# An Experimental Study of Catalytic Effects on Reaction Kinetics and Producer Gas in Gasification of Coal-Biomass Blend Chars with Steam

A thesis submitted in partial fulfilment of the requirements for the Degree of Master of Engineering in Chemical and Process Engineering

University of Canterbury

2011

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# Acknowledgements

There are many people whose support and contribution help the completion of this master's thesis. To all these people, I would like to say 'thank you'.

Firstly I am graceful to Professor Shusheng Pang, who is my principal supervisor and leader of the overall gasification program and who provided his invaluable expertise and guidance in conduction of this project.

Thanks to Dr. Tana Levi, who is the technology operations manager of CRL Energy Ltd in Wellington, New Zealand, and my co-supervisor of this project. Thanks are also going to Mr. Rodney Brown and all other staff of CRL Energy Ltd, who contributed their experience and guided me to complete my experiments in the laboratory at CRL Energy Ltd.

I would like to cherish the memory of Dr Tony Clemens, who was the previous project manager of CRL Energy Ltd and senior engineer on gasification research in New Zealand.

This project was sponsored by New Zealand Coal Association through CRL Energy Ltd.

Thanks to Qixiang Xu, who is my good friend and schoolmate.

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# Abstract

The objective of this thesis is to experimentally investigate the performance of steam gasification of chars of pure coal (lignite, sub-bituminous), pure biomass (radiata pine, eucalyptus nitens) and their blends. The influences of gasification temperature, types of coal and biomass, coal-biomass blending ratio, alkali and alkaline earth metal (AAEM) in lignite, on specific gasification characteristics (producer gas composition and yield, char reactivity) were studied. In addition, synergistic effects in co-gasification of coal-biomass blend char were also investigated. This project is in accordance with objectives of the BISGAS Consortium.

In this study, experiments were performed in a bench-scale gasifier at gasification temperatures of 850°C, 900°C and 950°C, respectively. Two types of coals (lignite and sub-bituminous) and two kinds of biomass (radiata pine and eucalyptus nitens) from New Zealand were selected as sample fuels. From these raw materials, the chars with coal-to-biomass blending ratios of 0:100 (pure coal), 20:80, 50:50, 80:20 and 100:0 (pure biomass), which were derived through the devolatilization at temperature of 900°C for 7 minutes, were gasified with steam as gasification agent. During the gasification tests, the producer gas composition and gas production were continuously analysed using a Micro gas chromatograph. When the gas production was undetectable, the gasification process was assumed to be completed and the gasification time was recorded. The gasification producer gas consisted of three main gas components: hydrogen (H<sub>2</sub>), carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>).

The results from gasification of chars of individual solid fuels (coal or biomass) confirmed that biomass char gasification was faster than coal char gasification. The influences of gasification temperatures were shown as: when gasification temperature increased, the  $H_2$  yield increased in coal char gasification but decreased in biomass char gasification. In the meantime, CO yields increased while CO<sub>2</sub> yields decreased in

both coal char and biomass char gasification. In addition, the char reactivity of all the pure fuel samples increased with elevated gasification temperatures.

The results from co-gasification of coal-biomass blend char exhibited that the syngas production rate, which is defined as the total gas production divided by the gasification completion time, was enhanced by an increase in gasification temperatures as well as an increase in the biomass proportion in the blend. The AAEM species played a significant catalytic role in both gasification of pure coal chars and co-gasification of coal-biomass blend chars. The presence of AAEM increased the producer gas yield and enhanced the char reactivity.

The positive synergistic effects of the coal-biomass blending char on syngas production rate only existed in the co-gasification of lignite-eucalyptus nitens blend chars. The other blend chars showed either insignificant synergistic effects or negative effects on the syngas production rate.

# **1** Introduction

## **1.1 Backgrounds**

New Zealand is currently faced with a series of issues involving energy supply and environmental protection, such as the substantial increase in energy demand, lack of good quality fossil fuels, and related environmental concerns for air pollutants and  $CO_2$  emissions. Therefore, it is in the interests of the nation to investigate and develop renewable energy, together with the possibility of using cleaner and more efficient energy conversion technologies at an industrial scale in the future.

Co-gasification of blended coal and biomass provides a promising opportunity for high efficiency energy conversion and environmentally friendly technology in New Zealand.

Firstly, it is well recognized that gasification is a clean and efficient way for converting solid fuel into hydrogen-rich fuel gases. The gases produced (which are also called producer gas) can be utilized directly as fuels for electricity and power generation or as a synthesis liquid fuel precursor for manufacturing methanol, Fischer-Tropsch oil, etc. (Chmielniak and Sciazko 2003; Weerachanchai et al. 2009). Furthermore, gasification feedstock is highly versatile; a wider range of solid fuels can be used, such as coal, biomass, plastic waste, petroleum coke and so on (Higman and Burgt 2003).

Secondly, the vast local coal reserves and abundant biomass in New Zealand should be sufficient in meeting energy demands for centuries. New Zealand's coal reserves are estimated to be 8.6 billion tons, in which lignite is 75%, sub-bituminous is 17% and bituminous is 8% (Clemens et al. 2006). 90% of the coal reserve is well suited to gasification. Besides, New Zealand has abundant woody biomass resources from the domestic forestry industry and agricultural sector. Every year, the plantation forest harvest is approximately 20 million m<sup>3</sup> (Forestry 2009), in which 4-5 million m<sup>3</sup> of wood residues (sawdust, bark or chips) are generated during the processing (Penniall 2008).

Finally, coal-biomass blends could thus make use of possible synergistic effects in cogasification by combining some of the characteristics of each feedstock alone. From environmental point of view, the addition of biomass to coal gasification could contribute to the reduction of  $CO_2$  emissions and the pollution caused by sulphur and ash contained in coal, as biomass characteristics are known to be  $CO_2$  neutral and low in sulphur and ash content (Fermoso et al. 2010). From an economical point of view, the blending of coal and biomass for co-gasification can provide a potential opportunity to build a large scale gasification based energy plant. The large scale plant can increase energy efficiency and reduce costs for unit energy product; however, high costs for transportation and handling of a large quantity of low density biomass (Kajitani et al. 2009) will hinder the commercialisation of such large scale plant (Kumabe et al. 2006). On the other hand, coal utilisation involves much lower costs for transportation and handling.

As mentioned above, the study of the co-gasification of coal and biomass, when applied to New Zealand, has an important significance.

## **1.2 Gasification**

Gasification is a thermo-chemical process which coverts solid fuel (coal and biomass) with gasification agents (air, oxygen or steam) into a producer gas which consists of  $H_2$ , CO, CO<sub>2</sub>, CH<sub>4</sub> and other minor hydrocarbons.

#### 1.2.1 Gasification Mechanism

It is generally agreed that the gasification process can be divided into two main stages after the initial short drying: devolatilization (pyrolysis) and char gasification as shown in Figure 1-1 (Bridgwater 2003; Liu and Niksa 2004; Pan et al. 1996).



Figure1-1: Process of co-gasification of coal and biomass

#### a) Devolatilization (pyrolysis)

As the temperature of the dry feedstock increase to  $300 - 500^{\circ}$ C, devolatilization takes place and the feedstock is decomposed into solid char, volatiles and a very small amount of unsaturated hydrocarbons, e.g., tars. The volatiles consist of H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O and C<sub>2</sub>H<sub>6</sub>. The char is the residual solids mainly consisting of solid carbon and metals (Ahrenfeldt and Knoef 2005; Gordillo et al. 2009).

Dry feed stock + Heat  $\rightarrow$  Char + Volatiles

#### b) Char gasification.

Char gasification is the slowest conversion process and thus it is the rate-determining step of the overall gasification process (Ahmed and Gupta 2011; Zhang et al. 2010). Char gasification consists of a series of heterogeneous reactions of the carbon in the chars with the gasification agent (Steam, Air, or Oxygen), and reactions among reactant and resultant gases. Hence, the char gasification directly depends on char reactivity with gasification agent (Asadullah et al. 2010).

The heterogeneous reactions among char, gasification agents and resultant gas in gasification process are described as follows (Klass 1998; McKendry 2002b). In these reactions, the standard enthalpy is shown with temperature at 298K.

#### (1) Steam reaction:

$$C + H_2 O \Leftrightarrow CO + H_2$$
  $\Delta H = 131.3 kJ / mol$ 

(2) Water-gas shift:

 $CO + H_2O \Leftrightarrow CO_2 + H_2$ 

$$\Delta H = -41.1 kJ / mol$$

#### (3) Boudouard reaction:

$$C + CO_2 \Leftrightarrow 2CO$$
  $\Delta H = 172.4 kJ / mol$ 

(4) Hydro-reaction:

$$C + 2H_2 \Leftrightarrow CH_4$$
  $\Delta H = -74.8kJ / mol$ 

(5) Steam methane reforming:

$$CH_4 + H_2O \Leftrightarrow CO + 3H_2$$
  $\Delta H = 206kJ / mol$ 

At the same time, oxidisation reactions may occur when air or oxygen is used as the gasification agent once the temperature is sufficiently high. The oxidisation reactions of the char, dry feedstock and the volatiles directly provide thermal energy for the demand of gasification.

### (6) Partial carbon combustion:

$$C + \frac{1}{2}O_2 \Longrightarrow CO$$
  $\Delta H = -110.5kJ / mol$ 

(7) Carbon combustion:

$$C + O_2 \Longrightarrow CO_2$$
  $\Delta H = -393.5 kJ / mol$ 

(8) Hydrogen combustion:

$$H_2 + \frac{1}{2}O_2 \Leftrightarrow H_2O \qquad \Delta H = -245.3kJ / mol$$

#### 1.2.2 Steam gasification

When steam is used as a gasification agent, gasification (which is also called steam gasification) is an attractive process for producing a hydrogen-rich gaseous fuel, as steam is a more reactive gas than other gasification mediums (Haykiri-Acma et al. 2006). Moreover, steam involvement in the reaction is important for enhancement of hydrogen yield in the producer gas through the **Reactions (1), (2) and (3)** (Umeki et al. 2009a). Compared with air-blown gasification and oxygen-blown gasification, steam gasification has obvious advantages:

- It produces a gas with higher heating value about 10 16 MJ/Nm<sup>3</sup> (Li et al. 2004b; Lv et al. 2004);
- It generates a hydrogen-rich gas with a 30-60 vol.% H<sub>2</sub> content (Yan et al. 2010).
- It reduces the diluting effect of N<sub>2</sub> from air (Umeki et al. 2009a).
- It is economically feasible as it eliminates the need for an expensive oxygen plant when oxygen is used as gasification mediums from the viewpoint of economical feasibility.
- Excess steam in steam gasification can be easily separated by condensation (Weerachanchai et al. 2009).

However, the steam gasification process as a whole is endothermic. Thus, for practical applications of the steam-only gasification, it is necessary to supply heat from an external source (Encinar et al. 2001; Umeki et al. 2009b).

## 1.3 Characteristics of the feedstock materials

Both biomass and coal are carriers of accumulated solar energy and thus are considered to be important solid fuels for energy supply. However, the differences in their natures and availability create differences in performance when utilized in energy production (Sjöström et al. 1999). In general, the compositions of coal and biomass have to be analyzed by two methods before being utilized and the information can be used to understand the effects of the fuel composition on the producer gas quality. One method is proximate analysis, in which the proportions of moisture content, ash content, volatile matter content and fixed carbon content are measured. The other method is ultimate analysis, which is elemental composition analysis. C, H, O, N and S are generally major elements in coal and biomass. Table 1-1 shows the proximate analysis and ultimate analysis of various coal and biomass.

Table 1-1: Analysis of composition of coal and biomass (Demirbas 2003; Higman and Burgt 2003)

		Biomass				Coal			
		Corn cobs	Wheat straw	Pine	Straw	Lignite	Sub- bituminous	Bituminous	
	Moisture	15.0	6.5	11.6	7.6	5.5	10.5	13.0	
Proximate	Ash	1.4	7.6	0.3	10.1	32.3	11.2	10.7	
analysis	Volatiles	76.6	69.2	74.5	68.8	24.9	34.7	37.0	
	Fixed carbon	7.0	16.7	13.6	21.5	37.3	43.6	39.3	
	С	48.4	41.4	46.9	43.4	77.3	76.4	78.4	
Ultimate analysis	Н	5.6	5.7	5.2	4.2	5.3	5.6	5.4	
	0	44.3	42.9	51.6	40.3	14.2	14.9	9.9	
	Ν	0.3	1.1	0.9	0.2	1.3	1.7	1.4	
	S	-	0.5	-	-	1.9	1.4	4.9	

## 1.3.1 Coal

As the traditional fossil fuel, the coal reserve is the most abundant and is also geographically more widely spread over the world (Sonobe et al. 2008). Coal can be further classified into lignite, sub-bituminous coal and bituminous coal, ranking from the lowest to the highest grades respectively (Lee et al. 2007).

Due to the higher fixed carbon content, coal gasification can generate producer gas with high calorific values. Furthermore, the low rank coal (such as lignite) contains significant amounts of inherent alkali and alkaline earth metal (e.g. calcium and magnesium), which can act as an excellent catalyst for gasification (Clemens et al. 1998). However, coal utilization has led to serious environmental concerns such as global warming due to the utilizing coal leads to an increase in the atmospheric  $CO_2$  concentration (Merrick 1984).

#### 1.3.2 Biomass

Biomass is widely considered to be as a renewable and environmentally friendly energy source for sustainable heat and power generation, as its utilization is known to be  $CO_2$  neutral (Bridgwater 1995; Demirbas 2001). The  $CO_2$  balance for biomass is about zero as plants in their growth phase remove  $CO_2$  from the atmosphere during photosynthesis process in the amounts comparable to the ones produced during biomass gasification (Chen et al. 2003; Smolinski et al. 2010). Renewable biomass resources include agricultural residues, short rotation woody crops and wood waste (e.g. sawdust, chips, bark, and forestry residues) (McKendry 2002a).

Biomass has a relatively high reactivity as it contains high atomic H/C ratio and has a high content of volatile matter (Kastanaki et al. 2002). In addition, high reactivity of biomass is also a consequence of the high surface area of biomass and the inherent alkali metals. For example, agricultural residues contain abundant calcium and potassium species (Ganga Devi and Kannan 1998; Jaffri and Zhang 2009). The high reactivity of biomass can facilitate the conversion of fuel and upgrade the quality of producer gas in gasification (Zhang et al. 2007). However, raw biomass has a low density and high moisture content, it caused the high cost for its collection, transportation and preparation, hence biomass gasification is relatively costly (Bahng et al. 2009; Fushimi et al. 2010; Kirubakaran et al. 2009).

# **1.4 Objectives of the project**

This study is part of a joint project based on New Zealand Coal Association initiative, CRL Energy hydrogen programme and University of Canterbury's biomass gasification programme. This thesis has focused on the understanding and experimentally testing of the behaviour of the co-gasification of coal and biomass. The two specific objectives of this study are:

- To review the previous studies in literature on influences of gasification condition (temperature), blending ratio of coal and biomass, and the presence of alkali and alkaline earth metals in the coal on the processes of gasification and co-gasification.
- To experimentally investigate the influences of gasification temperature, coalbiomass blending and catalytic elements in the coal on co-gasification performance (producer gas quality and char reactivity).
- To analyse the synergistic effect in co-gasification of coal-biomass blend char

### 1.4.1 Objectives of experiments

For the above purposes, a series of experiments were conducted, in which chars produced from various blends of coal and biomass were gasified in a bench scale gasifier with steam as the gasification medium.

Four variable operation parameters in the experiment design are considered as follows:

- Choice of feedstock;
- Gasification temperature;
- Blended ratio of coal and biomass;

• Presence of AAEM in solid fuels.

The following analyses were performed in the experimental runs:

- Producer gas production rate and producer gas composition;
- Accumulative producer gas production;
- Char reactivity.

## 1.4.2 Contribution of project

The experiment results obtained from this project will provide contributions to this field in two areas:

- Better understanding of the influences of different operational conditions and blending ratio on co-gasification of New Zealand coals and biomass.
- Providing data base for validation of theoretical results from gasification simulation models which has been carried out in a separate study.

# 2 Literature Reviews of Gasification and Co-gasification Studies

A literature review was conducted to better understand the existing research on gasification of coal, biomass and blended coal and biomass. The effects of operational conditions on gasification and co-gasification have been extensively investigated in recent years. However, the published gasification experiments were carried out by various researchers under different operational conditions, such as the feedstock resources (coal and biomass), gasification agent, and gasifier systems as well as varied temperature and pressure, which are listed in Table 2-1 for biomass gasification, Table 2-2 for coal gasification and Table 2-3 for co-gasification.

Authors of the experiments	•	Feedstock		Gasification	G	Operation conditions	
	Year	Coal	Biomass	agents	Gasifier	Temperature (°C)	Pressure
Franco et al.	2003	Х	Pinus pinaster, Eucalyptus globulus, Holm oak	Steam	Fluidised bed	700-900	Atmospheric pressure
Hanaoka et al.	2005	Х	Japanese oak, Red pine bark	Air - Steam	Downdraft fixed bed	900	Atmospheric pressure
Li et al.	2004	Х	Six sawdust species	Air	Circulating fluidized bed	700-850	Atmospheric pressure
Luo et al.	2009	Х	Pine sawdust	Steam	Fixed bed	600-900	Atmospheric pressure
Lv et al.	2004	X	Pine sawdust	Air - Steam	Fluidized bed	700-900	Atmospheric pressure

Table 2-1: The summary of reported biomass gasification experiments in literature

Table 2-1 (continued)

Smolinski et al.	2010	Х	Crops from Poland and Germany	Steam	A laboratory- scale fixed bed	650-900	Atmospheric pressure
Umeki et al.	2009	Х	Wood Chips	Steam	Updraft fixed bed	927	Atmospheric pressure
Wei et al.	2007	Х	Pine sawdust, legume straw	Steam	Downflow free-fall reactor	750-850	Atmospheric pressure
Yan et al.	2010	Х	Pine sawdust	Steam	Fixed bed	600-850	Atmospheric pressure

Table 2-2: The summary of reported coal gasification experiments in literature

Authors of the experiments	Year	Feedstock				Operation conditions		
		Coal	Biomass	Gasification agents	Gasifier	Temperature (°C)	Pressure	
Lee et al.	1998	Australian sub- bituminous coal	х	Air - Steam	Fluidized bed	750-900	Atmospheric pressure	
Tay and Li	2009	Victorian brown coal	Х	$O_2$ and $CO_2$	Fluidized bed and fixed bed	800	Atmospheric pressure	
Wang et al.	2009	Australian Newlands sub- bituminous coal	Х	Steam	Horizontal corundum tubular reactor	700-900	Atmospheric pressure	
Wu et al.	2006	Yanzhou coal	X	Steam	Fixed bed	900-1200	Atmospheric pressure	

Authors of the experiments		Feedstock		Gasification	G	Operation conditions	
	Year	Coal	Biomass	agents	Gasifier	Temperature (°C)	Pressure
Aznar et al.	2006	Coal	Plastic waste, Pine sawdust	Air	Fluidized bed	750-880	Atmospheric pressure
Alzate et al.	2009	A sub- bituminous coal	Pinus Patula, Cypress sawdust	Steam	A 304 steel cylindrical fluidized bed	850	50-60 psig
André et al.	2005	Lignite from Spain	Bagasse, Pine	Air - Steam	Fluidised bed	730-900	Atmospheric pressure
Collot et al.	1999	Daw Mill Coal	Silver birch Wood	Air - Steam	A fixed- bed and a fluidized bed	850/1000	25bar
Fermoso et al.	2009	Bituminous coals from China, Spain, South Africa	Olive pulp, Pine sawdust	Oxygen/ Steam mixture	fixed bed	1000	1 and 15 atm
Fermoso et al.	2009	A bituminous coal	Olive stone, Eucalyptus	Air - Steam	A stainless steel tubular reactor	850-1000	0.5 - 2 Mpa
Kajitani et al.	2009	Australian bituminous, Chinese bituminous	Cedar	Carbon dioxide	two stage entrained flow gasifier	1200-1300	0.5MPa
Kumabe et al.	2006	Mulia coal from Indonesia	Japanese cedar	Air - Steam	downdraft fixed bed	900	Atmospheric pressure

Table 2-3: The summary of reported co-gasification experiments in literature

# Table 2-3 (continued)

Lapuerta et al.	2008	Coal-coke	Pinus, Olive, Sawdust	Air	A circulating flow gasifier	1250	Atmospheric pressure
Li et al.	2009	A Chinese bituminous coal	Pine sawdust, Rice straw	Oxygen-rich air / Steam	A bench- scale fluidized bed	900	Atmospheric pressure
Mastellone et al.	2010	Lignite	Wood	Air - Steam	A bubbling fluidised bed	850	Atmospheric pressure
Pan et al.	2000	Black coal, Sabero coal	Pine Chips	Air - Steam	A fluidized bed	840-910	Atmospheric pressure
Pinto et al.	2003	Coal	Pine, Waste plastic	Air - Steam	A fluidized bed	750-890	Atmospheric pressure
Pinto et al.	2009	Colombian coal, Puertollano coal	Pine, Bagasse, Polyethylene	Steam and air/oxygen	A fluidized bed	850	Atmospheric pressure
Vélez et al.	2009	Colombian coal (sub- bituminous)	Sawdust, Rice, Coffee husk	Air - Steam	A fluidized bed	750-850	Atmospheric pressure
Yan and Lu	2009	Lignite	Herbaceous, Woody biomass	Air - Steam	A bubbling fluidized bed	900	Atmospheric pressure
Xu et al.	2011	Lignite	Wood	Steam	A bench scale gasifier	850, 900 and 950	Atmospheric pressure

# **2.1** Effect of operation temperature on producer gas in gasification studies of coal, biomass and their blends

The gasification temperature shows remarkable influence on the gasification performance of pure coal, pure biomass and their blends, since the balance between endothermic and exothermic gasification reactions is determined by the operation temperature. Therefore, the reactor temperature has a significant influence on the producer gas yields and composition (Pan et al. 2000).

When the gasification temperature was elevated, the gas yields were increased and the char and tar contents were reduced. These effects could be due to several reasons. Firstly, the increased temperature clearly favors the formation of volatile matter during the initial devocalization step. Secondly, endothermic reactions of tar cracking and char gasification are enhanced at elevated temperatures (Pinto et al. 2003; Wei et al. 2007).

The quality of producer gas is determined by the contents of each component in the producer gas. The main components of the producer gas are  $H_2$ , CO and CO<sub>2</sub>, and small quantities of minor hydrocarbons, such as CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>. It is thus important to understand how temperature influences the composition of producer gas.

#### 2.1.1 Hydrogen content

It has been found from the literature that elevated temperatures clearly favoured the formation of  $H_2$  in all of the aforementioned experimental studies (Detournay et al. 2010; Küçük and Demirbas 1997; Lee et al. 1998; Umeki et al. 2009a; Umeki et al. 2009b; Wang et al. 2009b; Yan et al. 2010), although their temperature ranges were different, as shown in Table 2-1, Table 2-2 and Table 2-3.

According to the thermodynamic principle, higher temperatures favoured the reactant direction in exothermic reactions and favoured the products direction in endothermic reactions. Therefore, the endothermic **Reactions (1), (2)** and **(6)** (given in **Chapter 1**) were enhanced with increased temperature, so that the equilibrium shifted towards the side with  $H_2$  formation, which resulted in a significant increase in  $H_2$  production (Lv et al. 2004).

Based on the gasification processes, the increase in gasification temperature led that a greater volatile matter which contained  $H_2$  was released during the devolatilization, the first steps of gasification (Lapuerta et al. 2008). And then, the rise in temperature clearly favoured a secondary cracking and reforming of tars and heavy hydrocarbons, leading to an increase in  $H_2$  generation (Franco et al. 2003; Pinto et al. 2003; Wei et al. 2007). Therefore, it could be inferred that higher temperatures are more favourable for hydrogen yield.

#### 2.1.2 Carbon monoxide content

The influence of gasification temperature on the CO content was also detected through a series of experiments; however, the results were conflicting. Several experiments indicated that raising the temperature resulted in an increase in the fraction of CO (Aznar et al. 2006; Detournay et al. 2010; Fermoso et al. 2009b; Lee et al. 1998) because the endothermic **steam gasification** (1) is significantly enhanced at higher temperatures. Furthermore, as the reaction temperature increased, carbon tended to react with  $CO_2$ , through the **Boudouard reaction** (4), displacing the equilibrium to CO formation.

However, other experiments (Luo et al. 2009; Lv et al. 2004; Wang et al. 2009b) displayed the opposite trend in which CO content decreased with an elevated temperature (Luo et al. 2009). A possible explanation is that CO content was mainly determined by **partial combustion reaction** (7) which is an exothermic reaction. Hence, higher temperatures were not favourable for CO production.

A few of further experiments were also reported (André et al. 2005; Smolinski et al. 2010) in which no significant changes in CO content were detected in the producer gas with increased gasification temperature.

#### 2.1.3 Carbon dioxide content

It was observed that the CO<sub>2</sub> content was significantly decreased with a rise in gasification temperature in the experiments reported by André et al. (2005); Aznar et al. (2006); Detournay et al. (2010); Lee et al. (2007); Pinto et al. (2003) and Smolinski et al. (2010). As thermodynamically predicted, at lower temperatures, the **carbon oxidation reaction (8)** is more significant than carbon gasification, as it is exothermic. Then, with a rising temperature, the combustion reaction is further inhibited so that less CO<sub>2</sub> was produced. Besides, the consumption of CO<sub>2</sub> through the **Boudouard reaction (4)**, which is an endothermic reaction, can also contribute to the reduced CO<sub>2</sub> content in the producer gas when the gasification temperature is increased.

However, one experiment by Luo et al. (2009) indicated a contrary trend for increased gasification temperature, with  $CO_2$  content increasing significantly with temperature raised from 600-900°C.

#### 2.1.4 Methane content

A lot of experiments (André et al. 2005; Lee et al. 1998; Pinto et al. 2003; Rezaiyan and Cheremisinoff 2005; Smolinski et al. 2010) have detected the same trend of  $CH_4$  content decreases with the rise in gasification temperature. This was believed to be caused by the exothermic **hydro-reaction** (5) in which high temperatures can inhibit the  $CH_4$  formation. Furthermore, the increased temperatures promote the endothermic **steam methane reforming reaction** (6), leading to the consumption of the methane.

However, reports from a few of other experiments (Fermoso et al. 2009b; Lapuerta et al. 2008) showed a different result: the production of  $CH_4$  remained almost constant and was not affected by the variation in reaction temperature. This indicated that  $CH_4$  was produced mainly during the devolatilization step.

#### 2.1.5 Overall views on gas production

As has been reported in the literature, the results were related to the fact that the fraction of  $H_2$ , CO, CO<sub>2</sub> and CH<sub>4</sub>, were linked together by the equilibrium of the reactions (1) to (8) under test conditions. Hence some authors suggested that either one or several reactions were more dominant at a certain temperature than the rest of the reactions. Conflicting results in producer gas composition were therefore caused by the difference in setting temperature.

In Yan et al. (2010)'s studies,  $H_2$  content and hydrogen yield increased significantly with temperatures ranging from 600 to 850 °C in which temperature range CO<sub>2</sub> and CH<sub>4</sub> molar fractions increased to reach the maximum value at a temperature of 700°C and then decreased. Contrastingly, CO content decreased between 600 and 700 °C and rose between 700 and 850 °C, with the minimum value obtained at 700°C.

The significant decrease in CO observed between  $600 - 700^{\circ}$ C, while contrary trends appeared for the content of other gases, indicates that the **water-gas shift reaction (3)** was more dominant than devolatilization.

With an increase in temperature from 700 to 800 °C, small decreases in  $CO_2$ ,  $CH_4$  and an increase in CO were detected, indicating that the **water-gas shift reaction (3)** and devolatilization reaction had less importance, whereas the **steam reaction (1)**, **Boudouard reaction (4)** and **steam methane reforming reaction (6)** had significant influence on gases compositions.  $H_2$  content increased significantly with the gasification temperature for the same reason.
At temperatures higher than  $800^{\circ}$ C, a dramatic decrease in CO<sub>2</sub>, CH<sub>4</sub> and an increase in CO were observed, which illustrates the **steam reaction** (1), **Boudouard reaction** (4) and **steam methane reforming reaction** (6) playing more prevailing roles while the converse reaction might have occurred.

The same results from another study (Vélez et al. 2009) showed that, for high temperatures, the steam reaction (1), Boudouard reaction (4) can be more influential than the water-gas shift reaction (3).

Therefore, at a certain gasification temperature, one or several reactions are more dominant than the rest. It is necessary to investigate that how gasification temperature influences the producer gas composition in this project.

# 2.2 Effect of blended coal and biomass on producer gas in cogasification studies

Previous studies as shown in Table 3-3 have been reported on the investigation of the catalytic effects in co-gasification of blended coal and biomass. In these literatures, the relationship between the composition of producer gas and the blending ratio in the coal-biomass blends were reviewed. In the experiments of the reported studies, the operating conditions such as gasification temperature and flow rate of gasification agent (steam, air or oxygen) were kept constant in each experiment. The experimental conditions of co-gasification are listed in Table 2-3 and the observations from ten studies are summarized as follows:

**Case 1**: In the experiments of Li et al. (2009), it has been found that the increase in biomass proportion in the coal-biomass blend led to increase  $H_2$  content and decrease CO content.

**Case 2**: A separate study of Lapuerta et al. (2008) showed an increase in CO,  $H_2$  and CH<sub>4</sub> with increasing of the biomass content in the blend fuel.

**Case 3**: Another study by André et al. (2005) showed that an increase in biomass content resulted in an increase in CO content and a decrease in  $H_2$  content. In this study, CO<sub>2</sub> remained relatively constant (showing an insignificant variation) and CH<sub>4</sub> content was slightly increased.

**Case 4**: In the study of Kumabe et al. (2006), the  $H_2$  content decreased and  $CO_2$  content increased with an increase in the biomass ratio in the coal-biomass blend. In contrast, the contents of CO and CH<sub>4</sub> were independent of the biomass ratio.

**Case 5**: Further experimental study about the gasification of biomass-coal pellets was performed by Alzate et al. (2009) who found that as the quantity of coal in the pellets increased, the  $H_2$  content in the producer gas was decreased while the  $CH_4$  content increased. The CO content changed when plotted against the coal-biomass ratio, showed as curvature, with the minimum value occurring at around 20% of coal in pellets. This trend is contrary to the tendency of  $CO_2$  change which was the maximum at around 20% of coal in the coal-biomass blend.

**Case 6**: Another recent study of Yan and Lu (2009) found that the  $H_2$ , CO and  $CH_4$  contents increased and only  $CO_2$  content decreased with an increases in the biomass (pine sawdust) ratio. In another experiment using a different biomass (straw), before the biomass percentage increased from 0% to 30%, the content of CO firstly increased, and then decreased as the straw proportion increased to 100%. The trends of other producer gas contents ( $H_2$ ,  $CO_2$  and  $CH_4$ ) were as similar as that from co-gasification of coal-pine blend but the CO content displayed a different trend - it increased at first and then decreased.

**Case 7**: From studies of de Jong et al. (1999) and Vélez et al. (2009), it was found that gasification of pure biomass produces a higher concentration of combustible syngas (hydrogen and carbon monoxide) than coal-biomass blends.

**Case 8**: Two studies conducted by Fermoso et al. (2009a; 2009b) have shown that the production of  $H_2$  and CO increased with additions of biomass. A slight increase in  $CO_2$  production was also observed. An increased in gas production was predictable, as biomass fuels are much more reactive than coal. It was also found from these two studies that the carbon conversion of the coal-biomass blends was higher than that of gasification of pure coal. This finding has indicated that the interactions between the coal and biomass fuels during the gasification have promoted the gasification rate due to the high reactivity of the biomass fuel.

In the mentioned studies above, it has been found that the effects of blended coal and biomass on producer gas were inconsistent. The results of those studies may be caused by several reasons:

Firstly, biomass has higher volatile matter content than coal (Kumabe et al. 2006; Yan and Lu 2009); therefore, the increase in biomass content in blends produced the more volatile matter during devolatilization and thus the contents of producer gas (such as  $H_2$ ,  $CH_4$ ) were increased.

Secondly, biomass has lower fixed carbon content than coal; hence the increase in biomass ratio reduced the total amount of gasified carbon in blends (Li et al. 2009). It caused that the **steam reaction** (1) and **Boudouard reaction** (4) was inhibited, leading to increase the  $CO_2$  content and decrease the  $H_2$  and CO content.

Thirdly, the high reactivity of biomass lead to a faster volatile release, causing the increase in the syngas production in the gasification processes (de Jong et al. 1999; Fermoso et al. 2009a; Lapuerta et al. 2008).

Finally, the variability in the feedstock materials, gasifier type and operation conditions are also believed to affect the results significantly.

From the above discussion, the influences of blended coal and biomass on the producer gas were not conclusive. An important factor for this is believed to the solid fuel (coal and biomass) characteristics which vary significantly with the type and location of fuels. However, few reports are found on gasification of New Zealand coal and biomass resources and their blends. Therefore, it is important to experimentally investigate the catalytic effects of New Zealand coal and biomass in gasification.

# 2.3 Effect of AAEM in the gasification studies

The overall efficiency of gasification is determined by the conversion rate of the solid chars which are generated from the initial devolatilization process. In turn, the rate of char gasification directly depends on the char reactivity (Asadullah et al. 2010; Tay and Li 2009) which are essentially influenced by the structural properties and the intrinsic reactivity of the chars. The structural properties include the surface area and porosity, while the intrinsic reactivity reflects the surface chemistry and catalytic effect of the inorganic compounds (Everson et al. 2006), such as alkali and alkaline earth metals (AAEM). The catalytic effect of AAEM is an important factor and also the most variable property of the coal-biomass blend in the co-gasification.

It is known that AAEM are active catalysts for gasification. Among these AAEM species, calcium (Ca) and potassium (K) are the most promising. The former is presented in the coal, whereas the latter is abundant in some herbaceous biomass

resources (Zhang et al. 2010). A series of studies (Li et al. 2004a; Matsumoto et al. 2009; Quyn et al. 2002; Wu et al. 2002) on the catalytic effect of AAEM species on char reactivity in individual coal or biomass gasification were investigated. From these studies, it was found that the presence of AAEM had a significant influence on the char structure as well as its reactivity in the gasification step (Huang et al. 2009; Mitsuoka et al. 2011).

#### 2.3.1 The mechanisms of AAEM in gasification

The mechanisms of AAEM may be explained by the following steps. These theories may explain why AAEM species exhibit positive catalytic effects on gasification performance.

Firstly, during the initial rapid pyrolysis of coal and biomass, AAEM species were easily desorbed from the solid surface into the volatile phase, where AAEM species (mainly Ca and K) were associated with the carboxyl and phenolic groups to form part of organic substance in coal or biomass (Quyn et al. 2003). Simultaneously, the organic molecules in the solid phase rearranged to form a micro-crystalline structure of char; therefore, the char structure changed and became more porous to promote the reactivity during gasification (Mitsuoka et al. 2011).

Secondly, during the volatile-char interactions, AAEM species in the vapour phase were re-adsorbed onto the surface of the porous char (Li et al. 2006; Li and Li 2006). the formation of intermediate alkali-surface compounds between AAEM species and carbon also increased the interlayer distance and caused total pore volume expansion, thus the C-C bonds existing between layers were weakened and the gasification reactions were enhanced (Huang et al. 2009). And then the re-adsorbed AAEM and the residual AAEM in solid char participates the char gasification process, which decreased the energy activation of gasification reactions (Leboda et al. 1998).

#### 2.3.2 The reactions of AAEM mechanism in gasification

Several researchers (Brown et al. 2000; Jaffri and Zhang 2008a; Jaffri and Zhang 2008b) have proposed the reactions scheme for explanation the effects of AAEM species during the gasification. As catalysts, AAEM species can participate in the gasification process by undergoing chemical or electronic interaction with the carbonaceous substrate. Specifically, an oxidation-reduction cycle by carbon takes place to form intermediate alkali-surface compounds. These are represented by [-COM] called a phenolic alkali metal surface oxide group and  $[-CO_2M]$ , which is known as a carboxylic alkali metal surface oxide group (Wang et al. 2009b):

$$M_2CO_3(s) + C(s) \leftrightarrow [-COM](s) + [-CO_2M](s)$$

During gasification the steam on carbon particle surface reacts with the intermediate alkali surface compounds to form  $H_2$  and CO as described in the following reactions:

$$[-COM](s) + H_2O(g) \leftrightarrow [-CO_2M](s) + H_2(g)$$

$$[-CO_2M](s) + C(s) \leftrightarrow [-COM](s) + CO(g)$$

$$[-COM](s) + CO_2(g) \leftrightarrow [-CO_2M](s) + CO(g)$$

The carbon particles react with  $H_2O$  at the carbon particle surface as the steam gasification reaction and Boudouard reaction:

$$C + H_2 O \Leftrightarrow CO + H_2$$

 $C + CO_2 \Leftrightarrow CO$ 

However, few reports have been found in literature on the effect of AAEM on the quality of producer gas in the gasification. In this project, as one of selected fuel samples, lignite contains significantly AAEM species, especially calcium (Clemens et al. 1998). Hence, the effects of AAEM in lignite on gasification characteristics (producer gas and char reactivity) will be investigated in this project.

# 2.4 Synergistic effects in co-gasification

The synergistic effects in co-gasification is defined as A few studies of the synergistic effects in co-gasification (Demirbas 2002; Lapuerta et al. 2008; Sjöström et al. 1999; Zhang et al. 2007) have found that the synergistic effects existed when coal and biomass were blended in co-gasification. Therefore, sufficient data are not available for explaining the observations. However, it might be suggested through the following mechanisms:

The effects may be caused by high volatile matter content and high reactivity in biomass. When coal-biomass blends are fed into the reactor, the biomass will react rapidly, releasing a high amount of volatile matter via the thermal or oxidative cleavage of the weakest covalent bonds in the organic matter. This matter then rapidly decomposes and forms a high number of free radicals, which react not only with the organic matter of the biomass, but possibly with the coal as well, thereby favouring decomposition and oxidation/gasification reactions in the coal. Furthermore, the hydrogen-rich light molecules produced from the devolatilization of the biomass and the cracking of violates may react with the volatiles produced from coal, thereby preventing recombination reactions and the formation of less reactive secondary char.

In order to investigate the synergistic effects in co-gasification of coal-biomass blend chars and explain the observations, four types of coal-biomass blend chars are used to exam the performance of synergistic effects in co-gasification.

# **3 Experiments and Methodology**

As a major part of this project, the proposed experimental work was carried out on a bench scale gasifier, where chars of pure biomass, pure coal and their blends were gasified with steam as gasification agent.

### **3.1 Materials**

Two different ranks of coals found in New Zealand (*Lignite* and *Sub-bituminous coal*), as well as two types of woody biomass, *Radiata pine* (*Pine*) and *Eucalyptus nitens* (*E. nitens*), were selected as solid fuels for the experiments. Lignite and sub-bituminous are both typical low rank coals and their reserves are enormous in New Zealand. Pine is the most common species in New Zealand plantation (Forestry 2009). E. nitens is a short rotation plantation hardwood species. All of the four fuel samples have abundant resources in New Zealand and suitable for energy resources.

	Pine	E. nitens	Lignite	Sub-bituminous		
Proximate analysis (% w/w as received basis)						
Fixed Carbon	13.9	12.7	34.1	42.4		
Volatiles	78	81.5	41.9	38.6		
Ash	0.34	0.38	4.9	5.4		
Moisture	7.8	5.4	19.1	13.6		
Ultimate analysis (% daf)						
Carbon	47.2	47.5	50.6	59.4		
Hydrogen	5.41	5.57	3.64	4.1		
Nitrogen	< 0.03	< 0.03	0.55	1.03		

Table 3-1: Proximate analysis and ultimate analysis of solid fuel samples

Table 3-1 presents the results from both the proximate and ultimate analysis for the four types of solid fuels tested. Proximate analysis and Ultimate analysis are two general methods to examine the composition of fuel species. The former one is used to measure the proportions of moisture content, ash content, volatile matter content

and fixed carbon content, while the latter one is used to analyze the elemental composition, such as carbon, hydrogen, oxygen, nitrogen and Sulfur

# **3.2 Solid fuel sample preparations**

### 3.2.1 Pulverization

Before the experiments, the four solid fuel feedstock materials were firstly pulverized through a ring mill and sieved to powders with particle size of less than 0.5 mm, as shown in Figure 3-1. In order to investigate the catalytic effects of the alkali and alkaline earth metals (AAEM) in the lignite, some lignite powder was acid-washed to remove the AAEM in the powder. The pulverized powders were maintained in the dry containers for the next treatment.



Figure 3-1: Solid fuel materials in the original forms as received and in the power form for the gasification experiments

The pulverized samples (coal and biomass) were thoroughly mixed with coal-tobiomass blending ratio in different batches of 0 wt%, 20 wt%, 50 wt%, 80 wt% and 100 wt% of coal. The identification numbers for the coal-biomass blends are given in Table 3-2.

	Pine	E. nitens
Lignite	No. 1	No. 2
Sub-bituminous	No. 3	No. 4
Acid-washed lignite	No. 5	No. 6

Table 3-2: Identification number for the blended coal and biomass

#### 3.2.3 Pelletization and charring processes

After the pulverization and blend process, the powders were compressed under a pressure of 1.6 MPa in a mould to produce cylindrical pellets approximately of ~10mm in length and 8 mm in diameter as shown in Figure 3-2 for the lignite-biomass pellets. The pelletization was to prevent the segregation of coal and biomass during charring.

Pellets	00	MO	80	BO	
Chars					•
	0% Lignite 100% P. Radiata	20% Lignite 80% P. Radiata	50% Lignite 50% P. Radiata	80% Lignite 20% P. Radiata	100% Lignite 0% P. Radiata
Pellets	IND.		-		
Chars				•	ði.
	0% Lignite 100% E. nitens	20% Lignite 80% E. nitens	50% Lignite 50% E. nitens	80% Lignite 20% E. nitens	100% Lignite 0% E. nitens

Figure 3-2: Samples of pellets and chars

Table 3-3	(a): Proximate	analysis	of lignite-	pine blend	d chars
	(	j~-~			

Lianita Dina	Proximate analysis (% w/w as dry basis)			
Liginte - Pine	Fixed Carbon	Volatiles	Ash	
0 - 100	95.9	2.1	1.9	
20 - 80	91.8	3.2	4.9	
50 - 50	87.4	4.3	8.3	
80 - 20	82.3	4.8	10.7	
100 - 0	81.4	5.0	12.9	

Table 3-3 (b): Proximate analysis of lignite-E. nitens blend chars

Lianita E nitana	Proximate analysis (% w/w as dry basis)				
Liginte - E. mtens	Fixed Carbon	Volatiles	Ash		
0 - 100	92.7	4.0	3.2		
20 - 80	89.4	4.2	6.0		
50 - 50	85.7	4.6	9.7		
80 - 20	84.5	5.1	10.4		
100 - 0	81.4	5.0	12.9		

Sub-bituminous -	Proximate analysis (% w/w as dry basis)			
Pine	Fixed Carbon	Volatiles	Ash	
0 - 100	95.9	2.1	1.9	
20 - 80	90.1	4.8	5.2	
50 - 50	88.2	4.9	8.7	
80 - 20	86.6	3.3	10.1	
100 - 0	85.4	3.7	10.9	

Table 3-3 (c): Proximate analysis of sub-bituminous-pine blend chars

Table 3-3 (d): Proximate analysis of sub-bituminous-E. nitens blend chars

Sub-bituminous - E.	Proximate analysis (% w/w as dry basis)			
nitens	Fixed Carbon	Volatiles	Ash	
0 - 100	92.7	4.0	3.2	
20 - 80	89.5	4.1	6.4	
50 - 50	87.6	3.6	8.8	
80 - 20	86.6	3.5	9.8	
100 - 0	85.4	3.7	10.9	

Sample char was produced by heating up the prepared pellets, which were placed into an oven for 7 minutes at a temperature of 900°C to remove the volatile components. The char samples for the lignite-biomass blends are also shown in Figure 3-2 under the corresponding un-charred pellets. The proximate analysis of coal-biomass blend chars is listed in Tables 3-3 (a) to 3-3 (d).

### 3.2.4 Acid washing

In order to investigate the effect of AAEM in the lignite on gasification performance, some lignite powder was washed using mid-acid to remove the AAEM. This was done in a beaker by stirring for 15 minutes in a 1 mol per litre solution of hydrochloric acid (HCl) at room temperature. The acid-washed powder sample was then filtered and washed repeatedly with distilled water until the washing gave no indication of

chloride in treatment with silver nitrate solution. Finally the washed lignite powder was pelletized and charred.

# **3.3 Experimental equipments and procedures**

### 3.3.1 Equipments

The bench scale gasification system is sketched in Figure 3-3 and its photo is shown in Figure 3-4. In the system, nitrogen gas is introduced as an inert gas carrier. This system contains a bench scale gasifier, a steam generator and a gas preheater, a water cooling system and a micro gas chromatograph.



Figure 3-3: Flow diagram of gasification apparatus

The gasifier is made of a special glass with 1.5mm in thickness which can stand high temperatures of over 1000°C. Its dimensions are 36mm in diameter and 350mm in

height. A porous quartz frits with a 4mm thickness is fixed inside and close to the bottom of the gasifier, above which the solid char particles were held during the gasification tests. The gasifier is placed and heated by an electrical oven. This oven's temperature is controlled at temperatures of up to 1200°C. One pair of K-type thermocouples are placed above the fritz to measure the temperature inside the gasifier.

The preheater is used for heating the mixture of steam and nitrogen up to 300°C. The water cooling system consists of a condenser and a water bottle, which were applied to reduce the temperature and to remove condensed water in producer gas, respectively. A dehumidifier absorbs the residual vapour in the producer gas. Finally, the MTI M200 micro gas chromatograph (Micro-GC) is used to analyse the gas content in producer gas.



Figure 3-4: Gasification apparatus

#### 3.3.2 Experiment procedures

For each experimental run, 1 gram of sample char was first fed into the bench scale gasifier. Then pure nitrogen gas was continuously supplied with its flow rate being manually controlled at 0.6 litres per minute by a valve and the flow rate was monitored by the gas flow meter. Before entering the gasifier, the nitrogen was preheated to 300°C through the pre-heater. When the gasifier was fully filled with heated nitrogen, the gasifier was heated to a set temperature (850°C, 900°C or 950°C) by controlling the electrical oven.

After the temperature inside the gasifier became stable at the set point, the water pump was turned on to inject the distilled water at a flow rate of 1.79 millilitres per minute into the steam generator which was also turned on once it was filled with water. Once being generated, the steam was mixed with the heated nitrogen; the steam-nitrogen mixture was then flowed into the top of the gasifier in which the steam reacted with the sample char.

The producer gas was generated and flowed out from the bottom of the gasifier with the carrier gas (nitrogen). The flow rate of the producer gas was measured by a flow meter and its composition (H<sub>2</sub>, CO, and CO<sub>2</sub>, as well as N<sub>2</sub>) was analysed by the MTI M200 Micro-GC. The sample gas was taken and analysed every 60 seconds. Each experiment was continued until all of the concentrations of H<sub>2</sub>, CO, and CO<sub>2</sub>, were less than 0.5%, which was shown on the GC monitor.

# **3.4 Methodology**

### 3.4.1 Experimental variations

The effects of experimental conditions on the gasification process and on the gas composition were evaluated. Apart from the sample char species as shown in Table 3-2, the variables investigated also included gasification temperature and blending ratio of coal and biomass.

In this study, a total number of 90 experimental runs were performed, which included six combinations of coal-biomass blends (lignite-pine, lignite-E. nitens, sub-bituminous-pine, sub-bituminous-E. nitens, acid-washed lignite-pine, acid-washed lignite-E. nitens), five blended ratios of coal to biomass (0-100, 20-80, 50-50, 80-20, 100-0) and three gasification temperatures (850, 900 and 950°C) as shown in Table 3-2 and Table 3-4. At least three runs were carried out for each data point to ensure data reliability.

Temperatures Blended ratio (coal : biomass)	850°C	900°C	950°C
0-100	Х	Х	Х
20-80	Х	Х	Х
50-50	Х	Х	Х
80-20	Х	Х	Х
100-0	Х	Х	Х

Table 3-4: The variables for gasification tests

In this study, the effects of experimental parameters as described above on producer gas composition and on gasification output parameters were analyzed, which included char reactivity, producer gas yield and production rate.

For each experimental run, the composition of the producer gas varied with elapsed time and this was recorded from the continuous micro-GC analysis. In the experiments, nitrogen acted as an inert and carrier gas, which flowed into the gasifier at a constant flow rate of 0.6 litres per minute. The results of gas yield and gas composition were analyzed from the experiments and the gas components of the producer gas analysed included hydrogen (H<sub>2</sub>), carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>).

The gasification output parameters (gas yield and gas composition) were calculated using the following methods:

#### 1) Producer gas yield

Producer gas yield (Y) was estimated as:

$$Y = \sum_{t=0}^{t} F(t) \times \Delta t \tag{3-1}$$

$$F(t) = \frac{F_{nitrogen}}{N_{Nitrogn}(t)} \times N_{one \ producer \ gas}(t)$$
(3-2)

, in which  $\Delta t$  is the time interval of 60 second, F(t) is producer gas flow rate (L/s) at a certain time interval,  $N_{Nitrogn}$  and  $N_{one \, producer \, gas}$  are, respectively, the nitrogen content and the gas content for H<sub>2</sub>, CO or CO<sub>2</sub> at the same certain time interval, which values were obtained from the micro GC analysis,  $F_{nitrogen}$  is the flow rate of nitrogen, 0.6 litre per minutes = 0.01 litre per seconds.

#### 2) Char reactivity

Char mass remained in the gasifier (m) at time t is determined as the difference between the original char mass  $(m_0)$  and the accumulated carbon  $m_{consumed}$  reacted:

$$m_{consumed}(t) = \sum_{t=0}^{t=i} \frac{[Y_{CO}(t) + Y_{CO_2}(t)] \times \Delta t}{v_0} \times M_{carbon} \dots (3-3)$$

$$m(t) = m_0 - m_{consumed}(t) \dots (3-4)$$

, in which  $Y_{CO}(t)$  and  $Y_{CO_2}(t)$  are the gas volume of CO and CO<sub>2</sub> at the certain time interval,  $v_0$  is the gas constant volume at reference conditions (22.4 litre/mole),  $M_{carbon}$  is molar weight of carbon, 12 gram/mole.

Once the reacted carbon is determined, the char conversion percentage (X) can be calculated by:

$$X(t) = 1 - \frac{m(t)}{m_0} \times 100\%$$
(3-5)

Char reactivity (r) at time *t* is related to the carbon conversion rate as the following equation:

$$r = \frac{1}{1 - X(t)} \frac{dX}{dt} = -\frac{1}{m(t)} \frac{dm}{dt}$$
(3-6)

#### 3) Syngas production rate

The average syngas (H<sub>2</sub>, CO or CO<sub>2</sub>) production rate (SPR) is calculated as:

$$SPR = \frac{Accumulative gas yield of producer gas}{Total gasification time}$$
(3-7)

### 4) The calculation for synergistic effect test

In order to investigate whether synergistic effects exist when coal and biomass were blended, the prediction has to be calculated from each individual fuel on the basis of the absence of synergistic effects.

$$X_{mix} = F_{coal}X_{coal} + F_{biomass}X_{biomass}$$
(3-8)

In which  $X_{coal}$  and  $X_{biomass}$  are the data from pure coal char and pure biomass char gasification,  $F_{coal}$  and  $F_{biomass}$  are the fraction of single fuel in the coal-biomass blend char, and  $F_{coal} + F_{biomass} = 100\%$ .

If the experimental results deviate from the predicted results  $X_{mix}$  by more than 5% (experimental error), then the occurrence of synergistic effects have been identified.

#### 3.4.3 Assumptions

In this project, several assumptions are stated.

- The component of char is 100% carbon only.
- Gas productions only include H<sub>2</sub>, CO and CO<sub>2</sub>.
- A less amount of hydrocarbon compounds, such as CH4, is negligible.

• The vapor in gas production after passing the water bottle is negligible.

#### 3.4.4 Error analysis

In each experimental test, three parameters have to be collected and recorded manually, which were 1) the mass of char before gasification, 2) the mass of ash after gasification, and 3) the volume of water from non-reacted steam (which is trapped in the water bottle after the water cooling system), as shown in **Appendixes A**. Hence, the reproducibility of experimental results has to be checked and a good agreement of the data among the three repeating runs was obtained, with experimental errors lower than 5%.

The error analysis was demonstrated in carbon balance and oxygen balance.

<u>Carbon balance:</u> all carbon elements in gas production are from the carbon in char reacted.

$$Carbon_{\exp} = M_{char} - M_{ash}$$
(3-9)

$$Carbon_{cal} = M_{carbon} \times (n_{CO} + n_{CO_2})$$
(3-10)

$$\% error = \frac{\left|Carbon_{exp} - Carbon_{cal}\right|}{Carbon_{exp}} \times 100\%$$
(3-11)

, where  $M_{char}$  is the mass of char before gasification (g),  $M_{ash}$  is the mass of ash after gasification (g),  $M_{carbon}$  is the molar mass of carbon, 12g/mol,  $n_{CO}$  is the molar number of CO and  $n_{CO_2}$  is the molar number of CO<sub>2</sub>.

Oxygen balance: the oxygen elements in gas production are from the oxygen elements in steam.

$$Oxygen_{exp} = \frac{Flow_{steam} \times t - V_{water}}{1000 \, ml/l} \times M_{water}$$
(3-12)

$$Oxygen_{cal} = (n_{CO} + 2 \times n_{CO_2})$$
(3-13)

$$\% error = \frac{|Oxygen_{exp} - Oxygen_{cal}|}{Oxygen_{exp}} \times 100\%$$
(3-14)

, where  $Flow_{steam}$  is the flow rate of steam, 1.79 ml/min, t is the total gasification completion time (min),  $V_{water}$  is volume of water trapped in water bottle,  $M_{carbon}$  is the molar volume of water, 55.6 mol/l,  $n_{CO}$  is the molar number of CO and  $n_{CO_2}$  is the molar number of CO<sub>2</sub>.

# **4 Results**

### 4.1 Char yields from devolatilization

Devolatilization, also termed as pyrolysis, is the first step prior to generation solid chars for char gasification. In this project, the devolatilization was conducted at a temperature of 900°C for 7 minutes for preparation of chars for steam gasification tests, where the coal-biomass blend pellets were made at the coal to biomass blending ratios of 100:0, 80:20, 50:50, 20:80 and 0:100. The char yields of coal-biomass blends at various blending ratios in the devolatilization process are demonstrated in Table 4-1.

As expected, the average char yield of pure coal is approximately 45% which is much higher than that of pure biomass (about 17%). Since coal has lower volatile matter and higher fixed carbon content, compared with biomass; the coal yields higher content of solid char in the devolatilization process (Haykiri-Acma and Yaman 2010). According to proximate analysis (Table 3-1), the pure lignite coal has 41.9 wt% volatile and 34.1 wt% fixed carbon whereas the sub-bituminous has 38.6% volatile and 42.4% fixed carbon. The corresponding values for pine are 78% and 13.9% while those for E. nitens are 81.5% and 12.7%.

The results of devolatilization of the four selected fuel samples follow the same trends as the proximate analysis and the char yields decreased in the following sequence: sub-bituminous coal produced the most amounts of char (49%), followed by lignite (41%), pine (18%) and E. nitens (15%). The char yield of coal-biomass blends was related to ratio of the coal to biomass and the char yield of each fuel. It has been observed that an increase in coal proportion in the coal-biomass blend increases the char yield of the blend. These results were presented in Table 4-1.

Coal / Biomass	Ratio	Char yield
	80 / 20	36%
Lignite-Pine	50 / 50	29%
	20 / 80	23%
	80 / 20	43%
Sub-bituminous-Pine	50 / 50	34%
	20 / 80	25%
	80 / 20	38%
Lignite-E. nitens	50 / 50	29%
	20 / 80	21%
	80 / 20	44%
Sub-bituminous-E. nitens	50 / 50	33%
	20 / 80	24%
Lignite	100	41%
Sub-bituminous	100	49%
Pine	100	18%
E. nitens	100	15%

Table 4-1: Char yield of coal-biomass blend from devolatilization

### 4.2 Results of individual coal and biomass char gasification

In this work, steam gasification of chars generated was experimentally investigated in a bench scaled gasifier. This section will present the results from steam gasification of four pure fuel chars (lignite, sub-bituminous, pine and E. nitens) whereas the results for the gasification of blended chars will be presented in the following section.

The producer gas compositions as a function of elapsed time are shown in Figures 4-1(a) to 4-1 (d) for steam gasification of lignite, sub-bituminous, pine and E. nitens at the gasification temperature of 950°C. In the figures, three major gas components of hydrogen (H<sub>2</sub>), carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>) are presented. The results for gasification temperature of 850°C and 900°C are included in Figures D-1 to D-4 in **Appendixes D**.

The generation of producer gas was determined by the reactions between char and the gasification agent described below. The main constituent of char was carbon. Therefore, in the steam char gasification, the main reaction was **Steam Gasification Reaction** (4-2), in which a large amount of hydrogen was produced.

$$C + H_2 O \Leftrightarrow CO + H_2 \tag{4-1}$$

CO and CO<sub>2</sub> may undergo the Water-Gas Shift Reaction (4-3) and the Boudouard Reaction (4-4):

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \tag{4-2}$$

$$C + CO_2 \Leftrightarrow 2CO \tag{4-3}$$

Based on these reactions, for both coal and biomass char gasification, the evolution of producer gas composition can be summarised as follows. Firstly,  $H_2$  content in producer gas was the highest confirming that the **Steam Gasification Reaction (4-1)** was the most dominant. Secondly, the CO content reached its peak value more rapidly than that of CO<sub>2</sub> content which can be attributed to the fact that the occurrence of the **Steam Gasification Reaction (4-1)** occurred prior to the **Water-Gas Shift Reaction** (4-2) and the **Boudouard Reaction (4-3)**. Thirdly, the CO and CO<sub>2</sub> contents in late stage of the gasification were approaching the equilibriums values determined by the **Water-Gas Shift Reaction (4-2)** and the **Boudouard Reaction (4-2)** and the **Boudouard Reaction (4-3)**.



(a)



(b)



(c)



(d)

Figure 4-1: The composition of producer gas from steam gasification of chars of lignite (a), sub-bituminous (b), pine (c) and E. nitens (d) at 950°C

# 4.3 Results of co-gasification of coal-biomass blend chars

Steam co-gasification of four coal-biomass blend chars (lignite-pine, lignite-E. nitens, sub-bituminous-pine and sub-bituminous-E. nitens), at the coal-biomass blending ratios of 100:0, 80:20, 50:50, 20:80 and 0:100, was carried out at gasification temperatures of 850, 900 and 950°C.

The gas composition results of co-gasification of coal-biomass blend chars, at the blending ratio of 50:50, with steam at the gasification temperature of 950°C are presented in Figure 4-2(a) for lignite-pine, in Figure 4-2(b) for lignite-E. nitens, in Figure 4-2(c) for sub-bituminous-pine and in Figure 4-2(d) for sub-bituminous-E.

nitens. The gas compositions for other blending ratios and gasification temperatures are presented in Figures E-1 to E-12 in **Appendix E**.

From Figures 4-2(a) to 4-2(d), it can be seen that for all of the coal-biomass blends, the producer gas contents for all of the gas components increased rapidly in the initial period to their peak values, and then decayed exponentially over a longer period of time until the completion of the gasification process. It is found that the evolution of producer gas content curves during the co-gasification of coal-biomass blend chars is similar to that of pure coal char gasification. This is unsurprising considering the much lower char yield of biomass than coal during the devolatilization; therefore, the coal char was more dominant in the co-gasification of the coal-biomass blend char. Hence, the curves of producer gas in coal-biomass blend char co-gasification resemble those of coal char rather than biomass char. Other authors also observed a similar behavior (Fermoso et al. 2010; Xu et al. 2011).



(a)



(b)



(c)



(d)

Figure 4-2: The composition of producer gas from steam gasification of coal-biomass blend chars of lignite-pine (a), lignite-E. nitens (b), sub-bituminous-pine (c) and sub-bituminous-E. nitens (d) at 950°C

# 4.4 Database and error analysis

The information and error analysis of all experimental tests are presented in the in Appendix G

# **5** Discussions

A series of gasification experiments have been performed in order to investigate the effects of types of coal and biomass, operation variances (gasification temperatures, blended coal-to-biomass ratio, AAEM present in lignite) on gasification reactivity, and producer gas composition and yields. Finally, the synergistic effects in co-gasification of coal-biomass blend chars are also investigated

### 5.1 Effects of fuel species

It is clear that the gasification of pure coal char and pure biomass char are quite different, based on the results of producer gas compositions as shown in Figures 4-1(a) to 4-1(d), both in terms of the gas composition values and the trends of changes with elapsed time. In addition, the completion time for gasification process is also different between the coal chars and the biomass chars. These differences can be due to the different characteristics between coal char and biomass char. Hence, it is important to examine the effects of feedstock species on producer gas composition and char reactivity.

### 5.1.1 Producer gas production

In Figure 4-1 (a) and Figure 4-1 (b), for the coal char gasification, the producer gas contents increase drastically initially before reaching their peak values (as listed in Table 5-1). After reaching their peak values, the curves decayed exponentially until coal char conversion was completed. The whole gasification process of lignite and sub-bituminous char took 1800 seconds and 2400 seconds, respectively.

In contrast to the sharp peaks displayed in coal char gasification, Figures 4-1 (c) and 4-1(d) display bell-shaped curves where producer gas compositions for the biomass chars remain fairly stable around the peak values for about 300 seconds after the initial heat-up stage. The curves then decrease rapidly towards the equilibrium values

while the gasification process is completed. The completion time of the gasification of pine and E. nitens chars was 1100 seconds and 1200 seconds, respectively.

Species	Lignite	Sub-bituminous	Pine	E. nitens
H <sub>2</sub>	33%	21%	31%	29%
СО	11%	5%	9%	12%
$CO_2$	10%	7%	10%	9%

Table 5-1: The maxima of producer gas content for each feedstock species at gasification temperature of 950°C

It is expected that the performance of gasification, in terms of gasification completion time and the shape of the producer gas curves, is related to the micro-structures of the coal char and the biomass char. As shown in Table 3-3, biomass char has higher fixed carbon content and lower volatile matter compared to coal char. Thus, char created from coal exhibits different micro-structures from that created from biomass, because the volatile matter is removed during the devolatilization. It has also been observed in other studies. The biomass chars have porosities with values from 40 to 50% and a pore sizes between 20 and  $30\mu$ m. On the other hand, coal have porosities ranging from 2 to 18% and a pore sizes of around 5  $\mu$ m (Encinar et al. 2001). Furthermore, in the scanning electronic microscopy (SEM) images (Diagram 5-1) were illustrated in the studies (Xu et al. 2011), it clearly demonstrated that for the biomass char, there are a large amount of finer voids between the carbonaceous matters forming the porous structure of thinner clusters. For the coal char, the carbonaceous materials are more likely to be segregated in the form of more compacted clusters.



Diagram 5-1: The SEM images of (a) pure biomass char and (b) pure coal char. All images have a magnification of ×350 (Xu et al. 2011).

Hence, compared with coal char, the biomass char is structurally more amorphous and porous (Kastanaki and Vamvuka 2006; Klose and Wölki 2005). During gasification, steam diffuses into the porous biomass char easily and reacts with the char mass at both the interior and the surface of the char. This creates a large effective reaction area which is maintained for a long time and enhances the intrinsic reactivity of the biomass char. Therefore, the producer gas curves of the biomass char gasification remained at around their peak values for approximately 5 minutes, during which time large amounts of biomass char were consumed.

On the other hand, the coal char has a more compact structure than the biomass char (Zhu et al. 2008), so steam reacts with the char mass largely at the surface area of the coal char but the resistance for the steam to penetrate into the coal char is higher than that into the biomass char. This can be confirmed by the observation in Figures 4-1(a) and 4-1(b) in which a sharp increase in the producer gas composition curves is observed during the initial period of coal char gasification, when the char surface was available for the reaction with steam. As the reaction processes, the producer gas composition the significantly reduced reaction area in the chars.

#### 5.1.2 Char reactivity

According to the producer gas composition from the char gasification, the char conversion percentage with elapsed time and char reactivity were calculated using the **Equations (3-5)** and **Equation (3-6)** in **Chapter 3**, respectively. The results for the gasification temperature of 850°C are shown in Figure 5-1 for the char conversion percentage and in Figure 5-2 for char reactivity. In the figures, the comparison among all of the tested coal and biomass fuels are presented. The results for other gasification temperatures of 850°C are include in Figures F-1 and F-2 in **Appendixes F**.



Figure 5-1: The effect of feedstock species on char conversion percentage at 850°C


Figure 5-2: The effect of feedstock species on char reactivity at 850°C

From Figures 5-1 and 5-2, it is found that the gasification of both biomass chars (pine and E. nitens) was completed at the same time (around 40 minutes) (Figure 5-1). The two biomass char samples bear a resemblance for the char reactivity as a function of char conversion percentage (Figure 5-2).

However, for the two coal samples, the completion time of lignite char conversion (50 minutes) was approximately half of that of sub-bituminous char (100 minutes) as shown in Figure 5-1. This can be explained by the difference in char reactivity as shown in Figure 5-2 in which the reactivity of lignite char was much higher than sub-bituminous char. From Figure 5-2, it is also found that the reactivity curves as a function of char conversion percentage are also different. The reactivity of sub-bituminous char remained relatively constant at 0.03min<sup>-1</sup> throughout whole gasification process. However, the reactivity of lignite char was sustained at 0.08min<sup>-1</sup> up to the char consumption of 30% and then gradually decreased with further char conversion. The higher reactivity of lignite might be explained by the catalysis of inherent alkali and alkaline earth metals (AAEM) in lignite, especially calcium

(Clemens et al. 1998). It is thought that the decrease in the reactivity at a high conversion percentage for lignite may be attributed to the deactivation of calcium when most of the char has been converted (Ganga Devi and Kannan 1998; Zhang et al. 2010).

The reactivity difference between the coal char and the biomass char can also be attributed to the difference in their char chemical structures and micro-structures. Pine and E. nitens chars are much more reactive and thus the completion time of steam gasification was shorter than coal chars, particularly for the sub-bituminous char. This trend agrees well with the results reported by other researchers (Haykiri-Acma et al. 2006). The coal consists mainly of C=C bonds, which requires high activation energy to be broken, hence coal has low reactivity. On the other hand, the cellulose and lignin of the biomass consist mainly of weaker R-O-R bonds, which are less resistant to thermal decomposition (Lapuerta et al. 2008; Ulloa et al. 2009). Furthermore, the carbon micro-structure in biomass char is porous and highly disordered (Kastanaki and Vamvuka 2006). These characteristics can accelerate the reaction rate between the solid carbon in the biomass char and steam.

In conclusion, biomass chars appeared more reactive than coal chars during the whole gasification process, since the completion time of biomass char gasification was much less than that of coal char. However, the catalytic effect of AAEM in lignite is significant at low conversion percentage; therefore, the lignite char had the highest reactivity among the four selected sample chars while the char conversion percentage was less than 40%. The more details on effect of AAEM in lignite will be discussion in **Chapter 5.2.3** 

In conclusion, the reactivity of biomass char is higher than that of coal char, this is due to the micro-structure of char, the former is more porous and the latter is more compact. Consequently, the total gasification completion time of coal char is longer than that of biomass char gasification. However, the presence of AAEM in lignite is other important factor on char reactivity.

# **5.2 Effects of operation variations**

The effects of three operation variation, gasification temperatures, coal-to-biomass blending ratio and AAEM in lignite, on producer gas composition and yield as well as char reactivity were investigated.

#### 5.2.1 Effects of gasification temperatures

The gasification temperature is an important operating variable with regard to the final composition of the producer gas and gas component distribution in the gasification of pure coal char, pure biomass char and/or their blend char (Pinto et al. 2003). In this project, gasification temperatures were varied from 850 to 950°C in 50°C increments. In this section, the results of the effects of gasification temperature on the yield of producer gas and char reactivity were presented.

#### 5.2.1.1 Producer gas production

## Gasification of pure char

The accumulative gas yield of the producer gas ( $H_2$ , CO and CO<sub>2</sub>) from steam gasification of lignite, sub-bituminous, pine and E. nitens were determined by the **Equations (3-1)** and (**3-2**) as described in **Chapter 3**. The results for the three main gas components ( $H_2$ , CO and CO<sub>2</sub>) are plotted in Figure 5-3 for  $H_2$ , in Figure 5-4 for CO and in Figure 5-5 for CO<sub>2</sub>.

The influences of gasification temperature on producer gas yields were the result of a series of complex reactions. In general, higher temperatures enhanced the endothermic gasification reaction (**Steam Gasification Reaction (4-1)** and

**Boudouard Reaction (4-3)**), the reverse direction of **Water-Gas Shift Reaction (4-2)** towards the left-hand side (formation of CO and H<sub>2</sub>O instead of CO<sub>2</sub> and H<sub>2</sub>).



Figure 5-3: The effect of gasification temperature on hydrogen yield

Figure 5-3 shows the effect of gasification temperature on the accumulative hydrogen production for the char gasification of four pure feedstocks. The rise of gasification temperature was found to give a reverse trend of hydrogen yield between coal char and biomass char, with an increase in the former and a decrease in the latter.

For lignite and sub-bituminous chars,  $H_2$  yield increased with a rise in temperature. The  $H_2$  yield for the lignite char was increased from 2.67 liters at 850°C to 2.94 liters at 950°C whereas that for the sub-bituminous chars was increased from 2.26 liters at 850°C to 2.40 liters at 950°C. Results obtained in other studies (Lee et al. 1998; Wang et al. 2009b) of coal char gasification indicated the same trend. On the contrary, for pine and E. nitens chars,  $H_2$  yields decreased with a rise in temperature from 2.98 liters at 850°C to 2.81 liters at 950°C for the pine char and from 3.05 liters at 850°C to 2.70 liters at 950°C for the E. nitens char. However, no studies were found in literature on this trend for the biomass char gasification.



Figure 5-4: The effect of gasification temperature on carbon monoxide yield

The results in Figure 5-4 show that an increase in the gasification temperature had a positive effect on the accumulative carbon monoxide (CO) production of all four feedstock chars. With gasification temperature increasing from 850°C to 950°C, the CO yield increased from 0.31 liters to 0.75 liters for the lignite char, from 0.38 liters to 0.74 liters for the sub-bituminous char, from 0.42 liters to 0.74 liters for the pine char and from 0.51 liters to 0.97 liters for the E. nitens char, respectively.



Figure 5-5: The effect of gasification temperature on carbon dioxide yield

On the contrary, the yield of carbon dioxide (CO<sub>2</sub>) decreased with the increase in gasification temperature as shown in Figure 5-5. With the gasification temperature increasing from 850 to 950°C, the accumulative CO<sub>2</sub> yields decreased from 1.16 liters to 1.04 liters for the lignite char, from 0.91 liters to 0.81 liters for the sub-bituminous char, from 1.29 liters to 1.18 liters for the pine char and from 1.18 liters to 0.94 liters for the E. nitens char, respectively. Based on the results shown in Figures 5-4 and 5-5, yields of CO and CO<sub>2</sub> complement one another. This trend agrees with the results reported by other researchers (Aznar et al. 2006; Detournay et al. 2010; Lee et al. 1998).

The complementary behaviour of CO and CO<sub>2</sub> can be explained by the **Water-Gas Shift Reaction (4-2)** and/or the **Boudouard Reaction (4-3)**. CO<sub>2</sub> was produced through the **Water-Gas Shift Reaction (4-2)** but as the gasification temperature increased, this exothermic reaction was inhibited, leading to a decrease in the CO<sub>2</sub> yield. However, when the gasification temperature increased, the **Boudouard**  **Reaction (4-3)** was more dominant than the **Water-Gas Shift Reaction (4-2)** thus  $CO_2$  was consumed. Hence, at a higher temperature, less  $CO_2$  was produced, resulting that an increase in CO yield in the gasification of both coal chars and biomass chars.

#### Co-gasification of coal-biomass blend char

The influence of gasification temperature in co-gasification is the combination between that in gasification of pure coal char and pure biomass char. Figures 5-14, 5-15 and 5-16 show the influence of gasification temperature on producer gas (H<sub>2</sub>, CO and CO<sub>2</sub>) yields obtained at different blended ratios. The hydrogen (H<sub>2</sub>) yield is shown in Figure 5-14, the carbon monoxide (CO) yield is shown in Figure 5-15 and the carbon dioxide (CO<sub>2</sub>) yield is shown in Figure 5-16. From these results, it can be seen that producer gas yields were significantly influenced by temperature.

As seen in Figure 5-14, the trend for the effects of gasification temperature is not consistent on the  $H_2$  yield in the co-gasification of coal-biomass blend char. For example, for the lignite-pine blends, at the blended ratio of 20:80,  $H_2$  yield tended to increase from 2.82 to 2.99 liters with gasification temperature increased from 850 °C to 950°C. On the contrary, at the blended ratio of 80:20, the  $H_2$  yield decreased from 2.84 to 2.32 liters with the same gasification temperature increased. However, for the sub-bituminous-E. nitens blends, a clear trend is observed that the  $H_2$  yield increased with the gasification temperatures increased for all of the blending ratios.

The main reason for these results is that coal and biomass showed different trends of hydrogen yield at elevated temperatures during their individual char gasification. These differences caused the inconsistent results of hydrogen yield with increasing temperatures during co-gasification of coal-biomass blends.

In Figures 5-15 and 5-16, it can be seen that the sub-bituminous- E. nitens blend chars with a blended ratio of 20:80 had the highest CO yield at 950°C, which was 0.86 litres; while the lowest CO<sub>2</sub> yield (0.19 litres) was produced for the lignite-pine blend chars with the blending ratio of 20:80 at 850°C. The lowest CO<sub>2</sub> yield (0.75 litres) was found for the sub-bituminous-E. nitens blend chars at the blending ratio of 80:20, and the highest CO<sub>2</sub> yield (1.44 litres) was for the lignite-E. nitens blend chars at the blending ratio of 20:80, both cases being observed for gasification temperature of 850°C.

From the results shown in Figures 5-15 and 5-16, a clear and consistent trend has been observed that the CO yield increased and the  $CO_2$  yield decreased with increase in gasification temperature. This trend holds for all of the coal-biomass blends and all of the blending ratios. For example, with the lignite-E. nitens blend at the blending ratio of 50:50, the CO yield was increased from 0.36 litres to 0.57 litres while the  $CO_2$  yield decreased from 1.35 litres to 1.08 litres when the gasification temperature increased from 850°C to 950°C.

The complementary behaviour of CO and CO<sub>2</sub> in co-gasification was the same as the evolutions of CO and CO<sub>2</sub> in gasification of both pure coal chars and pure biomass chars. This suggests that the effects of temperature on gasification reactions between a single fuel and blended fuels are the same. Higher temperatures inhibited the endothermic reactions, **Water-Gas Shift Reaction** (4-2) and **Boudouard Reaction** (4-3), and thus resulting in a decrease of CO<sub>2</sub> yield and an increase of CO yield when the temperature rose from 850°C to 950°C.

## 5.2.1.2 Char reactivity

## Pure chars (coal/biomass)

The variation of reactivity measured against char conversion percentage at the gasification temperatures of 850°C, 900°C and 950°C are displayed in Figures 5-6 to 5-9 presenting the results of lignite, sub-bituminous, pine and E. nitens, respectively.



Figure 5-6: The effect of gasification temperature on char reactivity in steam gasification of lignite char



Figure 5-7: The effect of gasification temperature on char reactivity in steam gasification of sub-bituminous char



Figure 5-8: The effect of gasification temperature on char reactivity in steam gasification of pine char



Figure 5-9: The effect of gasification temperature on char reactivity in steam gasification of E. nitens char

In all of the four fuel chars, it has been found that the char reactivity was increased with the gasification temperature and the completion time is inversely related to the char reactivity. It is also well-known that at higher gasification temperatures, the reaction acquires more energy which accelerates the reaction. The results concur with other researchers' findings (Wu et al. 2006).

#### **Coal-biomass blend chars**

The effects of gasification temperature on char reactivity in co-gasification were also investigated in this study and the results are shown in Figure 5-10 for lignite-pine blend, in Figure 5-11 for lignite-E. nitens blend, in Figure 5-12 for sub-bituminous-pine blend and in Figure 5-13 for the sub-bituminous-E. nitens, respectively, all at the blending ratio of 50:50. The results for other blending ratios are presented in Figures

F-4 to F-7 in **Appendix F**. From Figures 5-10 to 5-13, it can be seen that in the cogasification of both coal-biomass blend chars, the influence of gasification temperature on the char reactivity was consistent with that in the gasification of individual coal chars and biomass chars. The char reactivity as a function of conversion percentage was increased with the gasification temperature.



Figure 5-10: The effect of temperatures on char reactivity in co-gasification of 50%lignite-50%pine blend



Figure 5-11: The effect of temperatures on char reactivity in co-gasification of 50%lignite-50%E. nitens blend



Figure 5-12: The effect of temperatures on char reactivity in co-gasification of 50% sub-bituminous-50% pine blend



Figure 5-13: The effect of temperatures on char reactivity in co-gasification of 50% sub-bituminous-50% E. nitens blend

## 5.2.2 Effects of coal-to-biomass blending ratio

The characteristics of coal char and biomass char are different, such as the char reactivity, the char structure and the chemical composition of the char. It is important to study the interaction between coal char and biomass char during co-gasification. In this section, the effects of the blended coal-to-biomass ratio in the blend char on producer gas yield, char reactivity and syngas production rate are to be analyzed based on the experimental results.

## 5.2.2.1 Producer gas production

Figures 5-14, 5-15 and 5-16 show the effects of coal-to-biomass blending ratio on producer gas ( $H_2$ , CO and CO<sub>2</sub>) yields obtained at different temperatures. From the results presented in Figures 5-14 to 5-16, it is seen that the coal-biomass ratio in the

blends also influences the producer gas yield, to a certain extent. These three figures refer to the main producer gas components:  $H_2$ , CO and CO<sub>2</sub>.



Figure 5-14: Hydrogen yield in the co-gasification of various coal-biomass blend chars at three gasification temperatures

Figure 5-14 shows that the  $H_2$  yield from co-gasification of various coal-biomass blends at different blending ratio at three gasification temperatures. From the figure, it can be seen that the influence of the coal-biomass blending ratio has inconsistent trend of influence on the  $H_2$  yield. For the sub-bituminous-E. nitens blend chars at the gasification temperature of 850°C, the  $H_2$  yield increased from 2.1 litres at coalbiomass blending ratio of 20:80 to 2.4 litres at the blending ratio of 80:20. However, for lignite-E. nitens blend chars at the gasification temperature of 900°C, the  $H_2$  yield decreased from 3.1 litres at the coal-biomass blending ratio of 20:80 to 2.8 litres at the blending ratio of 80:20. It is interesting to notice that the blending ratio has insignificant influence on the  $H_2$  yield for sub-bituminous-pine blends and this is true for all of the gasification temperatures with the  $H_2$  yield varying between 2.35 and 2.45 litres

However, in Figure 5-15 and Figure 5-16, the blending ratio in the coal-biomass blends has a consistent trend on the CO and  $CO_2$  yields which decreased with the coal proportion or the coal to biomass ratio. This trend is true for all of the coal-biomass blends and at all of the gasification temperatures tested. One possible explanation for the CO and  $CO_2$  yield decrease with the coal proportion is that the fixed carbon content decreased with the increase in the proportion of coal in the blend chars, which is shown in Table 3-3. As mentioned before, the less fixed carbon content in the blend chars, the lower the yields of CO and  $CO_2$  production from the **Steam Gasification Reaction (4-1)** and **Boudouard Reaction (4-3)**.



Figure 5-15: Carbon monoxide yield in the co-gasification of various coal-biomass blend chars at three gasification temperatures



Figure 5-16: Carbon dioxide yield in the co-gasification of various coal-biomass blend chars at three gasification temperatures

## 5.2.2.2 Char reactivity

The reactivity of coal-biomass blend chars at various blending ratios was determined by a calculation based on the gas analysis of the producer gas. The evolution of char reactivity as a function of char conversion percentage for coal-biomass blend chars at the gasification temperature of 850°C is presented in Figure 5-17 to Figure 5-20. The results for other gasification temperatures (900°C and 950°C) are presented in Figures F-8 to F-11 in **Appendix F**. Figures 5-17 and 5-18 show the char reactivity for the lignite-biomass blended chars including pure lignite and pure biomass chars, whereas results for sub-bituminous-biomass blended chars are shown in Figures 5-19 and 5-20.



Figure 5-17: The effect of blended ratio on char reactivity for lignite-pine blend chars at the gasification temperature of 850°C

In Figure 5-17, the evolution of char reactivity of lignite-pine blend char was presented. At the initial gasification, the reactivity of the pure lignite char was highest, while the reactivity of pure pine char was lowest. It may be due to the effect of AAEM in lignite. In the meantime, the reactivity of lignite-pine blend char shifted between these pure char cases. Furthermore, the reactivity of lignite-pine blend char increased with an increase in the lignite proportion. Following the process, the reactivity of both pure lignite char and lignite-pine blend char decreased. In contract, the reactivity of pure pine char increased, after the char conversion reached 40%, it exceeded the pure lignite char. While the reactivity of lignite-pine blend char is less than those of pure pine char and pure lignite char, which indicated the negative synergistic effects occurred.



Figure 5-18: The effect of blended ratio on char reactivity for lignite-E. nitens blend chars at the gasification temperature of 850°C

In Figure 5-18, it is observed that the evolution of char reactivity could be divided into two parts. In the first part, at the lower char conversion stage (less than char conversion percentage of 40%), the reactivity of lignite-E. nitens blended chars was higher than those of pure lignite char and pure E. nitens char, it indicated that positive synergistic effects occurred during the co-gasification of lignite-E. nitens blend char. In the meantime, the reactivity of coal-biomass blend char increased with an increase in the coal proportion. As gasification processing, the reactivity of both pure lignite char and lignite-E. nitens blend char decreased. In contract, the reactivity of pure E. nitens char increased. In the second part, after the char conversion percentage of about 40%, the char reactivity of E. nitens become greater than that of pure lignite char and the lignite-E. nitens blend chars; while, the reactivity of lignite-E. nitens blend char shifted between these pure char cases.



Figure 5-19: The effect of blended ratio on char reactivity for sub-bituminous-pine blend chars at the gasification temperature of 850°C



Figure 5-20: The effect of blended ratio on char reactivity for sub-bituminous-E. nitens blend chars at the gasification temperature of 850°C

The char reactivity for the sub-bituminous-biomass blend chars is shown in Figure 4-19 (blending with pine biomass) and in Figure 5-20 (blending with E. nitens biomass). It was shown in these two figures that the char reactivity of pure biomass chars were significantly higher than that of both the pure sub-bituminous char and the subbituminous-biomass blend chars. Based on these findings, it can be concluded that blending of sub-bituminous and biomass reduced the biomass char reactivity in the steam gasification. However, the reactivity of the blended chars was similar to that of pure sub-bituminous chars.

It can be seen from these figures that the evolutions of coal-biomass blend char reactivity were more identical to those of coal chars, rather than biomass chars. This has further evidenced that the characteristics of coal-biomass blend char are close to that of coal char.

## 5.2.3 Effects of AAEM in lignite

In order to further examine the catalytic effects of AAEM in lignite on gasification performance. The gasification of acid-washed lignite char was carried out in the bench scaled gasifier as well.

#### 5.2.3.1 Producer gas production

The effects of AAEM on producer gas and gasification completion time are shown in Figure 5-21 and Table 5-2, respectively. In Figure 5-21, it is seen that for all of the lignite chars and acid-washed lignite chars, the production rate (litre per second) of producer gas peaked after a short time from start and then decreased rapidly with the elapsed time. However, from these results, it is clear that at the same gasification temperature, the peak values of producer gas generation from lignite char gasification

were much higher than those from gasification of acid-washed lignite chars. When the curves decayed exponentially from their peak values, acid-washed lignite gasification took much longer time, which at least double the time of raw lignite chars. In Table 5-2, the overall gasification completion time (minutes) of lignite char and acid-washed lignite char at different temperature is presented.



Figure 5-21: The comparison of producer gas in gasification of lignite and acidwashed lignite (AWL) chars

 Table 5-2: The comparison of the overall gasification completion time of lignite and acid-washed lignite chars at different temperatures

Temperature	850°C	900°C	950°C
Raw lignite	52 min	43 min	31 min
Acid-washed lignite	132 min	87 min	63 min

The effect of AAEM on producer gas yield is displayed in Figure 5-22. It is obvious that the removal of AAEM reduced the producer gas yield at the same tested temperatures. For example, at 850°C, the yield of producer gas in lignite gasification was 4.15 litres, while acid-washed lignite only generated 2.83 litres. The same trends are also found at the gasification temperatures of 900 and 950°C. The different results between lignite char gasification and acid-washed lignite char gasification is due to the promotion of AAEM on **Steam Gasification Reaction (4-1)** and **Boudouard Reaction (4-3)**, which was presented in the **Chapter 2.3.2**. As a result, AAEM increased the char consumption, so that more produce gas were generated in lignite char gasification.



Figure 5-22: The comparison of producer gas yields in gasification of lignite chars and washed lignite chars

#### 5.2.3.2 Char reactivity

The char reactivity of lignite, acid-washed lignite and sub-bituminous coal in gasification measured against the char conversion percentage at gasification temperature of 900°C is plotted in Figure 5-23. The results for other gasification temperature (850°C and 950°C) are presented in Figures G-3(a) and G-3(b) in **Appendix G**. Throughout the whole gasification process, the reactivity of char prepared from acid-washed lignite was lower than that of raw lignite and sub-bituminous coal. Obviously, the removal of AAEM from lignite reduced the char reactivity. Several authors reported that AAEM was particularly effective for gasification of chars (Bayarsaikhan et al. 2005; Mitsuoka et al. 2011; Wang et al. 2009a). In these studies, the coal char with added Ca (one common AAEM specie found in coal) had higher reactivity during the gasification than the raw coal char.



Figure 5-23: The comparison of char reactivity for lignite, acid-washed lignite and sub-bituminous chars at the gasification temperature of 900°C

Interestingly, the effect of AAEM was more significant at the low carbon conversion percentage (<50%). A possible explanation for this may be the deactivation of AAEM species with more char consumed in the late stage of the gasification. Previous researchers (Huang et al. 2009) found that the particles of Ca metals were inclined to agglomerate during the gasification processing, resulting in deactivation.

It is also interesting to notice from Figure 5-23 that the acid-washed lignite chars and the sub-bituminous chars had similar reactivity trends with values much lower than the raw lignite chars. The reactivity of both acid-washed lignite and sub-bituminous char remained largely constants at 0.03 and 0.05 min<sup>-1</sup>, respectively. This indicates that the sub-bituminous chars had very low level of AAEM.

In conclusion, the inherent AAEM species in lignite played catalytic roles in the steam gasification of char. In other words, the presence of AAEM had a positive influence by increasing the reaction rate and raising the producer gas yield (Encinar et al. 2001)

## **5.3** Synergistic effects in co-gasification of coal-biomass blend chars

In this project, the performances of synergistic effects in co-gasification of four types of coal-biomass blends (lignite-pine, lignite-E. nitens, sub-bituminous-pine and sub-bituminous-E. nitens) are studied. A new term, syngas production rate, is used to exam the co-gasification performance. Syngas production rate is dependent on the producer gas yield and the gasification completion time (related to the reactivity), and it is calculated by the **Equation (3-7)**.

The results of syngas production rate during the co-gasification for various blending ratios and different gasification temperature are presented in Figures 5-24 to 5-27 as bars, for blended chars of lignite-pine, lignite-E. nitens, sub-bituminous-pine and sub-

bituminous-E. nitens, respectively. In these four figures, it is shown that, compared with pure coal char, the pure biomass char had a higher syngas production rate because of its high surface areas due to a more porous structure and high char reactivity from the **Discussion 5.1**.

The effects of gasification temperatures were also shown, the increase in gasification temperatures enhanced the syngas production rate in all coal-biomass blend char, which is consistent with the conclusion in **Discussion 5.2.1** (high temperature increased the total producer gas yield and reduced the total gasification completion time).

Although the effects of coal-to-biomass blending ratio on producer gas yield and char reactivity are conflict and disorder in **Discussion 5.2.2**, these four diagrams demonstrated clearly the influences of coal-to-biomass blending ratio, the increase of biomass proportion in blend promote the syngas production rate.

## 5.3.1 Synergistic effects

In Figures 5-24, 5-26 and 5-27, the syngas production rate of these three coal-biomass blend chars were almost less than those of pure coal and pure biomass char. However, the case of lignite-E. nitens blend char in Figure 5-25 was different, which was greater than the pure lignite and pure E. nitens char. Those observations indicated the synergistic effect may exist during co-gasification.

In order to investigate the synergistic effect in the coal-biomass blend during cogasification, the experimental results of gas production rate are compared with those  $(Y_{mix})$  theoretically calculated using the following equation without considering the synergistic effects.

$$Y_{mix} = F_{coal}Y_{coal} + F_{biomass}Y_{biomass}$$

, where  $Y_{coal}$  and  $Y_{biomass}$  are the total producer gas yields from the steam gasification of pure coal chars and pure biomass chars,  $F_{coal}$  and  $F_{biomass}$  are the fractions of single fuel in the coal-biomass blend char, and  $F_{coal} + F_{biomass} = 100\%$ .

The calculated results are also included in Figure 5-24 to 5-27 for corresponding coalbiomass blends. The differences between the experimentally measured values and the calculation results can be used as a reflection of the synergistic effects of the coalbiomass blending. From the comparison in the Figures 5-24 to 5-27, it is found that synergetic effects occurred in all of the four different coal-biomass blend chars in the steam gasification because significant discrepancies have been observed between the experimental values and the calculated results.







Figure 5-25: The effect of temperature and blending ratio on gas production rate in steam gasification of lignite-E. nitens blend chars



Figure 5-26: The effect of temperature and blending ratio on gas production rate in steam gasification of sub-bituminous-pine blend chars



Figure 5-27: The effect of temperature and blending ratio on gas production rate in steam gasification of sub-bituminous-E. nitens blend char

In Figures 5-24, 5-26 and 5-27 for the blends of lignite-pine, sub-bituminous-pine and sub-bituminous-E. nitens, the producer gas production rates obtained in cogasification experiments were lower than the calculated values which indicate that the blending had a negative synergetic effect on the gasification reactions. On the contrary, as shown in Figure 5-25 (lignite-E. nitens blends), the producer gas production rates in the experiments were higher than the calculated values thus the lignite-E. nitens blend chars has a positive synergetic effect during co-gasification.

In the previous studies (Demirbas 2002; Fermoso et al. 2009a; Sjöström et al. 1999; Zhang et al. 2007), the synergistic effects in co-gasification when coal and biomass were blended have also been found, it may suggests that the synergistic effects depend on properties of fuel species (coal and/or biomass). In this study, the existing synergistic effects are discussed in the following chapters. The positive synergetic

effects in the co-gasification of lignite-E. nitens may be determined by the combination of the catalytic effect of AAEM in lignite and the intrinsic properties of E. nitens.

## 5.3.2 Effect of E. nitens

In the devolatilization, the synergistic effect occurred when E. nitens was blended with coal as shown in Figure 5-28 and Figure 5-29. Both Figures illustrate the char yield at different blend ratios of coal and biomass, as well as the straights lines calculated from **Equation (5-2)**.

In a similar way as for char gasification, the synergistic effects between coal and biomass during devolatilization can be reflected by the char yield ( $X_{mix}$ ) with devolatilization as a function of fuel fractions in the blend fuel and the char yields of pure coal and pure biomass. If there is no synergistic effect, the char yield is linearly related to the fractions and char yields of each fuel:

$$X_{mix} = F_{coal}X_{coal} + F_{biomass}X_{biomass}$$
(5-2)

Here  $X_{coal}$  and  $X_{biomass}$  are the char yields of pure coal and pure biomass during devolatilization,  $F_{coal}$  and  $F_{biomass}$  are the fractions of coal and biomass in the coalbiomass blends,  $F_{coal} + F_{biomass} = 100\%$ .



Figure 5-28: Char yield of coal-E. nitens blends at devolatilization temperature of 900°C



Figure 5-29: Char yield of coal-pine blends at devolatilization temperature of 900°C

When E. nitens as the biomass was blended with coal, deviation was observed between the experimental char yields and the calculated ones using **Equation (5-2)** as shown in Figure 5-28. In a general trend, the experimental char yields are higher than the calculated ones. Therefore, the synergistic effect was remarkable in coal - E. nitens blends during devolatilization. This behaviour was also observed in other pyrolysis studies (Jones et al. 2005; Sjöström et al. 1999; Sonobe et al. 2008; Zhang et al. 2007).

However, the result as displayed in Figure 5-29 for coal-pine blend chars show a fairly close agreement between the experimental char yield and the calculated ones using **Equation (5-2)**, indicating that the char yield was almost linearly related to the coal proportion in the coal-biomass blend. Hence, there was no significant synergistic effect between coal and pine in their blends during devolatilization. This finding is consistent with previous studies (Biagini et al. 2002; Kastanaki et al. 2002; Meesri and Moghtaderi 2002; Moghtaderi et al. 2004) in which no significant synergy was observed between coal and biomass during pyrolysis over the selected experiment conditions.

Based on the above observations, the occurrence of synergistic effect in coal-biomass blends during devolatilization depends upon the fuel type used. In this project, when E. nitens was blended with coal, the synergistic effect existed, which may be caused by intrinsic properties of E. nitens.

#### 5.3.3 Effect of AAEM in lignite

In order to investigate the effect of AAEM in co-gasification, the acid-washed lignite was blended with two types of biomass, pine and E. nitens, at the blended ratios of 20:80, 50:50 and 80:20. The differences in syngas production rate during co-gasification between acid-washed lignite-biomass blend and raw lignite-biomass

blend are shown in Figure 5-30 for blend chars of lignite-pine and acid-washed lignite-pine and in Figure 5-31 for acid-washed lignite-E. nitens and raw lignite-E. nitens.



Figure 5-30: The comparison of gas production rate between lignite-pine and acidwashed lignite-pine blend chars

The results showed that the raw lignite-biomass blend chars had much higher syngas production rate, as it took a shorter time to complete the gasification reaction and improved char reactivity. In Figure 5-30, at the same operation conditions (i.e. gasification temperature and blended ratio), the syngas production rate of raw lignite-pine blend char was almost three times higher than that of the char from acid-washed lignite-pine. Furthermore, as shown in Figure 5-31, the syngas production rate of raw lignite-E. nitens char was double of that of the acid-washed lignite-E. nitens.



Figure 5-31: The comparison of gas production rate between lignite-E. nitens and acid-washed lignite-E. nitens blend chars

These results suggested that the enhanced syngas production rate could be associated with the catalytic effects of AAEM in lignite. In other word, the removal of AAEM from lignite reduces the reactivity of coal-biomass blend char as well as the syngas production rate. From Figures 5-30 and 5-31, it also found that the acid-washed lignite-biomass blend chars had similar syngas production rates, which indicates that E. nitens and pine have a similar influence on co-gasification. Therefore, the AAEM species played a more dominant catalytic role in co-gasification than the intrinsic properties of E. nitens.

In conclusion, in the case of lignite-E. nitens blend char, it was suggested that the combination of the catalytic effect of AAEM in lignite and the intrinsic properties of E. nitens promoted the synergistic effects during the co-gasification. In addition, the AAEM species played a more dominant catalytic role in co-gasification than the intrinsic properties of E. nitens.

# **6** Conclusions

The characteristics of steam co-gasification of chars of pure coal, pure biomass and coal-biomass blends were experimentally investigated in this project in a bench scale gasifier. Two types of coals (lignite and sub-bituminous) and two kinds of biomass (pine and eucalyptus nitens) were selected as sample fuels. The chars with the blended coal-to-biomass ratio of 0:100 (pure coal), 20:80, 50:50, 80:20 and 100:0 (pure biomass), which were derived through the devolatilization at the temperature of 900°C for 7 minutes, were gasified with steam as gasification agent at gasification temperatures of 850°C, 900°C and 950°C. A series of gasification experiments have been performed in order to investigate the effects of operation variations (gasification temperature, types of coal and biomass, blended coal-to-biomass ratio and alkali and alkaline earth metal (AAEM) in lignite) on gasification reactivity, and producer gas composition and yields. In addition, the synergistic effects in co-gasification were also investigated.

In the devolatilization, it is found that pure coal has a higher char yield than pure biomass while some difference exists in different types of coal and biomass. The char yields of the four sample fuels are as follows: sub-bituminous coal (49%) > lignite (41%) > Pine (18%) > E. nitens (15%). It is also found that the char yield of the coal-biomass blend is decreased with the increase of biomass proportion in the blend. In addition, the synergistic effects in coal-biomass blends during devolatilization were also examined and it is observed that only coal-E. nitens blends exhibited noticeable synergistic effects on char yield during the devolatilization.

For the gasification performance, the producer gas composition with elapsed time were continuously analysed by using a Micro-GC from which the total gas yield was calculated. Based on the gas analysis results, char reactivity and char conversion rate were determined.

From the results of gasification of pure coal and pure biomass chars, it is found that the biomass char gasification was faster than coal char gasification due to the higher reactivity for the biomass char. Compared to the coal char, the biomass char has a more porous micro-structure, which enhances the reactions between the biomass char and the steam. The influences of varying gasification temperatures on producer gas and char reactivity were investigated as well. For producer gas, with increase in gasification temperature, the  $H_2$  yields in coal char gasification was increased but the  $H_2$  yields in biomass char gasification temperature increased. In both coal and biomass char gasification, as gasification temperature increased, the CO yields increased while  $CO_2$ yields decreased. The study also found that the reactivity of all four fuel samples chars increased with the increase in gasification temperature.

From the experiments on co-gasification of coal-biomass blend chars, syngas production rates as well as the parameters examined in the gasification of pure fuel chars above were investigated. For producer gas, the effects of gasification temperature and coal to biomass blending ratio on  $H_2$  yield were inconsistent. The increase in gasification temperatures enhanced the CO yield but reduced the CO<sub>2</sub> yield, while the increase of coal char proportion in blends decreased both the CO and CO<sub>2</sub> yields. In addition, the char reactivity as a function of conversion percentage was increased with the gasification temperature, and it was independent of the coal to biomass blending ratio. These trends were true for all of the coal-biomass blends and at all of the gasification temperatures tested. Syngas production rate is the total producer gas yield divided by total gasification completion time. The syngas production rate was enhanced by an increase in gasification temperatures as well as an increase in the biomass proportion in the blend.

In gasification of lignite char and co-gasification of lignite-E. nitens blend chars, the influences of AAEM were significant. The presence of AAEM not only increased the producer gas yield, but also enhanced the char reactivity, hence promoting the syngas production rate. For example, AAEM species in lignite led to lignite having the highest reactivity during lower char conversion.
The synergistic effects on syngas production rate were also examined during the cogasification of all coal-biomass blend chars. From the results, the positive synergistic effect was only found in the gasification of lignite-E. nitens blend chars, which is the result of the effect of AAEM in lignite and the intrinsic properties of the biomass. However, for the other blend chars, the synergistic effects were either insignificant or negative, indicating the AAEM was low in sub-bituminous coal or the interaction between the coal and the biomass inhibited the steam reaction with the chars. In overall, The AAEM species played an important catalytic role in gasification by reacting with the carbonaceous substrate in the char during the gasification process.

This project based on a bench scaled gasifier is a fundamental research on gasification of pure fuel chars and co-gasification of blended coal and biomass chars. The results can be applied to the study of co-gasification of coal-biomass in a large-scaled gasifier in the future. When biomass was blended with coal in this project, an increase of biomass percentage in coal-biomass blend accelerated the gasification rate, due to the high reactivity of biomass. In this study, AAEM species in lignite led to lignite having the highest reactivity during lower char conversion. Therefore, the application of inherent AAEM species in raw materials should be considered.

New Zealand has abundant resources for the feedstock fuels, namely radiata pine, eucalyptus nitens, lignite and sub-bituminous, therefore, the results from this study have strong potential in future application. In addition, the blending of coal with biomass can potentially reduce the costs for low density biomass and reduce the green house gas emission from pure coal.

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## A. Appendixes A - Checklist of experiments

Gasifier Setting Temperature (C)		850	900	950	
Coal	Lignite	A	cid washed	l-lignite	Sub-bituminous
Biomass		Pine	E. nitens		
Blended Ratio coal/biomass	0 / 100	20 / 80	50 / 50	80 / 20	100 / 0
Char Sample Weight (g)				(1g)	
Resin Condition Check			Yes	No	
GC Calibration			Yes	No	
Nitrogen Input (0.6L/min	<b>1</b> )		On	Off	
Gasifier Gas leak Check			Yes	No	
Cooling Water			On	Off	
Preheater & Oven			On	Off	
Steam (1.8ml/min)			On	Off	
GC Analysis Start		Run ID			
GC Shutdown			On	Off	
Steam & Oven Closed			On	Off	
Preheater Shutdown			On	Off	
Cooling water & Nitroge	n stop		On	Off	
Water (ml)	Before		After	·	Difference
Ash weight (g)			-		

Signature \_\_\_\_\_

# **B.** Appendixes **B** - Proximate analysis and ultimate analysis of solid fuel samples



#### CRL Internal Report of Analysis Page 1 of 1 17/06/09 Date Received: Description: Wood and Lignite char blends. Customer Reference: 100% lignite 80% lignite, 50% lignite, 20% lignite, 100% wood char 20% wood 50% wood 80% wood char char char char CRL Energy Ltd Reference: 88/071 88/072 88/073 88/075\* 88/074\* Analysis - As Received Basis Moisture (ISO 11722) 0.8 0.7 0.7 0.6 0.7 % Ash (ISO 1171) % 12.8 10.3 9.6 6.0 3.2 Volatile (ISO 562) % 5.0 5.1 4.6 4.2 4.0 Fixed Carbon (by difference) % 81.4 83.9 85.1 89.2 92.1 82.9 85.1 86.0 88.9 Total Carbon (LECO C) % 91.9 Analysis - Dry Basis 12.9 10.4 9.7 6.0 3.2 Ash %

Volatile	%	5.0	5.1	4.6	4.2	4.0
Fixed Carbon	%	82.1	84.5	85.7	89.7	92.7
Total Carbon	%	83.6	85.7	86.6	89.4	92.5

Date of Issue: 24/06/09

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### CRL Report of Analysis

Page 1 of 1

Description: Blended chars of sub-bituminous coal and wood.	Date Received:	24/06/09

Customer Reference	8:		100% Sub-bit char	80% Sub-bit, 20% wood char	50% Sub-bit, 50% wood char	20% Sub-bit, 80% wood char
CRL Energy Ltd Ret	erence:	88/169	88/170	88/171	88/172	
Analysis - As Receiv	ed Basis					
Moisture	(ISO 5068)	%	0.7	0.5	0.6	0.4
Ash	(ISO 1171)	%	10.8	9.8	8.7	6.4
Volatile	(ISO 562)	%	3.7	3.5	3.6	4.1
Fixed Carbon	(by difference)	%	84.8	86.2	87.1	89.1
Total Carbon	(LECO SC-144DR)	%	85.2	86.0	89.2	89.2

Analysis -	Dry	Basis

Ash	%	10.9	9.8	8.8	6.4
Volatile	%	3.7	3.5	3.6	4.1
Fixed Carbon	%	85.4	86.6	87.6	89.5
Toatal Carbon	%	85.8	86.4	89.7	89.6

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Page 1 of 1

Date Received: 30-Sep-10

Description: Wood, coal and char samples

			Air Dry Basis							
CRL Ref	Description		Moist ISO 11722	Ash ASTM D1102	Vois ISO 562	Fixed Carbon by difference	Total Carbon SC144-DR	Total Carbon ISO/TS 12902	Total Hydrogen ISO/TS 12902	Total Nitrogen ISOTS 12902
93/000	Pine	%	7.8	0.34	78	13.9		47.2	5.41	<0.03
93/001	e niten	%	5.4	0.38	81.5	12.7		47.5	5.57	<0.03
93/002	Lignite	%	19.1	4.9	41.9	34.1		50.6	3.64	0.55
93/003	Sub-bit	%	13.6	5.4	38.6	42.4		59.4	4.10	1.03
93/004	L-P 20/80 Char	%	0.85	4.9	3.2	91.1	89.6			
93/005	L-P 50/50 Char	%	0.76	8.2	4.3	86.7	85.6			
93/006	L-P 80/20 Char	%	0.67	10.6	7.0	81.7	83.3			
93/007	S-P 20/80 Char	%	1.1	5.1	4.7	89.1	87.8			
93/008	S-P 50/50 Char	%	1.1	8.6	9.6	80.7	82.8			
93/009	S-P 80/20 Char	%	0.34	10.1	3.3	86.3	85.9			
93/010	100% Pine Char	%	0.88	1.9	2.1	95.1	93.8			

				Dry	Basis			
Description		Ash	Vols	Fixed Carbon	Total Carbon	Total Carbon	Total Hydrogen	Total Nitrogen
Pine	%	0.37	84.6	15.0		51.2	5.87	<0.03
e niten	%	0.40	86.2	13.4		50.2	5.89	<0.03
Lignite	%	6.1	51.8	42.2		62.6	4.50	0.68
Sub-bit	%	6.3	44.7	49.1		68.8	4.75	1.19
L-P 20/80 Char	%	4.9	3.2	91.8	90.4			
L-P 50/50 Char	%	8.3	4.3	87.4	86.2			
L-P 80/20 Char	%	10.7	7.0	82.3	83.9			
S-P 20/80 Char	%	5.2	4.8	90.1	88.8			
S-P 50/50 Char	%	8.7	9.7	81.6	83.7			
S-P 80/20 Char	%	10.1	3.3	86.6	86.1			
100% Pine Char	%	1.9	2.1	95.9	94.7			
	Description           Pine           e niten           Lignite           Sub-bit           L-P 20/80 Char           L-P 50/50 Char           L-P 80/20 Char           S-P 20/80 Char           S-P 50/50 Char           S-P 50/50 Char           S-P 50/50 Char           S-P 80/20 Char           100% Pine Char	Description       Pine     %       e niten     %       Lignite     %       Sub-bit     %       L-P 20/80 Char     %       L-P 80/20 Char     %       S-P 20/80 Char     %       S-P 50/50 Char     %       S-P 50/50 Char     %       S-P 80/20 Char     %       S-P 80/20 Char     %       100% Pine Char     %	Description         Ash           Pine         %         0.37           e niten         %         0.40           Lignite         %         6.1           Sub-bit         %         6.3           L-P 20/80 Char         %         4.9           L-P 50/50 Char         %         8.3           L-P 80/20 Char         %         5.2           S-P 20/80 Char         %         8.7           S-P 50/50 Char         %         10.1           100% Pine Char         %         10.1	Description         Ash         Vols           Pine         %         0.37         84.6           e niten         %         0.40         86.2           Lignite         %         6.1         51.8           Sub-bit         %         6.3         44.7           L-P 20/80 Char         %         4.9         3.2           L-P 50/50 Char         %         8.3         4.3           L-P 80/20 Char         %         10.7         7.0           S-P 20/80 Char         %         5.2         4.8           S-P 50/50 Char         %         8.7         9.7           S-P 80/20 Char         %         10.1         3.3           100% Pine Char         %         1.9         2.1	Description         Ash         Vols         Fixed Carbon           Pine         %         0.37         84.6         15.0           e niten         %         0.40         86.2         13.4           Lignite         %         6.1         51.8         42.2           Sub-bit         %         6.3         44.7         49.1           L-P 20/80 Char         %         4.9         3.2         91.8           L-P 50/50 Char         %         8.3         4.3         87.4           L-P 80/20 Char         %         10.7         7.0         82.3           S-P 20/80 Char         %         5.2         4.8         90.1           S-P 50/50 Char         %         8.7         9.7         81.6           S-P 80/20 Char         %         10.1         3.3         86.6           100% Pine Char         %         1.9         2.1         95.9	Description         Ash         Vols         Fixed Carbon         Total Carbon           Pine         %         0.37         84.5         15.0           e niten         %         0.40         86.2         13.4           Lignite         %         6.1         51.8         42.2           Sub-bit         %         6.3         44.7         49.1           L-P 20/80 Char         %         4.9         3.2         91.8         90.4           L-P 50/50 Char         %         8.3         4.3         87.4         86.2           L-P 80/20 Char         %         5.2         4.8         90.1         88.8           S-P 20/80 Char         %         5.2         4.8         90.1         88.8           S-P 50/50 Char         %         8.7         9.7         81.6         83.7           S-P 80/20 Char         %         10.1         3.3         86.6         86.1           100% Pine Char         %         1.9         2.1         95.9         94.7	Description         Ash         Vols         Fixed Carbon         Total Carbon         Total Carbon           Pine         %         0.37         84.5         15.0         51.2           e niten         %         0.40         86.2         13.4         50.2           Lignite         %         6.1         51.8         42.2         62.6           Sub-bit         %         6.3         44.7         49.1         68.8           L-P 20/80 Char         %         4.9         3.2         91.8         90.4           L-P 50/50 Char         %         8.3         4.3         87.4         86.2           L-P 80/20 Char         %         5.2         4.8         90.1         88.8           S-P 20/80 Char         %         5.2         4.8         90.1         88.8           S-P 50/50 Char         %         5.2         4.8         90.1         88.8           S-P 80/20 Char         %         10.1         3.3         86.6         86.1           100% Pine Char         %         1.9         2.1         95.9         94.7	Description         Ash         Vols         Fixed Carbon         Total Carbon         Total Carbon         Total Carbon         Total Pine           Pine         %         0.37         84.6         15.0         51.2         5.87           e niten         %         0.40         86.2         13.4         50.2         5.89           Lignite         %         6.1         51.8         42.2         62.6         4.50           Sub-bit         %         6.3         44.7         49.1         68.8         4.75           L-P 20/80 Char         %         6.3         4.3         87.4         86.2         4.50           Sub-bit         %         6.3         4.3         87.4         86.2         4.75           L-P 20/80 Char         %         10.7         7.0         82.3         83.9         4.75           L-P 80/20 Char         %         5.2         4.8         90.1         88.8         4.9           S-P 20/80 Char         %         5.2         4.8         90.1         88.8         4.9           S-P 80/20 Char         %         10.1         3.3         86.6         86.1         4.9           100% Pine Char %         1.9

Date of Issue: 3-Dec-10

Signature: Ben Rumsey Research Officer

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# C. Appendixes C - Char yield of blended coal and biomass at devolatilization temperature of 900 $^\circ \rm C$

		Pellets weight		
Coal / Biomass	Ratio	[g]	Char weight [g]	Char/Pellet
Asid weehed Lignite /	80 / 20	10.06	3.87	0.38
Pine	50 / 50	13.38	4.03	0.30
	20 / 80	27.34	5.78	0.21
	80 / 20	47.27	17.17	0.36
Lignite / Pine	50 / 50	46.92	13.75	0.29
	20 / 80	57.68	13.03	0.23
	80 / 20	67.55	29.04	0.43
Subbituminous / Pine	50 / 50	55.72	18.68	0.34
	20 / 80	49.73	12.32	0.25
	80 / 20	11.19	4.27	0.38
Lignite / E.niten	50 / 50	16.91	4.97	0.29
	20 / 80	29.02 6.03		0.21
Subbituminaua /	80 / 20	9.95	4.35	0.44
F niten	50 / 50	8.63	2.85	0.33
Linton	20 / 80	9.57	2.27	0.24
Lignite	100	6.09	2.47	0.41
Acid-washed Lignite	100	6.65	2.90	0.44
Subbituminous	100	7.71	3.78	0.49
Pine	100	41.39	7.61	0.18
E.niten	100	11.10	1.65	0.15

Table C-1: the char yield of coal-biomass blend after devolatilization

# **D.** Appendixes **D** - Experimental results of steam gasification of pure coal char and pure biomass char



### **D-1 Steam gasification of lignite char**

(a)



(b)

Figure D-1: The composition of producer gas from steam gasification of lignite char

at 850  $^{\circ}\text{C}$  (a) and 900  $^{\circ}\text{C}$  (b)

### D-2 Steam gasification of sub-bituminous char



(a)



Figure D-2: The composition of producer gas from steam gasification of subbituminous char at 850  $^{\circ}C$  (a) and 900  $^{\circ}C$  (b)

### D-3 Steam gasification of pine char



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Figure D-3: The composition of producer gas from steam gasification of Pine char at  $850\ ^\circ C$  (a) and  $900\ ^\circ C$  (b)

### D-4 Steam gasification of E. niten char



(a)



Figure D-4: The composition of producer gas from steam gasification of E. niten chars at 850  $^{\circ}C$  (a) and 900  $^{\circ}C$  (b)

## **E.** Appendixes **E** - Experimental results of steam gasification of coalbiomass blend chars

### E-1 Steam gasification of lignite-pine blend chars

20% lignite – 80% pine blends



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Figure E-1: The composition of producer gas from steam gasification of lignite-pine blend chars with a blending ratio of 20:80 at 850°C (a), 900°C (b) and 950°C (c)

50% lignite – 50% pine blends





Figure E-2: The composition of producer gas from steam gasification of lignite-pine blend chars with a blending ratio of 50:50 at 850°C (a) and 900°C (b)

80% lignite – 20% pine blends







Figure E-3: The composition of producer gas from steam gasification of lignite-pine blend chars with a blending ratio of 80:20 at 850°C (a), 900°C (b) and 950°C (c)

### E-2 Steam gasification of lignite-E. nitens blend chars

20% lignite – 80% E. nitens blends









Figure E-4: The composition of producer gas from steam gasification of lignite-E. nitens blend chars with a blending ratio of 20:80 at 850°C (a), 900°C (b) and 950°C (c)

50% lignite – 50% E. nitens blends





Figure E-5: The composition of producer gas from steam gasification of lignite-E. nitens blend chars with a blending ratio of 50:50 at 850°C (a) and 900°C (b)

80% lignite – 20% E. nitens blends





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Figure E-6: The composition of producer gas from steam gasification of lignite-E. nitens blend chars with a blending ratio of 80:20 at 850°C (a), 900°C (b) and 950°C (c)

### E-3 Steam gasification of sub-bituminous-pine blend chars

20% sub-bituminous – 80% pine blends



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Figure E-7: The composition of producer gas from steam gasification of subbituminous-pine blend chars with a blending ratio of 20:80 at 850°C (a), 900°C (b) and 950°C (c)

50% sub-bituminous – 50% pine blends







(b)

Figure E-8: The composition of producer gas from steam gasification of subbituminous-pine blend chars with a blending ratio of 50:50 at 850°C (a) and 900°C (b)

80% sub-bituminous – 20% pine blends







Figure E-9: The composition of producer gas from steam gasification of subbituminous-pine blend chars with a blending ratio of 80:20 at 850°C (a), 900°C (b) and 950°C (c)

### E-4 Steam gasification of sub-bituminous-E. nitens blend chars





(a)





Figure E-10: The composition of producer gas from steam gasification of subbituminous-E. nitens blend chars with a blending ratio of 20:80 at 850°C (a), 900°C (b) and 950°C (c)

50% sub-bituminous – 50% E. nitens blends





(b)

Figure E-11: The composition of producer gas from steam gasification of subbituminous-E. nitens blend chars with a blending ratio of 50:50 at 850°C (a) and 900°C

80% sub-bituminous – 20% E. nitens blends






Figure E-12: The composition of producer gas from steam gasification of subbituminous-E. nitens blend chars with a blending ratio of 80:20 at 850°C (a), 900°C (b) and 950°C (c)

## Appendixes F – Char reactivity



### F-1 Effect of feedstock species on char conversion percentage

(a)



Figure F-1: The effect of feedstock species on char conversion percentage at 900 (a) and 950°C (b)



### F-2 Effect of feedstock species on char reactivity

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Figure F-2: The effect of feedstock species on char reactivity at 900 (a) and 950°C (b)

#### F-3 Effect of AAEM on char reactivity



(a)



Figure F-3: The comparison of char reactivity for lignite, acid-washed lignite and subbituminous chars at the gasification temperature of 850°C (a) and 950°C (b)

#### F-4 Effect of gasification temperature on char reactivity of coal-biomass blends

### Lignite – pine blend



(a)



Figure F-4: The effect of temperatures on char reactivity in co-gasification of lignitepine blend with a coal to biomass blending ratio of 20:80 (a) and 80:20 (b)



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Figure F-5: The effect of temperatures on char reactivity in co-gasification of lignite-E. niten blend with a coal to biomass blending ratio of 20:80 (a) and 80:20 (b)



(a)



Figure F-6: The effect of temperatures on char reactivity in co-gasification of subbituminous-pine blend with a coal to biomass blending ratio of 20:80 (a) and 80:20 (b)



(a)



Figure F-7: The effect of temperatures on char reactivity in co-gasification of subbituminous-E. niten blend with a coal to biomass blending ratio of 20:80 (a) and 80:20

#### F-5 Effect of coal to biomass blending ratio on char reactivity of blends

#### Lignite – pine blend



(a)



Figure F-8: The effect of blended ratio on char reactivity for lignite-pine blend chars at the gasification temperature of 900°C (a) and 950°C (b)





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Figure F-9: The effect of blended ratio on char reactivity for lignite-E. niten blend chars at the gasification temperature of 900°C (a) and 950°C (b)

#### Sub-bituminous - pine blend



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Figure F-10: The effect of blended ratio on char reactivity for sub-bituminous-pine blend chars at the gasification temperature of 900°C (a) and 950°C (b)



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Figure F-11: The effect of blended ratio on char reactivity for sub-bituminous-E. niten blend chars at the gasification temperature of 900°C (a) and 950°C (b)

# G. Appendixes G – Database and error analysis

File	Date of test	Lianite	Pine	Temp.	Pellet Mass	Water Trap	Ash (a)	Carbon	Gas production
		g			(g)	(ml)	, C.: (9)	balance Error	error
mg100.0.850la	Jul 09, 2009	100%	0%	850	1.0000	95	0.1740	1%	2%
mg100.0.850lc	Nov 02, 2009	100%	0%	850	1.0000	90	0.1494	1%	5%
mg100.0.850ld	Sep 13, 2010	100%	0%	850	1.0040	98	0.1655	1%	3%
mg100.0.900la	Jun 26, 2009	100%	0%	900	1.0000	70	0.1110	4%	4%
mg100.0.900lb	Jul 13, 2009	100%	0%	900	1.0000	79	0.1170	2%	1%
mg100.0.900ld	Jun 01, 2010	100%	0%	900	1.0079	75	0.1253	5%	2%
		1000/							===
mg100.0.950la	Jun 17, 2009	100%	0%	950	1.0000	45	0.0890	1%	5%
mg100.0.950lb	Jul 13, 2009	100%	0%	950	1.0000	53	0.0950	5%	4%
mg100.0.950ic	Jul 29, 2010	100%	0%	950	1.0060	60	0.0671	5%	3%
mg80 20 850lpa	Dec 16 2009	80%	20%	850	1 0000	115	0 1650	1%	3%
mg80 20 850lpb	Jun 24, 2010	80%	20%	850	1 0086	110	0 1375	1%	1%
mg80 20 850lpc	Aug 02 2010	80%	20%	850	1.0031	120	0.1631	5%	5%
ingeoizeicecipe	, lag 62, 2010	0070	2070	000			011001	• / •	• / •
mg80.20.900lpa	Jul 01, 2010	80%	20%	900	1.0061	95	0.1175	5%	1%
mg80.20.900lpb	Jul 01, 2010	80%	20%	900	1.0028	100	0.1148	1%	0%
mg80.20.900lpc	Aug 03, 2010	80%	20%	900	1.0048	80	0.1093	5%	2%
	, in the second s								
mg80.20.950lpa	Jul 30, 2010	80%	20%	950	1.0026	70	0.0736	5%	2%
mg80.20.950lpb	Jul 30, 2010	80%	20%	950	1.0020	75	0.0831	3%	3%
mg80.20.950lpc	Jul 30, 2010	80%	20%	950	1.0037	73	0.0659	4%	4%
				_					
mg50.50.850lpa	Aug 02, 2010	50%	50%	850	1.0018	160	0.1542	5%	3%
mg50.50.850lpb	Jun 21, 2010	50%	50%	850	1.0076	140	0.1172	1%	1%
mg50.50.850lpc	Jun 22, 2010	50%	50%	850	1.0051	165	0.1367	0%	0%
mgE0 E0 000lpg	Nov 02, 2000	E09/	E09/	000	1 0000	05	0.0725	29/	29/
mg50.50.900lpa	lup 21, 2010	50%	50%	900	1.0000	90	0.0725	3%	3% 1%
mg50.50.900lpc	Nov 02, 2009	50%	50%	900	1.0000	110	0.0839	1%	5%
111g30.30.900ipc	1100 02, 2003	5078	50 /0	300	1.0000	110	0.0024	1 70	578
mq50.50.950lpa	Nov 03 2009	50%	50%	950	1 0000	55	0.0630	2%	2%
mg50.50.950lpb	Jun 23, 2010	50%	50%	950	1.0019	70	0.0844	1%	3%
mg50.50.950lpc	Jun 24, 2010	50%	50%	950	1.0043	60	0.0887	5%	2%
0	,								
mg20.80.850lpa	Aug 03, 2010	20%	80%	850	1.0059	150	0.1575	5%	3%
mg20.80.850lpb	Jun 18, 2010	20%	80%	850	1.0064	170	0.1295	4%	3%
mg20.80.850lpc	Aug 11, 2010	20%	80%	850	1.0041	145	0.1812	1%	2%
mg20.80.900lpa	Jun 18, 2010	20%	80%	900	1.0024	95	0.0538	3%	3%
mg20.80.900lpb	Aug 11, 2010	20%	80%	900	1.0046	85	0.0850	5%	2%
mg20.80.900lpc	Jun 17, 2010	20%	80%	900	1.0045	95	0.0574	2%	1%
m #20, 00, 050lm a	hum 45, 2010	200/	000/	050	1.0000	57	0.0454	09/	20/
mg20.80.950lpa	Jun 17, 2010	20%	00% 90%	950	1.0000	57	0.0434	19/	2%
mg20.80.950lpb	Jun 17, 2010	20%	00% 90%	950	1.0060	55	0.0577	170	170
111g20.00.950ipc	Jun 17, 2010	2070	00 /0	330	1.0000	00	0.0320	078	578
mg0.100.850pb	May 04, 2010	0%	100%	850	1.0068	80	0.0136	5%	3%
mg0.100.850pc	May 07, 2010	0%	100%	850	1.0016	72	0.0145	5%	4%
mg0.100.850pd	Jun 23, 2010	0%	100%	850	1.0086	80	0.0156	4%	1%
mg0.100.900pa	Jun 23, 2010	0%	100%	900	1.0046	40	0.0115	3%	1%
mg0.100.900pb	Oct 28, 2009	0%	100%	900	1.0000	35	0.0102	2%	1%
mg0.100.900pc	May 06, 2010	0%	100%	900	1.0027	38	0.0123	4%	4%
mg0.100.950pa	Oct 28, 2009	0%	100%	950	1.0008	21	0.0046	2%	1%
mg0.100.950pb	May 04, 2010	0%	100%	950	1.0068	22	0.0053	5%	2%
mg0.100.950pc	May 11, 2010	0%	100%	950	1.0036	30	0.0062	5%	3%

G-1 Profile of lignite-pine blend char gasification

# G-2 Profile of lignite-E. nitens blend char gasification

File	Date of test	Lignite	E. nitens	Temp.	Pellet Mass (q)	Water Trap (ml)	Ash (g)	Carbon balance Error	Gas production error
mg100.0.850la	Jul 09, 2009	100%	0%	850	1.0000	95	0.1740	1%	2%
mg100.0.850lc	Nov 02, 2009	100%	0%	850	1.0000	90	0.1494	1%	5%
mg100.0.850ld	Sep 13, 2010	100%	0%	850	1.0040	98	0.1655	1%	3%
mg100.0.900la	Jun 26, 2009	100%	0%	900	1.0000	70	0.1110	4%	4%
mg100.0.900lb	Jul 13, 2009	100%	0%	900	1.0000	79	0.1170	2%	1%
mg100.0.900ld	Jun 01, 2010	100%	0%	900	1.0079	75	0.1253	5%	2%
mg100.0.950la	Jun 17, 2009	100%	0%	950	1.0000	45	0.0890	1%	5%
mg100.0.950lb	Jul 13, 2009	100%	0%	950	1.0000	53	0.0950	5%	4%
mg100.0.950lc	Jul 29, 2010	100%	0%	950	1.0060	60	0.0671	5%	3%
mg80.20.850lna	Jul 17, 2009	80%	20%	850	1.0000	87	0.0920	3%	2%
mg80.20.850lnb	Jul 07, 2009	80%	20%	850	1.0000	86	0.0760	5%	3%
mg80.20.850lnc	Jul 17, 2009	80%	20%	850	1.0000	91	0.0920	5%	4%
			1	1					
mg80.20.900lna	Jan 24, 2009	80%	20%	900	1.0000	65	0.0600	3%	3%
mg80.20.900lnb	Jul 08, 2009	80%	20%	900	1.0000	55	0.0600	1%	1%
mg80.20.900lnc	Jul 20, 2009	80%	20%	900	1.0000	68	0.0700	2%	3%
	14 04 0000	0.001	0.001	0.00	4				
mg80.20.950lna	Mar 01, 2009	80%	20%	950	1.0000	48	0.0600	4%	1%
mg80.20.950lnb	Jul 08, 2009	80%	20%	950	1.0000	42	0.0710	5%	4%
mg80.20.950Inc	Sep 27, 2010	80%	20%	950	1.0044	50	0.0696	3%	5%
m = E0 E0 9E0  = e	Fab 25, 2000	E00/	500/	050	1 0000	110	0.0700	E0/	20/
mg50.50.850ina	Feb 25, 2009	50%	50%	000	1.0000	110	0.0790	5% 50/	3%
mg50.50.850inb	Jun 25, 2009	50%	50%	000	1.0000	95	0.0800	5% 0%	4%
mg50.50.850ina	Sep 17, 2010	50%	50%	008	1.0042	110	0.0688	0%	0%
ma50 50 000lpa	Ech 25, 2000	50%	50%	000	1 0000	65	0.0740	<b>5</b> %	19/
mg50.50.900lna	I eb 23, 2009	50%	50%	900	1.0000	65	0.0749	J /0	4 /0
mg50.50.900lnc	Sep 13, 2010	50%	50%	900	1.0000	75	0.0700	2%	5%
111g00.00.000ine	000 10, 2010	5070	0070	500	1.0000	10	0.0701	270	570
mq50 50 950lpa	Feb 28, 2009	50%	50%	950	1 0000	45	0.0549	1%	1%
mg50 50 950lnb	Jul 02, 2009	50%	50%	950	1 0000	42	0.0730	2%	3%
mg50.50.950lnc	Jul 15, 2009	50%	50%	950	1.0000	35	0.0640	5%	1%
J									
				1					
mg20.80.850lna	Sep 27, 2010	20%	80%	850	1.0022	105	0.0516	1%	2%
mg20.80.850lnb	Jul 06, 2009	20%	80%	850	1.0000	130	0.0620	0%	5%
mg20.80.850lnc	Jul 16, 2009	20%	80%	850	1.0000	102	0.0600	5%	4%
mg20.80.900lna	May 14, 2009	20%	80%	900	1.0000	68	0.0500	5%	1%
mg20.80.900lnb	Sep 14, 2010	20%	80%	900	1.0000	75	0.0455	1%	1%
mg20.80.900lnc	Jul 16, 2009	20%	80%	900	1.0000	60	0.0530	4%	5%
mg20.80.950lna	Jun 10, 2009	20%	80%	950	1.0000	30	0.0550	1%	2%
mg20.80.950lnb	Jun 16, 2009	20%	80%	950	1.0000	35	0.0400	2%	4%
mg20.80.950lnc	Jul 17, 2009	20%	80%	950	1.0000	33	0.0500	2%	4%
mg.0.100.850na	Mar 15, 2009	0%	100%	850	1.0000	80	0.0950	4%	4%
mg.0.100.850nb	Sep 20, 2010	0%	100%	850	1.0034	75	0.0987	1%	4%
mg.0.100.850nc	Jul 14, 2009	0%	100%	850	1.0000	68	0.1040	5%	5%
			_	1					
mg.0.100.900na	Mar 15, 2009	0%	100%	900	1.0000	42	0.0500	1%	1%
mg.0.100.900nb	Jun 29, 2009	0%	100%	900	1.0000	35	0.0400	0%	4%
mg.0.100.900nc	Jul 14, 2009	0%	100%	900	1.0000	38	0.0580	5%	3%
0.400.777			1007		4.00.15			4	
mg.0.100.950na	Jul 29, 2010	0%	100%	950	1.0013	40	0.0311	1%	0%
mg.0.100.950nb	Jun 24, 2009	0%	100%	950	1.0000	28	0.0230	2%	0%
mg.0.100.950nc	Jul 13, 2009	0%	100%	950	1.0000	35	0.0150	5%	3%

# G-3 Profile of sub-bituminous-pine blend char gasification

File	Date of test	Sub- bitunimous	Pine	Temp.	Pellet Mass (g)	Water Trap (ml)	Ash (g)	Carbon balance Error	Gas production Error
mg100.0.850sa	Jul 21, 2009	100%	0%	850	1.0000	142	0.2800	3%	1%
mg100.0.850sc	May 05, 2010	100%	0%	850	1.0024	174	0.2916	4%	1%
mg100.0.850sd	May 14, 2010	100%	0%	850	1.0036	200	0.3016	1%	4%
mg100.0.900sa	Jul 22, 2009	100%	0%	900	1 0000	130	0 1560	4%	4%
mg100.0.900sc	May 06, 2010	100%	0%	900	1 0041	109	0.1727	3%	2%
mg100.0.900sd	May 14, 2010	100%	0%	900	1.0037	125	0.1727	5%	3%
111g 100.0.00000	1112010	10070	070	000	1.0001	120	0.1000	070	0/10
mg100.0.950sa	Jul 22, 2009	100%	0%	950	1.0000	88	0.1420	5%	2%
mg100.0.950sb	Aug 03, 2009	100%	0%	950	1.0000	90	0.0990	3%	0%
mg100.0.950se	Sep 14, 2010	100%	0%	950	1.0049	95	0.1256	4%	4%
ma90.20.950apa	Jul 26, 2010	000/	209/	950	1 0060	250	0.2750	20/	A0/
mg90.20.850spa	Jul 27, 2010	00%	20%	000 950	1.0000	200	0.2759	2 70	4 70
mg80.20.850spb	Jul 29, 2010	00% 90%	20%	000	1.0039	230	0.2009	170	1%
mgo0.20.8505pd	Jul 20, 2010	00%	20%	000	1.0044	230	0.2011	470	3%
mg80.20.900spa	Jul 22, 2010	80%	20%	900	1.0036	140	0.1507	4%	1%
mg80.20.900spc	Jul 22, 2010	80%	20%	900	1.0025	135	0.1625	3%	0%
mg80.20.900spd	Jul 23, 2010	80%	20%	900	1.0036	150	0.1717	5%	2%
mg80.20.950spa	Jul 23, 2010	80%	20%	950	1.0052	85	0.1171	5%	2%
mg80.20.950spb	Jul 23, 2010	80%	20%	950	1.0041	80	0.1208	4%	3%
mg80.20.950spc	Jul 26, 2010	80%	20%	950	1.0063	90	0.1172	2%	3%
mq50 50 850spa	Jul 20, 2010	50%	50%	850	1 0020	240	0 1544	2%	0%
mg50.50.850spb	Jul 21, 2010	50%	50%	850	1.0020	230	0.1044	5%	2%
mg50.50.850spc	Jul 21, 2010	50%	50%	850	1.0061	230	0.1300	4%	2%
ing00.00.0003pc	50121, 2010	5078	5078	000	1.0001	200	0.1701	- 70	2 /0
mg50.50.900spa	Jul 16, 2010	50%	50%	900	1.0024	140	0.1241	5%	2%
mg50.50.900spb	Jul 16, 2010	50%	50%	900	1.0046	140	0.1279	3%	0%
mg50.50.900spc	Jul 19, 2010	50%	50%	900	1.0024	145	0.1385	5%	2%
mg50 50 950cp2	Jul 19, 2010	50%	50%	050	1 0064	85	0.0671	5%	2%
mg50.50.950spa	Jul 20, 2010	50%	50%	950	1.0004	105	0.0071	5% 5%	2%
mg50.50.950spb	Jul 20, 2010	50%	50%	950	1.0042	100	0.0745	5%	3%
ing00.00.0000pc	50120, 2010	5078	5078	550	1.0044	100	0.0743	578	578
mg20.80.850spa	Jul 13, 2010	20%	80%	850	1.0013	210	0.1956	3%	2%
mg20.80.850spb	Jul 13, 2010	20%	80%	850	1.0040	200	0.1832	0%	1%
mg20.80.850spc	Jul 15, 2010	20%	80%	850	1.0035	220	0.2079	2%	3%
mg20.80.900spa	Jul 14, 2010	20%	80%	900	1 0058	115	0 1351	4%	2%
mg20.00.00005pa	Jul 14, 2010	20%	80%	900	1.0000	120	0.1001	- <del>1</del> /6	1%
mg20.00.9003pb	Jul 15, 2010	20%	80%	900	1.0012	120	0.1004	2%	0%
111g20.00.3003pc	50115, 2010	2070	0070	500	1.0010	120	0.1005	2 /0	078
mg20.80.950spa	Jul 09, 2010	20%	80%	950	1.0069	85	0.0550	5%	5%
mg20.80.950spb	Jul 09, 2010	20%	80%	950	1.0034	75	0.0605	3%	0%
mg20.80.950spc	Jul 14, 2010	20%	80%	950	1.0026	75	0.0592	1%	1%
ma0 100 850pb	May 04, 2010	0%	100%	850	1 0068	80	0.0136	5%	3%
mg0.100.850pc	May 07, 2010	0%	100%	850	1.0000	72	0.0130	5%	4%
mg0.100.850pd	Jun 23 2010	0%	100%	850	1.0086	80	0.0140	4%	1%
nigo. 100.000pu	Jun 23, 2010	0 /0	10070	550	1.0000	00	0.0100	- 70	1 /0
mg0.100.900pa	Jun 23, 2010	0%	100%	900	1.0046	40	0.0115	3%	1%
mg0.100.900pb	Oct 28, 2009	0%	100%	900	1.0000	35	0.0102	2%	1%
mg0.100.900pc	May 06, 2010	0%	100%	900	1.0027	38	0.0123	4%	4%
			1.005		1.04.7.7				
mg0.100.950pa	Oct 28, 2009	0%	100%	950	1.0008	21	0.0046	2%	1%
mg0.100.950pb	May 04, 2010	0%	100%	950	1.0068	22	0.0053	5%	2%
mg0.100.950pc	iviay 11, 2010	0%	100%	900	1.0036	30	0.0062	5%	3%

### G-4 Profile of sub-bituminous-E. nitens blend char gasification

					Pellet	Water		Carbon	Gas
File	Date of test	Sub-	E. nitens	Temp.	Mass	Trap	Ash (g)	balance	production
		bitunimous			(g)	(ml)	,	Error	Error
mg100.0.850sa	Jul 21, 2009	100%	0%	850	1.0000	142	0.2800	3%	1%
mg100.0.850sc	May 05, 2010	100%	0%	850	1.0024	174	0.2916	4%	1%
mg100.0.850sd	May 14, 2010	100%	0%	850	1.0036	200	0.3016	1%	4%
mg100.0.900sa	Jul 22, 2009	100%	0%	900	1.0000	130	0.1560	4%	4%
mg100.0.900sc	May 06, 2010	100%	0%	900	1.0041	109	0.1727	3%	2%
mg100.0.900sd	May 14, 2010	100%	0%	900	1.0037	125	0.1550	5%	3%
mg100.0.950sa	Jul 22, 2009	100%	0%	950	1.0000	88	0.1420	5%	2%
mg100.0.950sb	Aug 03, 2009	100%	0%	950	1.0000	90	0.0990	3%	0%
mg100.0.950se	Sep 14, 2010	100%	0%	950	1.0049	95	0.1256	4%	4%
m a 80 20 850ana	Son 17, 2010	909/	209/	950	1 0010	100	0 4027	00/	40/
mg80.20.850sha	Sep 17, 2010	00%	20%	950	1.0012	100	0.1037	0%	4%
mg80.20.850shb	Sep 15, 2010	00%	20%	950	1.0020	170	0.2220	3%	4%
mg80.20.850snu	Aug 12, 2010	80%	20%	850	1.0033	170	0.1997	Z %	270 5%
111900.20.0003110	30130, 2003	0078	2070	000	1.0000	150	0.1000	570	570
mg80 20 900sna	Jul 30, 2009	80%	20%	900	1 0000	120	0.0980	5%	.3%
mg80 20 900snc	Aug 13, 2010	80%	20%	900	1.0069	140	0.1208	5%	1%
mg80.20.900snd	Aug 05, 2009	80%	20%	900	1.0000	135	0.1220	3%	2%
	,								
mg80.20.950sna	Jul 31, 2009	80%	20%	950	1.0000	75	0.0910	5%	3%
mg80.20.950snb	Aug 06, 2009	80%	20%	950	1.0000	75	0.0960	4%	3%
mg80.20.950snc	Aug 12, 2010	80%	20%	950	1.0066	85	0.0908	5%	0%
mg50.50.850sna	Jul 23, 2009	50%	50%	850	1.0000	170	0.1930	2%	2%
mg50.50.850snb	Sep 21, 2010	50%	50%	850	1.0012	185	0.1942	1%	3%
mg50.50.850snc	Jul 28, 2010	50%	50%	850	1.0029	200	0.1858	4%	4%
mg50.50.900sna	Sep 21, 2010	50%	50%	900	1.0044	140	0.0918	0%	1%
mg50.50.900snb	Aug 04, 2009	50%	50%	900	1.0000	100	0.1120	1%	2%
mg50.50.900snc	Sep 24, 2010	50%	50%	900	1.0020	135	0.0996	4%	1%
mg50.50.950sna	Jul 23, 2009	50%	50%	950	1.0000	65	0.0820	2%	1%
mg50.50.950snb	Aug 04, 2009	50%	50%	950	1.0000	80	0.0920	4%	2%
mg50.50.950snc	Jul 29, 2010	50%	50%	950	1.0078	85	0.0870	5%	0%
mg20.80.850sna	Sep 20, 2010	20%	80%	850	1.0032	200	0.2059	4%	1%
mg20.80.850snb	Sep 18, 2010	20%	80%	850	1.0021	200	0.2172	4%	3%
mg20.80.850snc	Aug 12, 2010	20%	80%	850	1.0020	185	0.2539	3%	4%
mg20.80.900sna	Jul 27, 2009	20%	80%	900	1.0000	122	0.1150	5%	3%
mg20.80.900snb	Aug 06, 2009	20%	80%	900	1.0000	127	0.0940	5%	2%
mg20.80.900snc	Sep 13, 2010	20%	80%	900	1.0021	125	0.0760	2%	5%
mg20.80.950sna	Jul 27, 2009	20%	80%	950	1.0000	75	0.0820	4%	0%
mg20.80.950snb	Aug 06, 2009	20%	80%	950	1.0000	70	0.0710	5%	4%
mg20.80.950snc	Sep 14, 2010	20%	80%	950	1.0023	85	0.0404	2%	0%
mg.0.100.850na	Mar 15, 2009	0%	100%	850	1.0000	80	0.0950	4%	4%
mg.0.100.850nb	Sep 20, 2010	0%	100%	850	1.0034	75	0.0987	1%	4%
mg.0.100.850nc	Jul 14, 2009	0%	100%	850	1.0000	68	0.1040	5%	5%
mg.0.100.900na	Mar 15, 2009	0%	100%	900	1.0000	42	0.0500	1%	1%
mg.0.100.900nb	Jun 29, 2009	0%	100%	900	1.0000	35	0.0400	0%	4%
mg.0.100.900nc	Jul 14, 2009	0%	100%	900	1.0000	38	0.0580	5%	3%
mg.0.100.950na	Jul 29, 2010	0%	100%	950	1.0013	40	0.0311	1%	0%
mg.0.100.950nb	Jun 24, 2009	0%	100%	950	1.0000	28	0.0230	2%	0%
mg.0.100.950nc	Jul 13, 2009	0%	100%	950	1.0000	35	0.0150	5%	3%

# G-5 Profile of acid-washed lignite-pine blend char gasification

File	Date of test	Acid- washed Lignite	Pine	Temp.	Pellet Mass (g)	Water Trap (ml)	Ash (g)	Carbon balance Error	Gas productio n Error
mg100.0.850wla	May 20, 2010	100%	0%	850	1.0053	230	0.2516	4%	2%
mg100.0.850wlb	Jun 11, 2010	100%	0%	850	1.0052	235	0.3581	0%	0%
mg100.0.850wlc	Jun 14, 2010	100%	0%	850	1.0071	260	0.4015	0%	0%
mg100.0.900wla	May 17, 2010	100%	0%	900	1.0036	160	0.0872	4%	4%
mg100.0.900wlb	May 18, 2010	100%	0%	900	1.0033	165	0.1246	5%	4%
mg100.0.900wld	Jun 09, 2010	100%	0%	900	1.0060	135	0.1418	1%	3%
mg100.0.950wla	May 18, 2010	100%	0%	950	1.0036	95	0.0792	4%	0%
mg100.0.950wlb	Way 20, 2010	100%	0%	950	1.0056	115	0.0923	3% 40/	1%
mg100.0.950wic	Jun 11, 2010	100%	0%	950	1.0070	110	0.0781	470	0%
mg80.20.850wlpa	Aug 27, 2010	80%	20%	850	1.0011	240	0.2587	4%	4%
mg80.20.850wlpb	Aug 27, 2010	80%	20%	850	1.0019	230	0.2411	5%	5%
mg80.20.850wlpc	Aug 28, 2010	80%	20%	850	1.0011	235	0.2579	5%	4%
mg80.20.900wlpa	Aug 19, 2010	80%	20%	900	1.0031	180	0.1439	4%	5%
mg80.20.900wlpb	Aug 19, 2010	80%	20%	900	1.0037	175	0.1278	2%	3%
mg80.20.900wlpc	Aug 20, 2010	80%	20%	900	1.0010	175	0.1116	5%	3%
mg80.20.950wlpa	Sep 08, 2010	80%	20%	950	1.0025	115	0.0493	1%	1%
mg80.20.950wlpb	Sep 08, 2010	80%	20%	950	1.0011	120	0.0535	1%	2%
mg80.20.950wlpc	Sep 08, 2010	80%	20%	950	1.0033	110	0.0523	2%	2%
mg50.50.850wlpa	Aug 28, 2010	50%	50%	850	1.0047	230	0.1400	0%	4%
mq50.50.850wlpb	Aug 30, 2010	50%	50%	850	1.0020	240	0.1513	1%	3%
mg50.50.850wlpc	Aug 30, 2010	50%	50%	850	1.0045	240	0.1624	1%	3%
mg50.50.900wlpa	Aug 16, 2010	50%	50%	900	1.0021	150	0.0961	5%	5%
mg50.50.900wlpb	Aug 17, 2010	50%	50%	900	1.0017	160	0.0965	5%	2%
mg50.50.900wlpc	Aug 17, 2010	50%	50%	900	1.0043	155	0.0688	2%	2%
mg50.50.950wlpa	Sep 07, 2010	50%	50%	950	1.0012	105	0.0379	1%	5%
mg50.50.950wlpb	Sep 07, 2010	50%	50%	950	1.0028	95	0.0389	1%	5%
mg50.50.950wlpc	Sep 08, 2010	50%	50%	950	1.0039	100	0.0394	3%	4%
mg20.80.850wlpa	Sep 01, 2010	20%	80%	850	1.0012	220	0.0906	0%	3%
mg20.80.850wlpb	Sep 02, 2010	20%	80%	850	1.0035	225	0.0976	2%	5%
mg20.80.850wlpc	Sep 02, 2010	20%	80%	850	1.0019	225	0.1045	1%	4%
mg20.80.900wlpa	Aug 16, 2010	20%	80%	900	1.0030	115	0.0702	1%	1%
mg20.80.900wlpb	Aug 13, 2010	20%	80%	900	1.0041	115	0.0621	3%	3%
mg20.80.900wlpc	Aug 16, 2010	20%	80%	900	1.0084	125	0.0686	0%	3%
mg20.80.950wlpa	Aug 31, 2010	20%	80%	950	1.0025	75	0.0343	5%	5%
mg20.80.950wlpb	Sep 01, 2010	20%	80%	950	1.0031	80	0.0299	3%	0%
mg20.80.950wlpc	Sep 02, 2010	20%	80%	950	1.0023	80	0.0287	2%	3%
		00/	10051	050	4.0000	00	0.0165	<b>F</b> 0/	0.71
mg0.100.850pb	May 04, 2010	0% 0%	100%	850	1.0068	80	0.0136	5%	3%
mg0.100.850pC	lun 23 2010	0%	100%	850	1.0016	12 80	0.0145	5% //	4% 1%
111gu. 100.000µ0	Jun 23, 2010	0 /0	100%	000	1.0000	00	0.0150	₩70	1 70
mg0.100.900pa	Jun 23, 2010	0%	100%	900	1.0046	40	0.0115	3%	1%
mg0.100.900pb	Oct 28, 2009	0%	100%	900	1.0000	35	0.0102	2%	1%
mg0.100.900pc	May 06, 2010	0%	100%	900	1.0027	38	0.0123	4%	4%
mg0.100.950pa	Oct 28, 2009	0%	100%	950	1.0008	21	0.0046	2%	1%
mg0.100.950pb	May 04, 2010	0%	100%	950	1.0068	22	0.0053	5%	2%
mg0.100.950pc	May 11, 2010	0%	100%	950	1.0036	30	0.0062	5%	3%

File	Date of test	Acid- washed Lignite	E. nitens	Temp.	Pellet Mass (g)	Water Trap (ml)	Ash (g)	Carbon balance Error	Gas production Error
mg100.0.850wla	May 20, 2010	100%	0%	850	1.0053	230	0.2516	4%	2%
mg100.0.850wlb	Jun 11, 2010	100%	0%	850	1.0052	235	0.3581	0%	0%
mg100.0.850wlc	Jun 14, 2010	100%	0%	850	1.0071	260	0.4015	0%	0%
400.000.1	14 17 0010	1000/	00/		4 0000	100		40/	40/
mg100.0.900wla	May 17, 2010	100%	0%	900	1.0036	160	0.0872	4%	4%
mg100.0.900wib	Iviay 16, 2010	100%	0%	900	1.0033	100	0.1240	3% 40/	4%
mg100.0.900wid	Jun 09, 2010	100%	0%	900	1.0060	135	0.1416	170	3%
mg100.0.950wla	May 18, 2010	100%	0%	950	1.0036	95	0.0792	4%	0%
mg100.0.950wlb	May 20, 2010	100%	0%	950	1.0056	115	0.0923	3%	1%
mg100.0.950wlc	Jun 11, 2010	100%	0%	950	1.0070	110	0.0781	4%	0%
mg80 20 850wlpa	Aug 24, 2010	80%	20%	850	1 0008	230	0 2526	3%	2%
mg80 20 850wlnb	Aug 25, 2010	80%	20%	850	1.0000	230	0.2381	4%	4%
mg80.20.850wlnc	Aug 25, 2010	80%	20%	850	1.0038	220	0.2260	5%	1%
0	<b>U</b>								
mg80.20.900wlna	Aug 23, 2010	80%	20%	900	1.0036	175	0.0805	3%	5%
mg80.20.900wlnb	Aug 23, 2010	80%	20%	900	1.0040	175	0.1029	5%	3%
mg80.20.900wlnc	Aug 24, 2010	80%	20%	900	1.0035	170	0.0915	5%	0%
mg80 20 950wlpa	Sep 10, 2010	80%	20%	950	1 0023	120	0.0498	1%	5%
mg80.20.950wlnb	Sep 10, 2010	80%	20%	950	1.0025	110	0.0430	- 7%	1%
mg80.20.950wlnc	Sep 10, 2010	80%	20%	950	1.0040	120	0.0513	5%	5%
Ū	1 /								
mg50.50.850wlna	Aug 31, 2010	50%	50%	850	1.0030	235	0.2092	5%	4%
mg50.50.850wlnb	Aug 31, 2010	50%	50%	850	1.0033	225	0.1816	0%	3%
mg50.50.850winc	Sep 01, 2010	50%	50%	850	1.0018	235	0.2296	5%	3%
mg50.50.900wlna	Aug 20, 2010	50%	50%	900	1.0025	150	0.1584	5%	4%
mg50.50.900wlnb	Aug 20, 2010	50%	50%	900	1.0021	150	0.1438	5%	1%
mg50.50.900wlnc	Aug 23, 2010	50%	50%	900	1.0050	155	0.1529	4%	3%
	Son 06, 2010	E09/	E09/	050	1.0010	05	0.0202	09/	20/
mg50.50.950wina	Sep 00, 2010	50%	50%	950	1.0019	100	0.0393	0%	2%
mg50.50.950wind	Sep 07, 2010	50%	50%	950	1.0023	105	0.0403	1%	0%
9									
				_					
mg20.80.850wlna	Sep 03, 2010	20%	80%	850	1.0014	220	0.0648	4%	2%
mg20.80.850winb	Sep 03, 2010	20%	80%	850	1.0021	210	0.0623	2%	3%
mg20.80.850winc	Sep 06, 2010	20%	80%	850	1.0026	210	0.0741	1%	4%
mg20.80.900wlna	Aug 17, 2010	20%	80%	900	1.0028	120	0.0442	5%	3%
mg20.80.900wlnb	Aug 18, 2010	20%	80%	900	1.0045	130	0.0545	5%	2%
mg20.80.900wlnc	Aug 18, 2010	20%	80%	900	1.0077	110	0.0457	5%	1%
m a 20, 80, 050 uda a	Sep 02, 2010	200/	0.00/	050	1.0019	70	0.0202	29/	40/
mg20.80.950wina	Sep 03, 2010	20%	80%	950	1.0010	70	0.0263	<b>∠</b> %	4%
mg20.80.950wind	Sep 06, 2010	20%	80%	950	1.0038	75	0.0203	5%	4%
<u>g_</u> 0.00.000Willo	200,2010	-070	0070	000			5.0200	070	-73
mg.0.100.850na	Mar 15, 2009	0%	100%	850	1.0000	80	0.0950	4%	4%
mg.0.100.850nb	Sep 20, 2010	0%	100%	850	1.0034	75	0.0987	1%	4%
mg.0.100.850nc	Jul 14, 2009	0%	100%	850	1.0000	68	0.1040	5%	5%
mg.0.100.900na	Mar 15. 2009	0%	100%	900	1.0000	42	0.0500	1%	1%
mg.0.100.900nb	Jun 29, 2009	0%	100%	900	1.0000	35	0.0400	0%	4%
mg.0.100.900nc	Jul 14, 2009	0%	100%	900	1.0000	38	0.0580	5%	3%
mg.0.100.950na	Jul 29, 2010	0%	100%	950	1.0013	40	0.0311	1%	0%
mg.0.100.950nb	Jun 24, 2009	0%	100%	950	1.0000	28	0.0230	2%	0%
111g.0.100.950nc	Jul 13, 2009	0%	100%	900	1.0000	35	0.0150	5%	5%