CATALYTIC GASIFICATION OF BIOMASS FOR THE PRODUCTION OF SYNGAS WITH REDUCED TAR FORMATION

By

Scott Hurley

Supervisor:

Dr. C. Charles Xu (Lakehead University)

Co-supervisor:

Dr. Fernando Preto (CanmetENERGY)

Environmental Engineering

Lakehead University

Thunder Bay, Ontario, Canada.

August, 2009

Abstract

With increased concerns over greenhouse gas emission and decreasing fossil fuel supplies, biomass is increasingly seen as an alternative option for energy and chemical production. There are several technologies available to upgrade biomass to useful energy and fuel products, and one of the most promising is gasification. Tar formation is the major challenge for biomass gasification. Formation of tars represents not only a decrease in gasification efficiency, but would cause some operating issues such as fouling and potential clogging due to the condensation of tars as they cool downstream

In the first part of this thesis, several impregnated metal ions (iron, cobalt, nickel, and ruthenium) and a locally available raw iron ore (natural limonite) were examined for use as catalysts for gasification of pine sawdust in the media of air/CO_2 at 700°C and 800°C. Compared with air, CO_2 as a gasifying agent for biomass gasification showed a much lower reactivity. The yields of char and tar both increased with increasing CO_2 concentration in the feed gas. A higher temperature and a greater oxygen content in the feed gas led to higher gasification efficiency. It was observed that the addition of iron ore to the biomass feedstock simply by physical mixing did not alter the yields of all products significantly irrespectively of the types of gasification agent and the gasification temperature, which was likely due to the poor contact between the catalyst and the gas/vapor products during the gasification process. All the impregnated metal cations (Fe, Ni, Co and Ru), in particular Ni, Co and Ru, were very effective for promoting the gasification of the woody biomass at 700°C and 800°C, leading to a lower tar yield, a significantly decreased char yield and a greatly increased yield of CO_2-free gas. At 800°C, the impregnation of Fe, Ni, Co or Ru led to almost complete conversion of the solid biomass into gas and liquid products, producing an extremely low char yield (< 1-4 wt%), and a very high yield of combustible CO_2-free gas (ranging from 51.7 wt% for Fe to 84 wt% for Ru). The tar yield also reduced significantly from 32.1 wt% without catalyst to 19-27 wt% with the impregnated metal ions. The addition of all impregnated metal cations significantly enhanced the formation of both carbon monoxide and hydrogen.

The second part of this thesis investigated the potential for the use of catalytic bed materials within a pilot-scale bubbling fluidized bed gasifier at the CANMET Energy Technology Centre (CETC) in Ottawa for air blown gasification of woody biomass. The effects of bed materials (olivine, limestone, dolomite, and a crushed iron ore) and equivalence ratios (ER, 0.20-0.40) on tar formation and syngas composition were investigated with white pine sawdust and crushed peat. All bed materials were calcined prior to gasification within the reactor under combustion conditions. Increasing the equivalence ratio generally led to decreased tar yield. Combustible gas (methane, hydrogen, and carbon monoxide) yields were generally highest at medium ER values (0.25-0.30). Tar and combustible gas yields were lower for crushed peat as compared to pine sawdust for all ER values under similar conditions. Calcined limestone exhibited the highest catalytic activity for tar reduction at all ERs tested, leading to a very low tar yield of 3.5-8.3 g/kg biomass. Other bed materials were similar to each other in terms of tar reduction, though dolomite and iron oxide appeared to be slightly more active than olivine. Dolomite and limestone produced the highest combustible gas yields. Olivine, however, was the most physically/thermally stable bed material. In contrast, limestone, dolomite, and iron oxide all appeared to be inferior to olivine for use as bed materials in a fluidized bed gasifier due to their high rates of fragmentation.

Acknowledgements

I would like to express my thanks and appreciation to my supervisors, Professor C. Charles Xu and Dr. Fernando Preto, for their guidance during my studies and for the invaluable technical assistance and constructive criticism.

Greatly appreciated technical assistance was provided by the other members of Dr. Xu's lab group, notably Dr. Hanning Li, Ms. Linghong Zhang, and Ms. Jaclyn Donald. Support from other members of the Lakehead University Faculty of Engineering, Mr. Garry Rathje, and Mr. Kailash Bhatia, is appreciated. The natural limonite material was kindly provided by Dr. Andrew Conly of the Lakehead University Department of Geology.

Pilot-scale testing at CETC would not have been possible without the technical assistance of the following individuals: Mr. Guy Tourigny, Ms. Yuanyuan Shao, Mr. Bart Young, Ms. Irene Coyle, and Dr. Fernando Preto. Special thanks must be extended to Mr. Dave Wambolt for expertise and assistance with the difficult day to day operation of the reactor.

I am grateful for the financial support for my graduate studies from Ontario Ministry of Energy and Ontario Centers of Excellence (OCE) through the Atikokan Bioenergy Research Centre (ABRC) Program, as well as Research Assistantships provided by Dr. Xu through the NSERC Discovery Grant.

Last but not least, I'd like to thank my family and friends for their support and encouragement.

Table of Contents

List of Tables

List of Figures

CHAPTER 1

Introduction

1.1 Background

The fact that the majority of the global climate change observed over the past decades is very likely due to anthropogenic use of fossil fuels [1] as well as the fact that these fossil fuels themselves are diminishing in supply [2,3] while demand for energy increases has led to significant interest in renewable and carbon neutral energy sources. Traditionally, the world's energy demand is met by the following sources: 30% petroleum, 23% natural gas, 22% coal, 6% nuclear, and 19% renewable [4]. While it is among the oldest energy supplies used by human being, biomass is renewable and carbon-neutral and the replacement of fossil fuel sources with biomass would lead to a net reduction in anthropogenic CO_2 emissions [5, 6]. Several pathways for the conversion of biomass to useful products exist, and are outlined in Figure 1-1. This thesis will focus on gasification of biomass resources, specifically on catalytic gasification of pinewood sawdust and peat targeting syngas production with reduced tar formation.

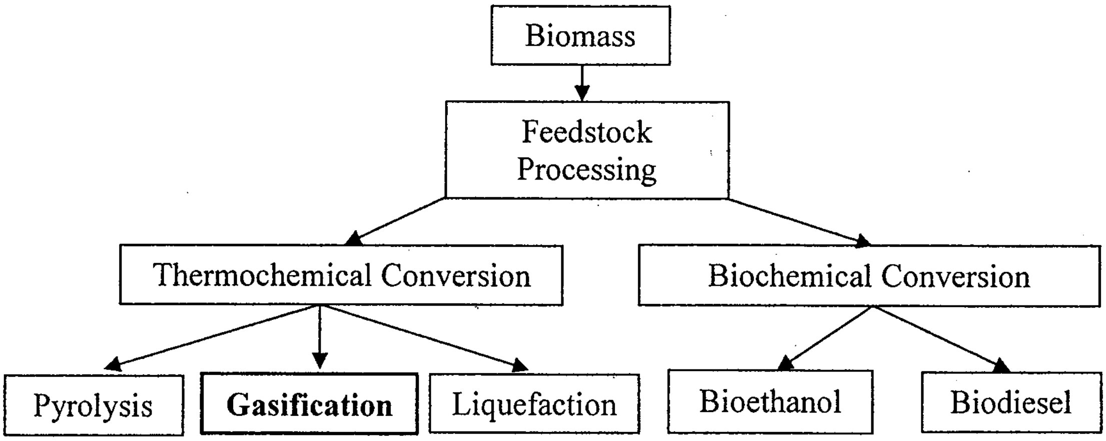


Figure 1-1. Major biomass conversion pathways [7].

Biomass gasification through the partial oxidation of the feedstock produces a low to medium-BTU product gas (also called producer gas or syngas) containing primarily CO, H_2, CH_4, CO_2 and trace higher hydrocarbons (C_2+C_3) [8]. While air, O_2 and steam are still the primary gasification agents, some recent research has also shown CO_2 can be a potential agent for gasification, which would allow for some hot flue gas recycling, as well as the use of CO_2 as a reactant via the reverse Boudouard reaction in the presence of catalysts [3, 6, 8-10]. Syngas from biomass gasification can be cleaned and used directly for power generation or catalytically modified to produce various chemical products such as methanol, dimethyl ether, Fischer-Tropsch oils, etc. [11].

Biomass gasification also produces some contaminants in the product gas, such as tars, NH_3, H_2S and SO_2, etc, and a major concern with biomass gasification is the high yields of tars [11-13]. These contaminants must be removed before the syngas is used for internal combustion, gas engines, and in particular for fuel cells and methanol synthesis, in order to achieve better efficiencies of the syngas applications. In an air-blown fluidized bed gasifier, typical tar contents in producer gas have been reported between 0.5 to 100 g/m^3 [11, 14, 15]. For many applications, with the exception of direct and immediate syngas combustion for heat or electricity production, these tar levels must be reduced, often to below 50 mg/m^3 [11]. Tars can have significant negative effects on gasification with respects to efficiency and operation. Specifically, the production of tars instead of combustible gases represents a decrease in gasification efficiency, and condensation and deposition of tars at temperatures below 350°C can lead to fouling and potential blockage of downstream equipment and piping [15].

Several methods exist for the reduction of gasification tars. Common methods for tar removal or reduction include (i) mechanical removal using cyclones, scrubbers and filters, (ii) in-furnace control through modification of reactor design and operating conditions, (iii) thermal cracking of tars, and (iv) catalytic cracking of tars [11].

Mechanical methods can be effective in capturing both tars and particulate matter from the gas stream. Bridgewater investigated the use of water scrubbers and found that tar concentration in the output gas could be reduced to as low as 20-40 mg/Nm^3 [16]. Scrubber systems, including venturi scrubbers, are however expensive options, and water-based systems generate a significant amount of contaminated water as secondary pollution that needs to be treated. Electrostatic precipitators (ESPs) are widely used in coal fired power plants due to their excellent efficiency at removing undesirable by-products. These systems can also be useful for the reduction of gasification tars and particulate matter. Paasen et al. examined the use of an ESP system for several different gasification systems (updraft, downdraft, and circulating fluidized bed), and found that the ESP system was able to almost completely remove heavy tars and particulate matters from the syngas, leading to the total tar reduction efficiency of 40-70% and 99% removal of the particulate matter [17].

The gasifier operating parameters, including temperature, pressure, equivalence ratio, ER (defined as the ratio of the amount of O_2 supplied to the gasifier to the O_2 amount required for complete combustion of the feedstock), gasification medium, residence time, feedstock type, preparation, and moisture content, etc. [3, 11, 12, 14]. Tar formation appears to increase with temperature to approximately 600°C, after which it decreases due to secondary thermal cracking reactions. Generally, tar yield also decreases with increasing equivalence ratio, as greater oxygen concentrations within the reactor allow for oxidation/gasification of tar compounds [11, 18]. The addition of secondary air above the fluidized bed can also effectively lower tar yields by creating a secondary reaction zone.

Different biomass feedstocks produce different tar yields under similar conditions. This is likely due to the varying proportions of cellulose, hemicelluloses and lignin within these sources. Hanaoka et al. found that high xylan concentrations lead to the greatest tar yields, followed by cellulose. High-lignin containing feedstocks produced the lowest tar yields [19]. In a gasification study of whole materials, it was found that waste paper produced the highest tar yield (60%), compared with 30-35% for sawdust and wood [11].

Catalytic gasification allows for tar removal at lower temperatures, generally as low as 600-800°C, than thermal tar cracking technologies. This has the advantages of avoiding more expensive heat resistant alloys for reactor construction [12], increasing thermal efficiency of the process, and preventing the combustible gas products from further thermal degradation due to the secondary reactions at high temperatures. The catalytic cracking of biomass derived tars has been widely studied [3, 5-18].

The most commonly used catalysts include nickel-based materials [3, 11, 12, 15], olivine [11, 12, 15, 20-22], and dolomite [11, 12, 15, 20-23]. Depending on the methods of catalyst addition, tar cracking catalysts can be **primary catalysts**, added to the gasification system (gasifier) as reactive bed materials [20-23] or directly to the biomass feedstock, or **secondary catalysts**, added to secondary guard beds and tar cracking reactors downstream of the gasifier [12]. Zhang et al. [12] investigated nickel-based catalysts as secondary catalysts, and found that they were able to reduce heavy tar concentrations in the producer gas by up to 99%, and these catalysts also increased hydrogen yield by 6-11% [12]. Nickel is generally considered an excellent catalyst for both the reduction of tars and the reforming of methane to increase pure syngas production (CO and H_2) [11-13], although commercial nickel catalysts can carry a significant cost. Poisoning and deactivation by sulphur and coke remains a major problem for the nickel-based catalysts [3, 11, 12].

Olivine and dolomite as natural minerals with the formulas $(Fe{\cdot}Mg)_2SiO_4$ and $CaMg(CO_3)_2$, respectively, have been demonstrated effective for gasification-tar cracking. These materials are particularly useful as reactive bed materials within a fluidized bed reactor [21]. While dolomite (calcined prior to use) tends to show greater catalytic activity than olivine, it is much more fragile and there are significant problems with attrition and the carryover of fine particles if used in the harsh environment of a fluidized bed [17, 21-23].

In the present study, a part of the research was focused on examining the catalytic activity of a natural iron ore (oxide) and several metal cations (iron, iron, cobalt, and ruthenium) for tar reduction in gasification of pinewood sawdust in air/CO_2 atmosphere with a bench-scale fixed-bed reactor. The second part of this study is concentrated on investigating the catalytic activity of several different bed materials (olivine, calcined dolomite, calcined limestone, and the crushed natural iron ore) for tar reduction in air-blown gasification of pinewood sawdust and peat with a pilot-scale fluidized bed gasifier at CanmetENERGY. Pinewood sawdust represents a common feed material for biomass gasification, and both pinewood and peat are potential alternative sources for energy production. Proximate and ultimate analyses of these materials are given in Table 5-1.

1.2 Research Objectives

The main objectives of this research are as follows:

(1) Investigate the catalytic gasification of pinewood sawdust in a fixed bed reactor, with an emphasis on the reduction of tar yield. The effects of temperature, CO_2/air concentration, and

catalyst type are investigated. The catalysts investigated in this study are crushed and directly mixed natural limonite (iron oxide), and a variety of wet-impregnated metal cations (iron, cobalt, nickel, ruthenium).

(2) Investigate the catalytic effects of various bed materials during the air-blown gasification of pinewood sawdust and crushed peat pellets in a pilot-scale fluidized bed reactor. The effects of bed materials (olivine, natural limonite, limestone, and dolomite) and varying equivalence ratio (ER) on syngas production and tar yield are studied.

1.3 Organization of Thesis

This thesis is composed of six chapters.

Chapter 1 – Introduction. This chapter gives a general introduction and a brief background literature review on biomass gasification and technologies for tar removal/reduction, as well as a description of the research objectives.

Chapter 2 – Literature Review. This chapter provides a detailed literature review on biomass gasification, fluidized bed gasification, and catalytic tar reduction technologies.

Chapter 3 – Catalytic Gasification of Woody Biomass in Air/CO_2 Media. This chapter provides some analysis of the feasibility catalytic gasification with CO_2 as a gasification agent for the production of syngas and the reduction of tar yield.

Chapter 4 – Pilot-scale Fluidized-bed Gasification of Pine Sawdust and Peat: Experimental Setup and Procedures. This chapter provides the details of the equipment and procedures used during the pilot-scale, fluidized bed gasification experiments, as also briefly outlined in Chapter 5.

Chapter 5 – Catalytic Gasification of Pinewood Sawdust and Peat in a Pilot-scale Air-blown Fluidized-bed Gasifier.

Chapter 6 – Conclusions. This chapter presents the overall conclusions and gives some recommendations for future work.

References

[1] IPCC, *2007: Climate Change 2007: Synthesis Report. Contribution of Working Groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* [Core Writing Team, Pachauri, R.K and Reisinger, A.(eds.)]. IPCC, Geneva, Switzerland

[2] S. Shafiee, E. Topal. *When will fossil fuel reserves be diminished?* Energy Policy 37 (2009) 181-189

[3] K. Sato, K. Fujimoto. *Development of new nickel based catalyst for tar reforming with superior resistance to sulphur poisoning and coking in biomass gasification.* Catalysis Communications 8 (2007) 1697-1701

[4] C. Song. *Fuel processing for low-temperature and high-temperature fuel cells: Challenges, and opportunities for sustainable development in the 21st century.* Catalysis Today 77(2002) 17-49

[5] A. Caputo, M. Palumbo, P. Pelagagge, F. Scacchia. *Economics of biomass energy utilization in combustion and gasification plants: effect of logistic variables.* Biomass and Bioenergy 28 (2005) 35-51

[6] L. Wang, C. Weller, D. Jones, M. Hanna. *Contemporary issues in thermal gasification of biomass and its application to electricity and fuel production.* Biomass and Bioenergy 32 (2007) 573-581

[7] A. Demirbas. *Progress and recent trends in biofuels.* Progress in Energy and Combustion Science 33 (2007) 1-18

[8] X.T. Li, J.R. Grace, C.J. Lim, A.P. Wakinson, H. Chen, J. Kim. *Biomass gasification in a circulating fluidized bed.* Biomass and Bioenergy 26 (2004) 171-193

[9] R. Raudaskoski, E. Turpeinen, R. Lenkkeri, E. Pongràz, R.L. Keiski. *Catalytic activation of CO_2: Use of secondary CO_2 for the production of synthesis gas and for methanol synthesis over copper-based zirconia-containing catalysts.* Catalysis Today (2009), doi:10.1016/j.cattod.2008.11.026

[10] S. Carabineiro, D. McKee, I. Silva. *Uncatalysed and catalysed CO_2 reaction using metal catalysts and binary vanadium mixtures supported on activated carbon.* Carbon 39 (2001)451-463

[11] J. Han, H. Kim. *The Reduction and control technology of tar during biomass gasification/pyrolysis: An overview.* Renewable and Sustainable Energy Reviews 12 (2008) 397-416

[12] R. Zhang, R. Brown, A. Suby, K. Cummer. *Catalytic destruction of tar in biomass derived producer gas.* Energy Conversion and Management 45 (2004) 995-1014

[13] D. Sutton, B. Kelleher, J. Ross. *Review of literature on catalysts for biomass gasification.* Fuel Processing Technology 73 (2001) 155-173.

[14] M. Asadullah, T. Miyazawa and K. Kunimori, *Catalyst development for the gasification of biomass in the dual-bed gasifier*, Applied Catalysis A: General 255 (2003) 169–180

[15] D. Lopamudra, K.J. Ptasinski and F.J.J.G. Janssen. *A review of the primary measures for tar elimination in biomass gasification processes*, Biomass and Bioenergy 24 (2003) 125–140

[16] A. Bridgewater. *The technical and economic feasibility of biomass gasification for power generation.* Fuel 14 (1995) 651-655

[17] S. Paasen, Rabou. *Tar removal with wet ESP: parametric study.* The Second World Conference and Technology Exhibition on Biomass for Energy, Industry and Climate Protection, (2004) 205–210

[18] P.M. Lv, Z.H. Xiong, J. Chang, C.Z. Wu and Y. Chen. *An experimental study on biomass air–steam gasification in a fluidized bed*, Bioresource Technology 95 (2004) 95–101

[19] T. Hanaoka, S. Inoue, S. Uno, T. Ogi and T. Minowa, *Effect of woody biomass components on air–steam gasification.* Biomass and Bioenergy 28 (2005) 69–76

[20] G. Hu, S. Xu, S. Li, C. Xiao, S. Liu. *Steam gasification of apricot stones with olivine and dolomite as downstream catalysts.* Fuel Processing Technology 87 (2006) 375-382

[21] J. Pecho, T.J. Schildhauer, M. Sturzenegger, S. Biollaz, A. Wokaun. *Reactive bed materials for improved biomass gasification in a circulating fluidized bed.* Chemical Engineering Science 63 (2008) 2465-2476

[22] J. Corella, M. Aznar, J. Gil, M. Caballero. *Biomass gasification in fluidized bed: Where to locate the dolomite to improve gasification?* Energy Fuels 13 (1999) 1122-1127

[23] A. Orío, J. Corella, I. Narvàez. *Performance of differne dolomites on hot raw gas cleaning from biomass gasification with air.* Industrial Engineering Chemistry Research 36 (1997) 3800-3808.

CHAPTER 2

LITERATURE REVIEW ON CATALYTIC GASIFICATION OF BIOMASS AND TAR REDUCTION

2.1. Introduction

Due to the concerns over climate changes and the declining fossil fuels reserve, it is of strategic significance to explore alternatives to fossil resources for both energy and chemical production. Among all the potential alternatives to fossil resources, biomass such as wood and woodwaste forestry residues (limbs, bark, tree tops), energy crops and agricultural residues (wheat/rice straws and corn waste) is promising because it represents an immense renewable and hence sustainable energy source (the global annual biomass production is about 6-8 times that the world energy consumption) [1,2]. Currently, the use of biomass accounts for approximately 12% of the world's total primary energy consumption [2, 3]. Although biomass resources are renewable, carbon-neutral, and massive in amount, they are very bulky and difficult to transport, handle, and store. Therefore, appropriate biomass conversion technologies are required to **upgrade** them into gas (hydrogen, syngas), liquid (ethanol, bio-diesel, bio-oils) and other solid fuels (pellets, bio-chars, bio-carbon) through a variety of bio-chemical and thermo-chemical conversion technologies.

Among all the conversion technologies, biomass gasification has attracted increasing research interest in the recent decades, as biomass gasification combined with gas turbine, internal combustion engines and gas burners has great potential for large-scale green power generation at higher efficiencies than the conventional pulverized coal-fired power generation. Gasification of biomass is achieved by partial oxidation of the feedstock using air, O_2 and steam or CO_2, producing a low to medium-BTU product gas (4-15 MJ/Nm^3), also called syngas. Syngas contains primarily CO, H_2, CH_4, CO_2 and trace higher hydrocarbons (C_2+C_3) [3], and the syngas can be cleaned and used directly for power generation or catalytically modified to produce various chemical products such as methanol, dimethyl ether, Fischer-Tropsch oils, etc. [4].

Biomass gasification also produces some contaminants in the product gas, such as tars, NH_3, H_2S and SO_2, etc, and a major concern with biomass gasification is the high yields of tars [4-6]. These contaminants must be removed before the syngas is used for internal combustion, gas engines, and in particular for fuel cells or methanol synthesis, in order to achieve better efficiencies of the syngas applications. In an air-blown fluidized bed gasifier, typical tar contents in producer gas have been reported between 0.5 to 100 g/m^3 [4, 7, 8]. For many applications, with the exception of direct and immediate syngas combustion for heat or electricity production, these tar levels must be reduced, often to below 50 mg/m^3 [4]. Tars can have significant negative effects on gasification with respects to efficiency and operation. Specifically, the production of tars instead of combustible gases represents a decrease in gasification efficiency, and condensation and deposition of tars at temperatures below 350°C can lead to fouling and potential blockage of downstream equipment and piping [8].

The biomass-derived tars consist of a wide range of condensable hydrocarbon and oxygen containing hydrocarbons compounds, which are mostly aromatics and complex poly-aromatic hydrocarbons (PAHs) [9]. Although the biomass-derived syngas with tar can be effectively cleaned with the wet scrubbing technology, hot gas clean-up technology, preferably employing using catalysts, to remove these contaminants at the "hot" state is advantageous with respect to energy efficiencies as it eliminates the need to cool the product gas and re-heat again for the syngas applications (internal combustion, gas engines, fuel cells and methanol synthesis, etc.). The hydrocarbons and tars formed during the gasification process could be removed at hot state through steam/dry reforming or cracking/hydro-cracking reactions as shown below [9]:

Steam reforming: $$C_nH_m + nH_2O \leftrightarrow nCO + (n+\frac{m}{2})H_2 \quad (1)$$

Dry reforming: $$C_nH_m + nCO_2 \leftrightarrow 2nCO + (\frac{m}{2})H_2 \quad (2)$$

Cracking: $$C_nH_m \leftrightarrow nC + (\frac{m}{2})H_2 \quad (3)$$

Hydro-cracking: $$C_nH_m + (\frac{4n-m}{2})H_2 \leftrightarrow nCH_4 \quad (4)$$

Without catalyst, the above tar removing reactions need to be carried out at high temperatures >900°C (due to the endothermic nature of these reactions and a high activation energy >250-350 kJ/mol). Dolomite and group VIII metals such as Ni, Fe, Co, etc. were the most common primary or secondary catalysts for the tar removing reactions [10, 11]. For instance, the use of dolomite and NiMo/Al_2O_3 could significantly reduce the activation energy of the steam reforming reaction of toluene to 123 kJ/mol and 56 kJ/mol, respectively, at 650-850°C [12].

Depending on the methods of catalyst addition, tar cracking catalysts can be the primary catalysts, added to the gasification system (gasifier) as reactive bed materials [14-16] or directly to the biomass feedstock, and the secondary catalysts, added to secondary guard beds and tar cracking reactors downstream of the gasifier [5]. Catalytic gasification allows for tar removal at lower temperatures, generally as low as 600-800°C, than thermal tar cracking technologies. This has the advantages of avoiding more expensive heat resistant alloys for reactor construction [5], increasing thermal efficiency of the process, and preventing the combustible gas products from further thermal degradation due to the secondary reactions at high temperatures.

This chapter overviews the following aspects of biomass gasification and tar reduction technologies, focusing on the formation and reduction of tars using catalysts: biomass gasification technologies, tar reduction technologies, catalysts for biomass gasification and tar reduction.

2.2. Biomass Gasification Technologies

Biomass gasification refers to the process by which biomass is heated under partially oxidizing atmosphere (air, O_2, steam, supercritical water or CO_2) to form a syngas (mainly CO, CO_2, hydrogen gas, methane, and trace higher hydrocarbons and water) as well as contaminants such as tars, NH_3, H_2S and SO_2, etc [4-6, 17, 18]. The overall reaction of biomass gasification may be described by the following generalized reaction:

$$\begin{aligned} Biomass + O_2\ or\ H_2O &\rightarrow CO + CO_2 + H_2O + H_2 + CH_4 + other\ HCs \qquad (5)\\ &\rightarrow tar + char + ash \\ &\rightarrow HCN + NH_3 + HCl + H_2S + other\ sulfur\ gases (SO_2, COS, etc.) \end{aligned}$$

The first stage of gasification is pyrolysis, occurring at temperatures in the range of 300°C, during which the volatile components of the biomass are evolved, leaving behind solid char. The volatile components will undergo cracking reactions into gas products (e.g., CH4, C) which would subsequently form final syngas product (CO, H_2, CO_2) by partial oxidation and steam reforming/gasification reactions. This char could also undergo gasification as it reacts with carbon dioxide and/or steam to produce carbon monoxide and hydrogen [19]. Some main reactions associated with gasification are outlined in Table 2-1. It is clearly seen that the reactions that contribute to the syngas (CO and H_2) formation are mainly highly endothermic, thermodynamically favored at high temperatures.

Table 2-1. Major reactions in the gasification of biomass [2, 20]

Reaction	**ΔH_{298} (kJ mol^{-1})**
Volatiles → $CH_4 + C$	Exothermic (mildly)
$C + 0.5O_2 \rightarrow CO$	-111
$CO + 0.5O_2 \rightarrow CO_2$	-254
$H_2 + 0.5O_2 \rightarrow H_2O$	-242
$C + H_2O \rightarrow CO + H_2$	+131
$C + CO_2 \rightarrow 2CO$	+172
$C + 2H_2 \rightarrow CH_4$	-75
$CO + 3H_2 \rightarrow CH_4 + H_2O$	-206
$CO + H_2O \rightarrow CO_2 + H_2$	-41
$CO_2 + 4H_2O \rightarrow CH_4 + 2H_2O$	-165

The re-condensation reactions of the thermally cracked volatile components would yield tars, which are aromatic-rich mixture of heavy hydrocarbons with a molecular weight greater than benzene. While coal gasification is an established technology, biomass tends to produce greater tar yields, and these tars tend to be heavier and more stable aromatic species [21]. In an air-blown fluidized bed gasifier, typical tar contents in producer gas have been reported between 0.5 to 100 g/m^3 [4, 7, 8]. While the relative proportions of these products can be manipulated through variable reaction parameters (temperature, fuel-air ratio, retention time, reactor type, etc), tar remains one of the main barriers to clean syngas production [22-25], as tar condenses at reduced temperatures, thereby fouling and blocking equipment downstream of the initial gasification process. Temperature, pressure, residence time, gasifying agent, type of feedstock, feed rate of biomass, flow rate of gasification medium and the use of catalysts, have significant effects on the compositions and heating values of the resulting gas as well as the tar formation [18, 26-28].

2.2.1 Air/Oxygen Gasification of Biomasss

In a typical biomass gasification process, the gasifying agents are commonly air, oxygen, steam, and CO_2 or their combinations. Compared with stream-blown gasification (highly endothermic), air-blown gasification is exothermic and hence can make the gasification an energy self-sufficient process. As such, it has been widely practiced on the scale of either research or industrial demonstration. However, air-blown gasification produces a syngas with a lower heating value (4-6 MJ/Nm^3) than steam gasification (13-20 MJ/Nm^3) [3]. This is due to the presence of inert N_2 from air and a high concentration of CO_2 in the product gas from air-blown gasification, and to the high contents of H_2 (by the steam reforming reactions) in the syngas from steam gasification [18]. Heating values of syngas derived from different gasification agents, in comparison to that of natural gas are shown in Table 2-2.

Table 2-2. Heating values of syngas derived from different gasification agents, in comparison to that of natural gas [2]

Gasification process	Heating value of syngas (MJ/Nm^3)
Air	4-6
Oxygen	10-15
Steam	13-20
Natural Gas	36

Gasification in an environment of pure oxygen is advantageous as it produces a syngas with a much higher heating value (10-15 MJ/Nm^3) than that produced by air due to the fact that it is not diluted by N_2, as shown in Table 2-2. In addition, the ease in separation of high purity CO_2 from the product gas stream by absorption/adsorption or membrane technology makes this technology more attractive with respect to greenhouse gas emission control. However, the cost associated with pure oxygen production by separation of oxygen from air, and the safety issue in using pure oxygen, would be the main barrier for commercialization of the oxygen-blown biomass gasification technology [21]. For air and oxygen gasification, a very effective operating parameter is the equivalence ratio (ER), defined as the ratio of O_2 content supplied to the reactor compared to the O_2 content required for complete combustion of the feedstock. For air/oxygen gasification, ER values of 0.25 to 0.35 are common. For instance, biomass was efficiently gasified in air at 800°C to produce a syngas consisting of 10 vol% H_2, 14 vol% CO, and 15 vol% CO_2 with trace amounts of CH_4 at an equivalence ratio of 0.35

[29]. In air-blown gasification, the products are strongly influenced by varying the ER. At an increased ER, the tar yield was found to be reduced significantly, likely due to the greater availability of oxygen to combust the volatiles formed in the pyrolysis zone of the gasifier [30, 31]. Increasing ER, however, showed negative effects on the quality of the product gas by reducing yields of combustible gases (H_2, CO) while simultaneously increasing CO_2 concentration in the gas product.

Air-blown fluidized bed gasification is one of the most cost effective methods available for the gasification of biomass [32]. Fluidized bed reactors provide excellent mixing and therefore better temperature control than fixed bed reactors [33, 34]. Due to solids mixing and particle entrainment, a single fluidized bed may not be able to achieve efficient solids and tar conversion. This may be mitigated through the use of a circulating fluidized bed (CFB) reactor, with cyclones which trap and recycle solids in order to increase total residence time [3, 34]. According to Li et al. [3], significant work is still required on the pilot and full-scale in order to fully understand biomass gasification in a CFB reactor. Moreover, another major advantage of fluidized bed systems is the potential to use catalytically active materials within the fluidized bed as the primary catalysts in order to decrease tar formation and increase combustible gas yield [5, 6, 21, 33, 35].

2.2.2 Steam and CO_2 Gasification of Biomasss

Steam gasification is able to produce a gaseous product that is free of N_2, with H_2 yields of greater than 50% (by volume) [30, 36]. A steam gasification operational parameter used is steam-biomass ratio (SB), which is analogous to ER, defined as: the ratio of H_2O (kg h^{-1}) to biomass (kg_{daf} h^{-1}) in the reaction. As with ER, the optimal value of SB shall be determined for a steam-gasification process in terms of heating value of the product gas and cost of steam supply. Herguido et al [36] observed that increasing SB from 0.5 to 2.5 led to a significant decrease in CO and tar yield, with slight increases in H_2 and CH_4 production. The decreases in tar and CO formation may be accounted for by the steam reforming reactions of the tars and CO as shown below. These reactions were found to be catalyzed effectively in the presence of nickel catalysts [37, 38] :

$$C_nH_x + nH_2O \rightarrow (n + x/2)H_2 + nCO \qquad (6)$$

$$CO + H_2O \rightarrow H_2 + CO_2 \qquad (7)$$

Pure steam gasification is highly endothermic, and the supply of sufficient heat to sustain the gasification reactions may be problematic. Therefore, steam gasification is often carried out in the presence of a small amount of air/oxygen in order to provide the necessary energy via partial combustion of the feedstock. A gasifying ratio (GR) is usually used and defined as the ratio of the feeding rate of (steam + O_2) ($kg\ h^{-1}$) to that of the biomass ($kg_{daf}\ h^{-1}$). In operation, an H_2O/O_2 ratio of approximately 3.0 was recommended for efficient air/steam gasification, with a GR of approximately 1.0 at a temperature of approximately 850°C [39]. Gil et al. also noted that as GR increases from 0.6 to 1.7, H_2 content and CO content decreased from 29% to 13% and 50% to 30%, respectively, while CO_2 content increased sharply from 14% to 37%, due to the excess combustion of the combustible gases. As would be expected, tar formation dropped significantly as GR was increased [39]. It was observed that under similar operating conditions, tar yield was greater in pure steam gasification than in air/steam gasification, and was the lowest under air/oxygen-blown gasification [30]. Increasing the feed O_2 content, however, would generally deteriorate the product gas quality with reduced concentrations of combustible gases [37, 40, 41].

Carbon dioxide can also be used as a gasification agent in a similar manner as steam. Scott et al. [42] investigated the rate of CO_2 gasification of various waste material chars. The reaction of CO_2 with carbonaceous material at atmospheric pressure was found to be relatively slower than the reactions of steam or oxygen, with an apparent order of reaction between 0-1.0 with respect to CO_2 [42-44]. Devi et al. [30] considered CO_2 as a promising gasification agent due to its potential in the enhancement of tar reduction by dry reforming with CO_2, as represented by the following reaction [30]:

$$C_nH_x + nCO_2 \rightarrow (x/2)H_2 + 2nCO \tag{8}$$

Due to the limitation with respect to reaction rate as mentioned above for the pure CO_2 gasification, the catalytic gasification of biomass in a steam/CO_2 atmosphere was investigated by García et al. [38]. Pinewood sawdust was gasified in steam/CO_2 with a co-precipitated Ni/Al catalyst. When compared to similar studies with pure steam gasification [37,38], catalytic gasification with CO_2 led to a decrease in both CH_4 and tar production and a corresponding increase in H_2 and CO production, indicating the dry reforming of CH_4 and tar to the combustible gas products. It was found that the reverse Bouduourd reaction is difficult, even at extremely high temperatures [45-49], and catalysts with high efficiencies are required. Iwaki et al. [45] attempted the CO_2 gasification of wastepaper using novel molten carbonate catalysts. They found that a mixture of lithium carbonate, sodium carbonate, and potassium carbonate showed the greatest catalytic activity, and found that CO_2 gasification in the presence of these catalysts was more effective than steam gasification.

2.2.3 Supercritical Water Gasification of Biomasss

Depending on the quality and condition of the biomass feedstock it may need to be dried first. Therefore biomass with high initial moisture content will require a higher energy input. Faaij et al [17] and Bridgewater [21] examined the technical and economic feasibility of the gasification of biomass wastes and residues for electricity production, and determined that a gasification process can be technically and economically feasible if the following issues are properly addressed: heavy metal distribution, efficient biomass drying, and cleaning of product gases on a full-scale. It is thus much advantageous if these types of low grade wet waste biomass feedstock can be gasified in the wet forms. This challenge has been addressed by the research and development of supercritical water gasification (SCWG) of biomass.

Supercritical water (SCW) is water or vapour at above its critical points: 374°C and 22.1 MPa. SCW has been chosen as an ideal gasification medium for biomass or lignocellulosic waste conversion primarily because it has strong solubility for organic compounds since water above its critical points becomes a weakly-polar solvent with low dielectric constant (ε) value and can thus dissolve many non-polar organics and light inorganic gases such as hydrogen and oxygen. SCW has very high reactivity for conversion of a variety of organic materials (biomass or hazardous wastes) due to its greatly increased value for its ion product ($K_w = [H^+][OH^-]$), e.g., at 400 °C and 50 MPa the value K_w is more than 100 times that at ambient conditions [50], which may efficiently hydrolyze biomass catalyzed by $[H^+]$ and $[OH^-]$ ions [51]. A wide range of biomass such as glucose and lignocellulosic wastes have been successfully gasified in SCW with or without catalyst (carbon or nickel, Pt) to produce hydrogen-rich gas products [52, 53]. Taking glucose as an example, up to 12 mol of pure hydrogen can be generated by SCWG of one mole of feedstock, as shown in the following stoichiometric equation:

$$C_6H_{12}O_6\,(s) + 6H_2O\,(l) \rightarrow 6\,CO_2\,(g) + 12H_2\,(g) \qquad \Delta H^\circ = 625.0\ \text{kJ/mol} \quad (9)$$

Compared to conventional steam gasification or reforming processes, SCWG can obtain a higher gasification-efficiency, a larger hydrogen yield and less tar and coke formation [52]. In addition, SCWG can utilize the wet biomass and wastes directly, eliminating the energy- and capital-intensive drying process. Thus, SCWG is particularly suitable for gasifying biomass with a high moisture content such as wastewater sludge, organic wastes or wastewater [54-56]. The SCWG has attracted significant interest since the 1980's especially in Europe and Japan, but so far there is no process demonstrated on a commercial scale. The major challenges for SCWG of biomass in a continuous flow reactor system are apparently related to the difficulty in the feeding of the slurry feedstock into a high-pressure system and the problems with reactor plugging by deposition of solid biomass particles, ashes and chars. These problems may be adequately addressed by properly designing the reactor system and development of highly active catalysts to minimize the formation of tar and char.

2.2.4. Applications of Biomass Gasification for Power Generation - Indirect Co-Firing

Co-firing biomass and coal has been regarded as one of the most cost-effective technologies for the use of bio-energy on a large scale in particular for power generation, as it makes use of the extensive infrastructure associated with the existing coal-based power systems, and requires only relatively modest additional capital investment to achieve a significant CO_2 reduction [57]. Co-firing is not a recent technology, but it has been remarkably progressing over the last 5-10 years, as it is presently being successfully practiced on a commercial scale in more than 150 power plants in the USA and Northern Europe [57, 58], which include pulverized coal boilers in large scale power plants (~ 700 MW) and bubbling or circulating fluidized beds boilers in smaller scale plants (~ 50 MW) [59, 60]. Co-firing biomass and coal results in noticeable benefits in reducing air pollutants (mainly CO_2 and SO_2 and often NO_x) [61]. However, direct co-combustion of biomass with coal in power generation boilers is associated with many technical challenges, among which the major one is the ash related issues (slagging, fouling, and corrosion) [57]. In addition, the co-firing of biomass with coal will produce fly ash that currently cannot be used in cement manufacturing since the biomass-derived fly ash does not comply with the ASTM and CSA standards for inclusion in cement admixtures for structural applications. This would cause loss in benefits for power generation plants not only due to the loss in the revenue from selling the fly ash to cement manufacturing industry, but the cost to dispose the co-firing fly ash. The above ash related issues (slagging, fouling, corrosion) as well as the unmarketable co-firing mixed fly ashes from biomass and coal, may be addressed by development of the so-called indirect co-firing or gasification-based co-firing technologies, in which solid biomass is first gasified to produce a syngas. This syngas is then injected into a boiler. The apparent advantages of gasified co-firing are: (1) it allows to handle the biomass fly ash separately from the that of coal fly ash without jeopardizing the marketing of the coal-derived fly ash, and (2) the syngas can be used directly in natural-gas or oil based power generation systems [62]. Co-firing with syngas is generally discussed in terms of natural gas-fired systems. The logistics of injecting a biomass-sourced syngas into a coal-fired boiler do not appear to have been studied in depth, although it was found that the addition of syngas in a coal-fired boiler led to unfavourable combustion conditions [63, 64]. A similar study by Kalisz et al. [65] concluded that indirect co-firing with a high quality syngas resulted in only slight operational changes, and a syngas thermal input of 20% could be reached. In contrast, with direct co-firing (co-combustion) methods, only a 5% thermal input was possible without significant pre-treatment or modification to the feeding lines [65]. Fiaschi and Carta [66] examined the co-firing of biomass-derived syngas with natural gas in a gas turbine as a potential method for the reduction of CO_2 emissions. In this research, a portion of oxygen and heat-rich exhaust from combustion was re-circulated to a gasifier, producing a syngas which was later mixed with natural gas. It was found that co-firing with approximately 30% gasification derived syngas led to a slight decrease in power output of only < 10% when compared to natural gas-fueled combustion [66]. Modeling has shown that the co-firing of biomass gas with natural gas would be more efficient if natural gas accounts for greater than 35% - 50% (energy basis) of the total fuel input in order to avoid major operational changes [67]. The biomass gasification-based indirect co-firing technology is promising for power generation, but the sustainable biomass supply can be an issue for large-scale application. The co-gasification of biomass with coal can be a means to establish economies of scale due to the much higher energy density in coal, as well as to smooth out the variability inherent within a biomass gasification system [68].

2.3 Tar Reduction Technologies

2.3.1 Tar Formation from Various Biomass Gasification Processes

Gasification operating parameters (temperature, pressure, residence time, gasifying agent and feedstock), have significant effects on the tar formation, compositions and heating values of the resulting gas. For example, different biomass feedstocks produce different tar yields under similar conditions. This is likely due to the varying proportions of cellulose, hemicelluloses and lignin within these sources. High xylan concentrations might lead to the greatest tar yields, followed by cellulose, while high-lignin containing feedstocks produced the lowest tar yields [28]. In a gasification study of whole materials, it was found that waste paper produced the highest tar yield (60%), compared with 30-35% for sawdust and wood [4]. As discussed previously, tar formation is strongly dependent on the gasification agents or atmospheres as well as temperature. In an air-blown gasification study it was found that increasing the gasification temperature led to a higher concentration of CO_2 accompanied with a decreased H_2 concentration in the gas product [69]. Compared with air/oxygen-blown gasification, using steam as the gasifying agent increased the tar yield, and the yields of H_2 and CO, and hence improved heating value of the product gas (LHV of 10-14

MJ/Nm^3, compared with only 4-8 MJ/Nm^3 for air-blown gasification) [70]. In air-blown gasification, the tar yields are in the range of 4-62 g/kg, much lower than the steam gasification of biomass (60-95 g/kg), as shown in Table 2-3.

Table 2-3: Typical gas composition and tar yields from gasification of pine wood chips in a bubbling fluidized bed with different gasifying agents (summarized from Gil et al. [70])

Gasifying agent	T(°C)	Gas Composition (vol%, db[a])							Tar yields (g/kg)
		H_2	CO	CO_2	CH_4	C_2H_n	N_2	H_2O[b]	
Air	780-830	5-16	10-22	9-19	2-6	0-3	42-62	11-34	4-62
Steam	750-780	38-56	17-32	13-17	7-12	2	0	52-60	60-95
Steam+ O_2	785-830	14-32	43-52	14 -36	6-8	3-4	0	38-61	2-46

[a] On a dry basis; [b] Moisture content in the producer gas.

The tar formation is also strongly dependent on the type of biomass gasifier. Basic types of biomass gasifier include counter-flow fixed-bed gasifier, concurrent flow fixed-bed gasifier, bubbling fluidized bed gasifier, and circulating fluidized bed gasifier, as schematically illustrated in Figure 2-1.

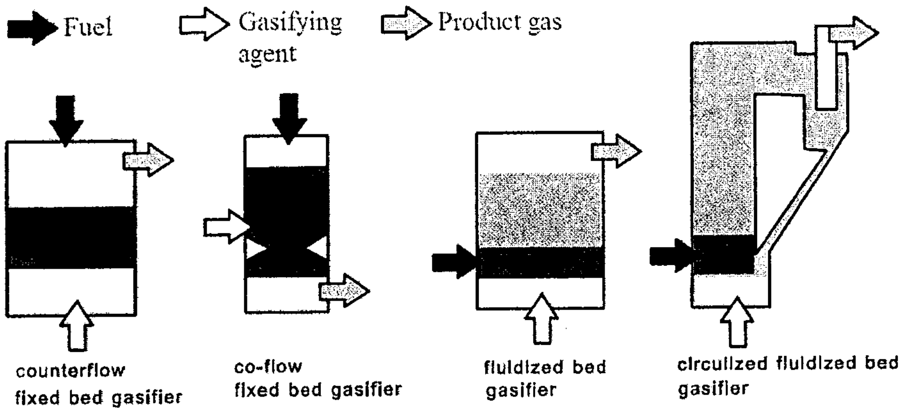


Figure 2-1 Basic types of biomass gasifier (modified from [71])

The gas quality of the product gas (tar content, particulate content and LHV values) from various air-blown biomass gasifiers are summarized in Table 2-4. The concurrent flow fixed-bed gasifiers generally produce a much lower tar yield compared with other types of gasifiers (counter-current flow fixed bed and fluidized bed gasifiers). This is likely resulted from the enhanced thermal cracking as the tar vapor pass through the high temperature zone within the co-current flow fixed bed gasifier.

Table 2-4. Gas quality of the product gas (tar content, particulate content and LHV values) from various air-blown biomass gasifiers [72, 73]

Gasifier	Fixed bed Co-current	Fixed bed Countercurrent	CFB
Tars (g/Nm^3)	0.01-6	10-150	2-30
Particles (g/Nm^3)	0.1-8	0.1-3	8-100
LHV (MJ/Nm^3)	4-6	4-5	4-6

The tar in the product gas must be cleaned before use for internal combustion systems, and direct-fired industrial gas turbines or methanol synthesis, since condensation and deposition of tars can lead to fouling and potential blockage of downstream equipment and piping [8]. The allowable limits for tar in the product gas depend on the end-use applications. For example, less than 50-100 mg/Nm^3, 5 mg/Nm^3, and <0.1 mg/Nm^3 is recommended for internal combustion systems, direct-fired industrial gas turbines, and methanol synthesis [73,74].

2.3.2 Primary Methods for Tar Reduction

Tar reduction technologies can be divided into two types: primary methods – treatment inside the gasifier, and secondary methods – gas cleaning after the gasifier. Primary methods are advantageous over secondary methods with respect to process simplicity and cost. In primary treatment, the gasification process is optimized to minimize tar formation. Primary treatment includes different approaches: (a) optimization of operating parameters and gasifier modification, and (b) addition of active bed materials (catalysts). As discussed above, gasification operating parameters (temperature, pressure, residence time, gasifying agent, ER and feedstock) and the type of biomass gasifier, have significant effects on the tar formation, compositions and heating values of the resulting gas. For instance, tar formation decreases with increasing temperature to > 600°C due to secondary thermal cracking reactions. Generally, tar yield also decreases with increasing ER, as greater oxygen concentrations within the reactor allow for oxidation/gasification of tar compounds [4].

Use of catalysts within the biomass gasification process is mainly for the primary, in-situ reduction of tar, or for catalytic gasification of biomass to produce a syngas at a lower temperature. Dolomite-based and nickel-based catalysts were widely used active material for tar reduction and catalytic gasification [30,33].

Mogtaderi [75] determined that maximum hydrogen production could be obtained at a low temperature of 600 °C in steam gasification of biomass with a nickel-based catalyst. Catalytic gasification allows for tar removal at lower temperatures, generally as low as 600-800°C, than thermal tar cracking technologies. This has the advantages of avoiding more expensive heat resistant alloys for reactor construction [5], increasing thermal efficiency of the process, and preventing the combustible gas products from further thermal degradation due to the secondary reactions at high temperatures. Catalysts can be added directly to the fluidized bed gasifier as a bed material [6]. The use of reactive bed materials within a fluidized bed reactor is of interest due to the high amount of tars produced during FBR gasification of biomass with a non-reactive quartz bed material [33]. Olivine and dolomite are particularly useful as reactive bed materials within a fluidized bed reactor [14]. While dolomite (calcined prior to use) tends to show greater catalytic activity than olivine, it is much more fragile and there are significant problems with attrition and the carryover of fine particles if used in the harsh environment of a fluidized bed [14, 76-78].

2.3.3 Secondary Methods for Tar Reduction

Primary measures are advantageous in terms of process simplicity and treatment costs, but they alone are difficult to meet the strict requirements on tar removal for some downstream applications of syngas. Secondary methods prove to be more effective for tar removal. Common methods for the reduction of gasification tars include (i) mechanical removal using cyclones, scrubbers and filters, and (ii) hot gas catalytic cracking of tars.

Mechanical tar removal methods include scrubbers, filters, cyclones, and electrostatic precipitators [73]. Several typical mechanical methods for tar removal are compared with hot gas catalytic tar cracking in Table 2-5. Sand bag filter and venturi scrubbers are highly efficient, being able to remove up to 95% of tar in the syngas at ambient temperature [4, 73], and able to reduce tars present in the gas stream to below 20-40 mg/Nm^3 [21]. Other methods such as wet scrubbers and water scrubber are also used to successfully remove tars and particulates from the gas stream [4,79]. Electrostatic precipitation is also very efficient for particle removal, while it can also achieve up to 60% tar removal [4].

Table 2-5. Mechanical methods for the reduction of tars formed during biomass gasification, compared with the catalytic tar cracking method [73]

Method	**Temp. (°C)**	**Tar Reduction (%)**	**Particle reduction (%)**
Sand bed filter	10-20	60-95	70-95
Wash tower	50-60	10-25	70-90
Venturi scrubber		50-90	
Fabric filter	~200	0-25	
Wet ESP	40-50	0-60	>99
Catalytic tar cracker	900	>95	

A common problem with the mechanical methods, however, is that they are cold gas clean-up methods requiring the producer gas to first be cooled to <150°C, and this gas cooling reduces the energy efficiency of the system [5]. Hot gas cleaning using catalytic cracking is thus more advantageous. As shown in Table 2-5, a catalytic tar cracker operating at a high temperature can obtain a high tar removal efficiency (95%). Secondary catalytic reactors are often used. Hot syngas from the biomass gasifier was fed into a downward fixed-bed (or fluidized bed) reactor in which catalysts are packed, or using catalyst coated filter located at the reactor outlet for tar removal [80, 81]. Ma et al [81] used porous alumina discs impregnated with nickel as the catalytic filters, and achieved a 99% reduction in tars at operating temperatures >800°C. For tar cracking/reforming, the most commonly used catalysts include nickel-based materials [4, 5, 82], olivine [4, 5], and dolomite [4, 5].

2.4. Catalysts for Catalytic Biomass Gasification and Tar Reduction

For catalytic cracking/reforming of biomass derived tars, Sutton [6] suggested the following criteria for developing useful catalysts (primary or secondary catalysts):

1. It is effective for the reduction of tars;
2. It is effective for reforming methane if syngas ($CO + H_2$) is desired;
3. Catalyst should yield a suitable syngas ($CO:H_2$) ratio for the desired final usage;
4. Catalyst should be resistant to fouling and deactivation;
5. The catalysts should be easily regenerated;
6. The catalysts should be resistant to mechanical attrition;

7. The catalysts should not be prohibitively expensive.

The most commonly used primary and secondary catalysts for tar reduction include nickel-based materials, dolomite, limestone, olivine and iron-based materials [4-6], as discussed in more details below. In addition, some clay minerals such as kaolinite, montmorillonite, and illite were also tested for tar cracking [6, 24, 83]. However, their activity is lower than those of dolomite or nickel based catalysts, due to the fact that clay-minerals cannot remain stable at the high temperatures (>800 °C) required for high-level tar removal.

2.4.1 Nickel-based catalysts

Nickel is the most widely used industrial catalyst [84], and as such a large body of literature exists on its application. The use of commercially available nickel catalyst at temperature greater than 740°C generally led to an increase in syngas production (hydrogen and carbon monoxide) and a subsequent decrease in methane and higher hydrocarbons and tar content [6]. Conversely, the methanation reaction is favoured over nickel catalysts at lower temperatures [6]. Zhang et al investigated the use of three nickel catalysts for tar reduction, and found that the use of Ni-based catalysts within a secondary catalytic reactor reduced tar yield by >99%, while simultaneously increasing hydrogen yield by 6-11% [5]. Nickel catalysts are commonly supported on alumina, silicate, ZrO_2, TiO_2, dolomite and MgO, etc. [27, 83], and can be used as primary catalysts within the gasifier or in a secondary catalytic reactor. Interestingly, the presence of oxygen-containing functional groups (-OH, -COOH, $-CH_3$, C=O) appears to be a pre-requisite for the supported nickel catalyst as a more efficient primary catalyst in biomass gasification.

Srivastava et al. [85] tested the steam gasification of functional group containing coal and non-functional group containing chars with a nickel catalyst. They determined that the gasification of coal led to a significantly higher gas yield than catalytic char gasification. Supported nickel (Ni/MgO) catalysts were also active in supercritical water gasification of biomass. The catalyst of 10 wt% Ni/MgO proved to be very active for the gasification of lignin in supercritical water at about 600°C [86]. Many commercial nickel based catalysts are very active for tar removal [80], although their activities depend also on the temperature of the catalytic bed, space-time, and catalyst particle size.

Poisoning and deactivation by sulphur and coke remains a major problem for nickel-based catalysts [4, 5, 82]. Nickel-based catalysts can be degraded through mechanical means (e.g., erosion and attrition), and these effects are increased in fluidized bed reactors. These catalysts can also be deactivated by surface fouling by coke [24], as well as poisoning by H_2S [30]. These problems with Ni catalyst with respects to catalyst deactivation and poisoning may be mitigated by increasing the reaction temperature [84, 87], using non-alumina (MgO or CeO_2) as catalyst supports or promoters (such as WO_3) [82, 88].

2.4.2 Dolomite and Limestone

Dolomite - a magnesium ore, $CaMg(CO_3)_2$ is a cheap and active catalyst for the gasification of biomass [6, 27, 82]. Dolomite can be used as either a bed material within a fluidized bed reactor or within a secondary catalyst bed located downstream. Corella et al. [15] compared these two addition methods and noted that there was no significant difference between the two with regard to product gas heating value. Both methods were reported to reduce tar yield significantly, and to a similar extent [15]. Sutton et al [6] concluded that dolomite as a catalyst for tar reformation increased gas yields at the expense of liquid yield, and is most active when calcined and used downstream at temperatures exceeding 800°C, while dolomite can be readily deactivated by carbon deposition and attrition.

Dolomite is also used as a support material for metal catalysts, notably nickel [27, 82]. Sato and Fujimoto [82] developed a nickel-based catalyst on a dolomite carrier material, doped by a sulphur-resistant WO_3 promoter, and obtained more than 90% of tar reduction during biomass gasification at 800-850°C in the presence of Ni-poisoning H_2S.

Limestone ($Ca(CO_3)_2$) is similar to dolomite, and the used of calcined limestone as a potential primary catalyst for fluidized bed gasification of bioamss has been investigated [89, 90]. While more studies are required, calcined limestone appears to be an excellent catalyst for both combustible gas production and tar reduction, and the use of calcined limestone has the potential for simultaneous hydrogen production and CO_2 capture in biomass gasification. When calcined, however, the material is fragile and may not be able to withstand the fluidization for long periods of time.

2.4.3 Olivine and Iron-based Catalysts

Olivine, a naturally occurring mineral containing magnesium, iron and silicon, is a potential option for use as a reactive bed material for tar cracking within a fluidized bed reactor [91]. A study by Rapagnà et al. [22] suggested that the catalytic activity of olivine was comparable to that of calcined dolomite, leading to a 90% reduction in tars when compared to a sand bed material. While dolomite still showed a slightly better catalytic efficiency (reducing tar content to 0.6 g/Nm^3 vs. 2.4 g/Nm^3 with olivine), olivine had significantly better resistance to physical attrition within the fluidized bed [22]. Calcined olivine has been used in a steam reforming reaction using naphthalene as a model compound [91] and in air-blown fluidized bed gasification of biomass [92]. Natural olivine alone without calcination showed little to no catalytic activity for dry reforming of methane and tar [93].

Iron-based catalysts are less expensive, but they exhibit a lower catalytic activity than nickel and other metal (Ru, Pt, etc.) catalysts, and they can be deactivated in the absence of hydrogen [24]. According to Nordgreen et al. [25] , while iron oxides do not seem to exhibit high catalytic activity, metallic iron obtained from hematite exhibited a high level of catalytic activity at temperatures exceeding 900 °C. Iron oxide in the form of hematite (Fe_2O_3) has been demonstrated by Sharypov et al. to be a useful catalyst for the hydro-cracking of coal tar and pyrolysis of biomass [94, 95]. Khelfa et al. found that the addition of a hematite catalyst during the steam gasification of *Miscanthus giganteus* (a high calorific value perennial grass) yielded a hydrogen rich product gas, with a peak gas yield of almost 95 wt% [96]. It was also found that the addition of 3 wt% hematite led to a decreased tar yield as compared to non-catalytic gasification, with a notable increase in the oxidation of phenolic species [96]. Uddin et al. [97] investigated the use of iron oxides as secondary catalysts for the gasification of a woody biomass (cedar), where the biomass was gasified in the first stage of a tubular reactor and the resulting tars were gasified downstream in a secondary bed. The iron oxide catalyst showed a high catalytic effect for increasing H_2 and CO_2 concentrations in the syngas by approximately 5 times while decreasing tar yield significantly.

Natural limonite ores containing mainly hematite and goethite (FeOOH), with a small amount of nickel have been used successfully as a catalyst in direct coal liquefaction [98], and for decomposition of coal volatiles [99]. In the study by Li et al [99], Indonesian limonite was used for the decomposition of coal volatiles from a coal carbonization process. For the tar decomposition experiments, the samples were reduced at temperatures above 650°C to obtain samples with mainly metallic iron. The Indonesian limonite showed a high conversion of tar resulting in only 0.3 wt% of the carbon remaining in the tar and the liquid fractions after the catalytic reactor [99]. An Australian limonite was found to be very active for hot gas decomposition of NH_3 to N_2 [100, 101].

In the following chapters, the gasification of both pinewood sawdust and peat in CO_2 and air environments with a variety of catalysts are studied. Chapter 3 focuses on the use of CO_2 as a gasification agent with both natural limonite and several impregnated metal catalysts. This research was carried out in a bench-scale fixed bed reactor as a means of conducting small scale preliminary tests prior to larger scale testing.

Chapters 4 and 5 focus on the air-blown gasification of pinewood sawdust and crushed peat pellets in a fluidized bed reactor with a variety of reactive bed materials. The effects of these bed materials and ER on tar yield and syngas production at the pilot-scale were studied.

2.5 Summary

(1) Gasification represents a promising utilization pathway for biomass as energy and chemical feedstock. The biomass gasification-based indirect co-firing technology is promising for power generation.

(2) Tar formation during biomass gasification, however, remains a significant issue that must be addressed. The production of tars instead of combustible gases represents a decrease in gasification efficiency, and condensation and deposition of tars at low temperatures would lead to fouling and potential blockage of downstream equipment and piping.

(3) Gasification operating parameters (temperature, pressure, residence time, gasifying agent and feedstock, and type of gasifier), have significant effects on the tar formation, compositions and heating values of the resulting gas. High xylan (hemi-cellulose) concentrations might lead to the greatest tar yields, followed by cellulose, while high-lignin containing feedstocks produced the lowest tar yields. Tar formation is strongly dependent on the gasification agents or atmospheres as well as temperature. A higher temperature and higher air-to-fuel ratio in air-blown gasification tend to produce less tar. Steam gasification of biomass would produce much higher tar yields than air/oxygen-blown gasification. The concurrent flow fixed-bed gasifiers generally produce a much lower tar yield compared with other types of gasifiers

(4) Primary measures for tar reduction (by optimizing the operating parameter and addition of primary catalysts in the gasifier) are advantageous in terms of

process simplicity and treatment costs, but they alone are difficult to meet the strict requirements on tar removal for some downstream applications of syngas.

(5) Secondary methods, by mechanical removal using cyclones, scrubbers and filters, and by hot gas catalytic cracking of tars, prove to be more effective for tar removal. In terms of the energy efficiency of the whole system, hot gas cleaning using catalytic cracking is more advantageous.

(6) The most commonly used primary and secondary catalysts for tar reduction include nickel-based materials, dolomite, limestone, olivine and iron-based materials. Poisoning and deactivation by sulphur and coke remains a major problem for the nickel-based catalysts. The major challenge of using dolomite, limestone olivine and other iron-based minerals in a fluidized bed gasifier is the mechanical strength of these materials, as the materials are fragile when calcined and hence may not be able to withstand the fluidization for long periods of time.

REFERENCES

[1]. Kucuk M, Demirbas A. Biomass conversion processes. *Energy Conversion Management* 1997; 38: 151-165.

[2]. McKendry P. Energy production from biomass (Part 1): overview of biomass. *Bioresource Technology* 2002; 83: 37-46.

[3]. X.T. Li, J.R. Grace, C.J. Lim, A.P. Wakinson, H. Chen, J. Kim. *Biomass gasification in a circulating fluidized bed.* Biomass and Bioenergy 26 (2004) 171-193

[4].] J. Han, H. Kim. *The Reduction and control technology of tar during biomass gasification/pyrolysis: An overview.* Renewable and Sustainable Energy Reviews 12 (2008) 397-416

[5]. R. Zhang, R. Brown, A. Suby, K. Cummer. *Catalytic destruction of tar in biomass derived producer gas.* Energy Conversion and Management 45 (2004) 995-1014

[6]. D. Sutton, B. Kelleher, J. Ross. *Review of literature on catalysts for biomass gasification.* Fuel Processing Technology 73 (2001) 155-173.

[7]. M. Asadullah, T. Miyazawa and K. Kunimori, *Catalyst development for the gasification of biomass in the dual-bed gasifier*, Applied Catalysis A: General **255** (2003) 169–180

[8]. D. Lopamudra, K.J. Ptasinski and F.J.J.G. Janssen. *A review of the primary measures for tar elimination in biomass gasification processes*, Biomass and Bioenergy **24** (2003) 125–140

[9]. L. Devi, K.J. Ptasinski, F. J. Janssen .Pretreated olivine as tar removal catalyst for biomass gasifiers: investigation using naphthalene as model biomass tar. *Fuel Processing Technology* 2005; 86: 6: 707-730

[10]. Coll, J. Salvado, X. Farriol, D. Montane. Steam reforming model compounds of biomass gasification tars: conversion at different operating conditions and tendancy towards coke formation. *Fuel Processing Technology* 2001; 74: 19-31

[11]. P. A. Simell; J.O. Hepola; A. Krause. Effects of gasification gas components on tar and ammonia decomposition over hot gas cleanup catalysts. *Fuel* 1997; 76: 1117-1127

[12]. G. Taralas, M.G. Kontominas, Kinetic modelling of VOC catalytic steam pyrolysis for tar abatement phenomena in gasification/pyrolysis technologies. Fuel, 83(2004): 1235–1245.

[13]. G. Hu, S. Xu, S. Li, C. Xiao, S. Liu. *Steam gasification of apricot stones with olivine and dolomite as downstream catalysts.* Fuel Processing Technology 87 (2006) 375-382

[14]. J. Pecho, T.J. Schildhauer, M. Sturzenegger, S. Biollaz, A. Wokaun. *Reactive bed materials for improved biomass gasification in a circulating fluidized bed.* Chemical Engineering Science 63 (2008) 2465-2476

[15]. J. Corella, M. Aznar, J. Gil, M. Caballero. *Biomass gasification in fluidized bed: Where to locate the dolomite to improve gasification?* Energy Fuels 13 (1999) 1122-1127

[16]. A. Orío, J. Corella, I. Narvàez. *Performance of differne dolomites on hot raw gas cleaning from biomass gasification with air.* Industrial Engineering Chemistry Research 36 (1997) 3800-3808.

[17]. Faaij, A., Van Ree, R., Waldheim, L., Olsson, E., Oudhuis, A., Van Wijk, A., Daey-Ouens, C., Turkenburg, W. *Gasification of biomass wastes and residues for electricity production.* Biomass and Bioenergy 12 (1997) 387-407.

[18]. Mahishi MR, Goswami DY. *Thermodynamic optimization of biomass gasifier for hydrogen production.* Int J Hydrogen Energy (2007), doi: 10.1016/j.ihydene.2007.05.018

[19]. Henrich, E., Bürkle, S., Meza-Renken, Z., Rumpel, S. *Combustion and gasification of pyrolysis chars from waste and biomass.* Journal of Analytical and Applied Pyrolysis 49 (1999) 221-241

[20]. J. Vélez, F. Chejne, C. Valdés, E. Emery, C. Londoño. *Co-gasification of Columbian coal and biomass in fluidized bed: An experimental study.* Fuel (2008), doi:10.1016/j.fuel.2008.10.1018

[21]. Bridgewater, A. *The technical and economic feasibility of biomass gasification for power generation.* Fuel 14 (1995) 651-655

[22]. S. Rapagnà, N. Jand, A. Kiennemann, P. U. Foscolo. *Steam-gasification of biomass in a fluidised-bed of olivine particles.* Biomass and Bioenergy 19 (2000) 187-197

[23]. Kirubakaran, V., Sivaramakrishnan, V., Nalini, R., Sekar, T., Premalatha, M., Subramanian, P. *A review on gasification of biomass.* Renewable and Sustainable Energy Reviews (2007), doi:10.1016/j.rser.2007.07.001.

[24]. Abu El-Rub, Z., Bramer, E., Brem, G. *Review of Catalysts for Tar Elimination in Biomass Gasification Processes* Ind. Eng. Chem. Res. (2004) 43, 6911-6919

[25]. Nordgreen, T., Liliedahl, T., Sjöström, K. *Metallic iron as a tar breakdown catalyst related to atmospheric, fluidised bed gasification of biomass.* Fuel 85 (2006) 689–694

[26]. Lv, P., Yuan, Z., Wu, C., Ma, L., Chen, Y., Tsubaki, N. *Bio-syngas procuction from biomass catalytic gasification. Energy Conversion and Management* 48 (2007) 1132-1139.

[27]. Srinakruang, J., Sato, K., Vitidsant, T., Fujimoto, K. *A highly efficient catalyst for tar gasification with steam.* Catalysis Communications 6 (2005) 437–440

[28]. T. Hanaoka, S. Inoue, S. Uno, T. Ogi and T. Minowa, *Effect of woody biomass components on air–steam gasification.* Biomass and Bioenergy **28** (2005) 69–76

[29]. I. Narvàez, A Orío, M. Aznar, J. Corella. *Biomass gasification with air in an atmospheric bubbling fluidized bed. Effect of six operational variables on the quality of produced raw gas.* Industrial and Engineering Chemistry Research 35 (1996) 2110-2120

[30]. Devi, L., Ptasinski, K., Janssen, F. *A review of the primary measures for tar elimination in biomass gasification processes.* Biomass and Bioenergy 24 (2003) 125 – 140

[31]. C. Kinoshita, Y. Wang, J. Zhou. *Tar formation under different biomass gasification conditions.* Journal of Analytical and Applied Pyrolysis 29 (1994) 169-181

[32]. M. Campoy, A. Gómez-Barea, F. Vidal, P. Ollero. *Air-steam gasification in a fluidized bed: Process optimization by enriched air.* Fuel Processing Technology (2009), doi: 10.1016/j.fuproc.2008.12.007

[33]. J. Pencho, T. Schildhauer, M. Sturzenegger, S. Biollaz, A. Wokaun. *Reactive bed materials for improved biomass gasification in a circulating fluidized bed reactor.* Chemical Engineering Science 63 (2008) 2456-2476

[34]. P. Garcia-Ibanez, A. Cabanillas and J.M. Sanchez. *Gasification of leached orujillo (olive oil waste) in a pilot plant circulating fluidised bed reactor. Preliminary results.* Biomass and Bioenergy 27 (2004) 183–194

[35]. C. Courson, L. Udron, A. Kienneman. *Grafted NiO on natural olivine for dry reforming of methane.* Science and Technology of Advanced Materials 3 (2002) 271-282

[36]. J. Herguido, J. Corella, J. Gonzàlez-Saiz. *Steam gasification of lignocellulosic residues in a fluidized bed at a small pilot scale: Effect of the type of feedstock.* Industrial and Engineering Chemistry Research 31 (1992) 1274-1282

[37]. L. Garcia, M. Salvador, J. Aruzo, R. Bilbao. *CO2 as a gasifying agent for gas production from pine sawdust at low temperatures using a Ni/Al coprecipitated catalyst.* Fuel Processing Technology 69 (2001) 157-174

[38]. L. García, M. Salvador, J. Arauzo, R. Bilbao. *Catalytic steam gasification of pine sawdust. Effect of catalyst weight/biomass flow rate and steam/biomass ratios on gas production and composition.* Energy and Fuels 13 (1999) 851-859

[39]. J. Gil, M. Aznar, M. Caballero, E. Francés, J. Corella. *Biomass gasification fluidized bed at pilot scale with steam-oxygen mixtures. Product distribution for very different operating conditions.* Energy and Fuels 11 (1997) 1109-1118

[40]. P.M. Lv, Z.H. Xiong, J. Chang, C.Z. Wu and Y. Chen. *An experimental study on biomass air–steam gasification in a fluidized bed.* Bioresource Technology 95 (2004) 95–101

[41]. Z.A. Zainal, A. Rifau, G.A. Quadir and K.N. Seetharamu. *Experimental investigation of a downdraft biomass gasifier.* Biomass and Bioenergy 23 (2002) 283–289

[42]. S.A. Scott, J.F. Davidson, J.S. Dennis, P.S. Fennell, A.N. Hayhurst, *The rate of gasification by CO_2 of chars from waste.* Proceedings of the Combustion Institute 30 (2005) 2151-2159

[43]. N.M. Laurendau, *Prog. Energy Combustion Science.* 4 (1978) 221-270

[44]. S. Kajitani, N. Suzuki, M. Ashizawa, S. Hara, *CO_2 gasification rate analysis of coal char in entrained flow coal gasifier.* Fuel 85 (2006) 163-169

[45]. H. Iwaki, S. Ye, H. Katagiri, K. Kitagawa. *Wastepaper gasification with CO2 or steam using catalysts of molten carbonates.* Applied Catalysis 270 (2004) 237-243

[46]. S. Carabineiro, D. McKee, I. Silva. *Uncatalysed and catalysed CO2 reaction using metal catalysts and binary vanadium mixtures supported on activated carbon.* Carbon 39 (2001) 451-463

[47]. H. Liu, C. Luo, S. Kato, S. Uemiya, M. Kaneko, T. Kojima. *CO_2/char gasification at elevated temperatures Part I: Experimental results.* Fuel Processing Technology 87 (2006) 775-781

[48]. H. Liu, C. Luo, S. Kato, S. Uemiya, M. Kaneko, T. Kojima. *CO_2/char gasification at elevated temperatures Part II: Clarification of mechanism through modelling and char characterization.* Fuel Processing Technology 87 (2006) 769-774

[49]. B.H. Hameed, M.I. El-Khaiary. *Equilibrium, kinetics and mechanism of malachite green adsorption on activated carbon prepared from bamboo by K_2CO_3 activation and subsequent gasification with CO2.* Journal of Hazardous Materials 157 (2008) 344-351

[50]. Marshall WL, Franck EU. Ion product of water substance, 0-1000 °C, 1-10,000 bars new international formulation and its background. J. Phys. Chem. Ref. Data. 1981;10(2):295-304.

[51]. Bobleter O. Hydrothermal degradation of polymers derived from plants. Prog. Polym. Sci. 1994;19:797-841.

[52]. Xu X., Antal M.J., 1998. Environmental Progress 17, 215-220.

[53]. Williams R.T., Onwudili J., 2006. Energy and Fuels 20, 1259-1265.

[54]. G.J. Dileo, P.E. Savage. *Catalysis during methanol gasification in supercritical water*, Journal of Supercritical Fluid*s* 39 (2006) 228–232.

[55]. K. Arai, R.L. Smith Jr., T.M. Aida, *Decentralized chemical processes with supercritical fluid technology for sustainable society*, Journal of Supercritical Fluids 47 (2009) 628–636

[56]. Y. Matsumura. *Evaluation of supercritical water gasification and biomethanation for wet biomass utilization in Japan.* Energy Conversion and Management 43 (2002) 1301-1310

[57]. Sjaak Van Loo, Jaap Koppejan (2008). The Handbook of Biomass Combustion & Co-firing, *Earthscan.*

[58]. Baxter, L. and Koppejan, J. (2004). Co-combustion of Biomass and Coal. *Euroheat and Power*, **1**, 34-39.

[59]. Boyland, D. M. (1996). Southern company tests of wood/coal co-firing in pulverized coal units. *Biomass and Bioenergy*, **10**, no 2/3, 139-147.

[60]. Prinzing, D. E., Hunt, F. E. and Battista, J. J. and Hughes, E. (1996). Co-firing biomass with coal at Shawville. *Proceedings of Bioenergy'96*, 121-128.

[61]. Philip C.W. Kwong, Christopher Y.H. Chao, J.H. Wang, C.W. Cheung, Gail Kendall (2007). Co-combustion performance of coal with rice husks and bamboo. *Atmospheric Environment*, **41**, 7462-7472.

[62]. Tillman, D. *Biomass cofiring: the technology, the experience, the combustion consequences*. Biomass and Bioenergy 19 (2000) 365-384.

[63]. K.-T. Wu, H.T. Lee, C.I. Juch, H.P. Wan, H.S. Shim, B.R. Adams, S.L. Chen. *Study of syngas co-firing and reburning in a coal fired boiler.* Fuel 83 (2004) 1991-2000

[64]. A. Demirbas. *Biomass resource facilities and biomass conversion processing for fuels and chemicals*. Energy Conversion Management 42 (2001) 1357–1378.

[65]. S. Kalisz, M. Pronobis, D. Baxter. *Co-firing of biomass waste-derived syngas in coal power boiler*. Energy 33 (2008) 1770–1778

[66]. D. Fiaschi, R. Carta. *CO_2 abatement by co-firing of natural gas and biomass-derived gas in a gas turbine*. Energy 32 (2007) 549-567

[67]. M. Rodrigues, A. Walter, A. Faaij. *Co-firing of natural gas and biomass gas in biomass integrated gasification/combined cycle systems.* Energy 28 (2003) 1115-1131

[68]. B. Ricketts, R. Hotchkiss, B. Livingston, M. Hall, *Technology status review of waste/biomass co-gasification with coal.* In Fifth European Gasification Conference, 8-10 April 2002, Noordwijk, The Netherlands

[69]. P.L. Spath, D.C. Dayton. Preliminary Screening—Technical and Economic Assessment of Synthesis Gas to Fuels and Chemicals with Emphasis on the

Potential for Biomass-Derived Syngas; National Renewable Energy Laboratory: Golden, CO., 2003. http://www.nrel.gov/docs/fy04osti/34929.pdf.

[70]. J. Gil, J. Corella, M. P. Aznar, M. A. Caballero. Biomass Gasification in Atmospheric and Bubbling Fluidized Bed: Effect of the Type of Gasifying Agent on the Product Distribution. *Biomass and Bioenergy* 1999; 17: 389-403.

[71]. U. Zuberbuhler, M. Specht, A. Bandi. Gasification of biomass – An overview on available technologies. http://www.zsw-bw.de/topics/fuel/REGbiomassconversion/renew_zu_en.pdf.

[72]. R.G. Graham, R. Bain. Biomass gasification: hot-gas cleanup. Biomass Gasification Working Group Report, International Energy Agency (IEA), 1993.

[73]. Ph. Hasler, R. Buehler, Th. Nussbaumer. *Evaluation of gas cleaning technologies for small scale biomass gasifiers*. In Biomass for Energy and Industry, 10th European Conference and Technology Exhibition, June 8-11, 1998, Wurzburg (Germany).

[74]. T.A. Milne, R.J. Evans. Biomass gasification "tars": their nature, formation and conversion. NREL, Golden, CO, USA, Report no. NREL/TP-570-25357, 1998.

[75]. Moghtaderi, B. *Effects of controlling parameters on production of hydrogen by catalytic steam gasification of biomass at low temperatures*. Fuel 86 (2007) 2422-2430

[76]. S. Paasen, Rabou. *Tar removal with wet ESP: parametric study*. The Second World Conference and Technology Exhibition on Biomass for Energy, Industry and Climate Protection, (2004) 205–210

[77]. J. Corella, M. Aznar, J. Gil, M. Caballero. *Biomass gasification in fluidized bed: Where to locate the dolomite to improve gasification?* Energy Fuels 13 (1999) 1122-1127

[78]. A. Orío, J. Corella, I. Narvàez. *Performance of differne dolomites on hot raw gas cleaning from biomass gasification with air*. Industrial Engineering Chemistry Research 36 (1997) 3800-3808.

[79]. J.C. Jansen, K. Jönsson and M. HagmanLa. *Biological detoxification of tar-water.* Water Sci Technol 46 (2002), pp. 59–65.

[80]. Aznar, M., Caballero, M., Gil, J., Martın, J., and Corella, J. *Commercial Steam*

Reforming Catalysts To Improve Biomass Gasification with Steam-Oxygen Mixtures. 2. Catalytic Tar Removal. Ind. Eng. Chem. Res. (1998) 37, 2668-2680

[81]. Ma, L., Verelst, H., Baron, G. *Integrated high temperature gas cleaning: Tar removal in biomass gasification with a catalytic filter.* Catalysis Today 105 (2005) 729–734

[82]. K. Sato, K. Fujimoto. *Development of new nickel based catalyst for tar reforming with superior resistance to sulphur poisoning and coking in biomass gasification.* Catalysis Communications 8 (2007) 1697-1701

[83]. Kimura T, Miyazawa T, Nishikawa J, Kado S, Okumura K, Miyao T, Naito S, Kunimori K, Tomishige K. *Development of Ni catalysts for tar removal by steam gasification of biomass.* Applied Catalysis B: Environmental 68 (2006) 160–170

[84]. P. Simell, E. Kurkela, P. Stahlberg, J. Hepola. *Catalytic hot gas cleaning of gasification gas.* Catalysis Today 27 (1996) 55-62

[85]. R. Srivastava, J. Sinha, S. K. Srivastava, S. Tripathi. *Nickel catalysed steam gasification of chars obtained from coal–alkali reaction at 600 °C.* Fuel 82 (2003) 93-96

[86]. T. Furusawa, T. Sato, H. Sugito,Y. Miura,Y. Ishiyama, M. Sato, N. Itoh, N. Suzuki. *Hydrogen production from the gasification of lignin with nickel catalysts in supercritical water.* International Journal of Hydrogen Energy 32 (2007) 699 – 704

[87]. W. Wang, N. Padban, Z. Ye, A. Andersson, I. Bjerle. *Kinetics of ammonia decomposition in hot gas cleaning.* Industrial and Engineering Chemistry Research 38 (1999) 4175-4182

[88]. M. Asadullah, S. Ito, K. Kunimori, M. Yamada, K. Tomishige, Biomass gasification to hydrogen and syngas at low temperature: Novel catalytic system using fluidized-bed reactor. J. Catal., 208 (2002): 255–259.

[89]. M.J. Llorente, R. Cuadrado, J.M. Laplaza, J.E. Garcia. *Combustion in bubbling fluidized bed with bed material of limestone to reduce the biomass ash agglomeration and sintering.* Fuel 85 (2006) 2081-2092

[90]. T. Weimer, R. Berger, C. Hawethorne, J.C. Abanades. *Lime enhanced gasification of solid fuels: Examination of a process for simultaneous hydrogen production and CO_2 capture.* Fuel 87 (2008) 1678-1686

[91]. L. Devi, M. Craje, P. Thune, K. Ptanski, F. Janssen. *Olivine as tar removal catalyst for biomass gasifiers: Catalyst characterization.* Applied Catalysis 294 (2005) 68-79

[92]. J. Corella, J. Toledo, R. Padilla. *Olivine or dolomite as in-bed additive in biomass gasification with air in a fluidized bed: Which is better?* Energy & Fuels 18 (2004) 713-720

[93]. C. Courson, L. Udron, A. Kienneman. *Grafted NiO on natural olivine for dry reforming of methane.* Science and Technology of Advanced Materials 3 (2002) 271-282

[94]. V. I. Sharypov, B. N. Kuznetsov, N. G. Beregovtsova, O. L. Reshetnikov, S. V. Baryshnikov. *Modification of iron ore catalysts for lignite hydrogenation and hydrocracking of coal-derived liquids.* Fuel 75 (1996) 39-42.

[95]. V.I. Sharypov, N.G. Beregovtsova, B.N. Kuznetsov, S.V. Baryshnikov, V.L. Cebolla, J.V. Weber, S. Collura, G. Finqueneisel, T. Zimny. *Co-pyrolysis of wood biomass and synthetic polymers mixtures: Part IV: Catalytic pyrolysis of pine wood and polyolefinic polymers mixtures in hydrogen atmosphere.* Journal of Analytical and Applied Pyrolysis 76 (2006) 265-270

[96]. A. Khelfa, V. Sharypov, G. Finqueneisel, J.V. Weber. *Catalytic pyrolysis and gasification of Miscanthus Giganteus: Haematite (Fe_2O_3) a versatile catalyst.* Journal of Analytical and Applied Pyrolysis 84 (2009) 84-88.

[97]. M. A. Uddin, H. Tsuda, S. Wu, E. Sasaoka. *Catalytic decomposition of biomass tars with iron oxide catalysts.* Fuel 87 (2008) 451–459

[98]. T. Kaneko, S. Sugita, M. Tamura, K. Shimasaki, E. Makino, L. Sikalalhi. *Highly active limonite catalysts for direct coal liquefaction.* Fuel 81 (2002) 1541-1549.

[99]. L. Li, K. Morishita, T. Takarada. Light fuel gas production from nascent coal volatiles using a natural limonite ore. *Fuel* 2007; 86:1570-1576

[100]. N. Tsubouchi, H. Hashimoto, Y. Ohtsuka, High catalytic performance of fine particles of metallic iron formed from limonite in the decomposition of a low concentration of ammonia. *Catalysis Letters* 2005; 105: 203-208.

[101]. N. Tsubouchi, H. Hashimoto, Y. Ohtsuka. Catalytic Performance of Limonite in the Decomposition of Ammonia in the Coexistence of Typical Fuel Gas Components Produced in an Air-Blown Coal Gasification Process. *Energy & Fuels* 2007;*21*: 3063–3069

CHAPTER 3

CATALYTIC GASIFICATION OF WOODY BIOMASS IN AIR/CO_2 MEDIA

Several impregnated metal ions (Fe (III), Co (II), Ni (II), and Ru (IV)) and a locally available raw iron ore (natural limonite) were examined for use as catalysts for gasification of pine sawdust in a fixed bed reactor in the media of air/CO_2 at 700°C and 800°C. Compared with air, CO_2 as a gasifying agent for biomass gasification showed a much lower reactivity. The yields of char and tar both increased with increasing CO_2 concentration in the feed gas. A higher temperature and a greater oxygen content in the feed gas led to higher gasification efficiency, as expected. It was observed that the addition of iron ore by simple physical mixing to the biomass feedstock did not alter the yields of all products significantly irrespectively of the types of gasification agent and the gasification temperature, which was likely due to the poor contact between the catalyst and the gas/vapor products during the gasification process. All the impregnated metal ion, in particular Ni (II), Co (II) and Ru (IV), were very effective in promoting the gasification of the woody biomass at 700°C and 800°C, leading to a lower tar yield, a significantly decreased char yield and a greatly increased yield of CO_2-free gas. At 800°C, the impregnation of Fe (III), Ni (II), Co (II) or Ru (IV) led to almost complete conversion of the solid biomass into gas and liquid products, producing an extremely low char yield (< 1-4 wt%), and a very high yield of combustible CO_2-free gas (ranging from 51.7 wt% for Fe to 84 wt% for Ru). The tar yield also reduced significantly from 32.1 wt% without catalyst to 19-27 wt% with the impregnated metal ions. The addition of all impregnated metal ions significantly enhanced the formation of both CO and H_2.

3.1. INTRODUCTION

Biomass can be an abundant source for energy, fuels, chemicals and materials [1, 2]. Biomass gasification is a viable process using gasification agents such as air/oxygen, steam, CO_2 or their combinations for converting biomass, in particular recalcitrant lignocellulosic biomass and agricultural/forestry waste streams, into low to medium BTU fuel gases (5-15 MJ/Nm^3). The gases produced (e.g. H_2, CO, CO_2, CH_4 and C_{2+}) can be utilized directly as fuels for heat and electricity generation, or as feedstocks for productions of methanol, ethanol, dimethyl ether, and Fischer-Tropsch oils, etc. [3].

In recent decades, there are growing concerns worldwide over climate change and greenhouse gas emissions. Reduction of greenhouse gas (mainly CO_2) emission may be achieved by sequestration of CO_2, enhancing energy end-use efficiency and promoting the use of renewable energy resources such as biomass. In addition to these, direct or indirect use of CO_2 from flue gases as a feedstock for producing chemicals, such as synthesis gas (through dry reforming of methane: $CO_2 + CH_4 \leftrightarrow 2H_2 + 2CO$, $\Delta H^{o}_{298\,K} = 247$ kJ/mol), methanol and urea, is more appealing not only because it can contribute to mitigation of greenhouse emissions, but also because it generate new opportunities for catalysis and industrial chemistry [4, 5]. The present state and perspectives of producing chemicals from CO_2 through heterogeneous catalytic reactions are briefly reviewed by Centi and Perathoner [5] and Raudaskoski et al. [6]. Synthesis gas, a mixture of hydrogen and carbon monoxide, is a key intermediate in the chemical industry. Presently, steam reforming, partial oxidation and auto-thermal reforming of natural gas is the dominant process for the production of syngas, which accounts for 48% of the world total hydrogen production [7]. However, from an environmental perspective, there is a growing interest in utilizing alternative renewable sources of raw materials (such as biomass, and bio-oils and bio-chars) and/or different kinds of flue and process gases (such as CO_2). In this context, syngas production by CO_2 gasification/reforming of biomass is an appealing scenario. A general reaction for CO_2 gasification/reforming of biomass may be shown below:

$$C_nH_xO_y + CO_2 \rightarrow H_2 + CH_4 + CO + C_2 \qquad (1)$$

Due to the highly endothermic nature of this reaction and reaction (2) below, it must be carried out at high temperature (>800°C) with additional energy supplied to facilitate the reaction. In practice, this energy may be supplied from renewable or non-fossil sources by combustion of biomass fuels or by in-process partial combustion of biomass using mixture of CO_2/air (or O_2) as the gasification medium. However, for better energy efficiency of the CO_2 gasification process, lower process temperatures are always desirable.

Carbon dioxide has been used as a gasification agent in a similar manner as steam does. Devi et al. [8] considered CO_2 as a promising gasification agent due to its potential in the enhancement of tar reduction by dry reforming with CO_2, as represented by the following reaction [8]:

$$C_nH_x + nCO_2 \rightarrow (x/2)H_2 + 2nCO \qquad (2)$$

However, reactivity of CO_2 towards carbonaceous material was demonstrated to be much lower compared with that of air, oxygen and steam [9-11]. The reaction of CO_2 with carbonaceous material at atmospheric pressure was found to be with an apparent order of reaction between 0-1.0 with respect to CO_2 [11-13].

The inherently low reactivity of CO_2 as a gasification agent for biomass gasification can be improved by using catalysts. Garcìa et al. [9] have successfully demonstrated that pinewood sawdust could be efficiently gasified in a fluidized bed using CO_2 as a gasifying agent and employing a Ni/Al co-precipitated catalyst as the bed materials. When compared to similar studies with pure steam gasification [9,14], catalytic gasification with CO_2 led to a decrease in both CH_4 and tar production and a corresponding increase in H_2 and CO production, indicating the dry reforming of CH_4 and tar to the combustible gas products. It was found that the reverse Bouduourd reaction is difficult, even at extremely high temperatures [15-18], therefore catalysts with high efficiencies are required. Iwaki et al. [15] attempted the CO_2 gasification of wastepaper, and they observed that CO_2 gasification in the presence of a mixture of lithium carbonate, sodium carbonate, and potassium carbonate was more effective than steam gasification.

As a primary measure to catalyze gasification and reduce tar formation, in-bed catalysts (either as bed materials or as additives to the feedstocks) have been widely investigated in air and/or steam gasification of biomass [19-22]. Typical examples of in-bed catalysts are calcined dolomite/limestone/olivine, and transitional metal-based catalysts [8, 19-22]. Nickel and noble metal catalysts (Ru, Pt, and Rh, etc.) were found to be highly effective in reducing tar formation and improving the quality of syngas [21]. Except for the research introduced above by Garcìa et al. [9,14], very little research was done on CO_2 gasification of biomass using in-bed catalysts of transition metals (Fe, Co, Ni, Ru).

The objectives of the present research are to investigate the feasibility of the gasification of woody biomass in CO_2/air media, and to examine the effects of a variety of catalysts on the gasification efficiencies and tar formation. The catalysts tested include several metal ions (Fe (III), Co (II), Ni (II), and Ru (IV)) pre-impregnated on the biomass feedstock, and a locally available raw iron ore (natural iron oxide) powder added directly by physical mixing. Natural iron oxides such as limonite have been shown to have a catalytic effect in the reduction of tars and production of useful products during the gasification and liquefaction of biomass [23-26]. The purpose of this research is to explore the potential of CO_2 as a gasification agent for efficient conversion of biomass to syngas using catalysts.

3.2. EXPERIMENTAL

3.2.1 Materials

The biomass used in this study was white pine sawdust obtained from a local sawmill in Southern Ontario. The sawdust sample was dried at 105°C for 24 hours and sieved to a particle size of < 2 mm prior to use. The proximate and ultimate analysis of the feedstock material is given in Table 3-1.

Table 3-1. Proximate and ultimate analysis of white pine sawdust feedstock

Proximate analysis (wt%, d.b.)[a]	
Ash (ASTM D 5142)	0.4
Volatiles (ASTM (D 5142)	84. 5
Fixed Carbon (by diff.)	15.1
Ultimate analysis (wt%, d.a.f.)[b]	
Carbon (ASTM D 5373)	52.7
Hydrogen (ASTM D 5373)	6.4
Nitrogen (ASTM D 5373)	0.1
Sulphur (ASTM D 5373)	<0.1
Oxygen (by diff.)	40.8

[a] On a dry basis; [b] On a dry and ash free basis.

3.2.2 Catalysts and their preparation

The iron ore material tested in this research as a catalyst was obtained from the former Steep Rock Mine site in Atikokan, Ontario. The ore was crushed and screened to below 300 μm and dried at 105°C in air for 24 h prior to use. The contents of major mineral elements in the iron ore were analyzed by ICP-AES, as shown in Table 3-2. The iron ore is composed mainly of iron and silicon (42 wt% and 31.1 wt%, respectively). Our X-ray diffraction (XRD) measurements showed that the iron is present in the forms of goethite (FeOOH) and hematite (Fe_2O_3) (as shown in Figure 3-1). For the tests with iron oxide catalyst, 2 grams of dried pine sawdust was mixed directly with 0.4 grams of crushed iron ore. As the iron ore contains 42.2 wt% Fe, yielding an Fe loading of approximately 8% (wt/wt) of the dry mass of the sawdust.

In addition, metal ions (Fe (III), Co (II), Ni (II), and Ru (IV)) were prepared by wet impregnation method using the sawdust and a solution of the individual metal nitrate compound: $Fe(NO3)_3\text{-}9H_2O$, $Ni(NO_3)_2\text{-}6H_2O$, $Co(NO_3)_2\text{-}6H_2O$ or $Ru(NO)(NO_3)_x(OH)_y$, for a metal loading at 2 % (wt/wt) of the dry mass of the sawdust. As a brief description of the wet impregnation process, the weighed metal nitrate compound was first dissolved in 200 ml 50% methanol/distilled water, and the solution was added into a flask with 2 g dried sawdust. The mixture was agitated for 30 min in an ultrasonic bath. The resulting suspension was subject to evaporation under reduced pressure at 80°C to remove the water and methanol, and the impregnated biomass was dried at 105°C for 24 hours prior to use.

Table 3-2: Contents of major mineral elements in the iron ore used

Mineral element content^a (wt%)												
Fe	Si	Cr	Al	S	Mn	Ca	K	Na	Ti	V	Pb	Mo
42.2	31.1	0.1	0.4	0.2	All < 0.05							

a. Determined by ICP-AES; DL = method detection limit.

The crystalline structures of the biomass loaded with various catalysts, either by physical mixing for the iron ore powder or by impregnation were evaluated by X-ray diffraction (XRD) analysis. The XRD measurements were carried out by using Ni-filtered Cu-Kα radiation with a Philips PW 1050-3710 Diffractometer, and the results are presented in Figure 3-1. The diffraction pattern of pine sawdust mixed with iron ore powder shows broad peaks at $2\theta = 16.0°$, 22.4°, typical of cellulose I_α (100) and I_α (200) [27]. The XRD signals of hematite and goethite were detected in this mixture. In contrast, the metal-related XRD signals were not detectable in all sawdust samples impregnated with metal ions. This strongly suggests excellent dispersion of the metal ions in the biomass. Interestingly, in these metal-impregnated sawdust samples two strong peaks at about $2\theta = 22°$ and 25° were detected, which are likely related to cellulosic structures of the sawdust. The peak at $2\theta = 22°$ is obviously ascribed to the diffraction of cellulose I_α (200), while the peak at $2\theta = 25°$ may be attributed to the thermally/chemically modified cellulose resulting from the metal ion impregnation process [28].

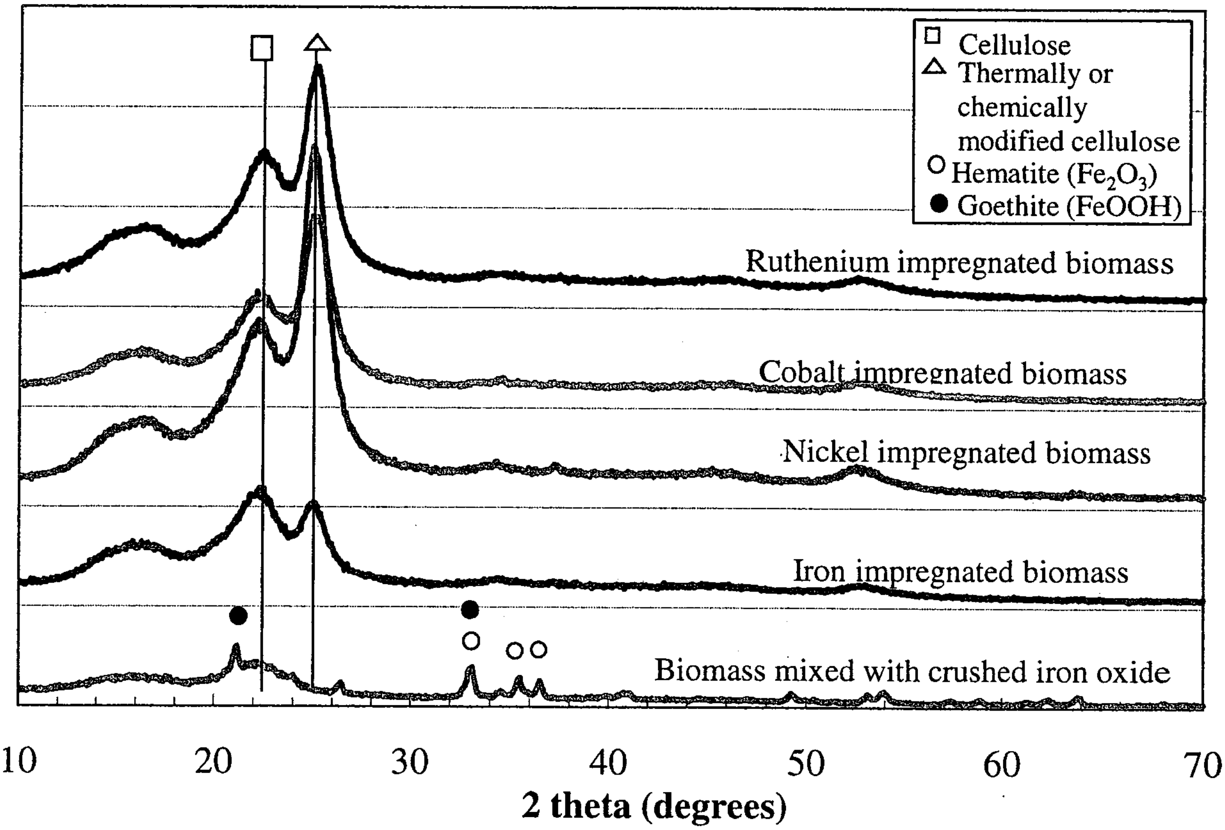


Figure 3-1. XRD patterns of the pine sawdust samples loaded with different types of metal catalysts prior to gasification.

3.2.3 Gasification apparatus, procedures and the product analysis

The gasification tests of pine sawdust were carried out with a fixed-bed stainless steel tubular reactor (15 mm ID), externally heated by an electrical furnace. In a typical test, 1.0g dried pine sawdust sample (with or without catalyst) was loaded into the reactor. The reactor with the sample was heated at a heating rate of 20°C/min from room temperature up to 700°C or 800°C, and soaked for 30 min at the temperature, in a stream of the selected gasification agent (100% air, or 100% CO_2 or 17 vol% CO_2 – 83 vol% air) at 100 ml/min. All tests took place at atmospheric pressure. The evolved gas products flowed through a demister packed with glass wool, an ice bath as the tar condenser, and finally through a wet test meter before being collected into a gas collection bag. After each test, the total volume of the gas was accurately measured by the wet test meter, and the gas compositions were analyzed by GC-TCD. The whole reactor system (reactor itself, demister and the tar condenser) was washed with acetone to dissolve all the tar formed in the gasification process. The residual solids (denoted as Char) were separated by filtration. After being dried at 105°C for 24 h in air, the solids were quantified by weighing. The acetone solution was evaporated at 40°C under reduced pressure to completely remove the acetone. The resulting liquid product was designated as "Tar" and its mass was quantified by weighing. In this study, the yields of Gas, Solids and Tar were calculated to the dry organic matters (i.e., on a dry and ash/catalyst-free basis). For this study, there is an inherent challenge associated with the calculation of Gas yield, due to different origins of the CO_2 in the product gas from the tests when CO_2 was employed as the gasification agent. The CO_2 collected in the product gas can originate from both the biomass and the feeding gas. In order not to over-estimate the gas yields, a conservative approach was adopted by evaluating "CO_2-free gas" (or combustible gases). Due to excluding CO_2 in the calculation of gas yield, the mass and carbon balances were not meaningful. However, in the tests with 100% air, the overall mass balances were found to be in the reasonable ranges of 95-110%. Two to three duplicate runs were conducted for most of the experimental conditions and the relative errors for the product yields between the runs under the same conditions were ensured within 10% of the reported value of yields for most of the conditions tested.

The compositions of gaseous products (consisting of mainly CO, H_2 and CH_4, and negligible amounts of C_2 and C_3 gases) were determined using an Agilent 3000 Micro-GC equipped with dual columns (Molecular Sieve and PLOT-Q) and thermal conductivity detectors. The tar products were analyzed with a Shimadzu gas chromatography/mass spectrometry (GC/MS)-QP2010S. The GC is equipped with a SHRXI-5MS capillary column (30m × 0.25mm × 0.25 μm). The column temperature was initially at 40°C, held for 2 min, and it was first raised up to 190°C at a heating rate of 12°C/min. The column was then heated up at a heating rate of 8°C/min to 290°C, followed by another isothermal hold for 30 min at this temperature. The obtained chromatographic peaks were identified using the WILEY8 library. Due to the very small amount of residual solids formed in most of the tests, the obtained chars were not analyzed further.

3.3. RESULTS AND DISCUSSION

3.3.1 Effects of CO_2 content in the feed gas

Gasification tests were conducted in a flow of gasification agent of various concentrations of CO_2 (100% air or ~0% CO_2, and 17% CO_2-83% air and 100% CO_2) at 700 °C and 800 °C, and the results are presented in Figure 3-2. The rationale behind the use an air/CO_2 mixture is the desire to partial combustion of the biomass feedstock in order to offset the endothermic heat effect of the CO_2 gasification reaction, and to achieve a heat self-sufficient (or auto-thermal) process. At both temperatures, the yields of char and tar both increased with increasing CO_2 concentration in the feed gas, e.g., at 700°C the char yield increased from 0.6 wt% with 100% air to 25.2 wt% with 100% CO_2, while at 800°C the tar yield climbed from 23.9 wt% with 100% air to 44.2 wt% with 100% CO_2. This is a result of the lower reactivity of CO_2 compared with other agent (e.g, steam and oxygen) as demonstrated by many studies [10, 11]. The amounts of char and tar were reduced by increasing operating temperature, as clearly shown by the comparison of Figures 3-2A and 2B. For example, in the CO_2-gasification the tar yield decreased from 44.2 wt% to 32.1 wt% and the char yield decreased from 21.2 wt% to 13.7 wt% as temperature increased from 700°C to 800°C. A higher temperature and a greater oxygen content in the feed gas would lead to higher gasification efficiency, as expected. .

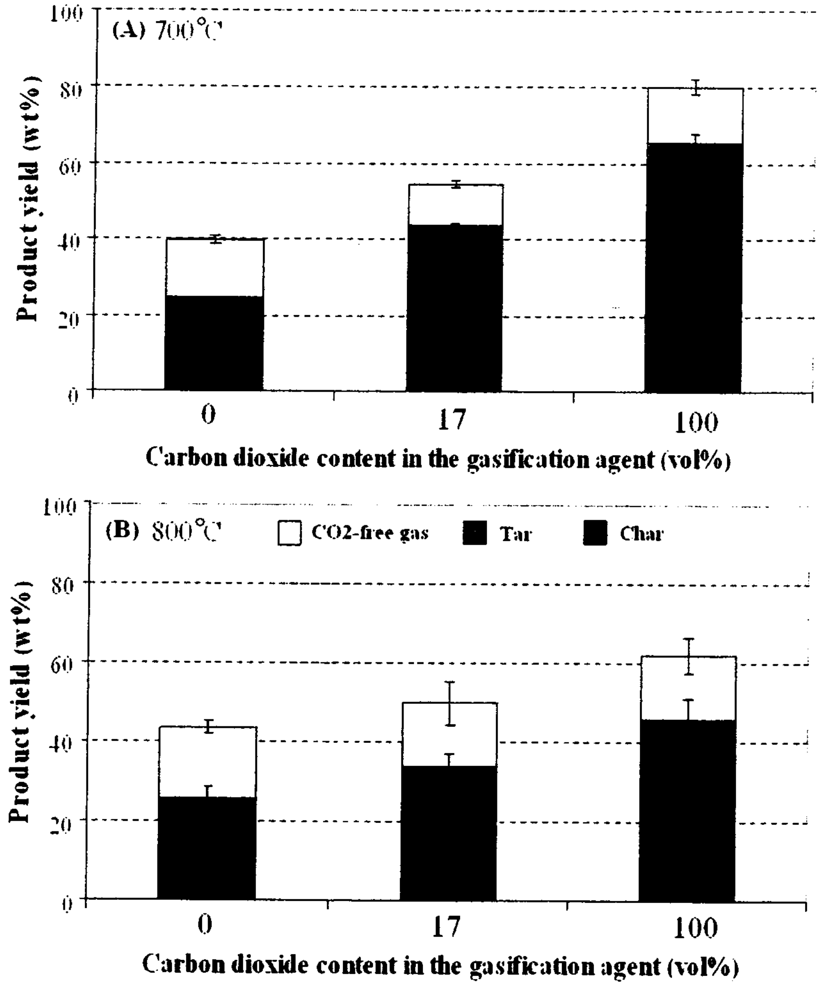


Figure 3-2. Effects of CO_2 concentration in the feed gas on the yields of CO_2-free gas, tar and char in gasification of pine sawdust at 700°C (A) and 800°C (B).

As shown in Figures 3-2A and 2B, the effect of CO_2 content in the feed gas on the yield of CO_2-free gas is less significant compared with those on the char and tar yields, as discussed above. At both temperatures, the average CO_2-free gas yields were in the range of 10-20 wt%, irrespective of the CO_2 content in the feed gas. Table 3-3 provides the formation of the main CO_2-free gas species (H_2, CH_4 and CO) during gasification of the pine sawdust in various types of feed gas at 700°C and 800°C. As shown in the Table, from all the tests under different conditions the yields of hydrogen, methane and CO were in the relatively narrow ranges of 0.42-0.66 mol/kg-biomass (equivalent to 9.4-14.8 liters at STP per kg of biomass fed), 0.42-0.77 mol/kg-biomass and 3.58-6.16 mol/kg-biomass, respectively. As such, the production of the main CO_2-free gas species was not significantly influenced by either CO_2 content in the feed gas or temperature. Generally, the yields of H_2 and CO were greater in the tests with 100% air than those with the CO_2-containing gasification agents, while the gasification in 100% CO_2 produced the greatest yields of CH_4, as shown in Table 3-3. The enhanced CH_4 at the expense of CO and H_2 might be a result of the methanation reaction: $CO + CO_2 + 7H_2 \rightarrow 2CH_4 + 3H_2O$.

Table 3-3. Formation of the main CO_2-free gas species (H_2, CH_4 and CO) during gasification of the pine sawdust in various types of feed gas at 700°C and 800°C.

	700 °C			800 °C		
	% CO_2 in the feed gas					
	0	17	100	0	17	100
Gas formation (mol/kg biomass):						
H_2	0.55	0.42	0.49	0.66	0.56	0.46
CH_4	0.56	0.42	0.77	0.46	0.48	0.57
CO	5.04	3.58	4.58	6.16	5.31	5.35

3.3.2 Effects of catalyst

Catalytic gasification was attempted in two ways in this research. First, a natural iron oxide material was crushed and mixed directly with the sawdust. Second, several metal ions (Fe (III), Co (II), Ni (II), and Ru (IV)) were impregnated onto the biomass prior to gasification.

It was observed that the addition of iron ore by simple physical mixing to the biomass feedstock did not alter the yields of all products significantly irrespective of the types of gasification agent at both temperatures. These results are less encouraging compared with those reported previously showing that iron based material (such as olivine) was an effective bed material for reducing tar formation in biomass gasification in a fluidized bed [23]. The performance discrepancy might be caused by the difference in reactor type (fluidized bed reactor is superior to the fixed bed reactor with respects to vapor-solid contact and mass/heat transfer efficiencies), and more likely due to the difference in compositions: olivine contains significant amount of magnesium and trace amount of nickel in addition to Fe and Si, while the iron ore used in this research contains mainly Fe and Si (Table 3-2). As the major issue of biomass gasification is related to the detrimental tar formation, a comparison of tar yields between the gasification tests with and without iron ore in various types of gasification agent is shown in Figure 3-3. At both temperatures of 700°C (Fig. 3-3A) and 800°C (Fig. 3-3B), the addition of crushed iron ore resulted in a slight increase in tar formation in the gasification runs with 100% air, although it did result in a small reduction in tar yields in the tests with 17% CO_2-83% air or 100% CO_2. Accordingly, addition of iron ore to the biomass feedstock by physical mixing does not seem to be an effective approach to reduce tar formation in biomass gasification at least in a fixed bed reactor. The authors' group will test iron ore as a bed material for biomass gasification in a fluidized bed reactor.

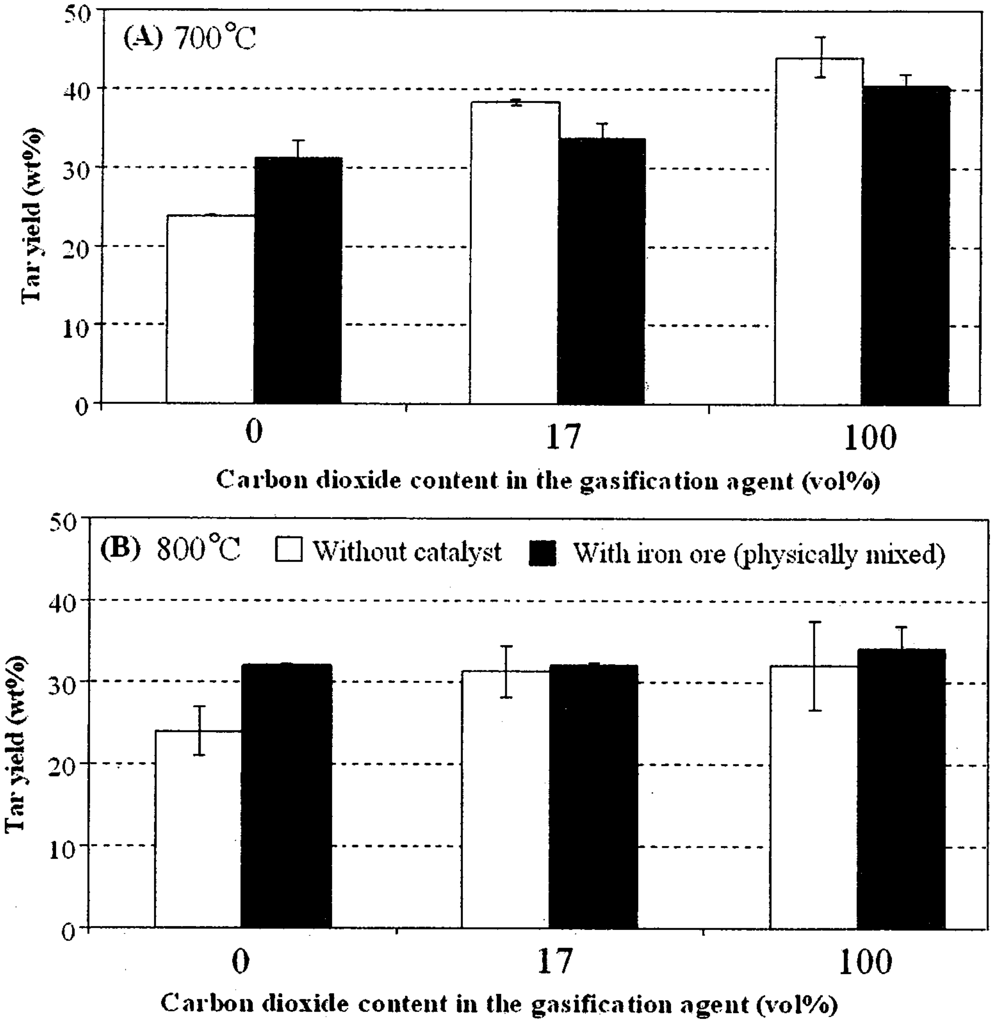


Figure 3-3. Effects of addition of iron ore (by physical mixing) on tar yields from the gasification of pine sawdust in various types of feed gas at 700°C (A) and 800°C (B).

Effects of the metal ion impregnated onto the pine sawdust on gasification of the biomass may be shown in Figure 3-4 that presents yields of CO_2-free gas, tar, and char from gasification of the pine sawdust in 100% CO_2 at 700°C and 800°C with various types of catalyst including the impregnated metals ions and physically mixed iron ore powder. As shown in Figure 3-4A, all the impregnated metal ions (Fe (III), Co (II), Ni (II), and Ru (IV)), in particular Ni (II), Co (II) and Ru (IV), were very effective for promoting the gasification of the woody biomass at 700°C, leading to a lower tar yield, a significantly decreased char yield and a greatly increased yield of CO2-free gas. In the 700°C gasification, all the impregnated metal ions reduced tar yield from 44.2 wt% without catalyst to

23.9~29.7 wt%, The impregnated Co (II) and Ru (IV) were found to be extremely active for enhancing the biomass gasification with respect to solid conversion, leading to the char yield as low as 4 wt%, compared with a char yield >20 wt% without catalyst or with the physically mixed iron ore powder or the impregnated Fe (III).

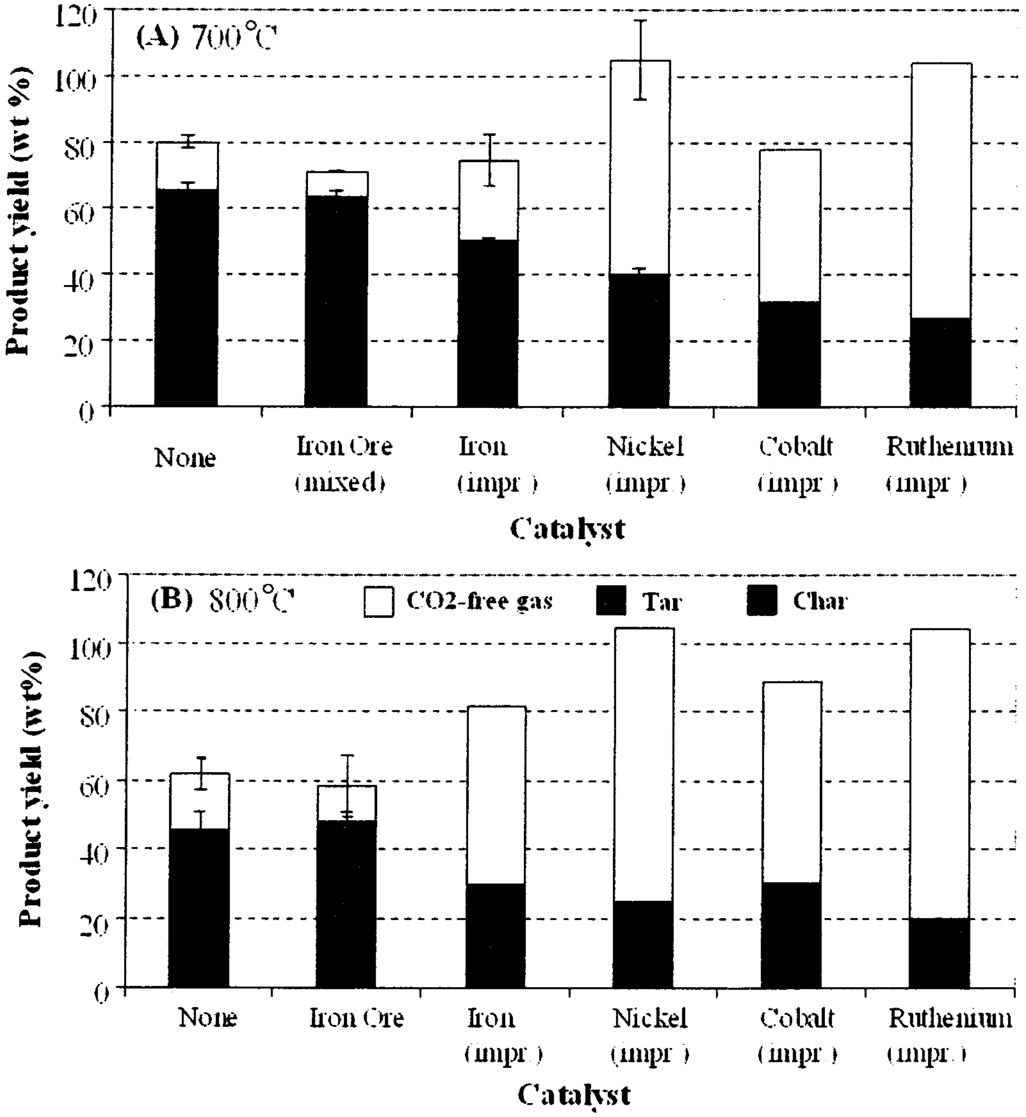


Figure 3-4. Yields of CO_2-free gas, tar, and char from gasification of pine sawdust in 100% CO_2 at 700°C (A) and 800°C (B) with various types of catalyst.

With respect to the yield of combustible (CO_2-free) gas, however, the impregnated Ni (II), Co (II) and Ru (IV) were very active catalysts, producing combustible (CO_2-free) gas at a yield of 64.7

wt%, 45.8 wt% and 77.4 wt%, respectively, compared with a gas yield of only 14.7 wt% in the gasification without catalyst. The impregnated Ru (IV) and Ni (II) are thus extremely active for promoting conversion of biomass to combustible (CO_2-free) gas, leading to 3-4 fold of increase in the yield of CO_2-free gas at 700°C. In addition, activity of all these impregnated metals was increased further as the gasification temperature increased to 800°C as shown in Figure 3-4B. At 800°C, the impregnation of Fe (III), Ni (II), Co (II) or Ru (IV) led to almost complete conversion of the solid biomass into gas and liquid products, producing an extremely low char yield (ranging from 0.9 wt% for Ru (IV) to 3.9 wt% for Co (II)), and a very high yield of combustible CO_2-free gas (ranging from 51.7 wt% for Fe (III) to 84 wt% for Ru (IV)). The tar yield also reduced significantly from 32.1 wt% without catalyst to 27.1 wt%, 23.0 wt%, 26.6 wt% and 19.3 wt% with the impregnated Fe (III), Ni (II), Co (II) and Ru (IV), respectively. The superb catalytic activities of the impregnated metal catalysts may be partially accounted for by their excellent dispersion states of these metal ions in the biomass as evidenced by the XRD measurements (Figure 3-1).

Effects of catalysts on yields of major combustible gas species of H_2, CH_4 and CO from gasification of pine sawdust at 700°C and 800°C in 100% CO_2 are shown in Figure 3-5. None of the catalysts tested showed noticeable effect on methane yield at either temperature. The methane formation from the gasification was in the range of 0.6-0.8 mol/kg-biomass, irrespective of whether or not a catalyst was used. The addition of impregnated metal ions did, however, have a significant effect on the formation of both carbon monoxide and hydrogen. The yield of CO during the gasification without catalyst at 700°C and 800°C was 4.7 and 5.3 mol/kg biomass, respectively. The yield was increased dramatically by the addition of impregnated metal catalysts. For example, at 800°C, the CO yield per kg of biomass (dry and ash-free) climbed to 17.7 mol, 28.0 mol, 20.0 mol and 29.0 mol with the impregnated Fe (III), Ni (II), Co (II) and Ru (IV) catalyst, respectively. . The yield of H_2 during the gasification without catalyst at 800°C was approximately 0.5 mol/kg biomass, which was increased to

1.3 mol/kg biomass, 2.5 mol/kg biomass, 2.1 mol/kg biomass and 3.1 mol/kg biomass due to the presence of the impregnated Fe (III), Ni (II), Co (II) and Ru (IV), respectively. Similar effects of the catalysts on CO and H_2 formation were observed at 700°C, as shown in Figure 3-5A. The above results are consistent with those reported previously by Garcìa et al. [9] for gasification of pine sawdust in a fluidized bed using CO_2 as a gasifying agent and employing a Ni/Al co-precipitated catalyst. For example, Garcìa et al. [9] also showed that the presence of the Ni/Al co-precipitated catalyst reduced tar formation, suppressed CH_4 formation, but enhanced the formation of CO and H_2.

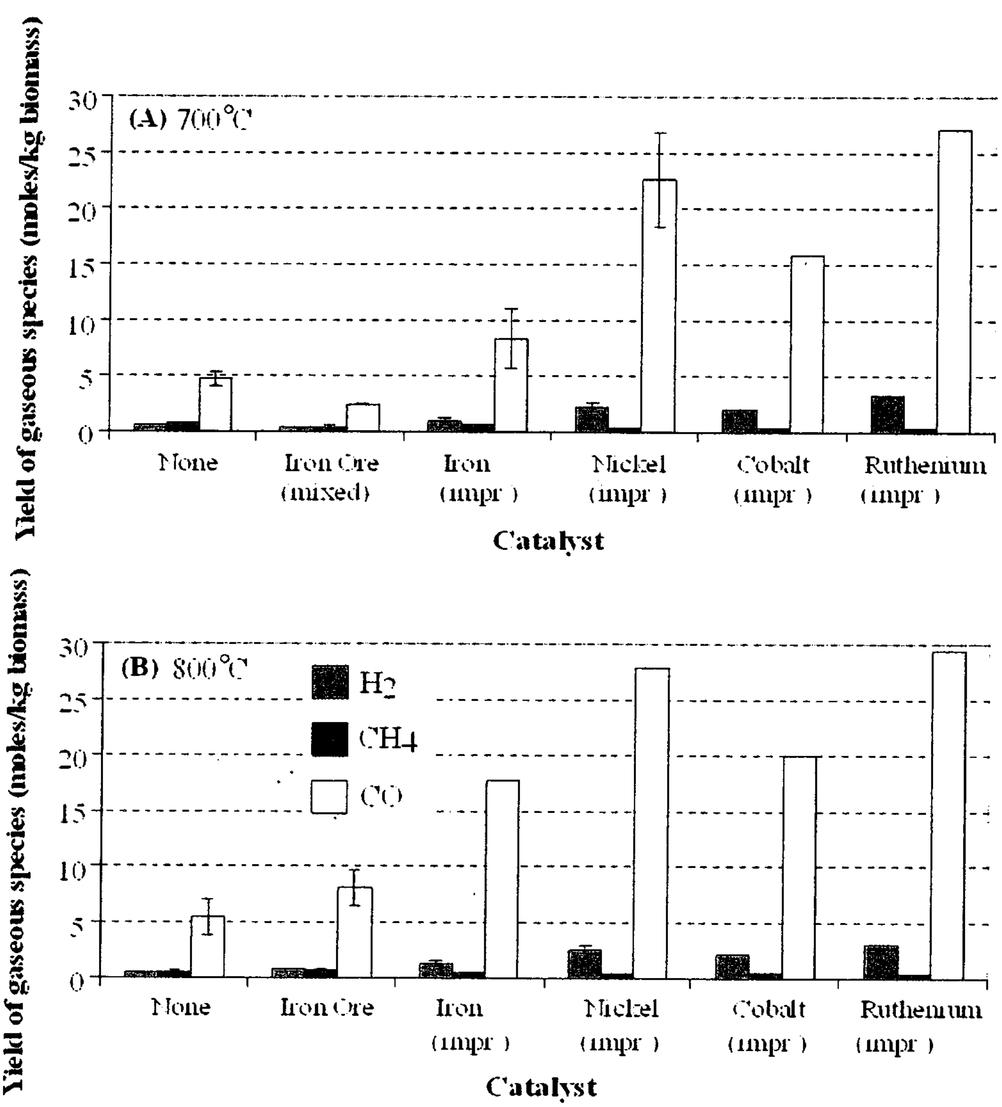


Figure 3-5 Effects of catalysts on yields of major combustible gas species of H_2, CH_4 and CO from gasification of pine sawdust at 700 °C (A) and 800°C (B) in 100% CO_2.

3.3.3 GC/MS analysis of tars

The tars obtained from gasification were analyzed using GC/MS. Typical results are presented in Figure 3-6 and Table 3-4 below. The relative concentration of a specific compound may be obtained qualitatively by the area % of the compound (defined by percentage of the compound's chromatographic area out of the total integration area). As clearly shown in the Figure and Table, all tars are a complex mixture of aromatic hydrocarbons (benzene, phenoics), aldehydes, ketones, with some amounts of organic acids (acetic acid, propenoic acid), ester, furans and alcohols, derived from the lignin and cellulosic components of the woody biomass. Although the gasifying agent (air or CO_2), temperature or the use of catalyst did result in some minor variation in the tar compositions (as revealed in Table 3-4), all the tars recovered from gasification of the pine sawdust under different conditions have similar compositions. For example, 4-hydroxy-4-methyl-2-pentanone was the dominant compound identified by GC/MS in all tars, with a relative composition of 17-27%. All tars analyzed contain a significant amount (4.8-9.2 area %) of a carbohydrate: 1,6-anhydro-ß-D-glucopyranose, which is most likely a degradation product from the cellulose in the pine sawdust [29]. Relatively high concentrations of phenolic compounds such as 2-methoxy-phenol and 1-hydroxy-2-methoxy-4-methylbenzene were present in almost all tars. As well known, the phenolic compounds were mainly originated from the degradation of the lignin component in the lignocellulosic biomass feedstock [30]. Lignin is a natural polymer of three main lignin building blocks (structural monomers), i.e., p-hydroxy-phenyl-propanol, guaiacyl-propanol and syringyl-propanol, linked mainly by two types of linkages: condensed linkages (e.g., 5-5 and β-1 linkages) and ether linkages (e.g., β-O-4 and α-O-4), while the ether linkages are the dominant linkages between the three main lignin building blocks. The phenol derivatives and benzene derivatives as observed in the tar products are mainly resulted from decomposition/de-polymerization of lignin by cleavage of its ether linkages at a high temperature.

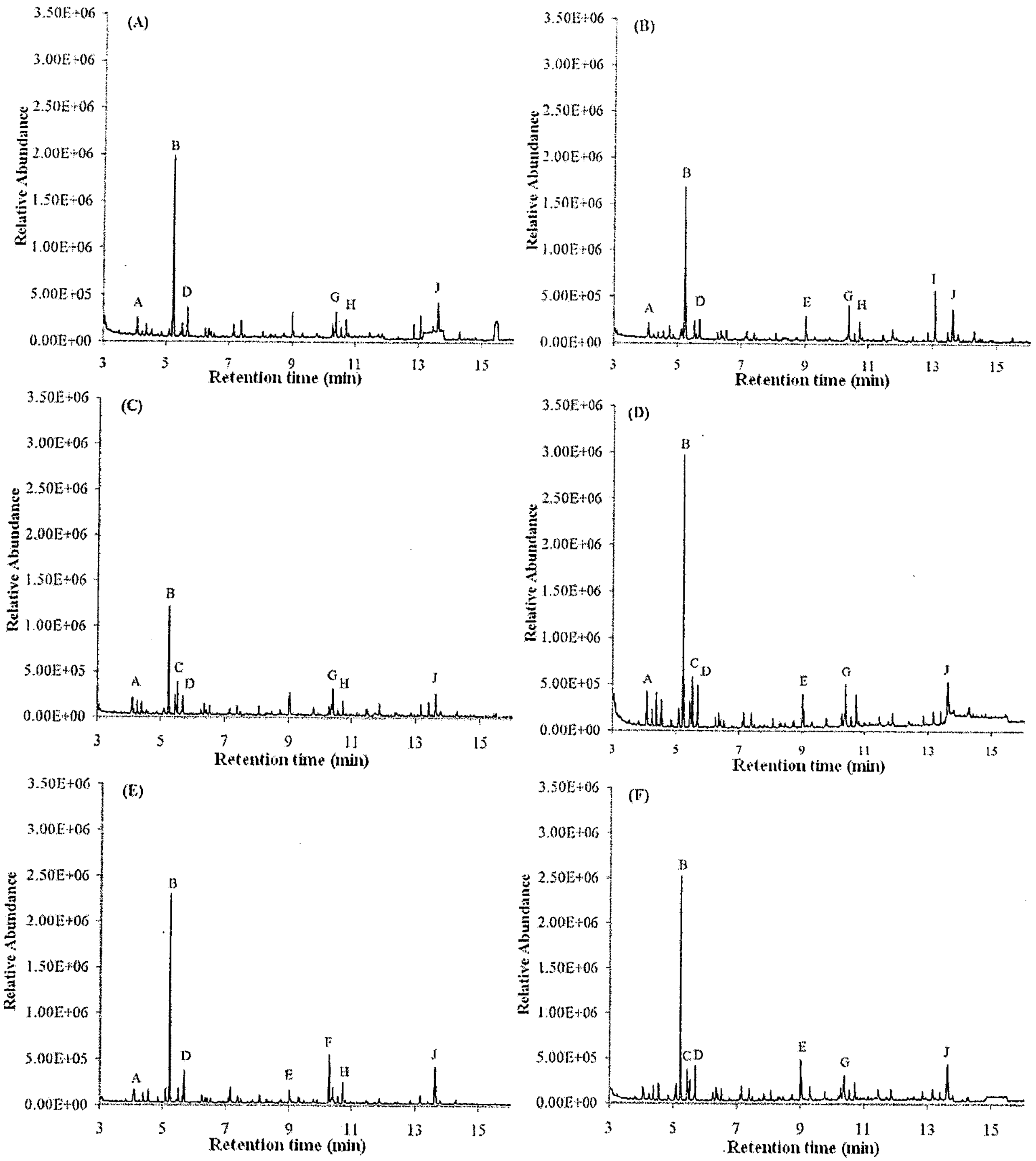


Figure 3-6. Chromatograms of the tar products from gasification of pine sawdust under the following conditions: **(A)** 100% air gasifying agent, 800°C, without catalyst; **(B)** 17% CO_2-83%air gasifying agent, 800°C, without catalyst; **(C)** 100% CO_2 gasifying agent, 800°C, without catalyst; **(D)** 100% CO_2 gasifying agent, 700°C, without catalyst; **(E)** 100% CO_2 gasifying agent, 800°C, with Ru (IV) catalyst; **(F)** 100% CO_2 gasifying agent, 800°C, with Ni (II) catalyst.

Table 3-4: GC/MS analysis results for the tars recovered from gasification of the pine sawdust under different conditions

Peak No.	RT (min)	Compound name	Area %					
			No Catalyst				Ru(IV)	Ni (II)
			800°C Air	800°C 17% CO_2-83%Air	800°C CO_2	700°C CO_2	800°C CO_2	800°C CO_2
	4.068	BENZENE, METHYL-						2.3
A	4.099	2-PROPANONE, 1-HYDROXY-	3.9	3.6	3.8	4.2	3.4	
	4.393	ACETIC ACID, ANHYDRIDE	2.2			3.0		
	4.558	3-PENTEN-2-ONE, 4-METHYL-				3.0		2.2
	5.104	2-FURANCARBOXALDEHYDE	1.4	1.9				
B	5.231	2-PENTANONE, 4-HYDROXY-4-METHYL-	24.3	22.7	17.4	22.2	27.4	20.4
C	5.449	2-FURANMETHANOL			4.1	3.3		4.0
	5.526	1,3-DIOXOLANE, 2,2,4-TRIMETHYL-	1.4	2.1	4.6	4.1	2.5	
D	5.699	1-METHOXY-2-ACETOXYPROPANE	4.4	3.8	3.7	3.6	4.4	4.2
	6.262	ETHANOL, 2-BUTOXY-	1.7	1.2				
	7.394	PHENOL	2.8	1.5			1.8	
E	9.015	PHENOL, 2-METHOXY-		4.4		4.6	2.4	7.0
	9.045	CYCLOPROPYLMETHANOL			6.7			
F	10.274	1-OCTENE					7.5	
	10.317	2,3,4,5-TETRAMETHYL-2-CYCLOPENTEN-1-ONE B					4.1	
G	10.389	1-HYDROXY-2-METHOXY-4-METHYLBENZENE	4.9	6.0	6.0	5.2		3.2
	10.566	2-PROPENOIC ACID, 2-METHYL-, ETHYL ESTER	1.7					
H	10.732	3-FURYLMETHANOL	3.0	3.1	2.4		3.8	
	11.463	1, 4-DIMETHOXY-2-METHYLBENZENE			2.8			
	11.883	3-PENTEN-2-ONE, 3-(2-FURANYL)-			3.5			
I	13.087	ALPHA.-D-GALACTOPYRANOSE, 1,2:3,4-BIS-O-(1-METHYLETHYLIDENE)-		7.4				
J	13.625	BETA.-D-GLUCOPYRANOSE, 1,6-ANHYDRO-	9.2	6.4	4.8	7.4	8.9	7.5
Total Area %			87.6	87.4	86.6	86.7	85.7	86.4

3.4. CONCLUSIONS

1. Compared with air, CO_2 as a gasifying agent for biomass gasification showed a much lower reactivity. The yields of char and tar both increased with increasing CO_2 concentration in the feed gas, In the CO_2-gasification of the pine sawdust, the tar and char yields at 700°C were as high as 44.2 wt% and 21.2 wt%, respectively. A higher temperature and a greater oxygen content in the feed gas led to higher gasification efficiency.

2. It was observed that the addition of iron ore to the biomass feedstock by simple physical mixing did not alter the yields of all products significantly irrespectively of the types of gasification agent and the gasification temperature, which was likely due to the poor contact between the catalyst and the gas/vapor products during the gasification process.
3. All the impregnated metal ions (Fe (III), Co (II), Ni (II), and Ru (IV)), in particular Ni (II), Co (II) and Ru (IV), were very effective in promoting the gasification of the woody biomass at 700°C and 800°C, leading to a lower tar yield, a significantly decreased char yield and a greatly increased yield of CO2-free gas. At 800°C, the impregnation of Fe (III), Ni (II), Co (II) or Ru (IV) led to almost complete conversion of the solid biomass into gas and liquid products, producing an extremely low char yield (< 1-4 wt%), and a very high yield of combustible CO_2-free gas (ranging from 51.7 wt% for Fe (III) to 84 wt% for Ru (IV)). The tar yield also reduced significantly from 32.1 wt% without catalyst to 19-27 wt% with the impregnated metal ions.
4. The addition of all impregnated metal ions had a significant effect on the formation of both carbon monoxide and hydrogen. At 800°C, the CO yield per kg of biomass (dry and ash-free) climbed to 28.0 mol and 29.0 mol with the impregnated Ni (II) and Ru (IV) ions, respectively, compared with only 5.3 mol/kg biomass without catalyst. The yield of H_2 during the gasification without catalyst at 800°C was approximately 0.5 mol/kg biomass, which was increased to 2.5 mol/kg biomass and 3.1 mol/kg biomass due to the presence of the impregnated Ni (II) and Ru (IV), respectively.
5. All tars are a complex mixture of aromatic hydrocarbons (benzene, phenolics), aldehydes, ketones, with some amounts of organic acids (acetic acid, propenoic acid), ester, furans and alcohols, derived from the lignin and cellulosic components of the woody biomass. 4-

hydroxy-4-methyl-2-pentanone was the dominant compound identified by GC/MS in all tars, with a relative composition of 17-27%. All tars analyzed contain a significant amount (4.8-9.2 area %) of a carbohydrate: 1,6-anhydro-ß-D-glucopyranose, derived from the cellulose in the pine sawdust. Relatively high concentrations of lignin-degraded phenolic compounds such as 2-methoxy-phenol and 1-hydroxy-2-methoxy-4-methylbenzene were present in almost all tars.

REFERENCES

[1].Z. Fang, T. Sato, R. Smith, H. Inomata, K. Arai, J. Kozinski, *Reaction chemistry and phase behaviour of lignin in high temperature and supercritical water. Bioresource Technology* 99 (2008) 3424-3430.

[2].V. Kirubakaran, V. Sivaramakrishan, R. Nalini, T. Sekar, M. Premalatha, P. Subramanian, *A review on gasification of biomass. Renewable and Sustainable Energy Reviews* (2007), doi:10.1016/j.rser.2007.07.001.

[3].P. McKendry, Energy production from biomass (part 3): gasification technologies. *Bioresource Technology* 83 (2002) 55-63.

[4].E.G. Baker, L.K. Mudge, M.B. Brown, Steam gasification of biomass with nickel secondary catalysts. Ind. Eng. Chem. Res. 26 (1987) 1335-1339.

[5].S. Rapagna, N. Jand, A. Kiennemann, P. Foscolo, Steam gasification of biomass in a fluidized bed of olivine particles. Biomass Bioenergy 19 (2000) 187-197.

[6].P. Weerachanchai, M. Horio, C. Tangsathitkulchai, Effects of gasifying conditions and bed materials on fluidized bed steam gasification of wood biomass. *Bioresource Technology* 100 (2009) 1419-1427.

[7].D. Sutton, B. Kelleher, A. Doyle, J.R.H. Ross, Investigation of nickel supported catalysts for the upgrading of brown peat derived gasification products. Bioresource Technology 80 (2001) 111-116.

[8].A.K. Dalai, E. Sasaoka, H. Hikita, D. Ferdous, Catalytic gasification of sawdust derived from various biomass. Energy Fuels 17 (2003) 1456-1463.

[9].P. Lv, Z. Yuan, L. Ma, C. Wu, Y. Chen, J. Zhu, Hydrogen-rich gas production from biomass air and oxygen/steam gasification in a downdraft gasifier. Renewable Energy 32 (2007) 2173-2185.

[10]. D. Sutton, B. Kelleher, J.R.H. Ross, Review of literature on catalysts for biomass gasification. Fuel Processing Technology 73 (2001) 155-173.

[11]. P. McKendry, Energy production from biomass: Part 1. Overview of biomass, Biosource Technology 83 (2002) 37– 46.

[12]. Z. Abu El-Rub, E.A. G. BramerBrem, Review of catalysts for tar elimination in biomass gasification process. Industrial and Engineering Chemistry Research 43 (2004) 6911-6919.

[13]. L. Devi, K. Ptasinski, F. Janssen. A review of the primary measures for tar elimination in biomass gasification processes. *Biomass and Bioenergy 24* (2003) 125-140.

[14]. J. Pencho, T. Schildhauer, M. Sturzenegger, S. Biollaz, A. Wokaun. Reactive bed materials for improved biomass gasification in a circulating fluidized bed reactor. *Chemical Engineering Science 63* (2008) 2456-2476

[15]. J. Han, H. Kim. The reduction and control technology of tar during biomass gasification/pyrolysis: An overview. *Renewable and Sustainable Energy Reviews 12* (2008) 397-416.

[16]. A. Uddin, H. Tsuda, S. Wu, E. Sasaoka. Catalytic decomposition of biomass tars with iron oxide catalysts. In Press. *Fuel* (2007), doi:10.1016/j.fuel.2007.06.021.

[17]. R. Zhang, R. Brown, A. Suby, K. Crummer. Catalytic destruction of tar in biomass derived producer gas. *Energy Conversion and Management 45* (2004) 995-1014.

[18]. T. Kimura, T. Miyazawa, J. Nishikawa, S. Kado, K. Okumura, T. Miyao, S. Naito, K. Kunimori, K. Tomishige. Development of Ni catalysts for tar removal by steam gasification of biomass. *Applied Catalysts B: Environmental 68* (2006) 160-170.

[19]. Z. El-Rub, E. Bramer, G. Brem, Experimental comparison of biomass chars with other catalysts for tar reduction. *Fuel 87* (2008) 2243-2252.

[20]. M.P. Anzar, M.A. Caballero, J. Gil, J.A. Martin, J. Corella, Commercial steam reforming catalysts to improve biomass gasification with steam-oxygen mixture. 2. Catalytic tar removal. Ind. Eng. Chem. Res. 37 (1998) 2668-2680.

[21]. E. G. Baker, L. K. Mudge, M. D. Brown, Steam gasification of biomass with nickel secondary catalysts. Ind Eng. Chem. Res. 26 (1987) 1335

[22]. D.N. Bangala, N. Abatzoglou, E. Chornet, Steam reforming of naphthalene on Ni-Cr/Al_2O_3 catalysts doped with MgO, TiO_2 and La_2O_3. AIChE J. 44 (1998) 927-936.

[23]. S. Rapagna, N. Jand, P. Foscolo, Catalytic gasification of biomass to produce hydrogen rich gas. Int. J. Hydrogen Energy 23 (1998) 551-.

[24]. Y. Cao, Y. Wang, J.T. Riley, W.-P. Pan, A novel biomass air gasification process for producing tar-free higher heating value fuel gas. Fuel Processing Technology 87 (2006) 343-353.

[25]. C. Pfeifer, R. Rauch, H. Hofbauer, In-bed catalytic tar reduction in a dual fluidized bed biomass stream gasifier. Industrial and Engineering Chemistry Research 43 (2004) 1634-1640.

[26]. M. Aresta, I. Tommasi, Carbon dioxide utilisation in the chemical industry. *Energy Convers. Manage.* **38** (1997) S373.

[27]. G. Centi, S. Perathoner, Heterogeneous catalytic reactions with CO_2: Status and perspectives. *Stud. Surf. Sci. Catal.* **153** (2004) 1-8.

[28]. R. Raudaskoski, E. Turpeinen, R. Lenkkeri, E. Pongrácz, R.L. Keiski, Catalytic activation of CO_2: Use of secondary CO_2 for the production of synthesis gas and for methanol synthesis over copper-based zirconia-containing catalysts. *Catalysis Today* (2009) doi:10.1016/j.cattod.2008.11.026.

[29]. R. Kothari, D. Buddhi, R.L. Sawhney, Comparison of environmental and economic aspects of various hydrogen production methods. Renewable and Sustainable Energy Reviews 12 (2008) 553-563.

[30]. L. Garcia, M. Salvador, J. Arauzo, R. Bilbao, CO_2 as a gasifying agent for gas production from pine sawdust at low temperatures using a Ni/Al coprecipitated catalyst. *Fuel Processing Technology 69* (2001) 157-174.

[31]. D. Roberts, D. Harris. Char gasification in mixtures of CO_2 and H_2O: Competition and inhibition. *Fuel 86* (2007) 2672-2678.

[32]. S. Kajitani, N. Suzuki, M. Ashizawa, S. Hara. CO_2 gasification rate analysis of coal char in entrained flow gasifier. *Fuel 85* (2006) 163-169.

[33]. T. Kaneko, S. Sugita, M. Tamura, K. Shimasaki, E. Makino, L. Sikalalhi. Highly active limonite catalysts for direct coal liquefaction. *Fuel 81* (2002) 1541-1549.

[34]. L. Li , K. Morishita, T. Takarada, Light fuel gas production from nascent coal volatiles using a natural limonite ore. *Fuel 86* (2007) 1570–1576.

[35]. C. Xu, T. Etcheverry. Hydro-liquefaction of woody biomass in sub- and supercritical ethanol with iron-based catalysts. ***Fuel*** 2008; 87:335-345.

[36]. Y. Yang, A. Gilbert, C. Xu. Production of bio-crude from forestry waste by hydro-liquefaction in sub-/super-critical methanol. AIChE J 55 (2009) 807-819.

[37]. G. Ponder, G. Richards, T. Stevenson, Influence of linkage position and orientation in pyrolysis of polysaccharides: A study of several glucans. *Journal of Applied and Analytical Pyrolysis 22* (1992) 217-229.

[38]. S. Karagoz, T. Bhaskar, A. Muto, Y. Sakata. Comparative studies of oil compositions produced from sawdust, rice husk, lignin and cellulose by hydrothermal treatment. *Fuel* 84 (2005) 875-884.

CHAPTER 4

PILOT-SCALE FLUIDIZED-BED GASIFICATION OF PINE SAWDUST AND PEAT: EXPERIMENTAL SETUP AND PROCEDURES

4.1 Introduction

In this study, catalytic gasification of pine sawdust and peat was carried out on a pilot scale (the feed rate can be adjusted to 5 - 25 kg/h) air-blown bubbling fluidized bed gasifier available at CanmetENERGY, Natural Resource Canada, in Ottawa. This chapter provides some details on the experimental setup and procedures. The experimental results will be discussed in Chapter 5.

4.2 Fluidized-bed Biomass Gasifier Setup

The biomass/peat gasification experiments were carried out at CanmetENERGY, Natural Resource Canada, in Ottawa, on a pilot scale, air-blown bubbling fluidized bed gasifier whose schematic diagram is given in Figure 4-1. A part of the fluidized bed system is also pictured in Figure 4-2. The system was originally designed as the circulating fluidized bed, but was operated in the bubbling bed regime in this study. The fluidized bed system is composed of a 5 inch (0.13m) ID 316 stainless steel cylindrical column and 236 inch (6 m) in height. The fuel feeding system consists of a belt feeder combined with a rotary airlock valve, and the feed rate can be adjusted to 5 - 25 kg/h by controlling the belt speed. From the main hopper, biomass is vibrated onto the belt feeder. The belt feeder sits on a scale, and feed rate is calculated using the fuel mass (on a dry basis), belt length and belt speed. The fuel feeding system is pictured in Figure 4-3.

The primary air and secondary air were introduced at locations shown in the Figure 4-1. The primary air, controlled at the computer control station, was injected below the fluidized bed distributor, while the secondary air, manually adjusted, was injected at various positions in and above the dense-phase reaction zone, as shown in Figure 4-1. The bed materials and the reaction zone of the unit were preheated using a propane gas burner. In these tests, an air-cooled fly ash deposition probe (2-in OD) was installed in the freeboard region. The tar sampling port was located at the outlet of the cyclone. A water cooled condenser was used to condense the tar vapor. After removal of tar, the gasification product gas was sampled for a series of on-line and off-line gas analyses. As shown in the Figure, the gasification flue gas was burned in an after burner and vented to the stack through an ID fan.

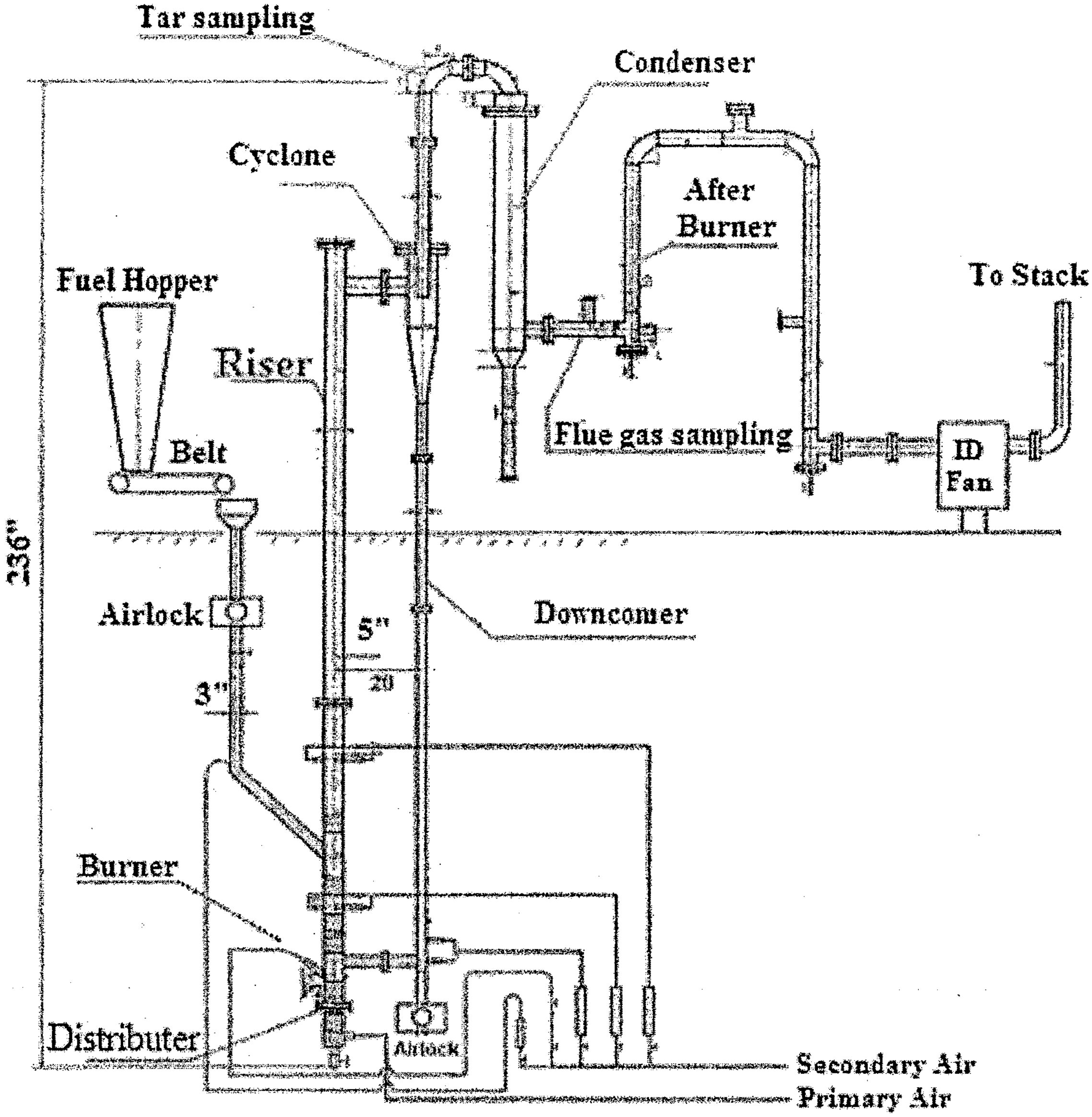


Figure 4-1 Schematic diagram of the air-blown fluidized bed gasification system at CanmetENERGY, Ottawa.

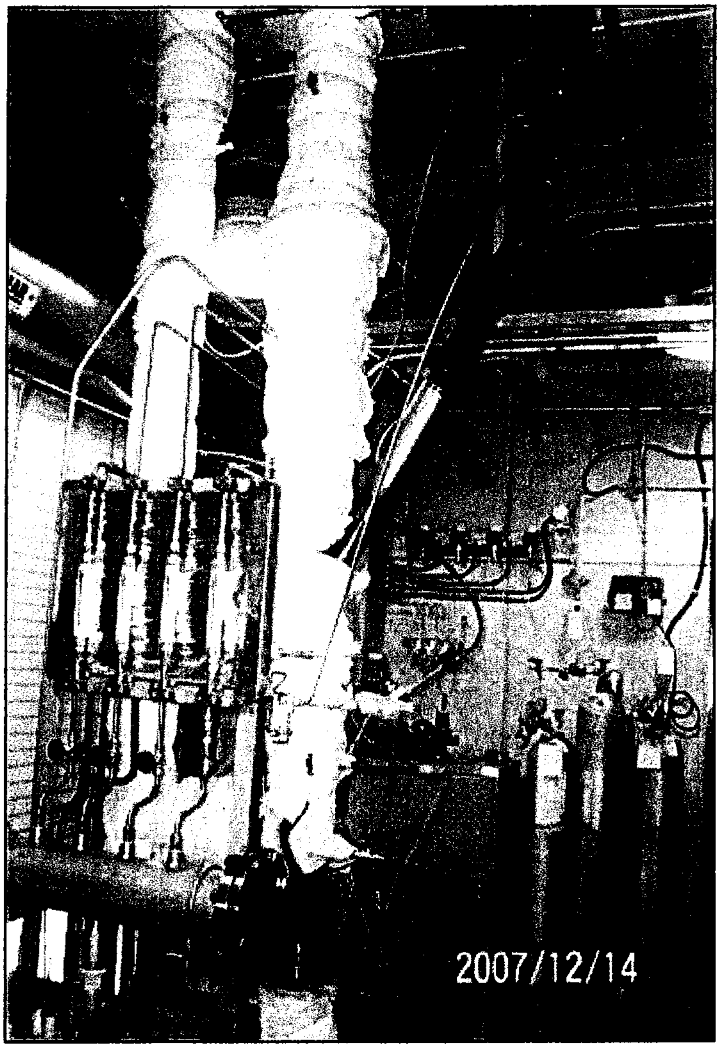


Figure 4-2 Picture of a part of the air-blown fluidized bed gasification system (first floor) at CanmetENERGY, Ottawa.

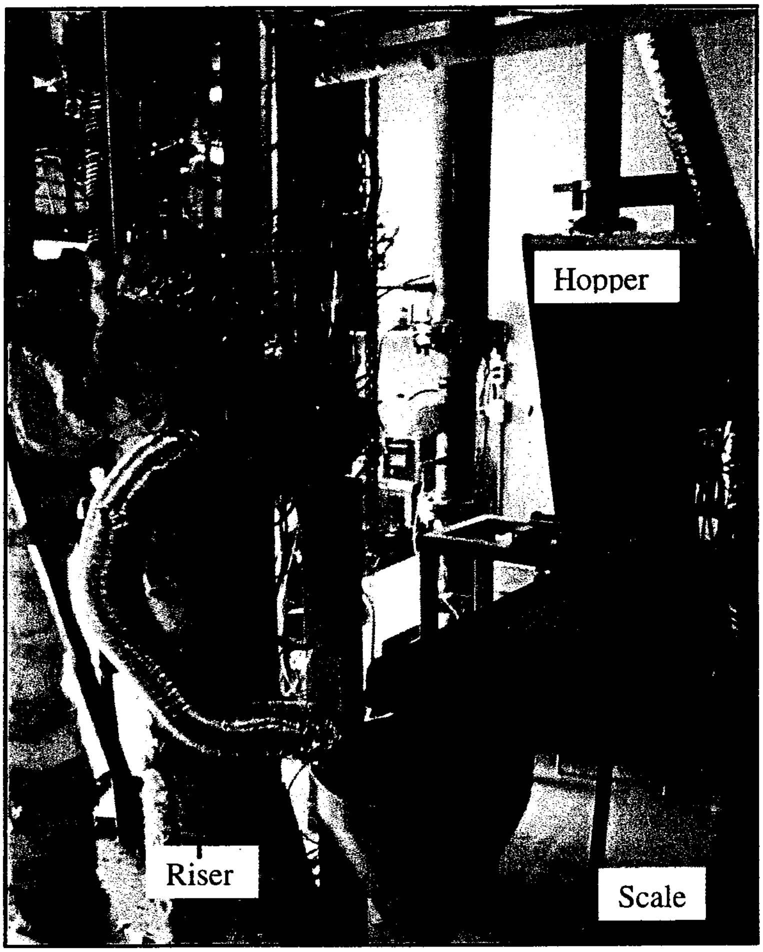


Figure 4-3. Feed system of fluidized bed reactor at CanmetENERGY, Ottawa (second floor) showing freeboard section of the riser.

4.3 Feedstock Preparation

White pine sawdust obtained from a sawmill in Southern Ontario contained a relatively high moisture content (38 wt%). This material was simultaneously crushed to remove large particles (> 10 mm) and dried to a moisture content of approximately 15-20% using a rotary dryer with a screening facility at CanmetENERGY, as illustrated in Figure 4-4. Pine sawdust was fed into the hopper where a screw feeder moved it to a chain-crusher. Propane heated air was blown through the system to dry the material and send crushed particles to the collection barrel. Particle size and moisture content was controlled by the speed of the screw feeder and chain-crusher, as well as blower-air temperature. The crushed and pre-dried material was then sieved to remove fine particles of <1 mm. Peat was received from Peat Resource Limited (an Ontario based peat fuel developing company) in pelletized form (10 mm OD x 30 mm long) at a moisture content of approximately 36 wt%. Due to poor fluidizability of the peat pellets and in order to obtain more representative results comparable to those from the pine sawdust, these pellets were crushed and sieved to 1-4 mm particle size. Some dried samples were ground into particles <60 mesh (250 μm) using an electrical grinder, and submitted for various analyses (proximate and ultimate and ash composition analysis results will be shown in Chapter 5). Compared with the peat, the white pine feedstock contains a much higher volatile matters (84.5 wt% db) and a much lower fixed carbon (15.1 wt% db) and ash (0.44 wt% db). Both feedstocks contain very close heating values (HHV, about 21 MJ/kg on a dry basis).

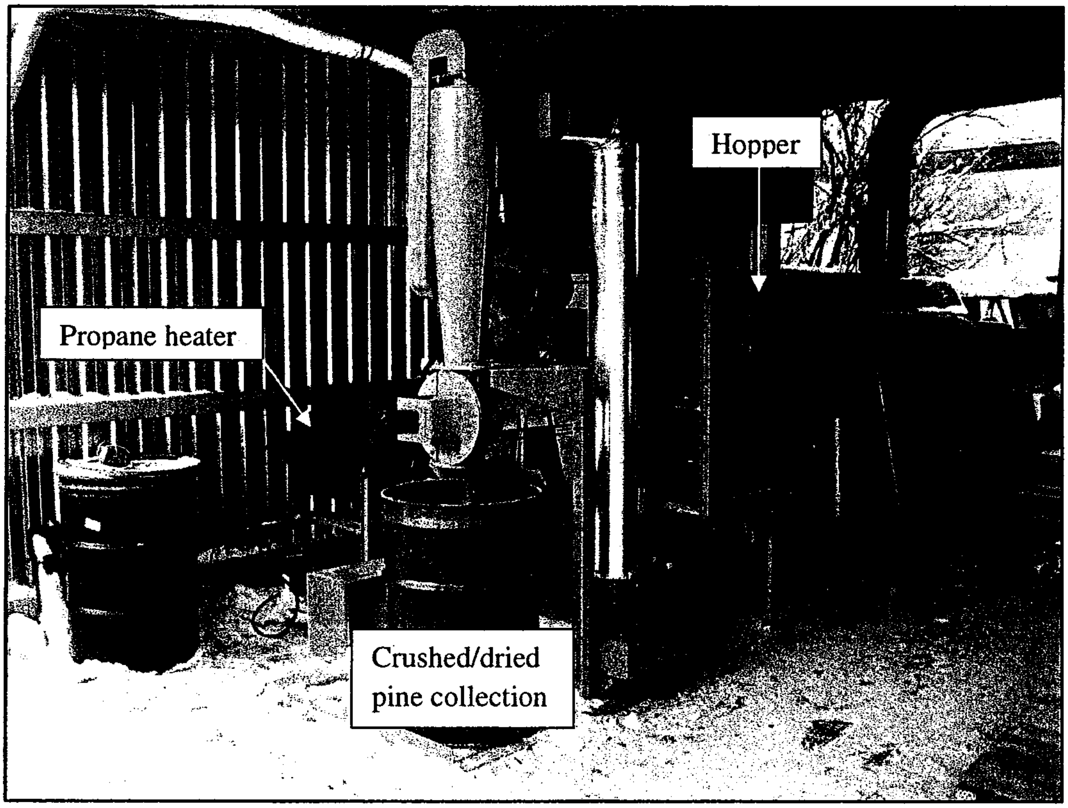


Figure 4-4. Pine sawdust crushing/drying at CanmetENERGY prior to gasification.

4.4 Bed Material Preparation

Olivine, limestone and dolomite were used as received at CanmetENERGY after crushing and sieving to ensure a uniform particle size (approximately 1 mm diameter). All bed materials were calcined in air at >750°C within the fluidized bed reactor during the warm-up combustion phase of each test using propane gas. Limonite iron ore (oxide) was obtained from the former Steep Rock Mine site in Atikokan, Ontario. The iron ore was crushed and sieved to a particle size of approximately 0.85 mm (due to its higher particle density) to facilitate the fluidization process. Analysis of the material by X-ray diffraction showed that the material is composed mainly of iron oxides, in the form of goethite (FeOOH) and hematite (Fe_2O_3). From ICP-AES analysis of the iron oxide, the Fe content of material was measured at 42.2 wt%.

Bed materials (fresh and used after the gasification tests) were analyzed by XRD analysis at the Lakehead University Instrumentation Laboratory. These results are presented and discussed in Chapter 5.

4.5 Gasification Procedures

For each run, about 13 kg bed materials were fed into the gasifier as the bed material, which was fluidized by the primary air at ~360 L/min and pre-heated using a propane gas burner. The online analyzers were calibrated using standard gases of H_2, CO, CO_2, CH_4, SO_2, NO, and O_2 at known concentrations. Fuel started to be fed into the reactor at ~4 kg/h after the bed zone attained a temperature over 750°C. The fluidized-bed unit was then warmed up in a combustion mode, at the equivalence ratio (ER) of ~1.4, during which it normally took 2-3 hours to reach steady state (with a relatively stable bed temperature). After that, the unit was switched to gasification mode operated at the desired equivalence ratio (ER = 0.20-0.40) by increasing the feed rate to 10-20 kg/h and decreasing the total air flow to ~300 L/min. Reactor temperature was maintained by the partial combustion of the biomass, without external heating. With some bed materials, a significant loss of material due to physical attrition and thermal fragmentation was observed, and additional bed materials were added during the tests in order to maintain the bed level. The bed level was carefully monitored via three pressure sensors at varying heights within the bed.

Operational parameters were monitored in real-time via the computer data-logger and readout. Data from the numerous pressure sensors, thermocouples, gas concentration sensors and flow-meters were recorded every three seconds. As the fluidized bed gasification operation attained steady state conditions (stable temperature and pressure, gas compositions), tar sampling was performed as detailed below.

4.6 Tar and Gas Sampling and Analysis

Gasification-derived tars are a notoriously difficult substance to both gasification operation and gas sampling, and there are several methods and protocols developed for capture and sampling of tars from gasification [1-3]. A fairly standard method involves the use of a train of impinger bottles filled with some organic solvent to capture tars from the producer gas. Carpenter et al. have examined the use of on-line molecular-beam mass spectrometry in order to avoid some of the limitations of impinger-based sampling, such as flow-rate dependent efficiency, line plugging, and tar loss due to condensation on the equipment [2,3]. This method however requires dedicated expensive infrastructure and equipment, and hence is not feasible for most biomass gasification research including the present study.

In this study, a non-iso-kinetic tar sampling system was used, using a train of impingers containing an isopropanol solvent, as illustrated in Figures 4-5 and 4-6. Product gas was drawn using a vacuum pump through a particulate filter into electrically heated lines (maintained at >350°C to prevent the condensation of tars), the tar was condensed at the impinge train, and the incondensable product gas flowed through a wet-gas meter and vacuum pump before it was finally vented. The impinger system was composed of six solvent-containing vessels, three in a water bath (20°C) and three in an ethylene glycol bath at -10°C, plus a final droplet trap. Tar sampling was started after reaching steady state gasification, and continued for 45-90 minutes. Total gas volume and sampling time were recorded with a wet gas meter. Following gasification, the solvent/tar mixture was collected. The impinger system and any piping below 350°C were washed with isopropanol, and the solvent/tar mixture filtered to remove any residual particulate matters. The isopropanol was evaporated at 50°C under reduced pressure with a rotary evaporator, and the tars were weighed for calculation of the tar yields and collected for further analyses (e.g., GC/MS and elemental analysis, etc.).

Online gas analysis of H_2, CO, CO_2, CH_4, SO_2, NO, and O_2 was carried out in all tests, but these online analysis data was used only for the operation monitoring and safety considerations, and to verify the steady state operational parameters. Gas samples were taken via gas bags collected at about 30 min intervals during the period of steady state gasification. These samples were analyzed off-line with an Agilent 6890A Series gas chromatograph (GC) with two thermal conductivity detectors (TCD-A & TCD-B). TCD-A consists of two columns to measure CO, CO_2, CH_4, C_2H_6, C_2H_4, C_2H_2, H_2S, O_2, Ar and N_2 with helium carrier gas. TCD-B consists of one column to measure H_2 concentration with argon carrier gas. Gas analyses for each test were averaged and normalized. The concentrations of inert gases (nitrogen and argon) at the gasifier input and output were used to calculate the total gas volume from the gasifier.

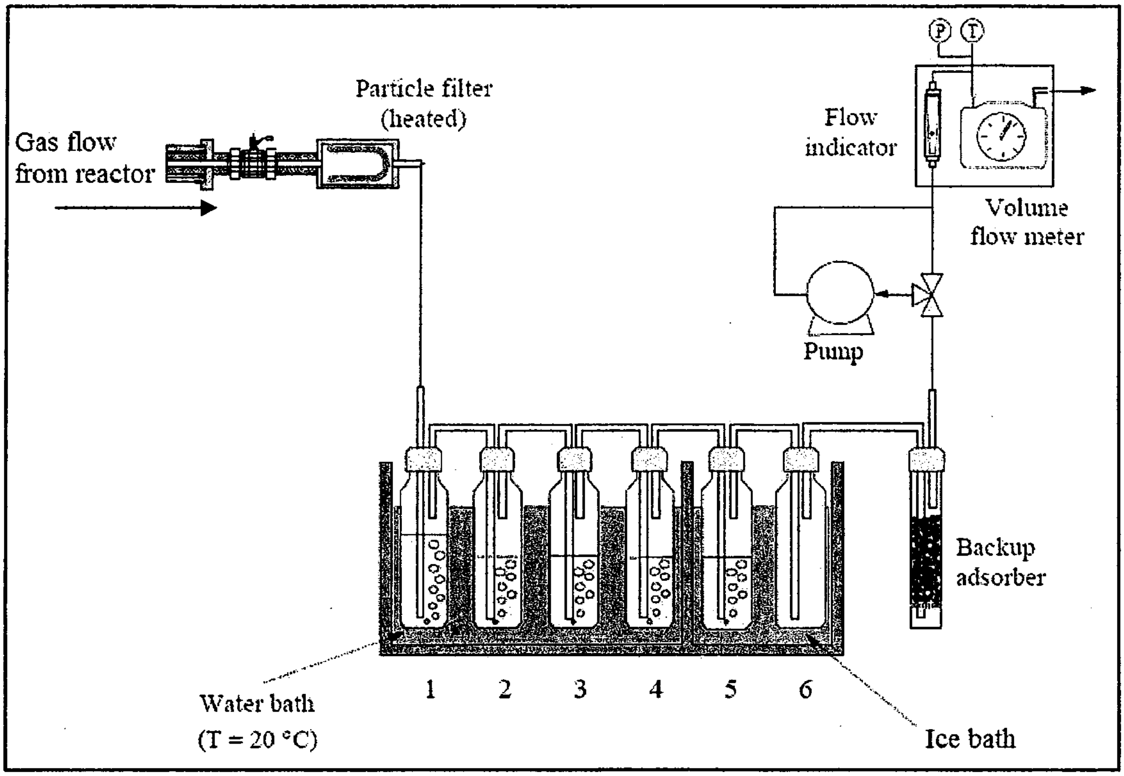


Figure 4-5. Schematic of the tar sampling system.

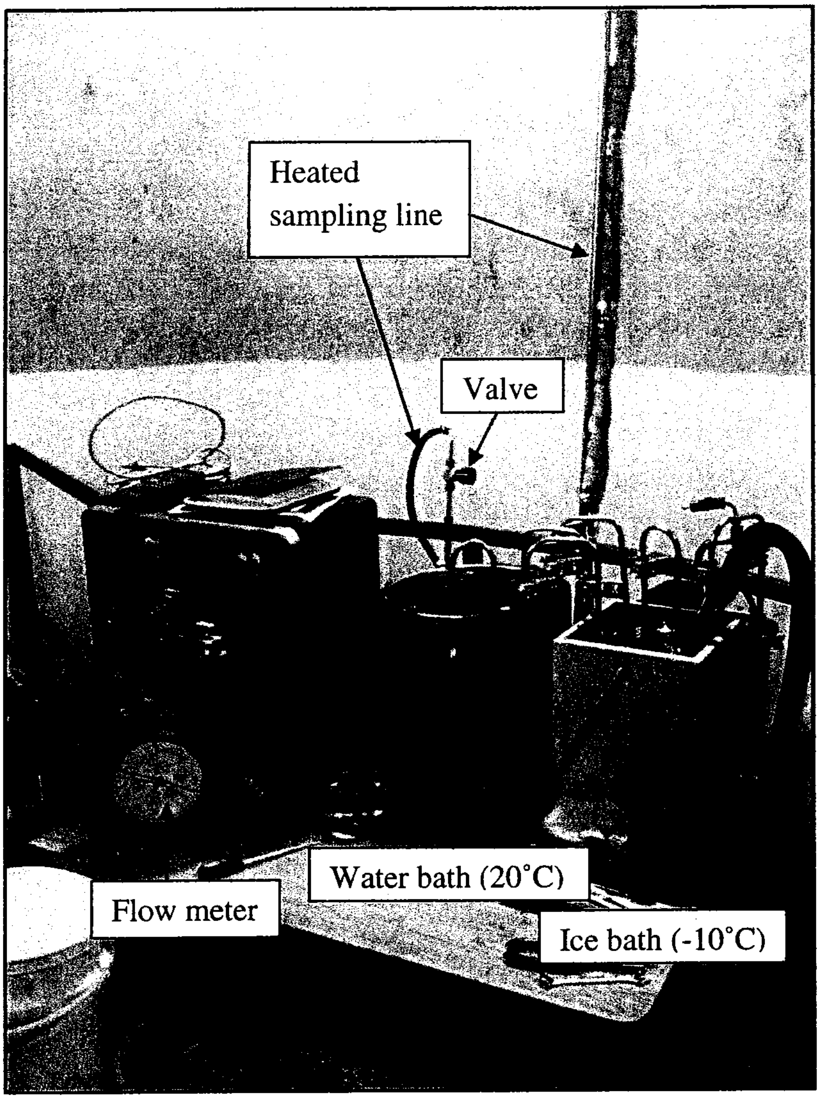


Figure 4-6. Photo of the tar sampling system and the heated sampling line from the gasifier.

References

[1] R. Zhang, R. Brown, A. Suby, K. Cummer. *Catalytic destruction of tar in biomass derived producer gas.* Energy Conversion and Management 45 (2004) 995-1014

[2] D. Carpenter, S. Deutch, R. French. *Quantitative measurement of biomass gasifier tars using a molecular-beam mass spectrometer: Comparison with traditional impinger sampling.* Energy and Fuels 21 (2007) 3036-3043

[3] W. van Kamp, P. de Wild, U. Zielke, M. Suomalainen, H. Knoef, J. Good, T. Lilidahl, C. Unger, M. Whitehouse, J. Neeft, H. Van de Hoek, J. Kiel. *Tar Measurement standard for sampling and analysis of tar and particles in biomass gasification product gas.* 14th European Biomass Conference and Exhibition (2005) 3-8

CHAPTER 5

CATALYTIC GASIFICATION OF PINE SAWDUST AND PEAT IN A PILOT-SCALE AIR-BLOWN FLUIDIZED-BED GASIFIER

Effects of bed materials (olivine, limestone, dolomite, and a crushed iron ore) and equivalence ratios (ER, 0.20-0.40) on tar formation and gasification efficiencies were investigated using pine sawdust and crushed peat pellets on a pilot-scale air-blown fluidized bed gasifier at CanmetENERGY in Ottawa. As expected, increasing the equivalence ratio generally led to decreased tar yield. Combustible gas (methane, hydrogen, and carbon monoxide) yields were generally highest at medium ER values (0.25-0.30). Tar and combustible gas yields were lower for crushed peat as compared to pine sawdust for all ER values under similar conditions. Calcined limestone exhibited the highest catalytic activity for tar reduction at all ERs tested, leading to a very low tar yield of 3.5-8.3 g/kg biomass. Other bed materials were similar to each other in terms of tar reduction, though dolomite and iron oxide appeared to be slightly more active than olivine. While dolomite and limestone produced the highest yields of H_2, olivine is more effective for CO formation, and for gasification of pine sawdust with olivine attained the maximum cold gas efficiency (74.8%) at ER = 0.30. Olivine was also the most attrition-resistant and thermally stable bed material among the four bed materials tested (including olivine, dolomite, limestone, and iron oxide) for biomass gasification in the fluidized bed reactor, leading to the best temperature control in the gasification operation.

5.1. INTRODUCTION

Biomass gasification is a viable thermo-chemical conversion technology using gasification agents such as air/oxygen, steam or CO_2 for converting biomass, in particular recalcitrant lignocellulosic biomass and agricultural/forestry waste streams, into low to medium Btu fuel gases (5-15 MJ/Nm^3). The gases produced (e.g. H_2, CO, CO_2, CH_4 and C_{2+}) can be utilized directly as fuels for heat and electricity generation, or as feedstocks for productions of methanol, ethanol, dimethyl ether, and Fischer-Tropsch oils, etc. [1]. Biomass gasification offers several advantages over other biomass conversion processes such as combustion, pyrolysis and bio-conversions, with respects to reduced CO_2 emissions, compact equipment requirements with a relatively small footprint, accurate combustion control, and high thermal efficiency.

The major challenge of biomass gasification is related to the formation tar, a highly variable mixture of condensable aromatic hydrocarbons (single ring to 5-ring aromatic compounds) along with other oxygen-containing hydrocarbons and complex PAH. Generally, an air/steam gasification process produces tar at approximately 20 g per Nm^3 of flue gas [2]. In an air-blown fluidized bed gasifier, typical tar contents in producer gas have been reported between 0.5 to 100 g/m^3 [3-5]. For many applications, with the exception of direct and immediate syngas combustion for heat or electricity production, these tar levels must be reduced, often to below 50 mg/Nm^3 [3]. Tars can have significant negative effects on gasification with respects to efficiency and operation. Specifically, the production of tars instead of combustible gases represents a decrease in gasification efficiency, and condensation and deposition of tars at temperatures below 350°C can lead to fouling and potential blockage of downstream equipment and piping [5].

The reduction of tar in biomass gasification has been the subject of a great number of studies [2, 3, 6-13]. Tar elimination approaches can be classified into two categories: primary measures and secondary treatments. Primary measures are in-furnace approaches to reduce tar formation by varying the operating conditions or by adding catalysts to the feedstocks, or using reactive bed materials (such as dolomite, olivine) in fluidized bed gasifiers [8, 9]. Secondary treatments include cold-gas mechanical methods (filter, scrubbers, etc.) and hot-gas catalytic processes to crack tar into gaseous products at a high temperature in a down-stream reactor (fixed bed or fluidized bed) which can be operated under different conditions than those of the gasifier [3, 7, 10-14]. Secondary catalytic treatment may also be regarded as hot gas cleanup. Common catalysts for hot gas cleanup include nickel/iron-based catalysts [10, 12, 14], biomass chars and other catalysts such as dolomite and olivine [12]. The most widely used catalysts for hot gas cleanup and tar cracking are alumina-supported nickel catalysts. Commercial nickel-based steam reforming catalysts were found to be very active for removal of tarry hydrocarbons and producing hydrogen-rich syngas [15-18]. A major problem has however been recognized for the alumina-supported nickel catalysts is the rapid deactivation of the catalyst due to the carbon deposition and nickel particle growth [16, 18].

Although secondary treatments as described proved to be effective for removing tar from biomass gasification, primary measures (i.e., treatments inside the gasifier) have been considered to be more economically viable [7, 8, 19]. Primary measures are not yet fully developed and have not to be implemented commercially. For instance, tar formation could be efficiently controlled below 10 mg/Nm^3 in air-blown fluidized-bed biomass gasification process, through injecting fuel gas and secondary air to the upper region of the fluidized bed reactor to maintain elevated temperatures for tar decomposition [19]. As with the control of operating parameters and novel design of gasifiers, the addition of catalysts in the gasifier has attracted growing interest in recent years for in-furnace tar control [7]. The in-bed catalysts could play important roles not only in increasing the reaction rate at low-temperature conditions inside the gasifier, but also by facilitating the tar conversion into valuable combustible gases via steam reforming, dry reforming, thermal cracking, hydro-reforming and hydrocracking, or water-gas reactions [7, 20]. Catalysts can be utilized either as bed materials or as additives to the feedstocks [21, 22]. Dolomites (CaO-MgO) have been the most commonly used catalyst for biomass gasification [7, 8]. Olivine was demonstrated to have much higher attrition resistance than that of dolomite, although its activity for reducing tar formation was similar to or less than that of dolomite [23]. Calcined limestone (CaO) proved to be very effective for tar elimination and improvement of hydrogen formation during steam gasification of biomass in a fixed bed [22] or a fluidized bed [20]. Char as the direct by-product from gasification processes can be an attractive less expensive catalyst for eliminating tar, but steam and dry reformation reactions would lead to loss of catalysts mass during the process [7]. Nickel and noble metal catalysts (such as Ru, Pt, and Rh) were found to be highly effective for reducing tar formation and improving the quality of syngas [7].

This research investigated air blown gasification of a woody biomass and peat with a pilot-scale bubbling fluidized bed gasifier employing catalytic bed materials. The effects of bed materials (olivine, limestone, dolomite, and a crushed iron ore) and equivalence ratios (ER, 0.20-0.40) on tar formation and syngas composition were discussed.

5.2. EXPERIMENTAL

5.2.1 Fluidized-bed biomass gasifier setup

The detailed configurations of the gasifier setup are given in Chapter 4.

5.2.2 Feedstock and bed materials preparation

The details of the feedstock and bed material preparation are given in Chapter 4. Proximate and ultimate analyses of the pinewood and peat feedstocks, as well as ICP-AES analysis of the natural limonite material used are given below:

Table 5-1. Proximate and ultimate analyses of white pine and peat feedstocks and ash compositions

Fuel Type	Peat	White Pine
Proximate analysis (wt %)		
Moisture (%)	35.8	38.0
Volatile matter (db)	68.6	84.5
Fixed carbon (db)[1]	29.4	15.1
Ash (db)	2.00	0.44
HHV (MJ kg^{-1})	21.4	20.6
Ultimate analysis (wt%, db)		
Carbon	56.1	52.5
Hydrogen	5.67	6.32
Sulfur	0.23	<0.05
Nitrogen	0.81	0.10
Oxygen[1]	35.2	40.6
Ash analysis (wt%, db)		
SiO_2	28.05	6.70
Al_2O_3	8.63	1.97
Fe_2O_3	5.56	1.46
TiO_2	0.48	0.09
P_2O_5	1.31	3.52
CaO	12.65	31.10
MgO	17.72	4.34
SO_3	12.73	2.80
Na_2O	2.84	0.36
K_2O	1.14	15.45

[1] by difference

Table 5-2 Limonite iron ore ultimate analysis

Major elements determined by ICP-AES (wt.%)											
Al	Ba	Ca	Mg	**Fe**	Mn	Na	K	P	S	Ni	Si
0.4	<0.1	<0.1	<0.1	**42.1**	<0.1	<0.1	<0.1	<0.1	0.2	<0.1	**3.1**

5.2.3 Operating procedures and tar and gas sampling and analysis

Operating procedures for gasification and tar, char, and gas sampling are outlined in Chapter 4.

5.3. RESULTS AND DISCUSSION

5.3.1 Effects of equivalence ratio

For air/oxygen blown gasification, equivalence ratio (ER) is defined as the ratio of actual air-to-fuel ratio to the stoichiometric air-to-fuel ratio for complete combustion. The quality of producer gas and gasification efficiency strongly depend on the value of ER employed. For gasification, the ER should be less than 1.0. An excessively low value of ER (<0.2) would result in incomplete gasification and excessive char formation, while a too high value of ER (>0.4) would normally produce more incombustible gases (CO_2, H_2O) at the expense of desirable products (H_2, CO and CH_4). In a practical gasification system, the ER is normally controlled at 0.2-0.3. In the present study, the value of ER was varied from 0.20 to 0.40 by varying both feed rate and total air flow rate. Figure 5-1 shows the yields of combustible gases (CO, H_2 and CH_4), tars, ash & char and CO_2 from gasification of the pine sawdust with olivine sand as the bed material at varying ERs. Hereafter, the product yield is defined as % of the product mass in relation to the input biomass (on a dry basis). As shown in Figure 5-1, with the olivine sand, the air-blown gasification of pine sawdust with an ER = 0.2-0.4 in the fluidized bed produced about 38-52 wt% combustible gases (CO, H_2 and CH_4), <8 wt% tars, <5 wt% ash & char and 65-70 wt% CO_2. Total yields were in the reasonable range of 105-125 wt%, all greater than 100% due to incorporation of oxygen from the air into the products during gasification and partial combustion. Generally, the results in Figure 5-1 suggest that the pine sawdust gasification with olivine sand as the bed material achieved a high biomass conversion (>95 wt%) at all ERs tested (0.2-0.4). Increasing ER led to a decrease in tar yield, as expected, leading to trace formation of tar at ER = 0.35 and 0.4. The ER however had less significant effects upon either char or CO_2 yield. It shall be noted that the lumped yield of solids (char and ash) was very minimal <5 wt% in all gasification runs, approximately in the same magnitude of the experimental error (5-10 %), so that the results could not warrant any meaningful discussion on the dependency of the char yield on the ER values. Furthermore, it is not meaningful to quantify char yields in particular when other bed materials such as limonite ore, limestone, and dolomite, were employed, as the collected bottom ash from the tests employing these bed materials contained a significant amount of entrained fines. The effects of ER on CO_2 yield are complex since the following completing and simultaneous reactions would co-exist and dominate in the air-blown gasification process:

Carbon combustion: $C + O_2 \rightarrow CO$ or CO_2 (1)

CO oxidation: $CO + O_2 \rightarrow CO_2$ (2)

Water gas shift: $H_2O + CO \rightarrow CO_2 + H_2$ (3)

CO_2 dry reforming/gasification: Tar/char + $CO_2 \rightarrow CO$ (+ H_2) (4)

As the ER increased, on one hand, more CO_2 would be produced from Eqs. (1) - (3). On the other hand, CO_2 reforming of tar (according to Eq. (4)) would consume CO_2, as evidenced by the greatly reduced tar yield when increasing the ER (Figure 5-1). The net result would be that: the CO_2 does not vary significantly with the value of ER, as shown in Figure 5-1. Similar observation was also reported by Orio et al [24].

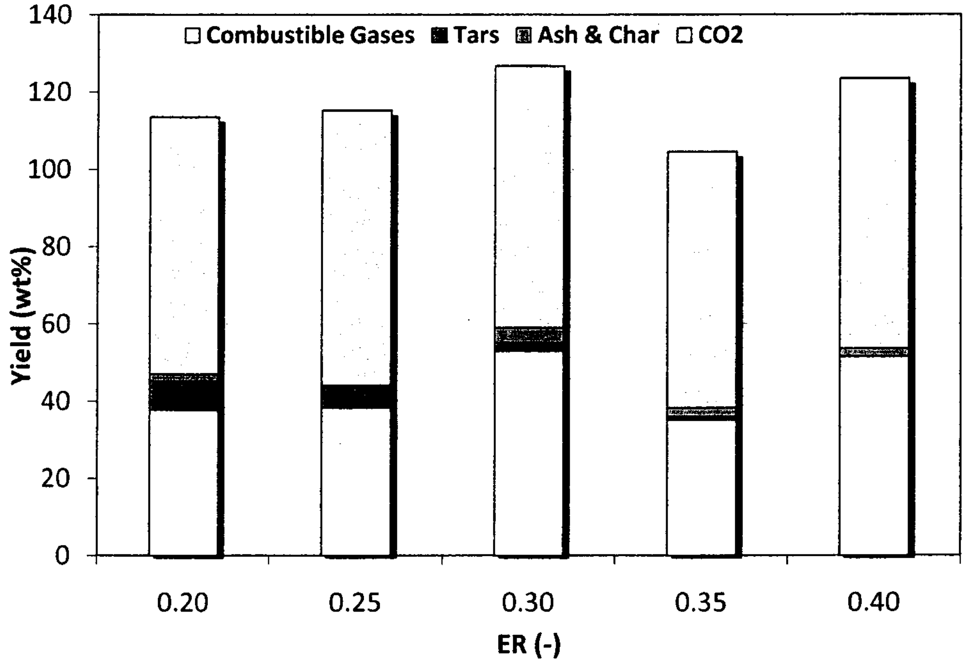


Figure 5-1 Product yields during gasification of white pine sawdust in a fluidized bed of olivine particles.

The effects of ER on the combustible gas formation are of interest in this study. As illustrated in Figure 5-1, the yield of total combustible gases increased with increasing ER, as expected, but it peaked at ER of around 0.3. A further increase in the value of ER to >0.3 decreased the yield of total combustible gas. As a matter of fact, with all bed materials combustible gas production appeared to be maximum in the medium value of ER (generally at

ER = 0.25 – 0.35). This variation of total combustible gas yield with the value of ER may be explained by the yield of individual gas species of CO, H_2 and CH_4, shown in Figure 5-2. Being typical for the air-blown gasification, for the whole range of ERs tested between 0.2 and 0.4, the yields of H_2 or CH_4 were much lower than that of CO: 2-4 mol/kg-biomass (db) for both H_2 and CH_4 vs. 11-17 mol/kg-biomass for CO. The variation of the total combustible gas yield with ER (in Figure 5-1) is thus dominated by the variation of CO formation (Figure 5-2), which peaked at a value of ER=0.3. A higher CO yield would be expected at a greater ER, due to the enriched oxygen environment for partial combustion of the carbonaceous materials to form CO. However, similar to the above discussion on CO_2 formation, the effects of ER on CO yield during air-blown gasification are also complex due to the co-occurring of the completing and simultaneous reactions (1) through (4). As the ER increased, more CO would be produced from the *carbon partial combustion* (Eq. (1)) and the *CO_2 dry reforming/gasification* (Eq. (4)), while the *CO oxidation* (Eq. (2)) and the *water gas shift* (Eq. (3)) reactions would consume CO. As shown in Figure 5-2, the generation of CO climbed again as the ER increased further from 0.35 to 0.4, while the yields of H_2 and CH_4 remained almost constant.

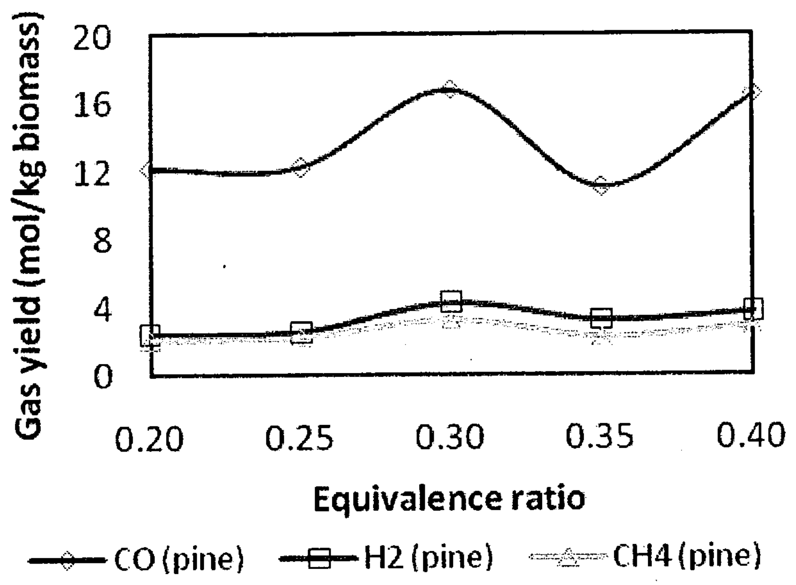


Figure 5-2 Yields of major combustible gases (CO, H_2 and CH_4) from the pine sawdust gasification with varying equivalence ratios.

5.3.2 Effects of bed material

Figure 5-3 presents the tar concentrations in the producer gas from air-blown gasification of pine sawdust at various ERs and bed materials. With any of the bed materials tested, increasing ER generally led to a decrease in tar yield, as reported previously [24] and discussed earlier (i.e. Figure 5-1). Among all the bed materials tested, calcined limestone showed the best performance for the reduction of tar formation. The tar concentrations with limestone at all ER values were much lower than those with other bed materials. For instance, the tar concentration with calcined limestone was below 5 mg/L at ER = 0.2, compared with >40 mg/L for the other three bed materials given the same ER. These results are very significant compared to many previous studies which demonstrated that dolomites were more active than calcites with respect to decomposition of tars [6, 25]. Dolomite and iron oxide showed similar activities, lower than limestone but higher than olivine sand, for tar reduction at a lower ER (<0.3).

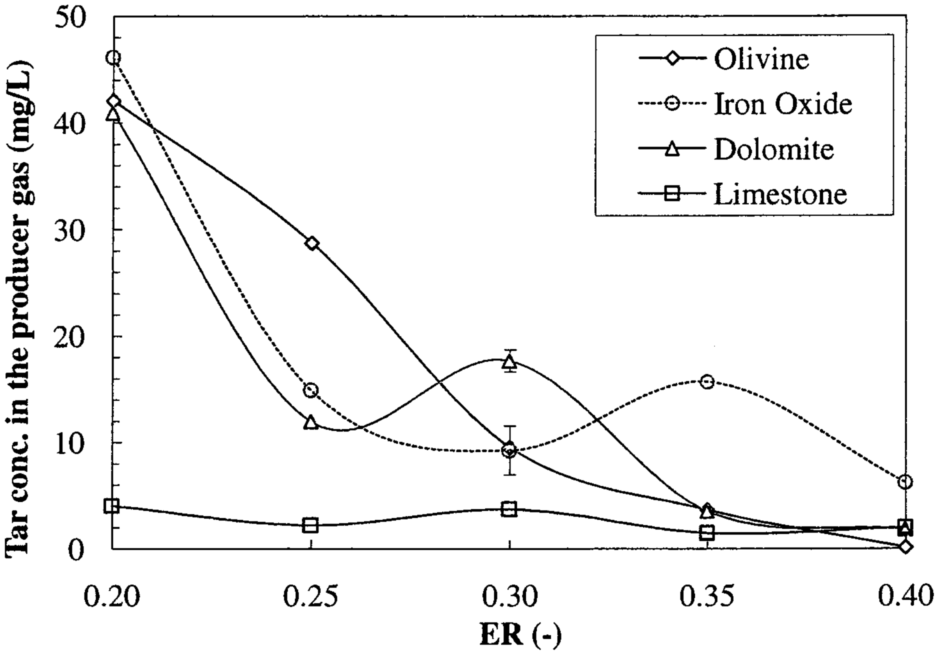


Figure 5-3. Tar concentrations in the producer gas from air-blown gasification of pine sawdust at various equivalence ratios and with different bed materials

An interesting observation from Figure 5-3 would be that dolomite and iron oxide appeared to lose their activities surprisingly at ER = 0.3-0.35, before they restored the activities at a higher ER (i.e., 0.4), leading to a peak of tar concentration in the producer gas at ER = 0.3 and ER = 0.35, respectively. Despite the experimental errors, the existence of these abnormal peaks was verified by several replicate tests, as indicated in the Figure 5-3. These abnormal trends for dolomite and iron oxide were not likely due to the changes in activities of dolomite and iron oxide, but more likely related to the bed temperatures in the operations with these two materials.

As such, we present the average fluidized bed dense phase temperatures for some typical testing runs in Figure 5-4. As clearly shown in the Figure, the average bed temperatures in the gasification operation were not constant at varying ERs, and a higher ER generally resulted in a higher bed temperature, which was expected due to enhanced partial combustion of the carbonaceous materials. For the entire range of ER (0.2-0.4), the bed temperatures in the operation with olivine could maintain fairly stable at 730-750°C, while the temperatures fluctuated between 680-830°C and 720-910°C for the dolomite and iron oxide, respectively, indicating poor bed temperature control in fluidization of these bed material more likely resulting from the severe attrition loss of these bed materials. Physical breakdown by attrition of iron oxide, dolomite, as well as limestone, was confirmed by the presence of a significant amount entrained fines in the bottom ash collected at the end of each run. The iron ore (oxide) showed the poorest resistance to physical/thermal breakdown during gasification. It is well known that tar cracking/conversion reactions are endothermic, so that a high bed temperature would thermodynamically and kinetically favor tar conversion [6, 20, 24, 26, 27]. The temperature profiles of dolomite and iron oxide coincidently showed a bottom peak at ER of around 0.35, which might account for the abnormal top peaks of the tar concentrations in the producer gas from these two bed materials at ER = 0.3-0.35, as shown in Figure 5-3. Although olivine sand showed a lower activity than the other three bed materials for tar reduction at an ER of 0.2-0.3, gasification of the pine sawdust with olivine showed a stable decrease in tar yield with increasing equivalence ratio, as revealed in Figure5-3. More importantly, the performance of olivine as the bed material for biomass gasification was the best amount all the four materials tested with respect to operational stability. Gasification of the feedstock with olivine could proceed very smoothly without significant loss of bed material fine particles due to the attrition in fluidization, which however was severe for the other three bed materials. The excellent performance of olivine sand was likely owing to its superior physical, chemical and thermal stability. Corella et al. [28] compared the biomass tar cracking capabilities of olivine and dolomite with a fluidized bed gasifier and they also concluded that olivine was much more stable than dolomite under fluidization at a high temperature.

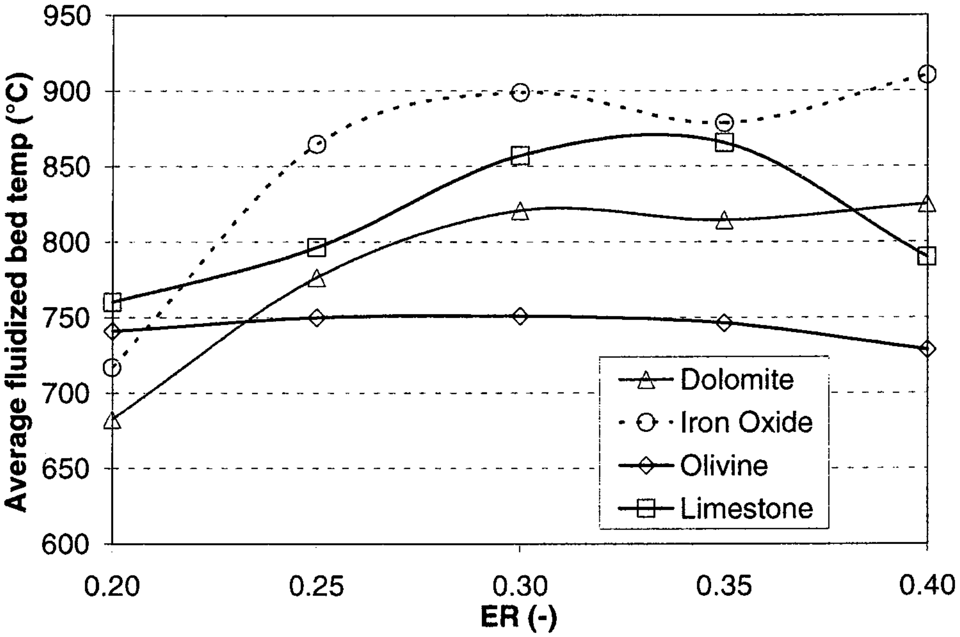


Figure 5-4 Average fluidized-bed dense-phase temperatures during gasification of pine sawdust at differing ER values with various bed materials.

The effects of bed materials on yields of the combustible gases, i.e., CO, CH_4 and H_2, from the pine sawdust gasification are shown in Figure5-5. Irrespective of the bed materials, the yields of these combustible gases generally peaked at ER of around 0.25-0.30, as was also shown before in Figures 5-1 and 5-2, which was expected. For biomass gasification, a low value of ER (e.g., 0.2) would result in incomplete gasification, while a high value of ER (e.g., 0.35, 0.4) would partially combust the combustible gases to form incombustible gases (CO_2, H_2O). From the results of the combustible gas yields, shown in Figure 5-5, the activities of these bed materials did not show an apparent sequence of priority, and the activity of these bed materials was strongly dependent on the value of ER. For instance, at ER = 0.2, olivine and limestone were more active for generation of CO and CH_4, while limestone and iron oxide were more active for H_2 formation. At ER = 0.3, olivine demonstrated to be the most active for the yields of CO (16 mol/kg-biomass) and CH_4 (~3.2 mol/kg-biomass), while dolomite produced the maximum yield of H_2 (~6.0 mol/kg-biomass).

Gasifier efficiency has been frequently used to evaluate gasification performance. It can be calculated based on the biomass feeding rate and the combustible gas (CO, H_2, CH_4) generation rate. Hot gas efficiency could provide a more useful measure of gasifier performance when the gas is to be used un-cooled for heat or power production. In this study, due to the fact that the gas was cooled and condensed prior to analysis, cold gas efficiency, as defined below, was employed for discussion.

$$Cold\ gas\ efficiency\ \left(\eta_{ceff}\right) = \frac{V_g q_g}{M_b C_b} \qquad (5)$$

Where: V_g = total combustible gas generation rate (m^3/s)

q_g = combustible gas heating value (kJ/m^3)

M_b = Biomass consumption rate (kg/s)

C_b = Biomass heating value (kJ/kg)

Figure 5-6 shows the calculated cold gas efficiencies of gasification of pine sawdust at varying ERs and with different bed materials. The cold gas efficiency for the gasification is highly dependent on both the equivalent ratios and the bed materials. For example, the efficiency ranges from 32.7% at ER = 0.20 with dolomite to a maximum of 74.8% at ER = 0.30 with olivine. Generally, as shown in the Figure, for each type of the bed materials the maximum gasifier efficiency attained at around ER = 0.25-0.30, which is in good agreement with the combustible gas formation results shown in Figures 5-2 and 5-5. In general, the use of limonite (iron oxide) bed material led to the lowest gasification efficiencies, compared with other three bed materials (olivine, limestone and dolomite). In a similar study by Cao et al. [19] achieved the maximum cold gas efficiency of approximately 56% from catalytic air-blown gasification of biomass with a small scale gasifier. As such, the maximum gasification efficiency (74.8%) obtained in the present study with olivine at ER = 0.30 in the fluidized bed gasifier is considerably higher than the literature one. This low efficiency by Cao et al. [19] is likely due to the small scale of the gasifier. Similar cold-gas efficiency values (54%-62%) were reported by Sheeba et al. [36] in air-blown gasification of coir pith in a fluidized bed reactor with silica sand.

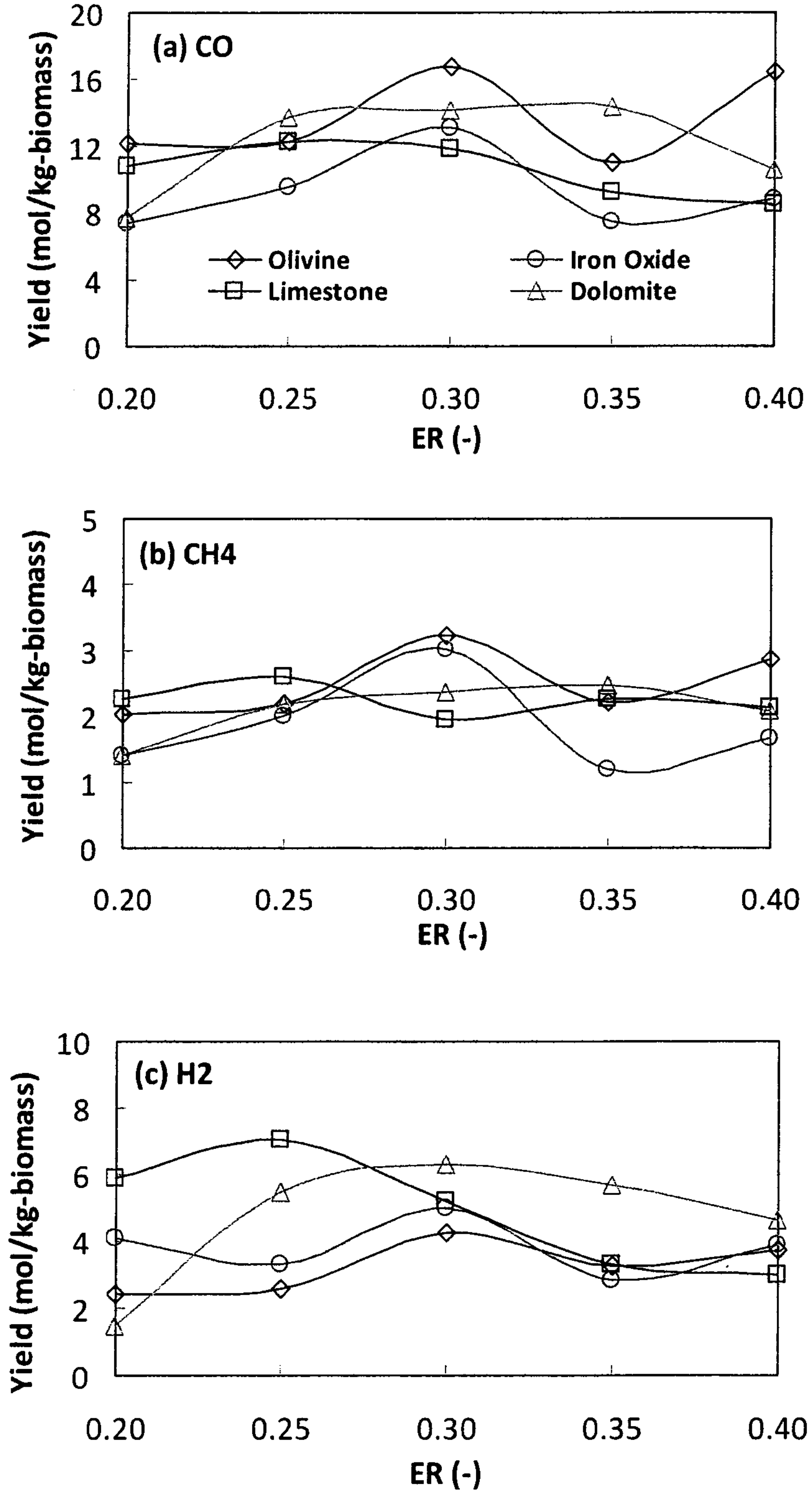


Figure 5-5 Yields of the major combustible gases of CO (a), CH_4 (b) and H_2 (c) from the pine sawdust gasification with various bed materials at varying equivalence ratios.

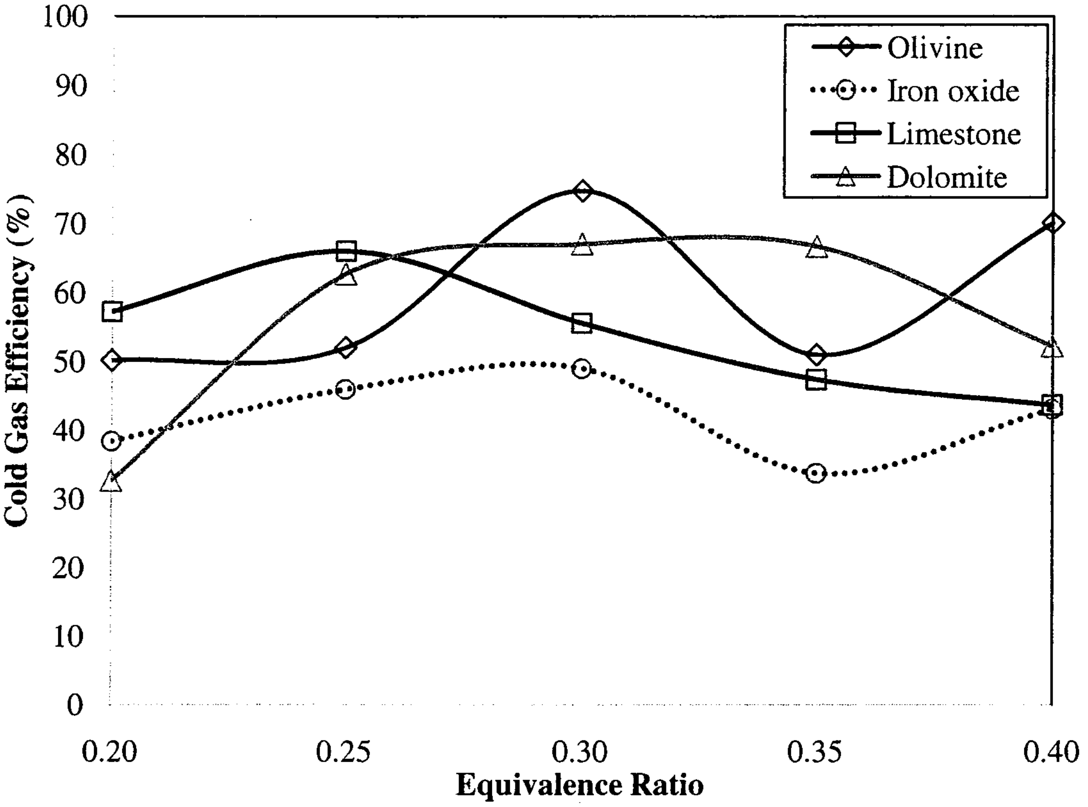


Figure 5-6. Cold gas efficiencies of gasification of pine sawdust at varying ERs and with different bed materials.

5.3.3 Effects of feedstock

In addition to the pine sawdust, crushed peat pellets were gasified in the fluidized bed reactor with olivine as the bed materials at ER ranging from 0.2 to 0.35. Figure 5-7 provides a comparison of tar concentrations in the producer gas between gasification of crushed peat pellets and pine sawdust with olivine. Similar as that observed for pine sawdust, the tar formation from peat decreased gradually as ER increased. More importantly, the gasification of peat resulted in a drastically lower tar yield compared with that of the woody biomass, in particular at a lower ER. For instance, the tar concentration in the producer gas was 15.8 mg/L at ER = 0.20 for peat gasification, compared with 42 mg/L for pine sawdust gasification. The greatly reduced tar formation from peat could be explained by the much lower volatile content of the peat used (68.4 wt% db) than that of the pine sawdust (84.5 wt% db).

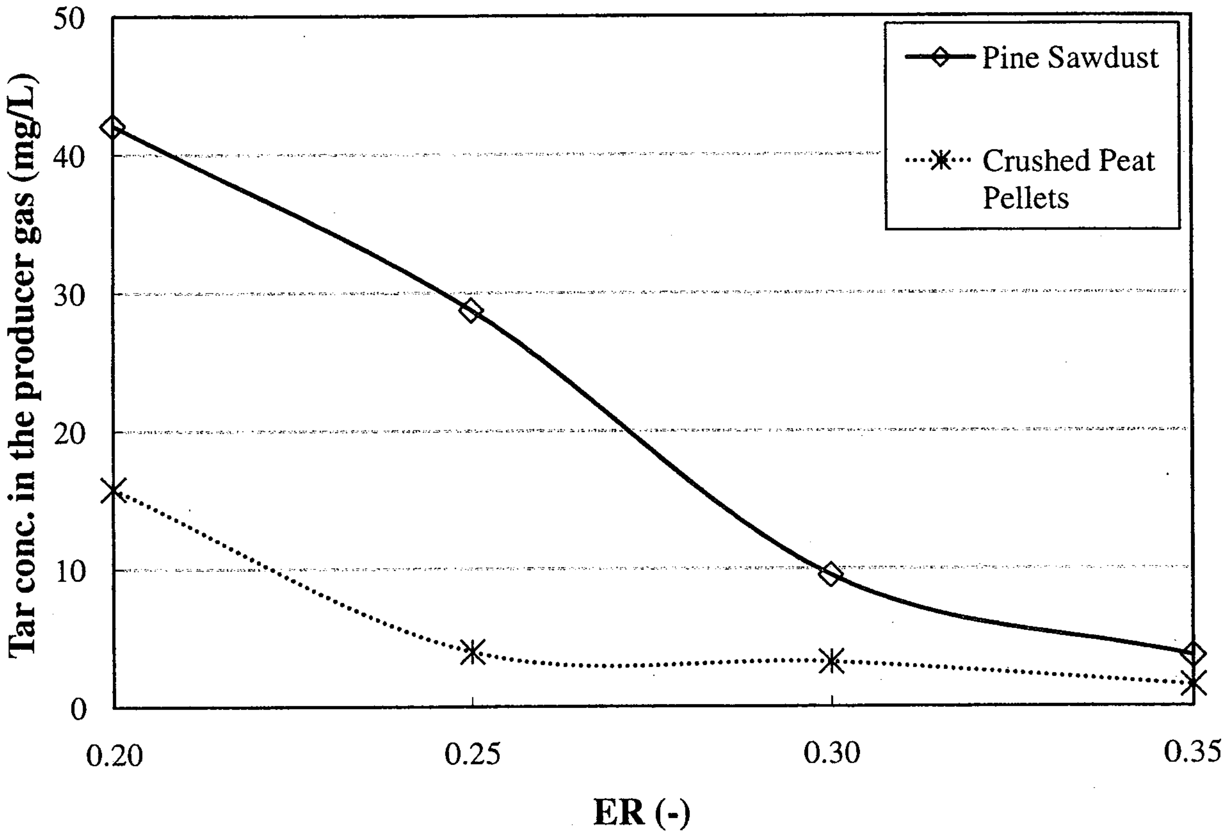


Figure 5-7 Tar concentrations in the producer gas from air-blown gasification of crushed peat pellets and pine sawdust with olivine at varying equivalence ratios

Comparison of yields of the major combustible gases of CO, CH_4 and H_2 between gasification of peat and pine sawdust is presented in Figure 5-8. As well known, in biomass gasification a significant amount of combustible gases was formed from volatile matters through thermal/catalytic cracking and through secondary reactions of the volatile-matter-derived intermediates, it is thus expected that gasification of peat (with a lower volatile content) would produce less combustible gases than gasification of pine sawdust, as evidenced by the results shown in Figure 5-8.

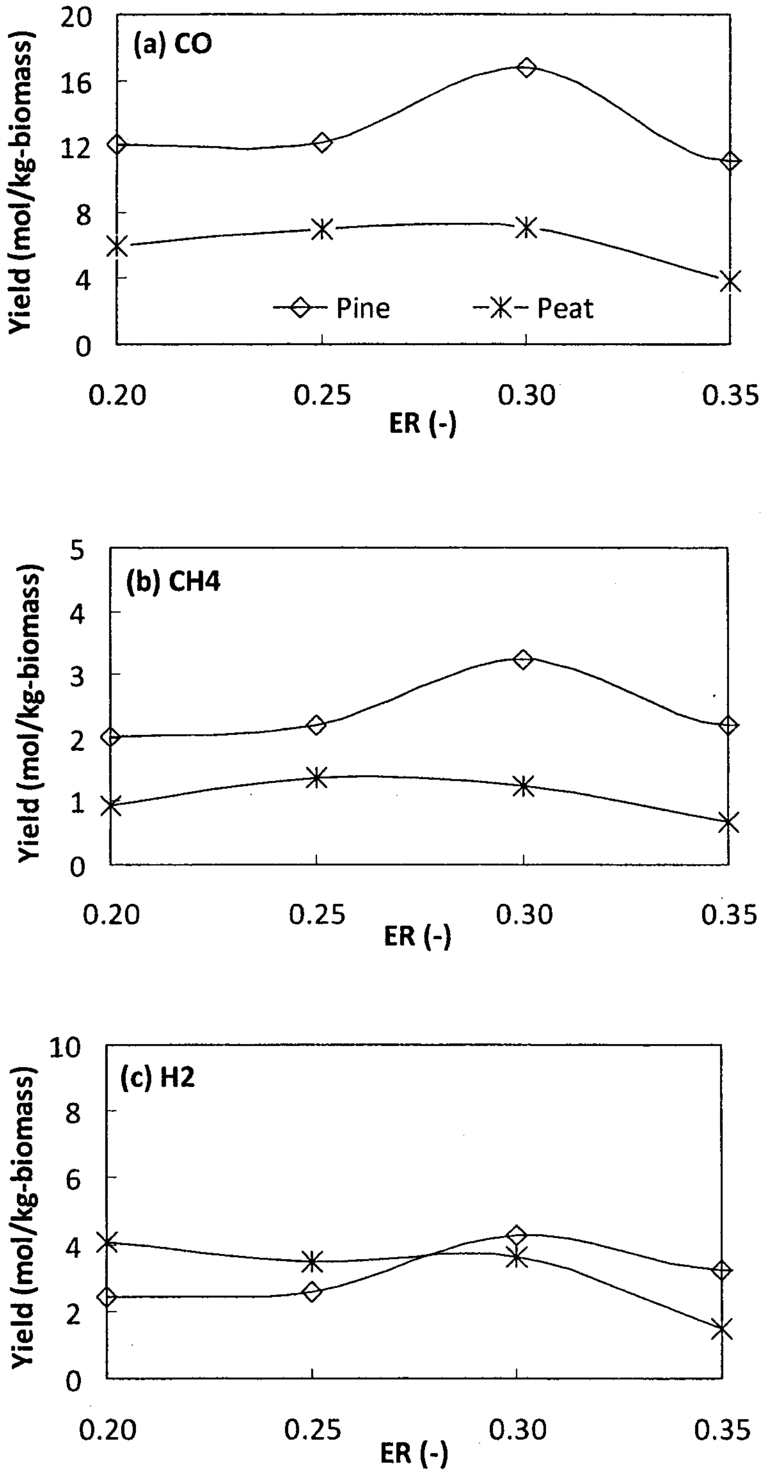


Figure 5-8 Yields of the major combustible gases of CO (a), CH_4 (b) and H_2 (c) from the gasification of peat and pine sawdust with olivine at varying equivalence ratios.

Figure 5-9 shows cold gas efficiencies for gasification of crushed peat pellets and pine sawdust at varying ERs with olivine bed material. The cold gas efficiency of peat gasification was lower than that of pine sawdust gasification, as concluded before on the formation of combustible gases (Figure 5-8). The efficiency for pine sawdust gasification increased from 50% at ER = 0.2 to a peak value of 74.8% at ER=0.30, while the efficiency for peat gasification was relatively constant at an ER ranging from 0.2 to 0.3, with a maximum cold gas efficiency of approximately 33%. The higher combustible gas production and higher gasification efficiencies for pine sawdust gasification is likely due to the higher volatile content of the sawdust versus peat (84.8 wt% vs. 70.0 wt, respectively).

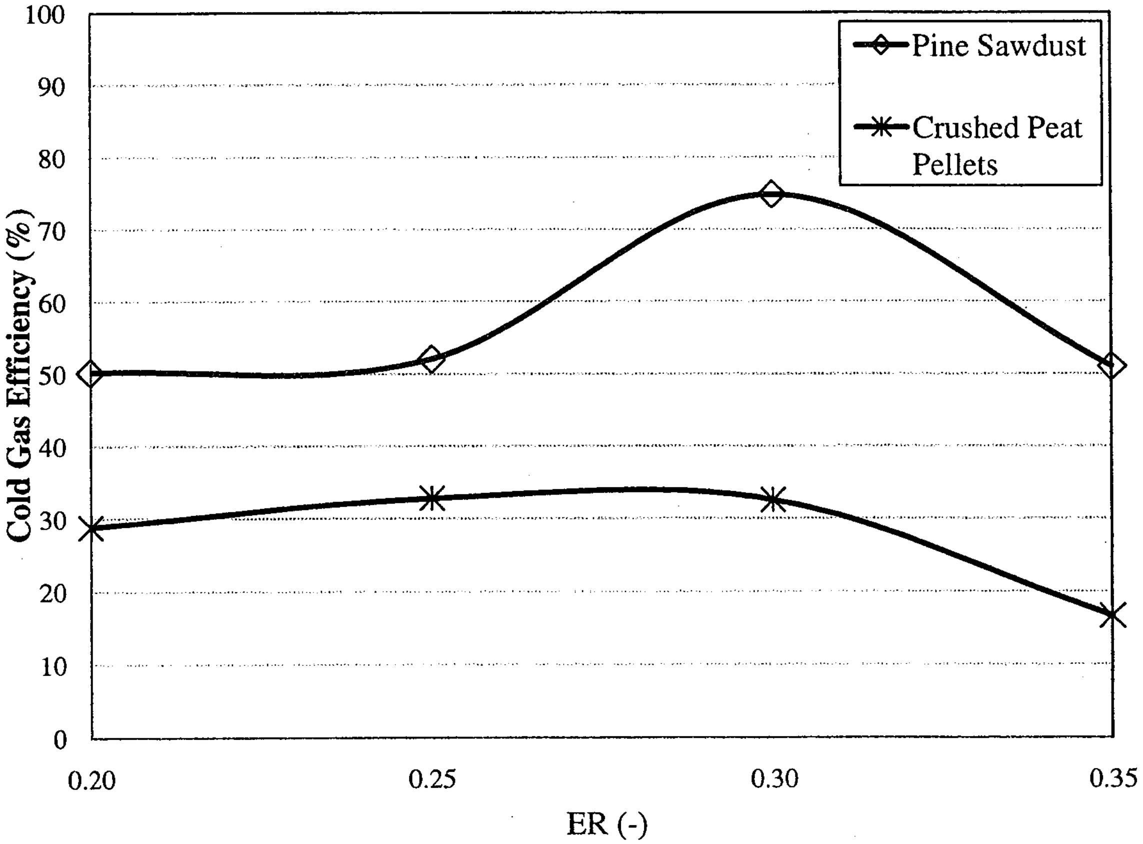


Figure 5-9. Cold gas efficiencies for gasification of crushed peat pellets and pine sawdust at varying ERs with olivine bed material.

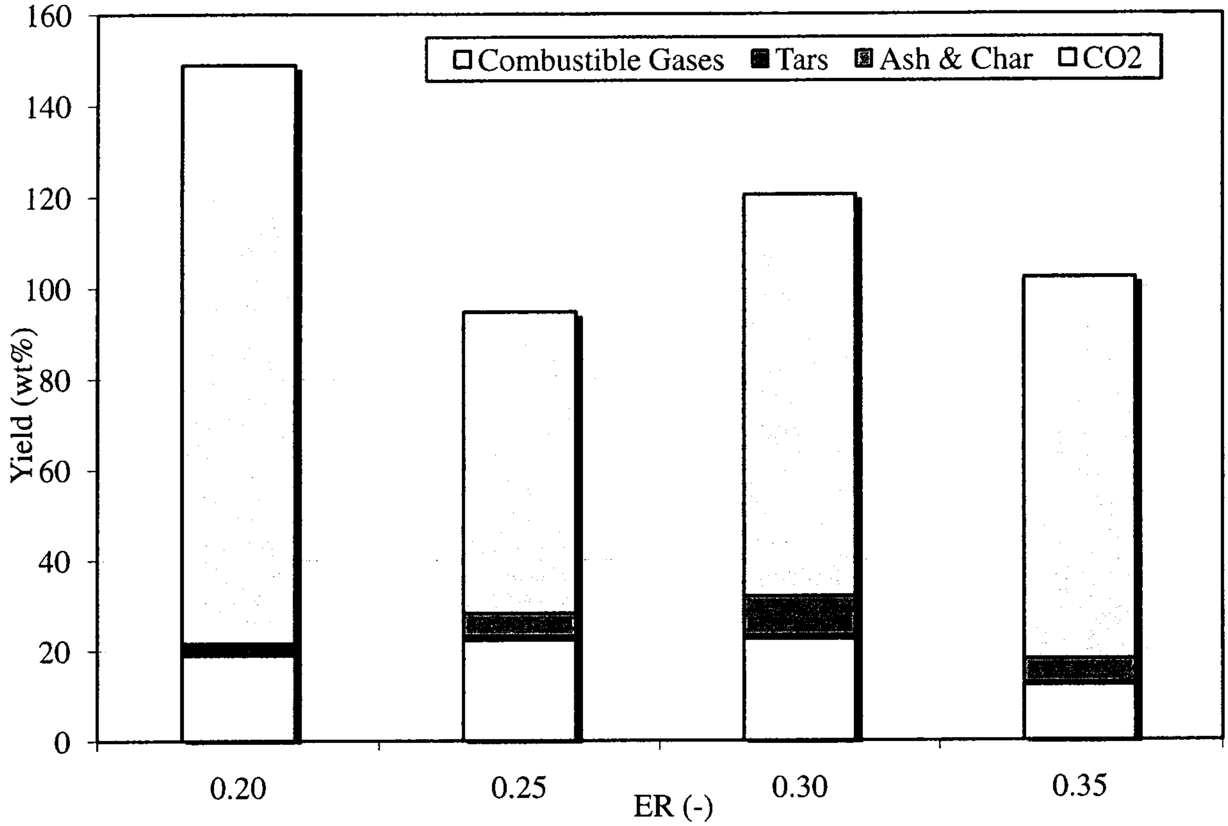


Figure 5-10. Product yields during gasification of crushed peat pellets in a fluidized bed of olivine particles.

Total product yields during gasification with crushed peat pellets are above 100 wt% for all ER values with the exception of ER=0.25. It is expected that total yield should exceed 100 wt% due to the incorporation of oxygen from the air gasification environment into the products. As compared with Figure 5-1, Figure 5-10 illustrates the lower combustible gas yields derived from peat gasification, as well as the higher CO_2 concentration.

5.3.4. Characterization of fresh and spent bed materials

The fresh and spent bed materials of olivine, crushed limonite (a natural iron oxide), limestone and dolomite were subject to X-ray diffraction (XRD) analysis to examine the changes in crystalline structures in the catalysts. Figure 5-10 shows the XRD profiles the fresh and spent bed materials of limonite iron oxide (a), limestone (b), and dolomite (c).

As shown in Figure 5-10a, the main crystalline species detected in the fresh limonite iron oxide were goethite (FeOOH) and hematite (Fe_2O_3), and quartz (SiO_2). In the spent limonite sample after gasification, the diffraction signals of goethite (FeOOH) almost completely diminished with increased hematite signals, suggesting the conversion of goethite (FeOOH) to hematite (Fe_2O_3) during the gasification process. The thermal degradation of goethite to hematite in high-temperature processes has been widely studied [29, 30], which can be generally described as the dehydration of goethite by the following equation:

$$2FeOOH + \textit{heat} \rightarrow Fe_2O_3 + H_2O \qquad (6)$$

This phase change through the above significant dehydration reaction could partially account for the low mechanical strength and high attrition of the limonite material in the fluidized bed gasifier during the experiments. The reactivity of natural limonite could be increased by reduction with H_2 [31]. The H_2-reduced limonite materials have proven to be highly effective secondary catalysts for tar cracking/reforming [32] and hot gas decomposition of NH_3 to N_2 [33, 34].

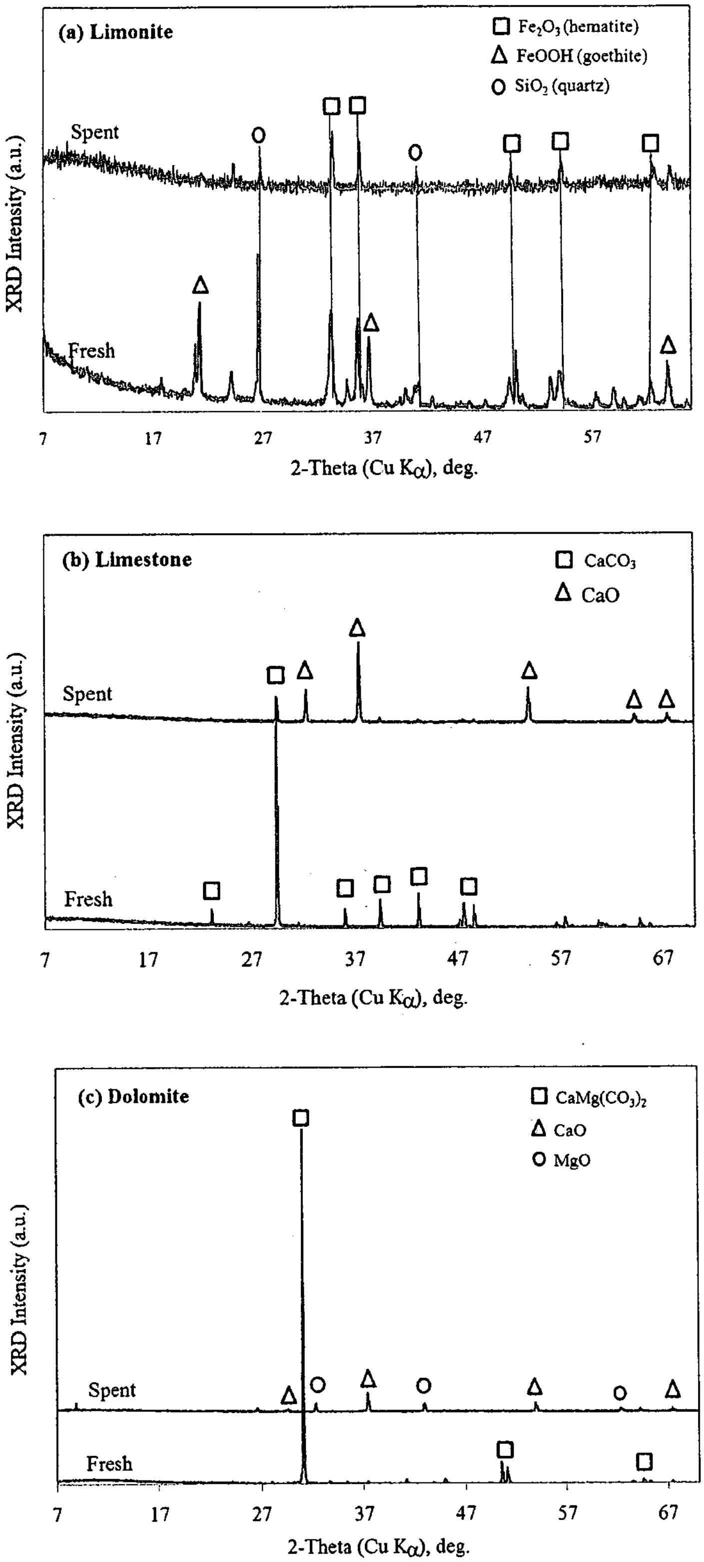


Figure 5-11. XRD profiles the fresh and spent bed materials of limonite iron oxide (a), limestone (b), and dolomite (c).

Both limestone and dolomite were calcined prior to the gasification tests, through reactions (7) and (8):

$$CaCO_3\ (\textit{limestone}) \rightarrow CaO\ (\textit{calcite}) + CO_2 \qquad (7)$$

$$CaMg(CO_3)_2\ (\textit{dolomite}) \rightarrow CaO + MgO + 2CO_2 \qquad (8)$$

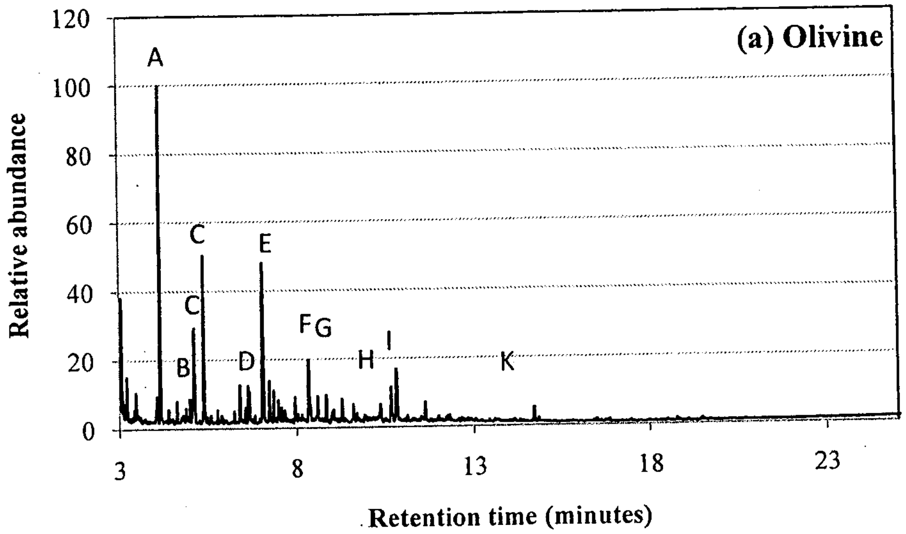
As revealed from the Figures 5-10b and 5-10c, calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) was the dominant species in the fresh limestone and dolomite, respectively, while in the spent catalysts, these species almost completely converted to lime (CaO), and CaO + MgO, respectively, as expected. Calcined limestone (CaO) and dolomites (CaO-MgO) have been commonly used as catalysts for biomass gasification [7, 8, 20, 22]. The phase transformation calcination through the above reactions would however decrease the mechanical strength of these materials, leading to a significant material loss in the fluidized bed gasifier as observed in this study.

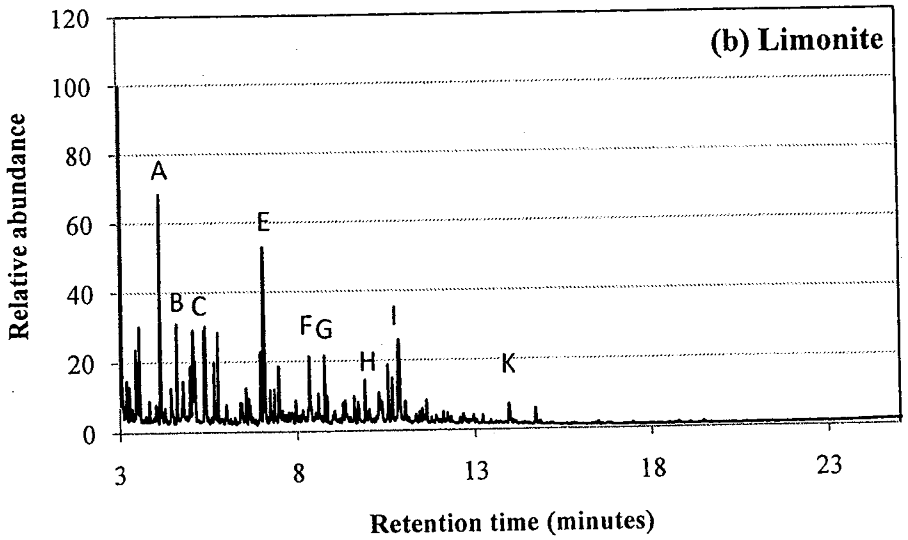
Olivine was demonstrated to have much higher attrition resistance than the other three materials (limonite, limestone and dolomite). XRD analysis of the fresh and spent olivine samples showed very complex signals due to the complexity of this mineral. Olivine represents a group of minerals including tephroite (Mn_2SiO_4), monticellite ($CaMgSiO_4$), and kirschsteinite ($CaFeSiO_4$). In the spent olivine sample separate magnesium or iron oxides signals were not detected, and all peaks were attributed to $(Mg_{1.8}Fe_{0.2})SiO_4$, suggesting that a complete calcination was not achieved at the present operating temperature (around 750°C). Devi et al. [35] found that calcination of olivine at temperatures exceeding 900°C for up to 10 hours was required for olivine calcination in order to improve its catalytic activation for biomass gasification and tar reduction in a fluidized bed.

5.3.5. GC/MS analysis of tars

Tars obtained from gasification were analyzed using GC/MS, and typical results are presented in Figure 5-11 and Table 5-3 below for the pine-sawdust derived tars from the air-blown gasification at ER = 0.25 with different bed materials. The relative concentration of a specific compound may be obtained qualitatively by the area % of the compound (defined by percentage of the compound's chromatographic area out of the total integration area). Gasification tars are a complex mixture of aromatic hydrocarbons, phenolic compounds, organic acids, esters and furans. In addition, all tars analyzed showed a significant amount of the carbohydrate 1,6-anhydro-beta.D.glucopyranose, apparently from the degradation of cellulose component in the feedstock (pine sawdust).

The phenol and benzene derivatives present in tar samples likely resulted from the high temperature depolymerisation of lignin, a natural polymer of p-hydroxy-phenyl-propanol, guaiacyl-propanol and syringyl-propanol [37]. Very high concentrations (up to 50%) of phenolic/aromatic compounds such as phenol, 2-methyl phenol and naphthalene, resulting from the partial degradation of lignin present in lignocellulosic materials, were detected in the tars from the gasification tests with olivine, limonite, and dolomite. Similar results were obtained in the air/CO_2 gasification of the sawdust as discussed previously in Chapter 3. Tars produced during gasification with limestone, however, exhibited a less complex GC-MS chromatogram with a very large signal attributed to 1,6-anhydro-beta.D.glucopyranose (relative concentration of 25%), compared with <10% in tars with the other bed materials. Apparently, this carbohydrate is associated with the degradation of cellulose in the pine sawdust [38]. As discussed before, the calcined limestone showed superior activity towards tar reduction during gasification (Figure 5-3). The GC/MS results suggest that the presence of calcined limestone in biomass gasification could effectively destroy the otherwise common phenolic compounds, which is an interesting finding of the present study. Furthermore, in the tar with calcined limestone the content of naphthalene (7.04 %) was significantly lower than that with other bed materials (10.9 - 13.2 %).





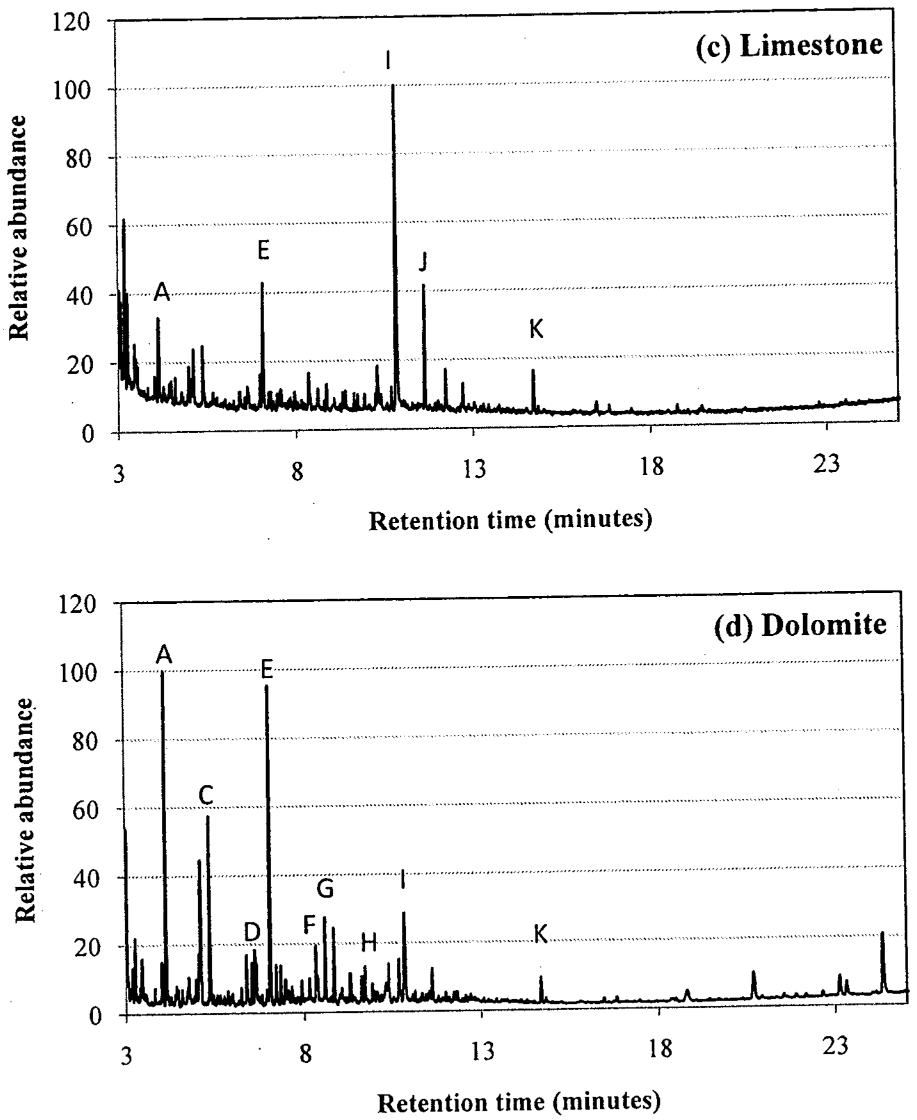


Figure 5-12. GC-MS chromatograms for the tar samples from the gasification tests at ER=0.25 with different bed materials.

Table 5-3. GC/MS analysis results for the tars recovered from gasification of the pine sawdust under different conditions

Peak No.	Retention Time (min)	Compound Identification	Rings	Area %			
				Olivine	Limonite	Limestone	Dolomite
	3.04	3-hydroxy-2-butanone	-	4.57	8.42	2.33	4.52
	3.19	Tetrahydro-2,2,4,4-tetramethyl furan		2.55	1.38	7.06	0.92
	3.27	Ethenyl benzyl	1		1.27	4.50	2.30
	3.43	4,5-dihydro-2-methyl 1H-imidazole	-		2.19		
	4.11	Cyclopenten-1-one	1	2.07			
A	4.16	Phenol	1	14.79	7.77	3.27	9.63
B	4.40	Benzene derivatives	1			1.39	0.89
	4.69	3-methyl-1,2-cyclopentanedione	1		5.02		
	5.02	2-oxo-proponal	-		3.98		
C	5.10	2-methyl phenol	1	14.60	5.62	2.86	13.73
D	6.39	Napthalene	2				12.67
	6.45	2,6-dimethyl phenol	1	2.64	1.64		1.80
	6.59	2-ethyl phenol	1	4.12	1.69	1.70	3.44
E	7.09	Napthalene	2	13.18	10.85	7.04	12.67
	7.38	2-propyl-2-pentanal	-	2.24			
F	8.30	4-methyl-1,2-benzenediol	1	3.40	1.59	1.96	2.22
G	8.50	Napthalene derivatives	2	1.15	0.96	1.05	5.12
	9.34	3-phenyl-2-propenal	-	1.79			
H	9.60	1,1'-biphenyl	2	0.96		0.77	1.10
I	10.70	1,6-anhydro-beta.D.glucopyranose	1	4.81	9.31	25.03	5.62
J	11.04	Acenaphthalene	3				
	11.58	1-acetoxy-cyclopenten-3-one	1	1.04	1.17	5.77	
K	14.70	Anthracene	3				1.07
L	24.34	1,2-benzenedicarboxylic acid esters	1				8.26
Total Area %				73.91	62.86	64.73	85.96

5.4. CONCLUDING REMARKS

(1). Olivine was the most attrition-resistant and thermally stable bed material among the four bed materials tested (including olivine, dolomite, limestone, and iron oxide) for biomass gasification in the fluidized bed reactor, leading to the best temperature control in the gasification operation.

(2) The pine sawdust gasification with olivine sand as the bed material achieved a high biomass conversion (>95 wt%) at all ERs tested (0.2-0.4). . While dolomite and limestone produced the highest yields of H_2, olivine is more effective for CO formation, and for gasification of pine sawdust with olivine the maximum cold gas efficiency (74.8%) was obtained at ER = 0.30.

(3) As expected, increasing ER led to a decrease in tar yield, leading to trace formation of tar at ER =0.35 and 0.4, while the ER had less significant effects upon either char or CO_2 yield. The yield of total combustible gases and gasification efficiency increased with ER as expected, but it peaked at ER of around 0.25-0.3.

(4). Although there were issues with attrition-resistance and thermal stability, limestone exhibited excellent catalytic tar cracking activity. Tar yields with limestone at all ER values were below 5 mg/L at ER = 0.2, compared with >40 mg/L for the other three bed materials given the same ER

(5). The gasification of peat resulted in drastically lower yields tar, but also the combustible gases (CO and CH_4 and H_2), compared with that of the woody biomass, in particular at a lower ER, which could be explained by the low volatile content of the peat used than that of the pine sawdust.

(6). All tars are a complex mixture of aromatic hydrocarbons (benzenes and phenolics), organic acids, esters and furans, as well as the carbohydrate 1,6-anhydro-beta.D.glucopyranose derived from lignocellulosic woody biomass. The tars from pine sawdust gasification with olivine, limonite, and dolomite bed materials contained high contents of phenolic/aromatic compounds. However, the tar with from pine sawdust gasification with calcined limestone consisted of a high concentration of cellulose-degraded carbohydrate, 1,6-anhydro-beta.D.glucopyranos, and much lower concentrations of phenolic/aromatic compounds.

REFERENCES

[1].P. McKendry, Energy production from biomass (part 3): gasification technologies. *Bioresource Technology* 83 (2002) 55-63.

[2].P. McKendry, Energy production from biomass: Part 1. Overview of biomass, Biosource Technology 83 (2002) 37– 46.

[3].J. Han, H. Kim. The Reduction and control technology of tar during biomass gasification/pyrolysis: An overview. Renewable and Sustainable Energy Reviews 12 (2008) 397-416.

[4].M. Asadullah, T. Miyazawa and K. Kunimori, *Catalyst development for the gasification of biomass in the dual-bed gasifier*, Applied Catalysis A: General **255** (2003) 169–180

[5].D. Lopamudra, K.J. Ptasinski and F.J.J.G. Janssen. *A review of the primary measures for tar elimination in biomass gasification processes*, Biomass and Bioenergy **24** (2003) 125–140

[6].D. Sutton, B. Kelleher, J.R.H. Ross, Review of literature on catalysts for biomass gasification. Fuel Processing Technology 73 (2001) 155-173.

[7].Z. Abu El-Rub, E.A. G. BramerBrem, Review of catalysts for tar elimination in biomass gasification process. Industrial and Engineering Chemistry Research 43 (2004) 6911-6919.

[8].L. Devi, K. Ptasinski, F. Janssen. A review of the primary measures for tar elimination in biomass gasification processes. *Biomass and Bioenergy 24* (2003) 125-140.

[9].J. Pencho, T. Schildhauer, M. Sturzenegger, S. Biollaz, A. Wokaun. Reactive bed materials for improved biomass gasification in a circulating fluidized bed reactor. *Chemical Engineering Science 63* (2008) 2456-2476

[10]. A. Uddin, H. Tsuda, S. Wu, E. Sasaoka. Catalytic decomposition of biomass tars with iron oxide catalysts. In Press. *Fuel* (2007), doi:10.1016/j.fuel.2007.06.021.

[11]. R. Zhang, R. Brown, A. Suby, K. Crummer. Catalytic destruction of tar in biomass derived producer gas. *Energy Conversion and Management 45* (2004) 995-1014.

[12]. T. Kimura, T. Miyazawa, J. Nishikawa, S. Kado, K. Okumura, T. Miyao, S. Naito, K. Kunimori, K. Tomishige. Development of Ni catalysts for tar removal by steam gasification of biomass. *Applied Catalysts B: Environmental 68* (2006) 160-170.

[13]. Z. El-Rub, E. Bramer, G. Brem, Experimental comparison of biomass chars with other catalysts for tar reduction. *Fuel 87* (2008) 2243-2252.

[14]. D. Sutton, B. Kelleher, A. Doyle, J.R.H. Ross, Investigation of nickel supported catalysts for the upgrading of brown peat derived gasification products. Bioresource Technology 80 (2001) 111-116.

[15]. M.P. Anzar, M.A. Caballero, J. Gil, J.A. Martin, J. Corella, Commercial steam reforming catalysts to improve biomass gasification with steam-oxygen mixture. 2. Catalytic tar removal. Ind. Eng. Chem. Res. 37 (1998) 2668-2680.

[16]. E. G. Baker, L. K. Mudge, M. D. Brown, Steam gasification of biomass with nickel secondary catalysts. Ind Eng. Chem. Res. 26 (1987) 1335

[17]. D.N. Bangala, N. Abatzoglou, E. Chornet, Steam reforming of naphthalene on Ni-Cr/Al_2O_3 catalysts doped with MgO, TiO_2 and La_2O_3. AIChE J. 44 (1998) 927-936.

[18]. S. Rapagna, N. Jand, P. Foscolo, Catalytic gasification of biomass to produce hydrogen rich gas. Int. J. Hydrogen Energy 23 (1998) 551.

[19]. Y. Cao, Y. Wang, J.T. Riley, W.-P. Pan, A novel biomass air gasification process for producing tar-free higher heating value fuel gas. Fuel Processing Technology 87 (2006) 343-353.

[20]. P. Weerachanchai, M. Horio, C. Tangsathitkulchai, Effects of gasifying conditions and bed materials on fluidized bed steam gasification of wood biomass. *Bioresource Technology* 100 (2009) 1419-1427.

[21]. C. Pfeifer, R. Rauch, H. Hofbauer, In-bed catalytic tar reduction in a dual fluidized bed biomass stream gasifier. Industrial and Engineering Chemistry Research 43 (2004) 1634-1640.

[22]. A.K. Dalai, E. Sasaoka, H. Hikita, D. Ferdous, Catalytic gasification of sawdust derived from various biomass. Energy Fuels 17 (2003) 1456-1463.

[23]. S. Rapagna, N. Jand, A. Kiennemann, P. Foscolo, Steam gasification of biomass in a fluidized bed of olivine particles. Biomass Bioenergy 19 (2000) 187-197.

[24]. A. Orio, J. Corella, I. Narvaez, Performance of different dolomite on hot raw gas cleaning from biomass gasification with air, Ind. Eng. Chem. Res. 36 (1997) 3800-3808.

[25]. J. Corella, M.P. Aznar, J. Delgado, M.P. Martinez, J.L. Arugües, *Studies in Surface science and Catalysis* 68 (1991) 249-252

[26]. Q. Yu, C. Brage, G. Chen, K. Sjöström, *Journal of Analytical and Applied Pyrolysis* 40 (1997) 481-489

[27]. C. Brage, Q. Yu, G. Chen, K. Sjöström, *Biomass & Bioenergy* 18 (2000) 87-91

[28]. J. Corella, J. Toledo, R. Padilla, *Energy & Fuels* 18(2004) 713-720

[29]. G. González, A. Sagarzazu, R. Villalba, *Materials Research Bulletin* 35 (2000) 2295-2308

[30]. H. Fan, B. Song, Q. Li, *Materials Chemistry and Physics* 98 (2006) 148-153

[31]. W. F. de Souza, I.R. Guimarães, L. Oliveira, M.C. Guerreiro, A. Guarieiro, K. Carvalho, *Journal of Molecular Catalysis A: Chemical* 278 (2007) 145-151

[32]. L. Li, K. Morishita, T. Takarada. Light fuel gas production from nascent coal volatiles using a natural limonite ore. *Fuel* 2007; 86:1570-1576

[33]. N. Tsubouchi, H. Hashimoto, Y. Ohtsuka, High catalytic performance of fine particles of metallic iron formed from limonite in the decomposition of a low concentration of ammonia. *Catalysis Letters* 2005; 105: 203-208.

[34]. N. Tsubouchi, H. Hashimoto, Y. Ohtsuka. Catalytic Performance of Limonite in the Decomposition of Ammonia in the Coexistence of Typical Fuel Gas Components Produced in an Air-Blown Coal Gasification Process. *Energy & Fuels* 2007;*21*: 3063–3069

[35]. L. Devi, M. Craje, P. Thüne, K. Ptasinski, F. Janssen, *Applied Catalysis A: General* 294 (2005) 68-79

[36]. K.N. Sheeba, J. Babu, S. Jaisankar, *Energy for Sustainable Development* (in press) doi:10.1016/j.esd.2009.06.002

[37]. S. Karagöz, T. Bhaskar, A. Muto, Y. Sakata. *Comparative studies of oil compositions produced from sawdust, rice husk, lignin and cellulose by hydrothermal treatment.* Fuel 84 (2005) 875-884

[38]. G. Ponder, G. Richards, T. Stevenson. *Influence of linkage position and orientation in pyrolysis of polysaccharides: A study of several glucans.* Journal of Analytical and Applied Pyrolysis 22 (1992) 217-229.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1. Summary and Conclusions

This study examined the catalytic gasification of biomass with a focus on the reduction of tar yield. In the first part, air/CO_2 gasification of pine sawdust with several different catalysts was examined. In the second part, air-blown gasification of pine sawdust and peat was carried out in a pilot-scale fluidized bed reactor at CANMET Energy in Ottawa, Ontario. The effects of different bed materials and equivalence ratios on syngas composition, gasification efficiency and tar yield were examined.

6.1.1. **Part I.** Catalytic Gasification of Woody Biomass in Air/CO_2 Media

1. Compared with air, CO_2 as a gasifying agent for biomass gasification showed a much lower reactivity. The yields of char and tar both increased with increasing CO_2 concentration in the feed gas, In the CO_2-gasification of the pine sawdust, the tar and char yields at 700°C were as high as 44.2 wt% and 21.2 wt%, respectively. A higher temperature and a greater oxygen content in the feed gas led to higher gasification efficiency.
2. It was observed that the addition of iron ore to the biomass feedstock simply by physical mixing did not alter the yields of all products significantly irrespectively of the types of gasification agent and the gasification temperature, which was likely due to the poor contact between the catalyst and the gas/vapor products during the gasification process.
3. All the impregnated metal cations (Fe, Ni, Co and Ru), in particular Ni, Co and Ru, were very effective for promoting the gasification of the woody biomass at 700°C and 800°Cr, leading to

a lower tar yield, a significantly decreased char yield and a greatly increased yield of CO2-free gas. At 800°C, the impregnation of Fe, Ni, Co or Ru led to almost complete conversion of the solid biomass into gas and liquid products, producing an extremely low char yield (< 1-4 wt%), and a very high yield of combustible CO_2-free gas (ranging from 51.7 wt% for Fe to 84 wt% for Ru). The tar yield also reduced significantly from 32.1 wt% without catalyst to 19-27 wt% with the impregnated metal ions.

4. The addition of all impregnated metal cations had a significant effect on the formation of both carbon monoxide and hydrogen. At 800°C, the CO yield per kg of biomass (dry and ash-free) climbed to 28.0 mol and 29.0 mol with the impregnated Ni and Ru catalyst, respectively, compared with only 5.3 mol/kg biomass without catalyst. The yield of H_2 during the gasification without catalyst at 800°C was approximately 0.5 mol/kg biomass, which was increased to 2.5 mol/kg biomass and 3.1 mol/kg biomass due to the presence of the impregnated Ni and Ru, respectively.
5. All tars are a complex mixture of aromatic hydrocarbons (benzene, phenoics), aldehydes, ketones, with some amounts of organic acids (acetic acid, propenoic acid), ester, furans and alcohols, derived from the lignin and cellulosic components of the woody biomass. 4-hydroxy-4-methyl-2-pentanone was the dominant compound identified by GC/MS in all tars, with a relative composition of 17-27%. All tars analyzed contain a significant amount (4.8-9.2 area %) of a carbohydrate: 1,6-anhydro-ß-D-glucopyranose, derived from the cellulose in the pine sawdust. Relatively high concentrations of lignin-degraded phenolic compounds such as 2-methoxy-phenol and 1-hydroxy-2-methoxy-4-methylbenzene were present in almost all tars.

Part II. Catalytic Gasification of Biomass in an Air-blown Pilot-Scale Fluidized Bed Reactor

(1) Olivine was the most attrition-resistant and thermally stable bed material among the four bed materials tested (including olivine, dolomite, limestone, and iron oxide) for biomass gasification in the fluidized bed reactor, leading to the best temperature control in the gasification operation.

(2) The pine sawdust gasification with olivine sand as the bed material achieved a high biomass conversion (>95 wt%) at all ERs tested (0.2-0.4). . While dolomite and limestone produced the highest yields of H_2, olivine is more effective for CO formation, and for gasification of pine sawdust with olivine the maximum cold gas efficiency (74.8%) was obtained at ER = 0.30.

(3) As expected, increasing ER led to a decrease in tar yield, leading to trace formation of tar at ER =0.35 and 0.4, while the ER had less significant effects upon either char or CO_2 yield. The yield of total combustible gases and gasification efficiency increased with ER as expected, but it peaked at ER of around 0.25-0.3.

(4) Although there were issues with attrition-resistance and thermal stability, limestone exhibited excellent catalytic tar cracking activity. Tar yields with limestone at all ER values were below 5 mg/L at ER = 0.2, compared with >40 mg/L for the other three bed materials given the same ER

(5) The gasification of peat resulted in drastically lower yields tar, but also the combustible gases (CO and CH_4 and H_2), compared with that of the woody biomass, in particular at a lower ER, which could be explained by the low volatile content of the peat used than that of the pine sawdust.

(6). All tars are a complex mixture of aromatic hydrocarbons (benzenes and phenolics), organic acids, esters and furans, as well as the carbohydrate 1,6-anhydro-beta.D.glucopyranose derived from lignocellulosic woody biomass. The tars from pine sawdust gasification with olivine, limonite, and dolomite bed materials contained high contents of phenolic/aromatic compounds. However, the tar with from pine sawdust gasification with calcined limestone consisted of a high concentration of cellulose-degraded carbohydrate, 1,6-anhydro-beta.D.glucopyranos, and much lower concentrations of phenolic/aromatic compounds.

6.2. Recommendations for Future Work

This thesis examined catalytic tar reduction during the gasification of biomass at both the bench scale (in a fixed-bed reactor with air/CO_2) and at the pilot scale (fluidized bed reactor with air). These experiments were successful and yielded encouraging results, however further research in certain areas is desirable.

For the air/CO_2 gasification of biomass, the following recommendations should be considered for future research:

- The wet-impregnation of metal cations onto biomass, while useful for examining activity of the metal catalysts, may not be practical for large scale operation. Future testing of catalysts of interest (notably cobalt, ruthenium and nickel) should involve the impregnation of catalyst ions onto a solid support, such as alumina, which could be more economically viable for the application of such catalysts to either as primary catalysts in the gasifier or as secondary catalysts in a guard bed downstream.
- Due to the limitation in the design and operation of the fixed-bed reactor system used in this study, it is possible that tars were evolved from the biomass early in the heating

process, before the added catalyst was heated and activated. In future tests, a modified reactor design is needed, e.g, employing a free-fall reactor or a fluidized bed reactor, to allow preheating of the catalyst material prior to biomass gasification and tar reduction.

With regard to the pilot scale fluidized bed gasification experiments, the following recommendations should be considered for future research:

- Limonite (iron oxide), calcined limestone, and to a lesser extent calcined dolomite showed poor mechanical resistance within the fluidized bed. These materials seem to be more suitable as secondary catalysts used downstream of the reactor within a secondary guard bed.
- Due to the relatively low reaction temperatures (approximately 750°C), olivine may not have been completely calcined prior to gasification. Pre-treatment of the olivine material at high temperature (>850°C) may increase the catalytic activity of this material.
- As a nature of the air-blown fluidized bed gasifier, temperature control was difficult during the tests, especially with bed materials prone to mechanical attrition. Temperature is known to have a significant effect on tar yield, and is therefore difficult to compare between different tests at varying equivalence ratios if these changes in air ratio led to significant temperature changes. A more efficient means of temperature control, through improved cooling or providing external heating may be recommended.
- In order to achieve ER value of 0.25 and below, the biomass feed system was running near maximum capacity while the primary air flow was operating at the minimum recommended flow required to maintain bed fluidization. As such, an increased capacity of the biomass feeding system is recommended.