800	43.91		20.23		10.13		24.93		0.80	
	900	47.22		25.67		7.01		19.89		0.21	
	700	38.68	39.91	19.11	16.84	11.18	10.80	28.88	30.55	2.15	1.90
10	800	42.38	42.03	20.58	22.51	10.16	10.38	25.81	24.24	1.06	0.85
	900	47.35	45.57	24.86	27.12	9.16	7.40	18.48	19.69	0.15	0.22

Table 4. Effect of silica sand on product gas compounds (vol.%) for sub-bituminous coal-corn stover co-gasification.

Biomass (wt.%)	Temp. (°C)	H_2		CO		CH_4		CO_2		$C_2 - C_4$	
		Expt.	Pred.	Expt.	Pred.	Expt.	Pred.	Expt.	Pred.	Expt.	Pred.
	700	39.63 ±1.03		18.58 ±0.21		11.57 ±1.03		27.92 ±1.43		2.31 ±0.45	
0	800	43.12 ±0.97		20.79 ±0.11		9.13 ±0.43		26.37 ±0.98		0.58 ±0.26	
	900	48.53 ±0.34		31.80 ±1.55		6.81 ±1.08		12.84 ±1.66		0.02 ±0.00	
	700	24.25 ±2.01	37.60	31.23 ±1.94	21.59	13.62 ±0.92	11.50	27.45 ±1.32	26.84	3.44 ±0.65	2.47
10	800	32.75 ±1.35	41.22	31.58 ±2.32	23.55	12.29 ±1.08	9.39	21.86 ±1.82	25.19	1.51 ±0.13	0.65
	900	41.00 ±2.28	46.53	31.00 ±0.79	33.77	9.69 ±1.13	7.18	18.08 ±1.01	12.47	0.23 ±0.04	0.05

4.   Discussion

Co-gasification results are presented in Table 1 to Table 4. Product yields (Table 1) and product gas compounds (Table 3) obtained using red mud were all in agreement with predicted yields. This indicated lack of synergy between sub-bituminous coal and corn stover. Experiments with silica sand (Table 2 and Table 4) showed similar characteristics of additivity between coal and biomass during thermal conversion.

Red mud appeared to promote cracking of char and tars into product gas as the yields were lower compared to those obtained using silica sand. Product gas yields obtained using red mud were slightly higher than product gas yields from silica sand experiments. This could be due to the difference between surface area of red mud and silica sand. Red mud particle size used was ≤ 125 μm and silica particle size averaged 251 μm. The high surface area for red mud may have enhanced heat and mass transfer.

Yields of major gas compounds (H_2, CO, CO_2, and CH_4) for single coal using red mud are similar to those from silica sand experiments. However, H_2 yields increased by 56% at 700°C, 31% at 800°C, and 15% at 900°C when coal and corn stover (10 wt.%) mixture was gasified using red mud compared to silica sand. At 700°C, H_2 concentration increased from 25 vol.% to 39%; at 800°C, H_2 increased from 33 vol.% to 42 vol.%; and at 900°C, H_2 increased from 41 vol.% to 47 vol.%. CO yields obtained from red mud co-gasification experiments were however lower than those of silica sand.

5.   Conclusions

1.   No synergetic effects were observed between coal and corn stover during co-gasification with red mud and silica sand.

2.   Char yields were lower and product gas yields higher with red mud compared to silica sand in co-gasification experiments.

3.   The addition of 10 wt.% of corn stover led to greater H_2 production with red mud

compared to silica sand.

6.   References

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