GASIFICATION OF BIO-OIL AND BIO-OIL/CHAR SLURRY

by

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B.Sc., Kyoto University, 2003
M.Sc., Kyoto University, 2005

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

in

The Faculty of Graduate Studies
(Chemical and Biological Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA

(Vancouver)

April 2010

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ABSTRACT

Economic utilization of biomass as a fuel has been limited by transportation cost. One suggested remedy to address the problems of processing biomass on a large scale is to pyrolyze solid biomass at numerous local sites and transport the resulting liquid or liquid/char slurry to a large centralized conversion plant. This research involves the gasification of biomass fast pyrolysis oil, so called bio-oil, and a slurry mixture of bio-oil and fast pyrolysis char into synthesis gas.

Kinetics of the reaction of steam with chars was studied using a thermo-gravimetric analyzer. Slurry Char was produced by pyrolysis of an 80 wt% bio-oil/20 wt% char mixture at nominal heating rates of 100–10,000°C/s. The resulting Slurry Char was subjected to steam gasification with 10–50 mol% steam at 800–1200°C. Reactivity of the Slurry Char increased with the pyrolysis heating rate, but was lower than that of Original Char. Kinetic parameters were established for a power-law rate model. Some measurements were initially done of gasification in CO₂.

A fluidized bed reactor, equipped with an atomization system, was constructed for gasification of bio-oil and slurry. The reactor contained either sand, or Ni-based catalyst. Experiments included gasification with pure steam and air. Effects of bed temperatures in the range 720–850°C, steam-to-carbon molar ratios of 2.0–7.5, and air ratios of 0–0.5 on gas composition and yields were tested. The carbon conversion of bio-oil to gas was found to be greater than that of slurry. The product gas composition was affected significantly by catalysis of the water-gas shift and the steam gasification. Greater yields of hydrogen and lesser yields of CO
and hydrocarbons were found when catalyst was used. On a dry, inert-free basis, gases of up to 61% H₂ were obtained. The data were compared with a thermodynamic equilibrium model. The product gas yield was reasonably predictable by the model.

A mass and energy balance model of steam gasification in a dual-bed gasifier-combustor revealed that energy requirements are sensitive to the steam/carbon ratio and to the recovery of latent heat in the produced gas.
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NOMENCLATURE

ADP  4-allyl-2,6-dimethoxyphenol

Ar  Archimedes number

BO  Bio-oil

C2+  Hydrocarbons having more than one carbon atoms in its molecule

C2–C4  Acetylene, ethylene, ethane, propylene, propane, iso-butane, 1-butene and butane

D  Diameter (m)

dp  Particle diameter (m)

E  Activation energy (J/mol)

g  Gravitational acceleration (m/s²)

Gc1HSV  Methane equivalent gas hourly space velocity (h⁻¹)

GHSV  Gas hourly space velocity (h⁻¹)

HAA  Hydroxyacetaldehyde

HAc  Acetic acid

HHV  Higher heating value (MJ/kg or GJ/m³)

H₂O/C  Steam to carbon molar ratio (mol/mol)

I.D.  Inner diameter (m)

K  Equilibrium constant

k  Rate constant (s⁻¹ Paⁿ)

k₀  Frequency factor (s⁻¹ Paⁿ)

L  Reactor length (m)
LHSV  Liquid hourly space velocity (h\(^{-1}\))

\(n\)  Reaction order regarding steam partial pressure.

O.D.  Outer diameter (m)

\(P\)  Pressure (Pa)

\(P_{\text{H}_2\text{O}}\)  Steam pressure (Pa)

\(R\)  Gas constant (J/(K·mol))

\(r(t)\)  Reactivity at the time \(t\) (s\(^{-1}\))

\(r_{\text{model}}\)  Reactivity calculated by model (s\(^{-1}\))

SEM  Scanning electron microscopy

SL  Bio-oil/char slurry

\(t\)  Time (s)

\(T\)  Temperature (K)

TGA  Thermogravimetric analyzer

\(U\)  Gas superficial velocity (m/s)

\(U_{\text{mf}}\)  Minimum fluidization velocity (m/s)

\(w(t)\)  Weight of char at the time \(t\) (mg)

\(w_0\)  Weight of char at the beginning of the gasification (mg).

\(w_f\)  Weight of char at the end of the gasification (mg).

\(X(t)\)  Fractional conversion

\(\Delta H^0_{298}\)  Heat of reaction at 298 K (kJ/mol)

\(\lambda\)  Air ratio (\(\lambda=1\) achieves the complete combustion of feedstock)

\(\mu\)  Viscosity (Pa·s)
\( \rho_g \)  
Gas density (kg/m\(^3\))

\( \rho_p \)  
Particle density (kg/m\(^3\))
ACKNOWLEDGEMENTS

I am most grateful to my supervisors, Drs. Naoko Ellis and A. Paul Watkinson for their invaluable advice, support and encouragement without which this thesis would not have been achieved successfully.

I would like to express my gratitude to Drs. John R. Grace and Peter V. Barr for kindly being members of my thesis committee and giving me critical and useful advice which have improved the quality of the thesis.

My gratitude is also due Dr. Yong-Hua Li for advice on experimental work, and Mr. Gordon Cheng and Mr. Doug Yuen in the machine shop for their assistance with mechanical aspects of my experimental setup, as well as Mr. Alex Thng, Mr. Graham Liebelt, Mr. Charles Cheung and Mr. David Roberts for construction of the setup. Special thanks are given to Mr. Horace Lam and Mr. Richard Ryoo in the Stores for helping me with all kinds of procurement. My former and present officemates, research fellows, visiting students and undergraduate summer students have made my program an unforgettably great experience.

I would also like to thank Dynamotive Energy Systems and VTT, Technical Research Centre of Finland Finland for providing bio-oil and fast pyrolysis char for the experimental study.

Finally, I am deeply indebted to my wife Hiromi for understanding my enrolment in a program of long duration, and providing consistent encouragement.
CO-AUTHORSHIP STATEMENT

I conducted all experimental work, data analysis, and prepared all the drafts of manuscripts (Chapters 2, 3 4 and 5) in this thesis. The drafts of manuscripts have been reviewed and strengthened through input given by my supervisors Dr. Naoko Ellis and Dr. A. Paul Watkinson.
CHAPTER 1 Introduction

1.1 Preface

Biomass is a promising renewable resource which can contribute to the substitution of dwindling fossil resources over many parts of the world. The increased interest in renewable and sustainable resources is a result of concerns about climate change caused by anthropogenic greenhouse gas, mainly CO$_2$ (IPCC, 2007), and demand for a secure supply of fuel, energy and chemicals. Biomass-derived fuels or chemicals obtained from short rotation forestry and other energy crops can contribute to reducing the net CO$_2$ emissions.

Increased biomass use for energy will be necessary to substitute for fossil fuels. Biomass is composed mainly of carbon, hydrogen and oxygen, and can be a source of chemicals and fuels. This need cannot be readily satisfied by other forms of sustainable energy: namely wind, solar, geothermal and hydro.

In Canada, wood residues from the forest industry are an available unused biomass source of 43.1 Mt-carbon/year. This is equivalent to an energy value of about 1.54 EJ/year, or 19% of the national fossil fuel use (Wood and Layzell, 2003). In addition, there exists a large quantity of unharvested trees killed by infection of bulate stain fungus distributed by pine beetles in the province of British Columbia, Canada. Approximately 580 million m$^3$ of trees (equivalent to 140 Mt carbon on the same basis (Wood and Layzell, 2003) ) have been killed since 1999 (Walton, 2009). Unharvested beetle killed trees increase the risk of wild fires due to their low water content; thus, the beetle killed trees need to be cut and used sooner than sound trees. Use
of the beetle killed trees for biomass to gas conversion is one of several promising options for efficient consumption.

Biomass can be converted to transportation fuels and chemicals by thermochemical processes. Production of synthesis gas from biomass is a key first step in the thermochemical route. Gasification of biomass may be carried out using either solid primary biomass or secondary products derived from pyrolysis processes. Steam gasification is a promising means to convert biomass since it produces synthesis gas, a mixture of hydrogen and carbon monoxide. The heat for this endothermic reaction can be provided by a separate combustion of char produced in the gasifier under conditions of incomplete carbon conversion. Therefore, there have been numerous studies on steam gasification of biomass using dual fluidized-bed gasifiers in which biomass is gasified by pure steam while residual carbon is combusted in a separated combustor (Shen et al., 2007; Pfeifer et al., 2009). In this way, steam gasification and combustion sections are completely separated, so that product gas from steam gasification can be obtained as non-diluted by N₂ even when the combustion part uses air for combustion agent. The heat generated in the combustor is recycled in the form of hot particles which flow to the gasifier (Shen et al., 2007).

Bio-oil, a product from the biomass fast pyrolysis process is a liquid with similar elemental composition to its original feedstock and with high bulk and energy density. When char, a byproduct of the fast pyrolysis process, is mixed with bio-oil, bio-oil/char slurry with even higher density is obtained (Table 1.1). This high bulk and energy density can reduce transportation costs to large scale centralized gasification plants; these costs have been a detrimental factor in large scale use of solid biomass resource. In addition, larger-scale
centralized conversion plants can be operated due to expanding economical transportation area when bio-oil/char slurry is used (Henrich et al., 2009). Although there are reported studies on steam gasification and partial oxidation of bio-oil, studies on slurry gasification have been limited to high temperature partial oxidation (1200–1600°C). In the present work, gasification of bio-oil/char slurry is studied in comparison to that of bio-oil. Firstly, the kinetics of gasification reactivity of bio-oil/char slurry in steam gasification is studied. Secondly, the partial oxidation air gasification performance of bio-oil/char slurry is studied using a lab-scale fluidized bed gasification setup, and the results are compared to those of bio-oil. Thirdly, steam gasification of bio-oil/char slurry is also studied using the setup, and compared to that of bio-oil. The gas compositions are compared with values calculated by equilibrium and modified equilibrium models.

1.2 Fast pyrolysis of biomass

Bio-oil is produced by fast pyrolysis of biomass. In the fast pyrolysis processes, biomass is heated to around 500°C within a few seconds in the absence of oxygen and decomposed to gas, vapour and char. The condensed liquid product from the vapour, bio-oil, is a dark brown coloured liquid of similar elemental composition to the feedstock biomass material (Bridgwater, 1999). The typical yield of the bio-oil from the fast pyrolysis processes is 75 wt% (Bridgwater, 1999), and reaches 90 wt% including char (Drift et al., 2006). The remaining product is wet gas, which can be used to provide the heat for the pyrolysis process. There are several reactor types for bio-oil production (e.g. fluid bed, transported bed, circulating fluid bed, rotating cone, ablative, vacuum), but the basic bio-oil producing procedures are quite similar (Bridgwater,
1999). The energy efficiency of the fast pyrolysis process is up to 90% (Ostman et al., 2001, Drift et al., 2006). This is competitive with the other biomass densification processes (i.e., wood pellet production; 88% (Bergman, 2005)).

Typical properties and components of bio-oil are shown in Tables 1.2 and 1.3 respectively (Bridgwater et al., 2001). A major factor of interest for a gasifier feedstock is its water content, which varies from 15 to 30 wt%, and affects the heating value. Due to organic acid compounds, bio-oil causes corrosion in fuel handling systems. In addition, bio-oil is thermally unstable, and also causes fouling in reactors due to oligomers and polymer precursors content which polymerize at high temperature (>80°C), and consequently, make bio-oil more viscous (Bridgwater, 1999). Therefore, upgrading or conversion to more stable fuels or chemicals is desirable for large scale usage in various purposes. Most of the char produced in wood pyrolysis has been separated from the crude bio-oil of Table 1.2.
Table 1.1  Bulk and energy densities of bio-oil, bio-oil/char slurry, wood pellets and wood chips (Sokhansanj, 2004; Bergman, 2005; Hamelinck et al., 2005)

<table>
<thead>
<tr>
<th></th>
<th>Bulk density (kg m$^{-3}$)</th>
<th>Energy density (GJ-HHV m$^{-3}$)</th>
<th>Energy density (MJ-HHV kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bio-oil</td>
<td>1200</td>
<td>22.9</td>
<td>19.1</td>
</tr>
<tr>
<td>Bio-oil/char slurry (80/20 wt%)</td>
<td>1300</td>
<td>29.7</td>
<td>22.8</td>
</tr>
<tr>
<td>Wood pellets</td>
<td>650</td>
<td>12.4</td>
<td>19.1</td>
</tr>
<tr>
<td>Wood chips</td>
<td>220</td>
<td>2.3</td>
<td>10.5</td>
</tr>
</tbody>
</table>
### Table 1.2  Typical properties of wood derived crude bio-oil (source: Bridgwater et al., 2001)

<table>
<thead>
<tr>
<th>Physical property</th>
<th>Typical value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water content</td>
<td>15-30 wt%</td>
</tr>
<tr>
<td>pH</td>
<td>2.5</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.2</td>
</tr>
<tr>
<td>Elemental analysis (water free oil basis)</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>55-58 wt%</td>
</tr>
<tr>
<td>H</td>
<td>5.5-7.0 wt%</td>
</tr>
<tr>
<td>O</td>
<td>35-40 wt%</td>
</tr>
<tr>
<td>N</td>
<td>0-0.2 wt%</td>
</tr>
<tr>
<td>Ash</td>
<td>0-0.2 wt%</td>
</tr>
<tr>
<td>HHV as produced (depends on water content)</td>
<td>16-19 MJ/kg</td>
</tr>
<tr>
<td>Viscosity (at 40°C and 25% water)</td>
<td>10-40 cp</td>
</tr>
<tr>
<td>Solids (char)</td>
<td>1 wt%</td>
</tr>
<tr>
<td>Vacuum distillation residue</td>
<td>Up to 50 wt%</td>
</tr>
</tbody>
</table>
Table 1.3 Representative chemical composition of fast pyrolysis liquid (source: Bridgwater et al., 2001)

<table>
<thead>
<tr>
<th>Major Components</th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>20-30</td>
</tr>
<tr>
<td>Lignin fragments: insoluble pyrolytic lignin</td>
<td>15-30</td>
</tr>
<tr>
<td>Aldehyde: acetaldehyde, hydroxyacetaldehyde, glyoxal, methylglyoxal</td>
<td>10-20</td>
</tr>
<tr>
<td>Carboxylic acids: formic, acetic, propionic, butyric, pentanoic, hexanoic, glycolic, (hydroxy acetic)</td>
<td>10-15</td>
</tr>
<tr>
<td>Carbohydrates: cellobiosan, a-D-levoglucosan, oligosaccharides, anhydroglucofuranose</td>
<td>5-10</td>
</tr>
<tr>
<td>Phenols: phenol, cresols, guaiacols, syringols</td>
<td>2-5</td>
</tr>
<tr>
<td>Furfurals</td>
<td>1-4</td>
</tr>
<tr>
<td>Alcohols: methanol, ethanol</td>
<td>2-5</td>
</tr>
<tr>
<td>Ketones: acetol (1-hydroxy-2-propanone), cycle pentanone</td>
<td>1-5</td>
</tr>
</tbody>
</table>
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The typical density of the bio-oil is 1200 kg/m$^3$, and the density of the mixture of bio-oil and pyrolysis char (bio-oil/char slurry) is 1300 kg/m$^3$ (Drift et al., 2006). With typical higher heating values of $\approx$18 MJ/kg, the large energy densities of bio-oil and bio-oil/char slurry on a volumetric basis compared to biomass feedstock and their forms as liquid reduce the cost for long distance transportation and traffic density (Henrich et al., 2009). The bulk and energy densities of bio-oil and bio-oil/char slurry are compared in Table 1.1 with those of wood pellets and wood chips. Transportation costs of bio-oil and bio-oil/char slurry are lower than for wood chips and wood pellets because of the higher energy densities and relative ease of handling due to their liquid form, making them efficient media for transportation.

1.3 Steam gasification of bio-oil

1.3.1 Reactions in steam gasification

Steam reforming of any oxygenated organic compounds proceeds according to the following overall reaction,

$$C_xH_yO_z + nH_2O \rightarrow n_1CO_2 + n_2H_2 + n_3CO + n_4CH_4 + n_6C_{2+} + n_7C_{(s)}.$$  \hfill(1.1)

where $C_xH_yO_z$ is the empirical formula of oxygenated organic compounds, and $x$, $y$ and $z$ can be determined by ultimate analysis, and stoichiometric coefficients $n_i$ can be calculated by gas analysis for gases, and by material balance of carbon for solid carbon, when no tar is generated. If only CO and H$_2$ are produced, the stoichiometric amounts are given in Equation (1.2),

$$C_xH_yO_z + (x - z)H_2O \rightarrow xCO + [(x + y/2 - z)]H_2.$$  \hfill(1.2)

If the oxygenated organic compound is a solid or heavy liquid, Reaction (1.2) is usually termed steam gasification. This reaction is followed by the methanation (1.3) and shift equilibria (1.4):
Chapter 1. Introduction

\[
\begin{align*}
\text{CO} + 3\text{H}_2 & \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}, \quad \Delta H^0_{298} = -205.8 \text{ kJ mol}^{-1} & (1.3) \\
\text{CO} + \text{H}_2\text{O} & \rightleftharpoons \text{CO}_2 + \text{H}_2, \quad \Delta H^0_{298} = -41.2 \text{ kJ mol}^{-1} & (1.4)
\end{align*}
\]

Depending on the conditions, the reverse Boudouard reaction may also occur,

\[
2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}, \quad \Delta H^0_{298} = -172 \text{ kJ mol}^{-1} & (1.5)
\]

Therefore, in the absence of solid carbon formation, the stoichiometric maximum yield of hydrogen that can be obtained is \(2 + (y-2z)/2x\) moles per mole of carbon in the feed material, as shown in following reaction, (Wang et al., 1996):

\[
\text{C}_x\text{H}_y\text{O}_z + (2x-z)\text{H}_2\text{O} \rightarrow x\text{CO}_2 + (2x+y/2-z)\text{H}_2
\]

(1.6)

According to Reaction (1.2), steam gasification of bio-oil proceeds according to,

\[
\text{CH}_{1.31}\text{O}_{0.47} + 0.53\text{H}_2\text{O} \rightarrow \text{CO} + 1.185\text{H}_2, \quad \Delta H^0_{298} = 108 \text{ kJ (mol carbon)}^{-1} & (1.7)
\]

where the elemental formula, \(\text{CH}_{1.31}\text{O}_{0.47}\) is calculated from the elemental composition of a bio-oil produced from poplar wood at NREL (Diebold et al., 1999) which has the composition 57.3 wt% C, 6.3 wt% H, 36.2 wt% O, 0.2 wt% N on a water free basis, containing 18.9 wt% moisture on a wet basis. The nitrogen amount in the bio-oil is regarded as negligible. The heat of reaction is calculated using estimated heat of combustion of bio-oil -462 kJ (mol-carbon)\(^{-1}\), -22.1 MJ (kg-water free bio-oil)\(^{-1}\) (Domalski et al., 1987). Details of the heat of reaction calculations are described in Appendix I. Because the steam gasification of bio-oil is an endothermic reaction, heat has to be provided for the reaction. If the shift reaction goes to completion, the maximum hydrogen yield corresponds to Reaction (1.8),

\[
\text{CH}_{1.31}\text{O}_{0.47} + 1.53\text{H}_2\text{O} \rightarrow \text{CO}_2 + 2.185\text{H}_2, \quad \Delta H^0_{298} = 67 \text{ kJ (mol-carbon)}^{-1} & (1.8)
\]

which is also an endothermic reaction. Therefore, steam gasification requires heat for endothermic reactions. From Reaction (1.8), 171g of \(\text{H}_2\) can be obtained from 1 kg of the bio-oil.
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at the maximum yield. However, the yield in practice is always lower than this value due to equilibrium reactions.

1.3.2 Catalyst screening and developing

As summarized in Table 1.4, gasification of bio-oil and its components has been studied extensively. Owing to its complex components and unstable properties, many researchers have chosen simpler model compounds for experimental studies. Firstly oxygenated organic compounds of light molecular weight (e.g., acetic acid) were used for catalytic steam gasification study. Secondly, heavier oxygenated organic compounds (e.g., glucose, cellulose, phenol, etc.) were used to study steam gasification. Those tests with model compounds were followed by work on bio-oil aqueous fraction extracted by water, separating the oil phase of potential materials to be used as a source for valuable chemicals. Crude or straight bio-oil steam gasification followed those studies. Various catalyst screening or development studies on steam gasification for bio-oil have been conducted, with optimization of the catalyst mixtures. Ni, Pt, Ru, etc. on base materials of Al₂O₃, ZrO₂, CeO₂ or mixtures of them have been mainly studied by researchers (Table 1.4). From those studies, Ni/Al₂O₃ catalyst with promoters (e.g. Mg, Ca, K), which is a common composition in commercial naphtha steam reforming, is also found to be highly effective for bio-oil steam gasification in terms of H₂ yield and conversion reducing carbon deposition on the catalyst, which deactivates catalysts. From their research on biomass steam or steam/O₂ gasification in a fast fluidized-bed gasifier, it was also reported by Aznar et al. (1998) that commercial naphtha steam reforming catalysts generally remove tar, at high effectiveness.
Table 1.4  Works on catalytic steam gasification of bio-oil, bio-oil aqueous fraction, model compounds of bio-oil and other biomass derived liquid

<table>
<thead>
<tr>
<th>Source</th>
<th>Reaction</th>
<th>Feed material</th>
<th>Reactor type, size</th>
<th>Catalyst</th>
<th>Operating conditions</th>
<th>Feed rate</th>
<th>( \text{H}_2 ) Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wang et al.,</td>
<td>Steam gasification</td>
<td>Model compounds: Acetic acid, Methanol, Cellulose</td>
<td>Packed bed micro</td>
<td>Ni-based Commercial cat. UCI G-90C 15% Ni on Al(_2)O(_3)/CaAl(_2)O(_4)</td>
<td>300-730°C ( \text{H}_2/\text{O}/\text{C} = 4.5\text{-7.5} )</td>
<td>( \text{G}_\text{HSV} = 336\text{-2240 h}^{-1} )</td>
<td>Steam</td>
</tr>
<tr>
<td>1996, 1997</td>
<td></td>
<td>Xylan, Levogluocan, Lignin, Aspen pyrolyzed vapour</td>
<td>reactor I.D. = 0.008 m</td>
<td>Low temp. shift cat. UCI C18HC 42% CuO, 47% ZnO, 11% Al(_2)O(_3)(support)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Phenol, Syringol, HAA in MeOH, ADP in MeOH</td>
<td></td>
<td>(expect to reform low-molecular-weight alcohols and aldehydes)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( d_\text{p} = 250\text{-}710 \times 10^{-6} \text{ m} )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0005 - 0.001 kg</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>When catalyst &lt;0.25 g, mixed with quartz chips (250-355 ( \times 10^{-6} \text{ m} ) )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ID = 0.008 m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Bed height &gt; 0.025 m</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wang et al.,</td>
<td>Steam gasification</td>
<td>Biooil aqueous fraction (poplar wood) Model compounds: Methanol, Acetic acid, Syringol, m-cresol</td>
<td>Fixed bed reactor I.D. = 0.0165 m ( L = 0.426 \text{ m} )</td>
<td>Commercial nickel-based catalysts UCI G-90C, UCI G-91, and dual-catalyst be of ICI 46-1 and 46-4</td>
<td>600-700°C ( \text{H}_2/\text{O}/\text{C} = 5\text{-35} )</td>
<td>( \text{G}_\text{HSV} = 760\text{-2450 h}^{-1} )</td>
<td>85% of stoichiometric potential from biooil aqueous fraction</td>
</tr>
<tr>
<td>1998</td>
<td></td>
<td></td>
<td></td>
<td>( d_\text{p} = 0.0024\text{-}0.004 \text{ m} ) 0.1 kg</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Catalysts can be easily regenerated by steam or CO2 gasification</td>
</tr>
<tr>
<td>Source</td>
<td>Reaction</td>
<td>Feed material</td>
<td>Reactor type, size</td>
<td>Catalyst</td>
<td>Operating conditions</td>
<td>Feed rate</td>
<td>H₂ Yield</td>
</tr>
<tr>
<td>------------------------------</td>
<td>-------------------</td>
<td>---------------------------------------------------------</td>
<td>-------------------------------------------------------------------------------------</td>
<td>---------------------------------------------------------------------------</td>
<td>--------------------------------------------------------------------------------------</td>
<td>----------------------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>Marquevich et al., 1999</td>
<td>Steam gasification</td>
<td>Model compounds: Acetic acid, xylose, glucose, sucrose in water 20% m-cresol, dibenzyl ether</td>
<td>2 Fixed bed reactors 1. I.D. = 0.0264 m ( L = 0.41 ) m for acetic acid and succharides 2. I.D. = 0.0127 m ( L = 0.28 ) m for m-cresol, dibenzyl ether, acetic acid</td>
<td>Rapid coking at ( T &lt; 650°C ) with acetic acid Oxygenated aromatics can be completely converted to gases at ( T &gt; 650°C ), ( H₂O/C = 3 ), ( G_{HSV} &gt; 850 ) h(^{-1} ) H₂ yield = 70-90% of stoichiometric value Sugars are difficult to reform 1. ( d_p = 0.0024-0.004 ) m, 0.1 kg, 50% ( \alpha )Al₂O₃ diluted, 2. ( d_p = 0.001-0.002 ) m, 0.01 kg</td>
<td>( 550-810°C, 500-750°C ) for acetic acid ( 725, 800,875°C ) (m-cresol, benzyl ether) ( H₂O/C = 3-6 ) 1.5-2bar Reaction completed at ( 600°C ) ( 650°C H₂O/C = 5 ) seems optimum</td>
<td>( 550-810°C, 500-750°C ) Acetic acid 784-5466 h(^{-1} ) M-cresol 8650 h(^{-1} ) Benzyl ether 11790 h(^{-1} ) Sugar 538-851 h(^{-1} )</td>
<td>67-90% of stoichiometric potential</td>
</tr>
<tr>
<td>Czernik et al., 1999, 2000, 2002, 2004</td>
<td>Steam gasification</td>
<td>Biooil aqueous fraction (pine sawdust, poplar wood, pine wood, peanut shells) Steam aqueous fraction of poplar wood Methane Crude glycerin Trap grease</td>
<td>Fluidized bed reactor ( D = 2 ) inch (nominal) C11-NK Sud-Chemie Entrained from reactor by 5%/day by attrition. Coke deposition at ( T = 800°C ) Low coke deposition at ( T = 850°C ) NREL prepared catalyst ( d_p = 300-500 \times 10^{-6} ) m, 0.15-0.25 kg</td>
<td>( 800-850°C, 870-950°C ) (methane) ( H₂O/C = Biooil aqueous fraction 7-9 Hemicellulose 9-14 Methane 3.85-7.1 Crude glycerin 2.1-2.6 Trap grease 2.7-5.0</td>
<td>( G_{HSV} = 770-1440 ) h(^{-1} ) 120-300 g/h 750°C Superheated steam 120-240 g/h</td>
<td>90% of stoichiometric value from bio-oil aqueous fraction</td>
<td></td>
</tr>
<tr>
<td>Source</td>
<td>Reaction</td>
<td>Feed material</td>
<td>Reactor type, size</td>
<td>Catalyst</td>
<td>Operating conditions</td>
<td>Feed rate</td>
<td>H₂ Yield</td>
</tr>
<tr>
<td>------------------------</td>
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<td>-----------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>Garcia et al., 2000</td>
<td>Steam gasification</td>
<td>Biooil aqueous fraction (poplar wood)</td>
<td>Packed bed micro reactor I.D. = 0.00785 m</td>
<td>Many Ni-based catalyst (commercial and research)</td>
<td>825-875°C H₂O/C = 4.9-11.0</td>
<td>G₁HSV = 62300-126000 h⁻¹ Steam (+ helium)</td>
<td>80-90% max. of stoichiometric potential</td>
</tr>
<tr>
<td>Magrini-Bair et al., 2002</td>
<td>Steam gasification</td>
<td>Bio-oil aqueous fraction (pine softwood)</td>
<td>Fluidized bed reactor D = 2 inch (nominal)</td>
<td>Ni, Mg, K were impregnated on 90% and 99% alumina particle dₚ &lt; 0.45 mesh (354 ×10⁻⁶ m)</td>
<td>850°C</td>
<td>150g/h steam 150g/h liquid</td>
<td>&lt; 95% of stoichiometric potential</td>
</tr>
<tr>
<td>Kechagiopoulos et al., 2004</td>
<td>Steam gasification</td>
<td>Model compounds of bio-oil and biogas: Ethylene glycol, Acetic acid, CH₃CO₂ mix at 6:4 with H₂O at H₂O/CH₃=0.75-5</td>
<td>Fixed bed</td>
<td>Sud-Chemie C11-9-09 EW dₚ = 180-500 ×10⁻⁶ m 5wt% Ni on calcium aluminate for acetic acid</td>
<td>450-750°C H₂O/C = 2.5-6</td>
<td>n.a.</td>
<td>&lt; 65-90% of stoichiometric potential</td>
</tr>
<tr>
<td>Rioche et al., 2005</td>
<td>Steam gasification</td>
<td>Bio-oil (beech wood) Model compounds: Acetic acid, Phenol, Acetone, Ethanol</td>
<td>Fixed bed I.D. = 0.015 m L = 0.3 m</td>
<td>Pt-CeZrO₂, Rh-CeZrO₂, Pd-CeZrO₂, Pt-Al₂O₃, Rh-Al₂O₃, Pd-Al₂O₃ 0.0001-0.0002 g</td>
<td>650-950°C H₂O/C = 2-100</td>
<td>G₁HSV = 43-3090 h⁻¹ 0.2 drop/s</td>
<td>&lt; 100% of stoichiometric potential (G₁HSV = 43 h⁻¹)</td>
</tr>
<tr>
<td>Galdámez et al., 2005</td>
<td>Steam gasification</td>
<td>Model compound: acetic acid</td>
<td>Fluidized-bed reactor was made of 316 stainless steel (SS316), and the distributor plate was composed of Inconel</td>
<td>Ni/Al catalyst (160-320 ×10⁻⁶ m), 0.2 kg</td>
<td>650°C H₂O/C=5.58 P=101 kPa</td>
<td>G₁HSV=13 000-62 000 h⁻¹</td>
<td>0.119 g H₂/g acetic acid (eq. 0.122 g H₂/g acetic acid) at G₁HSV=13000 h⁻¹</td>
</tr>
<tr>
<td>Source</td>
<td>Reaction</td>
<td>Feed material</td>
<td>Reactor type, size</td>
<td>Catalyst</td>
<td>Operating conditions</td>
<td>Feed rate</td>
<td>H₂ Yield</td>
</tr>
<tr>
<td>----------------------</td>
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<td>----------------------------------------------------------------------------</td>
<td>--------------------------------------------------------------------------------------</td>
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<td>----------------</td>
</tr>
<tr>
<td>Basagiannis and Verykios, 2006</td>
<td>Steam gasification</td>
<td>Model compound: acetic acid</td>
<td>microreactor consists of two 0.006 m O.D. sections of quartz tube, which serve as inlet and outlet to and from a quartz cell of 0.008 m o.d.</td>
<td>Al₂O₃ and La₂O₃, and Ni catalyst supported on La₂O₃/Al₂O₃ carrier, 0.0001–0.0001 kg(0.0005–0.005 m bed), particle size: 180–250 ×10⁻⁵ m;</td>
<td>550–800°C H₂O/HAc molar ratio: 3, P = 101 kPa.</td>
<td>Flow rate: 30 cm³/min; feed: 0.5% HAc, 1.5% H₂O in He</td>
<td>n.a.</td>
</tr>
<tr>
<td>Kechagiopoulos et al., 2006</td>
<td>Steam gasification</td>
<td>Bio-oil aqueous fraction Ethylene glycol Acetone Mixture of acetic acid, acetone and ethylene glycol</td>
<td>Fixed bed reactor, internal surface covered by alumina, I.D. = 0.01252 m, length = 0.712 m, high-temperature stainless steel</td>
<td>C11-NK Nickel based commercial naphtha reforming catalyst (Süd-Chemie, dₚ = 180–500 ×10⁻⁵ m) mixed with SiC of dₚ = 400 ×10⁻⁵ m average size</td>
<td>Ethylene glycol: 600–700°C, H₂O/C = 2–6 Acetone: 600–750°C, H₂O/C = 3–6 Ethylene glycol: 650–750°C, H₂O/C = 3–6 Bio-oil aqueous fraction: 600–900°C, H₂O/C = 8.2</td>
<td>Ethylene glycol: GHSV=1500 h⁻¹ Acetone: GHSV=1500 h⁻¹ Ethylene glycol: GHSV=1500 h⁻¹ Bio-oil aqueous fraction: GHSV=300–600 h⁻¹</td>
<td>Model compounds: &lt;90% at T&gt;600°C, H₂O/C &gt;3 Bio-oil aqueous fraction: &gt;60%</td>
</tr>
<tr>
<td>Takanabe et al., 2006</td>
<td>Steam gasification</td>
<td>Model compound: acetic acid</td>
<td>Fixed bed reactor</td>
<td>Pt/ZrO₂ catalyst, dₚ = 300–600 ×10⁻⁸ m, 0.00005–0.0002 kg</td>
<td>875 K, H₂O/C = 5</td>
<td>GHSV=40000–160000 h⁻¹, 87% at initial stage; GHSV=40000 h⁻¹</td>
<td></td>
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<tr>
<td>Basagiannis and Verykios, 2007</td>
<td>Steam gasification</td>
<td>Bio-oil aqueous fraction (beech)</td>
<td>Fixed bed</td>
<td>Ru/MgO/Al₂O₃, dₚ &lt;63 ×10⁻⁵ m, loaded on 1) a monolith (1200 channels per inch³), 0.024 m in diameter, 0.04 m in length and weighing 0.0066 kg (loading 1.7 g/in.³) and 2) a monolith (2400 channels per inch³) 0.00185 kg of catalyst was loaded on a monolith 0.025 m in diameter, 0.024 m in length and weighing 0.0024 kg (loading 2.2 g/in.³)</td>
<td>Acetic acid: 550–800°CBio-oil aqueous fraction: 700–800°C</td>
<td>Acetic acid: 290–470 cm³/min Bio-oil aqueous fraction: GHSV=4880–16570 h⁻¹</td>
<td>n.a.</td>
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<td>Source</td>
<td>Reaction</td>
<td>Feed material</td>
<td>Reactor type, size</td>
<td>Catalyst</td>
<td>Operating conditions</td>
<td>Feed rate</td>
<td>H₂ Yield</td>
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<tr>
<td>Czernik et al., 2007</td>
<td>Steam gasification</td>
<td>Bio-oil (hardwood) produced by Dynamotive</td>
<td>Fluidized bed reactor I.D.=2inch (nominal)</td>
<td>C11-NK Sud-Chemie (naphtha steam reforming) 4 laboratory formulated catalysts $d_p=300-500 \times 10^{-6}$ m</td>
<td>850°C H₂O/C=5.8</td>
<td>GₐHSV=920 h⁻¹</td>
<td>80–90% of stoichiometric potential</td>
</tr>
<tr>
<td>Davidian et al., 2007</td>
<td>Gasification</td>
<td>Bio-oil (beech wood residue)</td>
<td>Double envelope stainless steel reactor</td>
<td>Ni/Al₂O₃ catalyst ($d_p=200–300 \times 10^{-6}$ m) and K/La₂O₃-Al₂O₃ catalyst ($d_p=50–100 \times 10^{-6}$ m)</td>
<td>700°C</td>
<td>1–15 mL/h</td>
<td>40% with K/La₂O₃-Al₂O₃ catalyst</td>
</tr>
<tr>
<td>Ramos et al., 2007</td>
<td>Steam gasification</td>
<td>Model compound: acetol</td>
<td>Fluidized bed reactor (316 stainless steel), with Inconel distributor plate, inner section of 13.14 cm²,</td>
<td>Mixture of sand (0.264 kg) and catalyst (Ni–Al, Ni–Al–La, and Ni–Co–Al) (0–0.003 g), (both are $d_p=160–320 \times 10^{-6}$ m)</td>
<td>Non-catalytic: 450–650°C Catalytic: 600 and 650°C H₂O/C=1.3–6</td>
<td>GₐHSV=5947–22323 h⁻¹</td>
<td>i.e. 0.166 g H₂/g acetol with Ni–Al catalyst (eq. 0.171 g H₂/g acetol), 650°C, H₂O/C=4.6, GₐHSV=5947 h⁻¹</td>
</tr>
<tr>
<td>Wang et al., 2007</td>
<td>Steam gasification</td>
<td>Bio-oil</td>
<td>Fixed bed micro reactor</td>
<td>12CaO·7Al₂O₃ catalyst, doped with Mg, K or Ce (0.0002 kg, $d_p=180–250 \times 10^{-6}$ m)</td>
<td>250–750°C H₂O/C=1.5, 4.0 and 9.0</td>
<td>GₐHSV=10000 h⁻¹</td>
<td>2–2.5 mole H₂ yield/mole C fed at S/C=1.5–9.0, GₐHSV=10000 h⁻¹</td>
</tr>
<tr>
<td>van Rossum et al., 2007</td>
<td>Steam gasification and partial oxidation</td>
<td>Bio-oil (beech or pine wood chip)</td>
<td>Fluidized bed reactor, SS310S, Diameter=0.108 m, Height=0.72 m (Freeboard, diameter=0.196 m, height=0.33 m)</td>
<td>Nickel-Alumina catalyst: -Ni–K-La on alumina fluidizable catalyst ($d_p=200–300 \times 10^{-6}$ m) -KATALCO 23 (commercial methane reforming fixed bed catalyst) -KATALCO 46 (commercial naphtha reforming fixed bed catalyst) ($d_p=200–300 \times 10^{-6}$ m) -Sand ($d_p=150–450 \times 10^{-6}$ m) -Mixture of catalyst and sand</td>
<td>523–914°C H₂O/C=1.0–3.2 $\lambda$=0–26% $p&lt;100$ kPa</td>
<td>0.2–2.5 kg h⁻¹ bio-oil to 4–9 kg bed material</td>
<td>Steam gasification: 0–20% (stoichiometric) under non-catalytic 23–48% (stoichiometric) under catalytic Partial oxidation: 15% under non-catalytic at $\lambda$=23% 38–40% under catalytic at $\lambda$=23–26%</td>
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<tr>
<td>Source</td>
<td>Reaction</td>
<td>Feed material</td>
<td>Reactor type, size</td>
<td>Catalyst</td>
<td>Operating conditions</td>
<td>Feed rate</td>
<td>H₂ Yield</td>
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<tr>
<td>Bimbela et al., 2007, 2009</td>
<td>Steam gasification</td>
<td>Model compound: 50wt% acetic acid aqueous solution, 19.73wt% acetal aqueous solution, and 6.54wt% n-butanol aqueous solution</td>
<td>Micro reactor, fixed bed, I.D.=0.009 m, quartz tube, height=0.025 m</td>
<td>Sand layer followed by coprecipitated Ni–Al catalyst layer ( d_p =200–320 \times 10^{-6} \text{ m} )</td>
<td>550, 650, and 750°C Acetic acid 23% aqueous solution, ( \text{H}_2\text{O}/\text{C}=5.58 ) for acetic acid and acetal, and 14.70 for n-butanol ( P ): atmospheric</td>
<td>G₁, HSV=4789–134400 h⁻¹ (acetic acid) G₂, HSV=34430–172493 h⁻¹ (acetal) G₃, HSV=7759–46222 h⁻¹ (1-butanol)</td>
<td>Acetic acid: G₁, HSV=18000: achieved equilibrium composition G₂, HSV=18000: decreased ( \text{H}_2 ), ( \text{CO} ) and ( \text{CO}_2 ) yields with increasing ( \text{G}_1 ), HSV Acetal: G₂, HSV=34430–56928 h⁻¹; achieved equilibrium composition at initial stage G₃, HSV&gt;172493 h⁻¹; decreased ( \text{H}_2 ) yields with increasing ( \text{G}_3 ), HSV 1-butanol: G₃, HSV=7759 h⁻¹; achieved equilibrium composition G₂, HSV=11617 h⁻¹; decreased ( \text{H}_2 ) yields with increasing ( \text{G}_2 ), HSV</td>
</tr>
<tr>
<td>Domine et al., 2008</td>
<td>Steam gasification</td>
<td>Bio-oil (beech)</td>
<td>Fixed envelope, double envelope stainless steel tubular reactor</td>
<td>Cordierite monolith (0.002 kg, 0.02 m diameter, 0.017 m length) coated by either ( \text{Pt/CaO}_2\text{ZrO}_2\text{O}_2 ) or ( \text{Rh/CaO}_2\text{ZrO}_2\text{O}_2 )</td>
<td>700 and 780°C ( \text{H}_2\text{O}/\text{C}=2.5, 5 ) and 10 ( P ): n.a.</td>
<td>1–5 mL/h</td>
<td>Best performance with ( \text{Pt/CaO}_2\text{ZrO}_2\text{O}_2 ): 70% at 780°C, ( \text{H}_2\text{O}/\text{C}=10 ) with &lt;1% methane</td>
</tr>
<tr>
<td>Vagia and Lemonidou, 2008</td>
<td>Steam gasification, inert gasification</td>
<td>Acetic acid and acetone</td>
<td>Quartz tube reactor, I.D.=0.01 m, 0.02 m diameter</td>
<td>Ni, Rh or Ir on ( \text{CaO}_2\text{Al}_2\text{O}_3 ) and 12( \text{CaO}_7\text{Al}_2\text{O}_15 ), ( d_p =108–180 \times 10^{-6} \text{ m} ), 0.00005 kg with 0.0001 kg of quartz particles</td>
<td>550–750°C ( \text{H}_2\text{O}/\text{C}=0 ) or 3, ( P=101 \text{ kPa} )</td>
<td>Acetic acid: G₁, HSV=34500 h⁻¹ Acetone: G₃, HSV=28500 h⁻¹</td>
<td>Highest hydrogen yield is achieved with the 5 wt% ( \text{Ni/Al}_2\text{O}_3 ) catalyst, while the 0.5 wt% ( \text{Rh/Al}_2\text{O}_3 ) catalyst presents the highest resistant to coking</td>
</tr>
<tr>
<td>Wu et al., 2008</td>
<td>Steam gasification</td>
<td>Bio-oil (sawdust)</td>
<td>Two-stage fixed bed reactor system, Two of I.D.=0.02 m, height=0.8 m stainless steel.</td>
<td>1st stage: dolomite, ( d_p =0.002–0.003 \text{ mm} ) 2nd stage: YWC-95, Wuxi Quangya Co., Inc. Ni/MgO commercial catalyst, ( d_p =0.002–0.003 \text{ mm} )</td>
<td>700–900°C ( \text{H}_2\text{O}/\text{C}=1–16, ( P=101 \text{ kPa} )</td>
<td>GHSV=1800–14400 h⁻¹</td>
<td>81.1% at 800°C, G₁, HSV no more than 3600 h⁻¹</td>
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<td>Source</td>
<td>Reaction</td>
<td>Feed material</td>
<td>Reactor type, size</td>
<td>Catalyst</td>
<td>Operating conditions</td>
<td>Feed rate</td>
<td>H₂ Yield</td>
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<tr>
<td>Yaseneva et al., 2008</td>
<td>Steam gasification</td>
<td>Ethanol</td>
<td>quartz reactor (i.d. 0.0025 m) packed with a catalyst (0.00025 - 0.0005 mm fraction) diluted with a quartz sand</td>
<td>Al₂O₃ based catalyst doped with Ce-Zr and different components (Cu, Cu-Ni, Ru, Pt, La, Pr, Sm), ( d_p = 250 - 500 \times 10^{-6} ) m, 0.00018 kg, diluted in a 1:10 weight ratio with quartz sand</td>
<td>650–800°C</td>
<td>Volume composition EtOH: H₂O: N₂ = 1:4:5 fed into the reactor with the total flow rate 9 l/h</td>
<td>The highest H₂ yield was performed with Ru/CeₓZrᵧSm₀.₅/Al₂O₃</td>
</tr>
<tr>
<td>Marda et al., 2009</td>
<td>Partial oxidation</td>
<td>Bio-oil/methanol mixture (50/50wt%)</td>
<td>Microreactor, i.d. = 11 mm (20 mm at entrance)</td>
<td>Quartz wool</td>
<td>625–850°C O:C ratio 0.7–1.6</td>
<td>n.a.</td>
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<tr>
<td>Hu and Lu, 2009 (a, b)</td>
<td>Steam gasification</td>
<td></td>
<td>Fixed bed reactor, Ni/Al₂O₃ catalyst + quartz (50/50%)</td>
<td></td>
<td>(a) 300–800°C H₂O/C=6 ( P=101 ) kPa</td>
<td>(a) LHSV=10.1 h⁻¹</td>
<td>n.a.</td>
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<td>(b) 200–600°C H₂O/C=6 ( P=101 ) kPa</td>
<td>(b) LHSV=12.2 h⁻¹</td>
<td></td>
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<td></td>
<td>Steam gasification and partial oxidation</td>
<td>Model compound: acetic acid</td>
<td>Fixed bed reactor, Pt/ZrO₂ or Pt/CeO₂ catalyst 100 mg ( d_p = 300–600 \times 10^{-6} ) m</td>
<td></td>
<td>700°C H₂O/C=5 ( P=101 ) kPa</td>
<td>GHSV=80000 h⁻¹</td>
<td>Pt/ZrO₂: 85% max. at initial (steam gasification) ~74% for 4 h (1% O₂ partial oxidation) Pt/CeO₂: ~90% max at initial (steam gasification) 65–75% for 10 h (1% O₂ partial oxidation)</td>
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<tr>
<td>Source</td>
<td>Reaction</td>
<td>Feed material</td>
<td>Reactor type, size</td>
<td>Catalyst</td>
<td>Operating conditions</td>
<td>Feed rate</td>
<td>H₂ Yield</td>
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</table>
| Medrano et al., 2009 | Steam gasification        | Model compound: acetol and acetic acid | Fluidized bed reactor, I.D. = 25.4 mm, quartz tube | Mixture of sand and Ni-alumina catalyst ($d_p = 160\text{–}320 \times 10^{-6}$ m), bed height = 0.07 m, $U/U_{mf} = 6$ theoretically calculated | $650°C$ $H_2O/C=5.58$ $P=101$ kPa | Acetol: $G_{C1}\text{HSV}=8200$ h$^{-1}$ $-\infty$ (25000 h$^{-1}$ for modified catalyst) $U/U_{mf}=6$ Acetic acid: $G_{C1}\text{HSV}=6800$ h$^{-1}$ (25000 h$^{-1}$ for modified catalyst) $U/U_{ref}=10$ i.e., Acetol: 0.0047 at $G_{C1}\text{HSV}=\infty$ 0.0822 at $G_{C1}\text{HSV}=51459$ h$^{-1}$ 0.1342 at $G_{C1}\text{HSV}=25561$ h$^{-1}$ 0.1624 at $G_{C1}\text{HSV}=14628$ h$^{-1}$ 0.1664 at $G_{C1}\text{HSV}=8247$ h$^{-1}$ Ca/Al ratio 0.12, Mg/Al ratio 0.26, performed the best attrition durability for each mix. Ca/Al and Mg/Al ratio affected catalyst performance of acetic acid. Mg/Al mol ratio = 0.26 showed best catalyst activity durability.
1.3.3 Steam gasification using fluidized bed reactors

The fixed bed reactor designed for conventional steam reforming of natural gas and naphtha is not suitable for thermally unstable complex liquids obtained from lignocellulosic biomass because of their tendency to decompose thermally and form carbon deposits in the upper layer of the catalyst and in the reactor freeboard (Czernik et al., 2002). However, using a fluidized-bed reactor, gasification of these complex liquids can be efficiently carried out with the aid of a commercial nickel catalyst. From the studies in Table 1.4, various biomass materials (pine sawdust-derived bio-oil aqueous fraction, steam aqueous fraction of poplar wood, methane, crude glycerine, and trap grease) have been steam-gasified in fluidized bed reactors with catalysts. H\textsubscript{2} yields from various biomass-derived materials including straight bio-oil have approached or exceeded 80% of those theoretically possible for stoichiometric conversion at the gasification temperature around 800°C with Ni based catalyst. Bio-oil was also gasified with steam using the same equipment (Czernik et al., 2007). So far, their work has been limited to bio-oil aqueous fraction or straight bio-oil; bio-oil/char slurry has not been studied. Gasification properties of the slurry probably differ from those of bio-oil due to char content. The solid char may be expected to be less reactive than bio-oil. Therefore, a gasification study with slurry is worth conducting to develop gasification technology for this feedstock.

1.3.4 Feeding bio-oil and bio-oil/char slurry into a high-temperature gasifier

Feeding bio-oil and bio-oil/char slurry into a high-temperature gasifier is a technical challenge because of its high viscosity and polymerization tendencies. Bio-oil is composed of numerous oxygenated compounds and rapidly polymerizes when heated to more than 80°C.
Researchers who have conducted straight bio-oil gasification in fluidized bed reactors have used cooling devices for bio-oil feeding to prevent bio-oil from polymerizing and plugging in feeding lines (Czernik et al., 2007; Galdámez et al., 2005; van Rossum et al., 2007, 2009). In the present study, much effort has been made to design and install a working system for steady bio-oil and/or bio-oil/char slurry feeding and atomization. A cooling jacket was installed which fully surrounds the atomizing nozzle. In early work before the cooling jacket was added, plugging happened easily. Therefore, a cooling device is considered necessary for bio-oil and bio-oil/char slurry feeding unless devices which mechanically remove polymerized materials are installed.

1.3.5 Catalyst attrition in fluidized bed reactor

Although numerous gasification studies have been conducted using commercial reforming catalysts, those catalysts were not specially designed for fluidized beds, but rather for fixed beds. Attrition of the catalyst in fluidized bed reactors is of importance. There appear to be no commercial attrition-resistant steam reforming catalysts available. Conventional catalysts are susceptible to attrition, and in prior work they were entrained from the reactor at a rate of 5%/day (Czernik et al., 2002). Attrition-resistant research catalysts were developed by Magrini-Bair et al. (2002); however, these are not commercially available. The support materials are 90 and 99% alumina particles made by Coorstek, Inc. with surface areas of 0.2 and 1.0 m²/g, respectively, an order of magnitude less surface area than Ni-based commercial catalyst (8.8 m²/g, Sud-Chemie C11-NK). Attrition losses of the catalysts were less than 0.5 wt%/day. Moreover, the smaller surface area did not significantly affect catalyst performance. Those attrition-resistant catalysts make the gasification system more feasible. Although attrition of
catalyst is of importance when investigating process feasibility, conventional commercial catalysts are still effective for examining activity for short times. In addition, commercial catalysts are readily available and uniform in properties; the present study used a commercial catalyst for experiment.

1.3.6 Synthesis gas production by gasification of bio-oil/char slurry

Gasification of bio-oil/char slurry with oxygen has been reported (Dinjus et al., 2004). The gasification was carried out in a 3–6 MW entrained flow gasifier at 26 bar. Slurry consisted of bio-oil and 23–26 wt% of char and 3 wt% of straw ash with char diameter of 10–1000 µm. Slurry throughput was 0.35–0.5 t/h. Temperature was 1200–1600°C. The O₂ gas feeding amount corresponded to λ=0.4–0.6 (where λ is the ratio of oxygen used to the stoichiometric amount for complete combustion). N₂ was used for purging in the system. Complete carbon conversion (>99%) was obtained at high gasification temperature (>1000°C). Also, tar-free synthesis gas was obtained at 1200°C. This gasification process was thermodynamically controlled by available O₂ and the approximate raw synthesis gas composition could be estimated from the water-gas shift equilibrium,

\[
\frac{[[\text{CO}_2]-[\text{H}_2]]}{[[\text{CO}]-[\text{H}_2\text{O}]}} = K(T). \tag{1.9}
\]

An example product gas composition was 47% CO, 21% H₂, 18% CO₂, and 15% N₂ at 1200°C, λ=0.48, with char size of 94 µm (<90%). Tar was not obtained at this condition. In this study, synthesis gas was obtained from bio-oil/char slurry by autothermal (partial oxidation) gasification in which pure oxygen was fed as gasifying agent, and provides heat for the
endothermic gasification reactions. For example, the partial oxidation gasification of bio-oil proceeds according to,

$$\text{CH}_{1.31}\text{O}_{0.47} + 0.265\text{O}_2 \rightarrow \text{CO} + 0.655\text{H}_2,$$

(1.10)

$$\Delta H^0_{298} = -20 \text{ kJ mol}^{-1} \text{ (per atomic mol carbon),}$$

or -0.97 MJ kg$^{-1}$ (H$_2$O free bio-oil).

Exothermic Reaction (1.10) can be controlled by the oxygen feed rate. This process needs a facility for pure oxygen production that requires extra energy for the gasification, and a large scale process for sufficient efficiency. The present study of steam gasification of bio-oil/char slurry using a fluidized bed reactor with catalyst has not been reported. This approach produces a nitrogen-free synthesis gas from bio-oil/char slurry without air separation, by using steam as the gasifying agent. On the bench scale, electrical heaters provide the heat for this endothermic process. To investigate the feasibility, and for comparison of the process efficiency with that of steam gasification, catalytic gasification by partial oxidation of bio-oil/char slurry with/without steam is also investigated in the present study.

### 1.3.7 Equilibrium modeling

Li (2002) investigated equilibrium modeling on biomass gasification in a circulating fluidized bed to predict the maximum achievable yield of desired products from a reaction system after infinitely long time for given operating conditions. This analysis is useful to understand the process, and provides a useful design aid for evaluating the possible limiting behaviour of the complex reacting system. Kinetic modifications were introduced to apply the model to such systems as a fluid bed gasifier operating at about 850°C which did not fully
achieve equilibrium due to kinetic limitations. The present study uses a similar approach to predict product gas composition, and to obtain understanding of the process.

1.3.8 Research objectives

The objectives of the present study are to investigate the following:

(1) Steam gasification reactivity of char made from bio-oil/char slurry

To estimate the properties in gasifiers, the reactivity of bio-oil/char slurry is needed. Assuming char in the slurry limits the overall gasification rate in a gasifier, the steam gasification reactivity of char made from the slurry is subject to investigation. After determining the effects of temperature and steam partial pressure on conversion over time, a kinetic model is proposed.

(2) Steam gasification of bio-oil and bio-oil/char slurry in a fluidized bed reactor

(2.1) Effect of operating conditions on product gas compositions and yields

The effect of gasification temperature, steam to carbon feeding ratio, oxygen to carbon feeding ratio (for partial oxidation), space velocity of feed, and catalysis on product gas composition and yield are to be analyzed. The effect of char contained in the slurry on product gas is also studied.

(2.2) Steam versus partial oxidation gasification

In steam gasification, heat for the gasification is supplied solely by superheated steam and heat from external electrical furnace through the reactor wall. Since oxidation reactions provide heat for the endothermic reactions, steam gasification with partial
Chapter 1. Introduction

oxidation is of interest for easy operation without large amount of heat transfer through the reactor wall. The effect of oxygen feed rate on the product gases is studied.

(3) Comparison with an equilibrium model

Experimental results are compared with values calculated by equilibrium models (e.g. Li, (2004)) at which the conversion to gas is the achievable maximum. A kinetically modified model is also compared with the results to test if the product gas composition and yield can be predicted by the model even when kinetic effects are not negligible.

1.4 Thesis outline

The thesis is presented in a manuscript-based format. The thesis consists of the introduction chapter (Chapter 1), followed by research papers (manuscript-chapters) and a concluding chapter. In the manuscript-chapters, three studies on bio-oil and bio-oil/char slurry are shown. Chapter 2 shows the study on reactivity change between a fast pyrolysis char and the char made from rapid pyrolysis of a bio-oil/char slurry. By the analysis of rapid pyrolyzed Slurry Char, the reactivity of the slurry injection into the high temperature reactor system is investigated. Chapters 3 and 4 describe gasification studies using a lab-scale fluidized bed reactor with a bio-oil and a bio-oil/char slurry: Chapter 3 focuses on pure steam gasification of the bio-oil and the slurry; and Chapter 4 focuses on partial oxidation of the bio-oil and the slurry. Chapter 5 shows a case study of steam gasification in a dual-bed gasifier system, showing mass and energy balance. In Chapter 6, the comprehensive conclusions are given and recommendations for further works are presented.
1.5 References


Chapter 1. Introduction


Chapter 1. Introduction


CHAPTER 2 Steam Gasification Reactivity of Char from Rapid Pyrolysis of Bio-Oil/Char Slurry

2.1 Introduction

Biomass is considered a promising renewable resource which contributes to the world-wide needs for substitution of fossil resources. It is available in large amounts, and can be converted to transportation fuels and chemicals. Pyrolysis of biomass yields vapours, gas and char. In fast pyrolysis processes, biomass is heated to around 500°C within a few seconds in the absence of oxygen. The condensed product, bio-oil or pyrolysis oil, is a brown coloured liquid having similar elemental composition to the feedstock biomass (Bridgwater et al., 2001). As a high density liquid (typically 1200 kg/m³), bio-oil can be readily stored, and pumped, leading to reduced transportation cost compared to dry biomass. When mixed with char, a product of the same process, bio-oil/char slurry of density 1300 kg/m³ and energy density 30 GJ-HHV/m³ can be prepared (80 wt% bio-oil/20 wt% char). Steam gasification of the slurry yields synthesis gas which is an attractive product, since high quality fuels and chemicals can be produced via Fischer-Tropsch synthesis. Therefore a study of steam gasification of bio-oil and its slurry has been undertaken.

Bio-oil is composed of many oxygenated compounds derived originally from cellulose, hemi-cellulose and lignin. Thus, simple and light model compounds such as acetic acid, acetone, and other light oxygenated compounds which are components of bio-oil, were first studied in steam reforming (Wang et al., 1997; Wang et al., 1998; Czernik et al., 1999; Marquevich et al.,

1 A version of this chapter has been submitted for publication. Sakaguchi, M., Watkinson, A. P. and Ellis, N. Steam gasification reactivity of char from rapid pyrolysis of bio-oil/char slurry.
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1999; Garcia et al., 2000; Magrini-Bair et al., 2002; Rioche et al., 2005). After the light model compounds, heavier and more complex components such as phenols and hemicellulose, were gasified with steam (Czernik et al., 2002; Kechagiopoulos et al., 2006; Basagiannis and Verykios, 2007). With the idea of an integrated bio-oil use, the bio-oil aqueous fraction, rich in hemicellulose, was gasified, and the non-aqueous fraction, rich in pyrolitic lignin, was retained for production of valuable chemicals (Czernik et al., 2002). When heavy model compounds or lignin-derived compounds were gasified with catalyst, carbon tended to deposit on the catalyst surface, resulting in deactivation. Probably because of the difficulty in gasifying heavy compounds, whole bio-oil steam gasification research started only recently (Czernik et al., 2002; van Rossum et al., 2007; Wu et al., 2008; Davidian et al., 2007; Iojoju et al., 2007; Domine et al., 2008). On the other hand, steam gasification reactivity of wood char, similar to Original Char in a bio-oil/char slurry, was investigated earlier (Barrio et al., 2001), giving kinetic parameters for n-th order and Langmuir-Hinshelwood kinetic models. Similarly, sawdust was gasified with steam in a fluidized bed continuous gasifier, giving kinetic parameters for the n-th order kinetic model (Kojima et al., 1993). In this process, it can be assumed that the sawdust was pyrolyzed instantly after injection, and the resulting char was gasified by steam at a slow rate. The kinetic parameters are comparable to values from steam gasification of wood char. Despite much work on steam gasification of bio-oil and wood char, research for bio-oil/char slurry is limited to studies of oxygen blown pressurized entrained flow gasification at 1200-1600°C, to produce synthesis gas (Dinjus et al., 2004; Henrich, 2005). In addition, up to now, steam gasification kinetics have been studied for bio-oil and wood char only separately. The kinetic study of steam
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gasification of bio-oil/char slurry has not been reported, even though the kinetics of steam gasification of the slurry are important for a gasifier design.

We report on the gasification reactivity of bio-oil/char slurry, applicable to a steam-blown fluidized bed gasifier operating at temperatures of 800–1200°C. In the present study, it was assumed that the slurry is injected into a high-temperature gasifier, and rapidly pyrolyzed: the bio-oil components are first evaporated and/or decomposed rapidly, and then the resultant char is gasified with steam. Since the pyrolyzed bio-oil components might result in carbon deposition on the surface of the resultant char, steam gasification reactivity of the resultant char might be different from Original Char by the rapid pyrolysis upon injection. Therefore, steam gasification reactivity of char made by rapid pyrolysis of bio-oil/char slurry (Slurry Char) was analyzed, simulating injection of the slurry into a gasifier. The effect of heating rate during char preparation, and the steam concentration on the gasification rate were further analyzed. Kinetic parameters were determined according to the $n$-th order kinetic model, and compared with values from the literature.

2.2 Experimental section

Two bio-oils were used in the present study. Bio-oil A produced from birch and aspen forest thinning in Finland was provided by VTT, Technical Research Centre of Finland. Bio-oil B, produced from wood in a commercial scale fast pyrolysis plant, was provided by Dynamotive Energy Systems corporation in Canada. Original Chars A and B were the by-products of bio-oil production through fast pyrolysis (~500°C, a few seconds), separated from hot pyrolyzed gas by a cyclone, provided by Dynamotive Energy Systems corporation. Bio-oil B and Original Char B
were produced from the same feed stock at the same plant at yields of 60–75 wt%, and 15–20 wt%, respectively. Proximate analysis of the Original Chars and the ultimate analysis of Original Chars and the bio-oils are shown in Tables 2.1 and 2.2. Two bio-oil/char slurries were prepared by mixing 80 wt% bio-oil and 20 wt% Original Char: 1) a mixture of 80 wt% bio-oil A and 20 wt% Original Char A (slurry A); and 2) a mixture of 80 wt% bio-oil B and 20 wt% Original Char B (slurry B). Prior to mixing, char samples were crushed and sieved to a particle size below 38 µm. Particle sizes of the Original Chars were measured using a Mastersizer 2000 (Malvern Instruments): Original Char A was 18.7 µm and Original Char B was 14.6 µm (median). Prepared slurry samples were pyrolyzed using a Pyroprobe 1000 (CDS Analytical Inc.) in which heating rate can be set at nominal values of 10–100,000°C/s. The slurry (ca. 20 mg) was placed in a quartz tube (O.D. = 2.5 mm, I.D. = 1.9 mm and Length = 25 mm). The tube was inserted in a coiled electric heating element made of platinum, which was then placed in a small chamber (ca. 20 ml) with nitrogen purge at a flow rate of 100 ml/min. After purging the chamber with nitrogen for 5 minutes, the slurry was pyrolyzed by the heating element. The heating rate and temperature are electronically controlled by the Pyroprobe 1000. The quartz tube was heated to 800–1200°C at heating rate settings of 100, 1000 and 10,000°C/s on the equipment, and the final temperature was held for 30–60 seconds. It was not possible to check if the actual heating rates were equal to the nominal heating rates given by settings of the instrument. After pyrolysis, the resulting char (Slurry Char) was collected from the quartz tube and ground to a particle size below 38 µm. Slurry Char was gasified with steam in a thermogravimetric analyzer (TGA) (TA instruments Q600), which consists of a horizontal balance beam which holds a sample pan with
thermocouple in contact with the pan. Either Original Char or Slurry Char (ca. 2 mg) was placed on an alumina pan, dried at 110°C for 5 minutes in nitrogen, and then heated to gasification temperature at the heating rate of 50°C/min. The final temperature was maintained for 5-15 minutes while distilled water was injected into the furnace through a syringe pump, generating steam inside the TGA furnace. For smooth steam generation, a diffuser was placed in the furnace at the water tubing outlet. Steam was mixed with nitrogen in the furnace and reacted with the Slurry Char. The steam pressure was calculated assuming ideal gas. From the precision of the water pump and the mass flow controller in TGA, the accuracy of steam pressure was calculated to be ±3.2%. To reduce diffusion effects between the sample and bulk gas phase, a shallow sample pan (0.5 mm depth) was used. The total gas flow rate for each gasification temperature was set as shown in Table 2.3. From preliminary experiments with varying total gas flow rate, it was found that the gasification took place with very little effect of diffusion between 800–1000°C. Above 1000°C, a diffusion resistance appeared to significantly affect the gasification kinetics. BET surface area of partially gasified Slurry Char was measured with N₂ at 77 K via a multi-point method used with a Micrometritics ASAP2020 surface area analyzer. The data from Original Char and Slurry Char were compared.
Table 2.1  Proximate analysis of Original Char in wt%

<table>
<thead>
<tr>
<th>Sample</th>
<th>Moisture</th>
<th>Volatile Matter (dry basis)</th>
<th>Fixed Carbon (dry basis)</th>
<th>Ash (dry basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Char A</td>
<td>2.8</td>
<td>24.2</td>
<td>75.8</td>
<td>2.4</td>
</tr>
<tr>
<td>Char B</td>
<td>2.3</td>
<td>27.1</td>
<td>67.1</td>
<td>5.8</td>
</tr>
</tbody>
</table>

Table 2.2  Ultimate analyses of bio-oil and Original Char in wt%; ash for char is shown in Table 2.1

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>O (by diff.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>*Bio-oil A</td>
<td>41.2</td>
<td>6.9</td>
<td>&lt;0.3</td>
<td>51.9</td>
</tr>
<tr>
<td>*Bio-oil B</td>
<td>44.3</td>
<td>6.9</td>
<td>&lt;0.3</td>
<td>48.8</td>
</tr>
<tr>
<td>Char A</td>
<td>80.1</td>
<td>3.6</td>
<td>0.05</td>
<td>13.8</td>
</tr>
<tr>
<td>Char B</td>
<td>73.7</td>
<td>3.5</td>
<td>0.12</td>
<td>16.9</td>
</tr>
</tbody>
</table>

*Ultimate analysis of bio-oils was done by Canadian Microanalytical Service Ltd., Delta, British Columbia

Table 2.3  Total flow rate for gasification analysis

<table>
<thead>
<tr>
<th>Gasification temperature, °C</th>
<th>Flow rate, ml/min*</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>200</td>
</tr>
<tr>
<td>900</td>
<td>300</td>
</tr>
<tr>
<td>1000–1200</td>
<td>400</td>
</tr>
</tbody>
</table>

*Flow rate was set as large as possible in order to reduce diffusion effect around the char sample.

Flow rates at 800–900°C were lower due to steam generation restriction in the TGA furnace.
2.3 Treatment of experimental results

In the present study, the char reactivity at a given time was defined as:

\[ r(t) = -\frac{1}{w(t) - w_f} \frac{d(w(t) - w_f)}{dt} \]  \hspace{1cm} (2.1)

The degree of conversion, \( X(t) \) was obtained by:

\[ X(t) = 1 - \frac{w(t) - w_f}{w_0 - w_f} \] \hspace{1cm} (2.2)

Combining Equations 2.1 and 2.2 gave reactivity as a function of degree of conversion:

\[ r(X) = \frac{1}{1 - X} \frac{dX}{dt} \] \hspace{1cm} (2.3)

In this study, steam gasification reactivity of chars was evaluated using Equation 2.3.

Kinetic parameters for steam gasification reactivity of the Original Char and Slurry Char at \( X=0.5 \) were obtained for \( n \)-th order kinetic model instead of Langmuir-Hinshelwood kinetic model, assuming the kinetics is simply controlled only by steam pressure and temperature at the targeted temperature range.

\[ r = kP_{n,0}^n \] \hspace{1cm} (2.4)

where \( k = k_0 \cdot \exp \left( -\frac{E}{RT} \right) \) \hspace{1cm} (2.5)

as is commonly used for general char gasification kinetics (Barrio et al., 2001; Kojima et al., 1993).
Char steam gasification was carried out three times for each experimental condition, and a mean of each condition is shown on results figures with error bars indicating standard deviations. Kinetic parameters were determined by multiple regression of linearized form of Equations 2.4 and 2.5,

\[ \ln r = \ln k_0 - \frac{E}{RT} + n \ln P_{H_2O} \]  

Estimated kinetic parameters are shown with 95% confidence intervals. Those kinetic parameters were also determined by non-linear fitting in which the sum \( \Sigma ((r_{model} - r)^2/r^2) \) was used to minimize non-uniform errors. The weight function \( 1/r^2 \) equalizes all data points distributed in 2 orders of magnitude.

2.4 Results and discussion

Figures 2.1 and 2.2 show a typical weight loss curve and gasification rate \( X(t) \) change during a gasification experiment in the TGA. The first weight loss is release of volatiles in the char, followed by the second weight loss by steam gasification. The initial weight \( (w_0) \) and the final weight \( (w_f) \) for the steam gasification are indicated in the figures.
Figure 2.1  Typical Slurry Char weight loss curve during steam gasification experiment with TGA (Slurry Char B, 900°C, 10 kPa steam) (The final temperature was maintained for 5-15 minutes while distilled water was injected into the furnace through a syringe pump, generating steam inside the TGA furnace.)

Figure 2.2  Typical Slurry Char steam gasification rate $dX/dt$ during experiments (Slurry Char B, 900°C, 10 kPa steam) (The final temperature was maintained for 5-15 minutes while distilled water was injected into the furnace through a syringe pump, generating steam inside the TGA furnace.)
2.4.1 The effect of pyrolysis heating rate

Figure 2.3 shows the reactivity of Slurry Char A prepared by rapid pyrolysis at 900°C and heating rates of 100°C/s, 1000°C/s and 10,000°C/s as a function of conversion. The reactivity increased with the degree of conversion in a similar manner for all samples. The reactivity of Slurry Char A was close to that of Original Char A at $X=0.2$ and $X=0.4$, while it was 11~27% lower than the value for Original Char A at $X=0.6$ and 21~38% lower at $X=0.8$. For the Slurry Char, a higher pyrolysis heating rate resulted in higher gasification reactivity, and the reactivity difference between Original Char and Slurry Char became larger in the final stages of the reaction. This can be explained by differences in surface area. At $X=0.5$, BET surface area was 920 m$^2$/g in Original Char A, and 790 m$^2$/g for Slurry Char A formed by rapid pyrolysis at the heating rate of 100°C/s. This difference in surface area is consistent with the difference in reactivity from Original Char A to Slurry Char A. Considering that the gasification rate at 900°C is largely controlled by reaction rate at the char surface rather than diffusion resistance (as is explained below), then the surface area will affect the reactivity at this temperature. Therefore, rapid pyrolysis of bio-oil/char slurry made the resulting char less reactive in steam than Original Char produced with the bio-oil. As well, the lower the heating rate, the less reactive is the resultant char. For efficient steam gasification of bio-oil/char slurry, the system should be chosen such that the heating rate of slurry is as high as possible in order that the resulting char be most reactive.
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2.4.2 Effect of gasification temperature and steam pressure

Figure 2.4 shows the results of steam gasification reactivity of Original Char B and Slurry Char B at $X=0.5$ as a function of temperature at different steam partial pressures: 10, 30 and 51 kPa. Steam gasification reactivity of Slurry Char B was close to that of Original Char B. At $P_{\text{H}_2\text{O}}=10$ kPa, maximum reactivity was $\sim 0.04$ s$^{-1}$ whereas at higher steam pressure of 30 and 51 kPa, the maximum reactivity reached higher than 0.1 s$^{-1}$. At a fixed steam partial pressure of 30 kPa, the reactivity increased from 0.004 s$^{-1}$ to 0.1 s$^{-1}$, a factor of 250, as the temperature was raised from 800°C to 1200°C. Figures 2.5 and 2.6 show the effects of steam partial pressure on reactivity at $X=0.5$, for temperatures of 800–1000°C of the two chars, Original Char B and Slurry Char B, respectively. Increasing steam pressure from 10 to 51 kPa (a factor of 5.1) raised the reactivity typically by about 80%.
Figure 2.4  Reactivity of chars at \( X = 0.5 \); steam partial pressure at: (a) 10 kPa, (b) 30 kPa, and (c) 51 kPa
Figure 2.5  Original Char B steam gasification reactivity, steam effect \((X=0.5)\); continuous lines show \(n\)-th order reaction model

Figure 2.6  Slurry Char B reactivity as a function of steam partial pressure and temperature \((X=0.5)\); continuous lines show \(n\)-th order reaction model
2.4.3 \textit{n}-th order kinetics

The kinetic parameters for the \textit{n}-th order kinetic model were determined for the Slurry Char B and Original Char B, which were pyrolyzed at the heating rate of 1000°C/s. Data obtained from the gasification at 800–1000°C and steam partial pressure at 10–51 kPa were used for determining the parameters, \(k_0\), \(E\) and \(n\). Parameters obtained from linearized model fitting and non-linear fitting are close. The results are compared in Table 2.4 with values from the literature. Activation energies and frequency factors obtained in this study are similar to those of wood chars obtained by Barrio et.al. for 750–950°C and \(P_{H2O}=10–51\) kPa (Barrio \textit{et al.}, 2001), while the reaction orders were somewhat smaller. Compared with Kojima \textit{et al.} for 850–950°C and \(P_{H2O}=0–58\) kPa (Kojima \textit{et al.}, 1993), activation energy in the present work was higher, but reaction order was similar. As can be seen, those parameters from the literature are obtained from a similar range of temperature and steam pressure to those in the present study, and are therefore roughly comparable. The discrepancies may come from uncertainty of fitting method, or from the differences in char origin. Figures 2.7 and 2.8 show Arrhenius plots of the steam gasification for Original Char B and Slurry Char B. The plot of \(\ln k\) vs \(1/T(K)\) was linear up to 1000°C in a similar manner for both chars. Above 1000°C, the rate became less sensitive to temperature, which is attributed to increased diffusional resistance and/or \(H_2\) inhibition due to increased \(H_2\) production by steam gasification at the higher temperatures.
### Table 2.4: Kinetic parameters determined and literature value for comparison

<table>
<thead>
<tr>
<th>Reference</th>
<th>Char origin</th>
<th>$E$ (kJ mol$^{-1}$)</th>
<th>$k_0$ (s$^{-1}$Pa$^{-n}$)</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work (800–1000°C)</td>
<td>Fast pyrolysis of wood</td>
<td>235 ± 12</td>
<td>6.5×10$^5$ (9×10$^4$–5×10$^6$)</td>
<td>0.41 ± 0.13</td>
</tr>
<tr>
<td>Least-square fitting of linearized model</td>
<td>Bio-oil/char slurry</td>
<td>219 ± 13</td>
<td>3.4×10$^5$ (4×10$^4$–3×10$^6$)</td>
<td>0.34 ± 0.14</td>
</tr>
<tr>
<td>This work (800–1000°C)</td>
<td>Fast pyrolysis of wood</td>
<td>236</td>
<td>4.5×10$^5$</td>
<td>0.45</td>
</tr>
<tr>
<td>Non-linear fitting Bio-oil/char slurry</td>
<td>218</td>
<td>2.7×10$^5$</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>Barrio et al., 2001</td>
<td>Birch</td>
<td>237</td>
<td>3.30×10$^6$ ± 6×10$^4$</td>
<td>0.57 ± 0.03</td>
</tr>
<tr>
<td>(750–950°C)</td>
<td>Beech</td>
<td>211</td>
<td>2.15×10$^5$ ± 1×10$^5$*</td>
<td>0.51 ± 0.05</td>
</tr>
<tr>
<td>Kojima et al., 1993 (850–950°C)</td>
<td>Sawdust</td>
<td>179</td>
<td>1773</td>
<td>0.41</td>
</tr>
</tbody>
</table>

* The units were converted to s$^{-1}$Pa$^{-n}$
Chapter 2. Steam Gasification Reactivity of Char from Rapid Pyrolysis of Bio-oil/Char Slurry

Figure 2.7  Arrhenius plot of Original Char B steam gasification ($X=0.5$); dotted line indicates linear relationship for 800–1000°C

Figure 2.8  Arrhenius plot of Slurry Char B steam gasification ($X=0.5$); dotted line indicates linear relationship for 800–1000°C
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2.5 Conclusion

Steam gasification study of char originally produced with bio-oil, and char produced by pyrolysis of bio-oil/char slurry leads to the following conclusions:

(1) At 900°C, as conversion increased, the reactivity of Slurry Char became less compared to that of Original Char. This deactivation was consistent with surface area change by rapid pyrolysis. At X=0.5 and 900–1200°C, the reactivity of Slurry Char was very close to that of Original Char. At 800°C, the lowest gasification temperature tested, Slurry Char was more reactive than Original Char.

(2) Raising the pyrolysis heating rate of bio-oil/char slurry resulted in a higher reactivity of Slurry Char. Therefore heating rate of bio-oil/char slurry injected into a steam gasification reactor is an important factor for the gasifier system design.

(3) The kinetic parameters of steam gasification of Slurry Char and Original Char according to the n-th order kinetic model were determined at X=0.5: $E=235$ kJ/mol, $k_0=1.69\times10^6$ and $n=0.41$ for Slurry Char B, and $E=219$ kJ/mol, $k_0=7.38\times10^5$ and $n=0.34$ for Original Char B. These activation energies and reaction orders are similar to respective values for wood char found in the literature.

(4) At temperatures above 1000°C, the temperature sensitivity of the reactivity decreased, presumably due to the importance of diffusional resistances.
2.6 References


Chapter 2. Steam Gasification Reactivity of Char from Rapid Pyrolysis of Bio-oil/Char Slurry


CHAPTER 3  Steam Gasification of Bio-Oil and Bio-Oil/Char Slurry in a Fluidized Bed Reactor

3.1 Introduction

Biomass is a promising renewable resource which can contribute to the substitution of fossil resources over many parts of the world. It can be converted to transportation fuels and chemicals by thermochemical or biological processes. Production of synthesis gas from biomass is a key first step in the thermochemical route. Gasification of biomass may be carried out using either solid primary biomass or secondary products derived from pyrolysis processes. Pyrolysis of biomass yields vapours, gas and char. In rapid pyrolysis processes, biomass is heated up in the absence of oxygen to around 500°C within a few seconds and decomposed to gas, vapour and char. The condensed liquid product from the vapour, bio-oil, is a dark brown-coloured liquid of similar elemental composition to the feedstock biomass material (Bridgwater et al., 2001). As a high density liquid (typically 1200 kg/m³), bio-oil can be readily stored, and pumped, leading to reduced storage and transportation cost compared to dry biomass. When mixed with the by-product char from the same process, a bio-oil/char slurry of density 1300 kg/m³ can be prepared (at 80 wt% bio-oil/20 wt% char). The slurry has an energy density 24% higher than the original biomass fed to the pyrolyzer. As energy dense slurry reduces not only transport cost but also traffic density substituting truck transport by rail transport, a concept of many local pyrolysis facilities connected with a large scale centralized fuel synthesis plant has been studied (Henrich et al., 2009). Possibly due to the difficulty in gasification of heavy compounds, whole bio-oil

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2 A version of this chapter will be submitted for publication. Sakaguchi, M., Watkinson, A. P. and Ellis, N. Steam gasification of bio-oil and bio-oil/char slurry in a fluidized bed reactor.
steam gasification research has started only recently. Despite the extensive works on steam gasification of bio-oil (e.g. Czernik et al., 2007; Marda et al., 2009; van Rossum et al., 2007), research for bio-oil/char slurry is limited to studies of oxygen-blown, pressurized, entrained-flow gasification at 1200–1600°C (Dinjus et al., 2004; Henrich, 2005). There has been no study on pure steam gasification of bio-oil/char slurry reported. Partial oxidation, conducted by introducing pure oxygen or air, results in decomposition of the feedstock as well as supplying heat for endothermic gasification reaction. Compared to partial oxidation, pure steam gasification can increase synthesis gas yield by preventing combustion of synthesis gas by introduced oxygen. In the present study, the steam gasification of bio-oil/char slurry was investigated using a lab-scale fluidized bed reactor filled with either Ni-based naphtha steam reforming catalyst, or silica sand. The components and yield of the product gas, and carbon conversion to gas were compared with those from bio-oil. The experimental results from both the slurry and bio-oil were compared with the values predicted by an equilibrium model, to determine how close the product gas was to the equilibrium at each experimental condition. Partial oxidation (air gasification) of the bio-oil and the slurry is reported separately (Chapter 4).

3.2 Experimental equipment and methodology

Bio-oil and char, produced from wood in a commercial-scale fast pyrolysis plant, were provided by Dynamotive Energy Systems Corporation of Canada. Char was the by-product of the bio-oil production, in which it is separated from hot pyrolyzed gas by a cyclone. Bio-oil and char were produced from the same feedstock at the same plant. Proximate analysis of the char and the ultimate analysis of the char and the bio-oil are shown in Tables 3.1 and 3.2, respectively. Water content of the bio-oil was 25.2 wt%. Bio-oil/char slurry was prepared by mixing 80 wt%
bio-oil and 20 wt% char. Prior to mixing, char was crushed and sieved to a particle size below 38 μm. Particle size of the char was 5.9 μm (median), measured using a Mastersizer 2000 (Malvern Instruments). The bio-oil and the prepared slurry were stored in sealed containers at 5°C.

### Table 3.1 Proximate analysis of Original Char in wt%

<table>
<thead>
<tr>
<th>Moisture</th>
<th>Volatile Matter (dry basis)</th>
<th>Fixed Carbon (dry basis)</th>
<th>Ash (dry basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3</td>
<td>27.1</td>
<td>67.1</td>
<td>5.8</td>
</tr>
</tbody>
</table>

### Table 3.2 Ultimate analyses of bio-oil and Original Char in wt%; bio-oil is shown in the wet basis and char is shown in the dry ash free basis

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
<th>O (by diff.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bio-oil</td>
<td>42.5</td>
<td>7.2</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>49.7</td>
</tr>
<tr>
<td>Char</td>
<td>76.5</td>
<td>3.7</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>19.2</td>
</tr>
</tbody>
</table>

*Ultimate analysis was done by Canadian Microanalytical Service Ltd., Delta, British Columbia

### 3.2.1 Fluidized bed material

A commercial naphtha steam-reforming catalyst, RK-212, from Haldor-Topsoe was used as bed material for catalytic steam gasification. Silica sand (from TEC MINERALS, Eagle Lake, Texas) was also used as a bed material for non-catalytic steam gasification. Metal analysis of both the materials is shown in Table 3.3. Both catalyst and sand were crushed and sieved into the particle size between 180 and 355 μm. The bulk and particle densities, Archimedes’ numbers and the ranges of calculated minimum fluidization velocity, $U_{mf}$, are shown in Table 3.4. Both particles are around the boundary of group A and B particles on Geldart’s particle classification. The catalyst and the sand surfaces were characterized by scanning electron microscopy (SEM) after the steam gasification experiments.
Chapter 3. Steam Gasification of Bio-oil and Bio-oil/Char Slurry in a Fluidized Bed Reactor

Table 3.3  Metal analysis of the catalyst (RK-212) and the sand (*analyzed by whole rock fusion analysis, measured by ICP)

<table>
<thead>
<tr>
<th></th>
<th>RK-212</th>
<th>Sand</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>60.99</td>
<td>0.64</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>3.36</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.15</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>K₂O</td>
<td>1.32</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>13.98</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>wt%</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.85</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.04</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>SO₃</td>
<td>0.14</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>2.50</td>
<td>98.14</td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.01</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>486</td>
<td>167</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>8</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>140200</td>
<td>41</td>
<td>ppm(wt)</td>
</tr>
<tr>
<td>Sr</td>
<td>74</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>&lt;1</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>*L.O.I. at 1000°C</td>
<td>2.00</td>
<td>0.26</td>
<td>wt%</td>
</tr>
<tr>
<td>SUM</td>
<td>99.36</td>
<td>99.67</td>
<td>wt%</td>
</tr>
</tbody>
</table>

*Analysis was done by Loring Laboratories Ltd., Calgary, Alberta.

**L.O.I.: Loss on ignition after 30 min fusion at 1000°C.
### Table 3.4 Particle and fluidization properties of catalyst and sand in the steam gasification experiments (particle size: $d_p=180–355$ μm; gas viscosity: $\mu=3.7–4.5 \times 10^5$ Pa·s; gas density: $\rho_g=0.2$ kg/m$^3$)

<table>
<thead>
<tr>
<th></th>
<th>Bulk density (g/cm$^3$)</th>
<th>Particle density, $\rho_p$ (g/cm$^3$)</th>
<th>$Ar$</th>
<th>$U_{mf}$ [m/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>1.3</td>
<td>3.7</td>
<td>21–240</td>
<td>0.02–0.09</td>
</tr>
<tr>
<td>Sand</td>
<td>1.7</td>
<td>2.7</td>
<td>16–180</td>
<td>0.02–0.07</td>
</tr>
</tbody>
</table>

The minimum fluidization velocity was calculated as, $U_{mf} = 0.00075 (\rho_p - \rho_g)gd_p^2/\mu$ (simplified form when $Ar<10^3$ (Wen and Yu, 1966; Grace, 1982))
3.2.2 Gasification setup

Steam gasification experiments were carried out in a lab-scale fluidized bed reactor as shown in Figure 3.1. The reactor was made of 310 stainless steel, and comprised of 3-inch diameter (nominal) pipe (I.D.=77.9 mm, h=800 mm) with a perforated plate distributor. It was surrounded by a 9 kW furnace which supplies heat of reaction for the endothermic steam gasification reaction. The reactor was charged with 0.6 L (bulk) of either the catalyst or the sand, which corresponded to a fixed bed height of ~0.13 m for both bed materials. The bed was fluidized by superheated steam generated by a steam generator, which is comprised of a furnace of 7 kW output and a 2.5 inch diameter (nominal) 316L stainless steel pipe (I.D.=63 mm and length=1 m) filled with ceramic Raschig rings. Water was fed into the steam generator by a diaphragm pump. The bio-oil and slurry were fed from the side of the fluidized bed by a peristaltic pump through an atomizer nozzle which was fully surrounded by a cooling jacket to keep the feedstock temperature less than 80°C to avoid plugging by thermal decomposition. An aircap for airbrush (VLA-3 aircap with VLB aircap body, Paasche Airbrush Co.) was installed as the atomizer nozzle on a 6.35 mm O.D. (4.57 mm I.D.) 316 stainless tubing (outer tube), and 3.18 mm O.D. (1.40 mm I.D.) 316 stainless tube was placed inside to feed the bio-oil and slurry. Atomizing gas (N₂) was fed in the outer tube, atomizing feedstock material at the nozzle. The schematic for the atomizer is included in Appendix C.

Various configurations and tests were conducted with the bio-oil and the slurry to ensure proper atomization. The feedstock was sprayed at the end of the atomizer through a 1.6 mm diameter hole with nitrogen. Excess steam in the product gas was condensed and separated by a condenser. Fine char and catalyst particles which could be generated in the reactor were captured...
by an internal cyclone in the reactor, and a filter after the condenser. Product gas flow was measured by a volumetric flow meter combined with a thermocouple and a pressure transducer with which the product mass flow rate was determined. The concentrations of H₂, N₂, CO, CO₂ and CH₄ were measured by micro gas chromatograph CP-4900 (Varian, Inc.) with COX column and thermal conductivity detector, and C₂–C₄ components (acetylene, ethylene, ethane, propene, propane, iso-butane, 1-butene and butane) were measured by gas chromatograph/mass spectroscopy, GC-3800/MS-4000 (Varian, Inc.) with a capillary column, CP-PoraBOND Q fused silica, 25 m x 0.25 mm. Temperatures and product gas flow rates were recorded during experiments. BET surface areas of unused and used catalysts both for bio-oil and slurry gasification were measured with N₂ at 77 K via a multi-point method used with a Micrometritics ASAP2020 surface area analyzer.
Figure 3.1 Schematic of the steam gasification fluidized bed experimental apparatus
3.2.3 Experimental procedure and calculations

When the catalyst was used as a bed material, 50% H$_2$ – 50% N$_2$ mixture was first introduced after two hours at 400°C for activation. To atomize the bio-oil and slurry, N$_2$ was injected as an atomizing gas. When the sand was used as a bed material, the reactor was heated up to the gasification temperature with air/N$_2$ injection. The bio-oil and the slurry were fed at 2.7–5.3 g/min and 3.3–3.5 g/min, respectively, with 12 L/min STP of nitrogen. Water was introduced to the steam generator at the feed rates of 6.2–19.4 g/min and 12.9–13.8 g/min for bio-oil and slurry steam gasification, respectively. The steam temperature entering the reactor was in the range of 700–800°C, and the superficial gas velocity of 7–10U$_{mf}$ for the catalyst, and 4–10U$_{mf}$ for the sand. As the feed changes to gas, $U$ at the exit of the reactor is always larger than that at entrance. The ratios for the product gas in the reactor were $U/U_{mf}$=9–16 for the catalyst and $U/U_{mf}$=7–15 for the sand. It was ensured that the experimental conditions were set for bubbling fluidization to occur. After each steam gasification experiment, methanol was introduced to the atomizer to clean the nozzle, and then an air/N$_2$ mixture was introduced to remove carbon residue in the reactor which could possibly accumulate during the experiment.

In the present study, the hydrogen and carbon yields are described in mole% of elemental hydrogen and carbon in each component of the product gas produced from the feedstock without inherent water: 1) H$_2$, CH$_4$ and C$_2$–C$_4$ components shown above for the hydrogen yield, and 2) CO, CO$_2$, CH$_4$ and C$_2$–C$_4$ components for the carbon yield. The carbon conversion to gas is the sum of the carbon yield of each product gas component. Unconverted carbon in the gasifier is calculated from the carbon balance. Due to the unconverted carbon accumulation, a true steady
state cannot be achieved. However, since product gas yield during c.a. 1 hour successive
duration was stable, carbon balance calculation was applied as if the process was in steady state.

Bio-oil and slurry are gasified by steam according to,

\[ C_x H_y O_z + (x - z)H_2O \rightarrow xCO + \left( x + \frac{y}{2} - z \right)H_2 \]  

where \( C_x H_y O_z \) is the empirical formula of bio-oil or slurry. For the bio-oil, \( x=1, y=2.03 \) and
\( z=0.88 \), whereas for the slurry, \( x=1, y=1.60 \) and \( z=0.67 \), including contained water. Hydrogen
yields larger than 100% can be possible when the steam gasification reaction is followed by the
water-gas shift reaction,

\[ CO + H_2O \rightleftharpoons H_2 + CO_2 \]  

by which CO reacts with steam yielding more \( H_2 \). When the hydrogen yield is more than 100%,
the exceeded portion of hydrogen is from the steam fed to the system.

Steam conversion is the percentage of steam, the sum of fed water into the reactor and
contained water in the feedstock, consumed by the steam gasification reaction and the water-gas
shift reaction, and is calculated by dividing increased atomic hydrogen in the product gas by the
sum of atomic hydrogen contained in the water in the feedstock and in the fed water.

The steam to carbon ratio (\( H_2O/C \)) is the molar ratio of the steam plus the inherent water
of the feedstock (bio-oil water content is 25.2 wt%) introduced to the reactor and the carbon in
the feedstock.

The gas hourly space velocity, \( G_{C1}HSV \) is defined as the volume of methane, assuming
100% of carbon in the feedstock is converted to methane, at standard temperature and pressure
per unit bulk volume of catalyst per hour.
3.3 Results and discussion

Table 3.5 shows a typical product gas composition and heating value from steam gasification of bio-oil and bio-oil/char slurry. The nitrogen concentration was c.a. 33% from atomizing the feedstock, and the steam concentration was c.a. 50%. Dry and nitrogen free composition were compared with values in the literature shown in Table 3.6 (Czernik et al., 2007; van Rossum et al., 2007) obtained from similar and different reactors, respectively, and catalysts as those used in the present study. The H₂ produced is close to that in (van Rossum et al., 2007), and significantly below that in (Czernik et al., 2007).

<table>
<thead>
<tr>
<th>Bed material</th>
<th>Feed (Run name)</th>
<th>Basis</th>
<th>H₂</th>
<th>CO</th>
<th>CO₂</th>
<th>CH₄</th>
<th>C₂⁺</th>
<th>N₂</th>
<th>H₂O*</th>
<th>HHV-MJ/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand</td>
<td>Bio-oil</td>
<td>Wet, N₂ included</td>
<td>3.7</td>
<td>3.4</td>
<td>1.3</td>
<td>1.2</td>
<td>0.4</td>
<td>32.6</td>
<td>57</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>Dry, N₂ free</td>
<td></td>
<td>35</td>
<td>33</td>
<td>13</td>
<td>11</td>
<td>4</td>
<td>-</td>
<td>-</td>
<td>15.8</td>
</tr>
<tr>
<td></td>
<td>Slurry</td>
<td>Wet, N₂ included</td>
<td>3.7</td>
<td>2.6</td>
<td>1.5</td>
<td>0.9</td>
<td>0.2</td>
<td>33.8</td>
<td>57</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>Dry, N₂ free</td>
<td></td>
<td>39</td>
<td>28</td>
<td>16</td>
<td>10</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>12.4</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Bio-oil</td>
<td>Wet, N₂ included</td>
<td>13.1</td>
<td>2.4</td>
<td>5.5</td>
<td>0.7</td>
<td>0.1</td>
<td>32.3</td>
<td>45</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td>Dry, N₂ free</td>
<td></td>
<td>57</td>
<td>10</td>
<td>24</td>
<td>3</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>9.4</td>
</tr>
<tr>
<td></td>
<td>Slurry</td>
<td>Wet, N₂ included</td>
<td>11.6</td>
<td>1.6</td>
<td>4.9</td>
<td>0.2</td>
<td>0.0</td>
<td>33.8</td>
<td>47</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>Dry, N₂ free</td>
<td></td>
<td>59</td>
<td>8</td>
<td>25</td>
<td>1</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>8.3</td>
</tr>
</tbody>
</table>

*H₂O concentration was calculated by H elemental balance. Due to measurement errors and undetectable components (i.e., water) of the micro-GC, the total concentration is < 100%.
### Table 3.6 Product gas composition (in mol%, dry N₂ free basis) from steam gasification of bio-oil found in the literature

<table>
<thead>
<tr>
<th>Reference</th>
<th>Bed material</th>
<th>Feed</th>
<th>H₂O/C</th>
<th>H₂</th>
<th>CO</th>
<th>CO₂</th>
<th>CH₄</th>
<th>C₂+</th>
</tr>
</thead>
<tbody>
<tr>
<td>Czernik et al., 2007,</td>
<td>Ni based catalyst</td>
<td>Bio-oil</td>
<td>5.8</td>
<td>~70</td>
<td>~9</td>
<td>~20</td>
<td>~1</td>
<td>n.a.</td>
</tr>
<tr>
<td>fluidized bed reactor</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Van Rossum et al., 2007,</td>
<td>Sand</td>
<td>Bio-oil (pine)</td>
<td>1.9</td>
<td>26.8</td>
<td>44.7</td>
<td>5.6</td>
<td>15.6</td>
<td>6.7</td>
</tr>
<tr>
<td>spouted bed reactor</td>
<td>Ni-K/La on alumina</td>
<td>Bio-oil (beech)</td>
<td>3.1</td>
<td>52.8</td>
<td>10.2</td>
<td>25.1</td>
<td>9.1</td>
<td>1.4</td>
</tr>
<tr>
<td>KATALCO 46 (for naphtha</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>reforming)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>This work</td>
<td>Sand</td>
<td>Bio-oil</td>
<td>5.5</td>
<td>35</td>
<td>33</td>
<td>13</td>
<td>11</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Catalyst</td>
<td>Bio-oil</td>
<td>5.5</td>
<td>57</td>
<td>10</td>
<td>24</td>
<td>3</td>
<td>0</td>
</tr>
</tbody>
</table>
3.3.1 Effect of catalysis and temperature on bio-oil steam gasification

Figure 3.2 shows the hydrogen and carbon yields from the bio-oil steam gasification at \( \text{H}_2\text{O}/\text{C} \approx 5.5 \), \( \text{G}_{\text{HSV}} = 340 \text{ h}^{-1} \), and three different temperatures between 747 and 832°C for the non-catalytic steam gasification, and 725 to 803°C for the catalytic steam gasification. The difference between 100% and the total carbon conversion shows the amount of residual carbon and tar generated by the reaction. After catalytic steam gasification experiments, there was no evidence of tar formation downstream of the reactor, while tar was always found after non-catalytic steam gasification experiments. Under the catalytic conditions, the \( \text{H}_2 \) yield and \( \text{CO}_2 \) yield were significantly greater than those obtained under the non-catalytic conditions (sand), and the hydrocarbons and CO yields at the catalytic conditions were less than those for non-catalytic conditions. This significant change in the product gas components yields was caused by: 1) the catalysis of the steam gasification (Reaction (3.1)) by which hydrocarbons react with \( \text{H}_2\text{O} \) yielding \( \text{H}_2 \), \( \text{CO} \) and \( \text{CO}_2 \); and 2) water-gas shift reaction (Reaction (3.2)) by which CO reacts with \( \text{H}_2\text{O} \) yielding \( \text{H}_2 \) and \( \text{CO}_2 \). In addition, the total carbon conversion to gas was higher under the catalytic steam gasification than under the non-catalytic steam gasification (sand). This indicates that the injected bio-oil was evaporated and successfully decomposed and/or steam gasified better under the catalytic conditions than under the non-catalytic conditions. With increasing temperature, the \( \text{H}_2 \) yield and the \( \text{CO} + \text{CO}_2 \) yield, leading to the total carbon conversion to gas, increased under the non-catalytic steam gasification. However, under catalytic steam gasification, no clear relationships were found between both the carbon and hydrogen yields, and the gasification temperature. The hydrocarbon yield was not clearly affected by the
gasification temperature under the non-catalytic conditions either. Figure 3.3 shows the steam conversion at steam gasification of the bio-oil and the slurry with catalyst and sand. Catalyst strongly promoted reactions involving steam, while little water was involved in steam gasification under non-catalytic conditions. Thus, the gasification process under the present non-catalytic conditions is mostly thermal decomposition, without involving the water-gas shift reaction and the steam gasification reaction.
Chapter 3. Steam Gasification of Bio-oil and Bio-oil/Char Slurry in a Fluidized Bed Reactor

Figure 3.2  Effect of catalysis on: a) carbon yield (mol% - atomic) as CO, CO₂, CH₄ and hydrocarbons (C₂-C₄) ; and b) hydrogen yield (mol% - atomic) as H₂, CH₄ and hydrocarbons (C₂-C₄) on the dry feed stock basis; under steam gasification, H₂O/C=5.5, GcHSV ≈ 340 h⁻¹

Figure 3.3  Steam conversion by steam gasification of the bio-oil and the slurry under catalytic and non-catalytic conditions

63
3.3.2 Effect of space velocity and H₂O/C ratio under non-catalytic steam gasification

Figure 3.4 shows the effect of the space velocity of the bio-oil on the hydrogen and carbon yields at three different GCHSV values between 210–400 h⁻¹ (changed by feedstock feed rate from 2.7 to 5.3 g/h, keeping the same volume of the sand), T≈790°C and H₂O/C≈5.5. Figure 3.5 shows the effect of the steam to carbon ratio on the hydrogen and carbon yields at three different H₂O/C between 2.7–7.5, T≈800°C and GCHSV≈320 h⁻¹. Due to measurement error of the micro-GC, the error range of hydrogen yield is much wider than that for carbon yield. Under the bio-oil steam gasification conditions set by the present study, both the space velocity of the feedstock and the steam to carbon ratio did not clearly affect the product gas yield and composition.
Chapter 3. Steam Gasification of Bio-oil and Bio-oil/Char Slurry in a Fluidized Bed Reactor

Figure 3.4 Effect of space velocity on: a) carbon yield (mol% - atomic) as CO, CO₂, CH₄ and hydrocarbons (C₂-C₄); and b) hydrogen yield (mol% - atomic) as H₂, CH₄ and hydrocarbons (C₂-C₄) on the dry feed stock basis; at T≈800°C and GᵥHSV≈320 h⁻¹ under non-catalytic steam gasification

Figure 3.5 The effect of steam to carbon ratio on: a) carbon yield (mol% - atomic) as CO, CO₂, CH₄ and hydrocarbons (C₂-C₄); and b) hydrogen yield (mol% - atomic) as H₂, CH₄ and hydrocarbons (C₂-C₄); at H₂O/C≈5.5 and T≈790°C under non-catalytic steam gasification
3.3.3 Effect of feedstock and temperature on the product gas yield under catalytic steam gasification

Figure 3.6 shows the hydrogen and carbon yields from bio-oil and slurry catalytic steam gasification at $H_2O/C \approx 5.5$, $G_{C_1HSV} \approx 340 \text{ h}^{-1}$, and three temperatures between 725 and 803°C for bio-oil steam gasification, and three temperatures between 755 and 815°C for the slurry steam gasification. The carbon conversion to gas, and especially the CO yield from the slurry steam gasification was less than from the bio-oil steam gasification. The slurry yielded more unconverted carbon under steam gasification than the bio-oil, probably because the slurry initially contained 20 wt% char, which was 31% of total carbon content in the slurry. This might easily become residual carbon due to the lower reactivity of the char than for the gaseous components involved in the reaction system. However, the total carbon conversion differences between slurry and bio-oil decreased with increasing temperature (by: 24% at 725–755°C; 19% at 773–784°C; and 14% at 803–815°C). These decreased differences in carbon conversion were mainly caused by increasing carbon conversion of slurry with increasing temperature.

As the carbon from the char was 31% of the total carbon content in the slurry, the unconverted carbon at the low temperature of 755°C seems to be unconverted char with residue from bio-oil, while that at the high temperature of 815°C may mainly from the originally contained char. In addition, the carbon conversions to gas from the bio-oil were similar at different temperatures in the 725-803°C range. This shows that the char promoted generation of residual carbon at low temperature, but not at high temperature. Figure 3.7 shows the effects of catalysis and feedstock on the carbon and hydrogen yields. Comparing the catalytic and non-catalytic (sand) conditions, the total carbon conversion under the catalytic conditions was higher
than that under non-catalytic conditions by c.a. 20%: catalyst significantly suppressed the production of residual carbon. The carbon conversion to gas from the slurry was about 70%. It seems that residual carbon was highly suppressed, but char remained unreacted, as gas produced from the char would contribute to the total carbon conversion to gas by 0.1% (assuming no residual carbon accumulation) according to the char’s steam gasification reactivity (Chapter 2). Therefore, a high gasification temperature is required to suppress residual carbon generation, but it is difficult to convert the char effectively by steam. Thus, for continuous steam gasification, this residual carbon should be removed, for example, in a dual-bed gasifier (Pfeifer et al., 2009) in which the carbon residue is transported to a separate combustion process with the bed material to be burnt and recycled back to the steam gasification reactor. The heat of combustion of the carbon residue is essentially transported back to the gasifier by the enthalpy of the bed material. This helps supply the heat for the endothermic condition of the steam gasification reaction, and reduce external energy input. There were no clear relationships between the hydrogen yield and the gasification temperature from the experimental results in the present study.
Chapter 3. Steam Gasification of Bio-oil and Bio-oil/Char Slurry in a Fluidized Bed Reactor

Figure 3.6  Effect of temperature on: a) carbon yield (mol% - atomic) as CO, CO$_2$, CH$_4$ and hydrocarbons (C$_2$-C$_4$); and b) hydrogen yield (mol% - atomic) as H$_2$, CH$_4$ and hydrocarbons (C$_2$-C$_4$), under catalytic steam gasification at H$_2$O/C≈5.5, and G$_{C1HSV}$≈340 h$^{-1}$

Figure 3.7  Comparison of feedstock under catalytic and non-catalytic steam gasification on: a) carbon yield (mol% - atomic) as CO, CO$_2$, CH$_4$ and hydrocarbons (C$_2$-C$_4$); and b) hydrogen yield (mol% - atomic) as H$_2$, CH$_4$ and hydrocarbons (C$_2$-C$_4$) at H$_2$O/C≈5.6 and G$_{C1HSV}$≈320 h$^{-1}$
3.3.4 Comparison with thermodynamic equilibrium

The data were compared with values calculated assuming thermodynamic equilibrium. To predict the product gas composition, the modeling approach for gasification of carbonaceous materials of Li et al. (2001) was applied. In the model, the system which included C, H, O, N and S, was simplified to 42 gaseous species and two solid species. The model was solved by minimizing Gibbs free energy of the system using the RAND algorithm. To take kinetic effects into account, such as unconverted carbon and hydrocarbons which influence real processes by kinetics and/or mass transfer, elemental abundances in the steam gasification system were adjusted, as done by Li et al. (2004): unconverted carbon, and carbon and hydrogen in hydrocarbons in the product gas were initially withdrawn from the elemental abundances before the equilibrium calculation. Then, the hydrocarbons were added to the result of the equilibrium calculation. The experiments of Li et al. used different feedstocks (dry biomass), a different circulating fluid bed gasifier, and were limited to partial oxidation where methane was the only hydrocarbon reported. Rather than use their empirical equations, in the present study the amounts of unconverted carbon and hydrocarbons were substituted one by one using experimental data. The present model was validated by comparing predictions for a simple C-H-O system, the H₂O + C(s) reaction with those reported by Massey (1979). The discrepancy was less than 1%. Figure 3.8 compares the H₂ and CO yields between data from the present work and values from references (Czernik et al., 2007; van Rossum et al., 2007), and kinetic modified model-predicted values for both obtained data and values from the references. The H₂ yield was close to that predicted at equilibrium for both the bio-oil and the slurry under the catalytic steam gasification conditions, whereas the non-catalytic steam gasification yielded much less H₂.
(Figure 3.8b). The CO yield was greater under non-catalytic conditions and less under catalytic conditions due to the catalysis of the water-gas shift reaction, yielding H$_2$ and consuming CO, making the reaction system close to equilibrium under excess amount of steam (Figure 3.8a). Therefore, the product gas yield from catalytic steam gasification is predictable reasonably well once the parameters for the kinetic modified model, carbon conversion and hydrocarbon yield, are determined empirically from the actual gasification system. The value from Czernik et al. (2007) was close to the equilibrium model, while data from van Rossum et al. (2007) differed from equilibrium, even with catalyst, probably due to the different reactor type, i.e., a spouted bed reactor which could affect the kinetic modification. Under non-catalytic conditions, the carbon yield as CO was much higher and the hydrogen yield as H$_2$ was much lower. This is the same tendency as data from the present study. From the comparison, it is found that application of the kinetically-modified model to the present study resulted in good agreement, but this was not the case for the values from other researchers; model validity for different reactor types should be studied in more detail.
Chapter 3. Steam Gasification of Bio-oil and Bio-oil/Char Slurry in a Fluidized Bed Reactor

Figure 3.8  

3.3.5 Catalyst deactivation and attrition of bed material

A test of catalyst de-activation effects was done as follows. An experimental run of bio-oil partial oxidation was first conducted with catalyst. Then three runs were carried out at different conditions. After each run the usual burn-out of combustible material on the catalyst was done. Then the conditions of the first run were repeated. Figure 3.9 shows catalyst deactivation behaviour in the carbon and hydrogen yields from bio-oil partial oxidation from the 1st run with the catalyst and 5th run with the same catalyst after 4 runs of different conditions for approximately 250 min and 4 times burn-out. Catalyst activity for the water-gas shift reaction was reduced as shown by the CO yield increase by 2% and CO$_2$ yield decrease by 7%. In addition, catalyst activity for steam gasification was also decreased since the hydrogen yield as CH$_4$ was increased by 5%. Due to the deactivation in the water-gas shift and steam gasification reaction, total atomic hydrogen yield was reduced by 37%. This deactivation may be caused by accumulation of melted ash (metal oxides) from bio-oil or slurry, which is shown below in SEM images. This shows de-activation can be a critical issue for a process. Further study should be undertaken which focuses on new types of catalysts which can maintain activity for longer times, or on gasification or burn-out conditions which do not lead to de-activation.

Catalyst was subject to attrition by fluidization. Approximately 3% of catalyst was lost by attrition per 1 hour of gasification run, whereas less than 1% of sand was lost per 1 hour of gasification. Since the catalyst is a major design restriction due to its cost, this significant attrition loss should be reduced. Magrini-Bair et al. (2002) have developed a fluidizable catalyst for steam gasification of bio-oil, for which attrition was suppressed from 28.7 wt%/day (C11-NK,
commercial catalyst) to 0.5 wt%/day (their original catalyst) with similar gasification conditions to this study.

Figure 3.9 Catalyst deactivation after 250 min of bio-oil partial oxidation (comparison of 1st run and 5th run on the same catalyst bed at \( \lambda = 0.5 \) and \( \sim 845^\circ C \))

### 3.3.6 Surface changes after the bio-oil and the slurry gasification

The surface of the catalyst and the sand are of importance in terms of activity, as blocking the surface by ash or carbon deposits may cause active surface area decrease and catalyst deactivation. Figure 3.9 shows SEM images of unused fresh catalyst and sand. The surface of the catalyst was highly porous, while the surface of the sand was very smooth with very little pore structures. The subsequent SEM images (Figure 3.10 and 3.11) were taken after
gasification of the bio-oil and/or the slurry gasification and partial oxidation runs. Figure 3.10 shows the surfaces of the catalyst after gasification of: a) the bio-oil; and b) the slurry. The surface became smoother than that of the fresh catalyst, probably due to ash derived by the bio-oil or the slurry. However, highly porous surfaces were also found in places. It is suspected that the attrition of the catalyst may have created the appearance of porous surfaces. The BET surface areas (N₂, 77K) of unused and used catalysts for bio-oil and slurry gasifications were measured as: 6.7, 5.6 and 5.3 m²/g, respectively. The catalyst surface area decreased through the gasification operations. In addition, needle-shaped crystals were found in places from both the catalyst after the bio-oil and slurry gasification. Those crystals are probably metal oxides derived from the ash contents contained in bio-oil and bio-oil/char slurry. Metal analysis of the used catalysts was conducted (Table 3.7), however, it did not reveal the composition of the crystals due to their rather limited amounts.
Table 3.7. Metal analysis of the catalyst (RK-212) and the sand after gasification (*analyzed by icp after digestion by aqua regia)

<table>
<thead>
<tr>
<th></th>
<th>Unused Catalyst</th>
<th>Used catalyst, Bio-oil</th>
<th>Used catalyst, Slurry</th>
<th>Unused sand</th>
<th>Used sand, Bio-oil</th>
<th>Used sand, Slurry</th>
<th>Unit</th>
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<td>Al</td>
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<td>Fe</td>
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<td>0.11</td>
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<td>K</td>
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<td>8.32</td>
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<td>0.01</td>
<td>0.02</td>
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<tr>
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<td>9</td>
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<td>6</td>
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<td>3</td>
<td>8</td>
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</tr>
</tbody>
</table>

*Ag, Au, Cd, Co, P, Sb and U contents were under detection limit.
Figure 3.11 shows SEM images of the sand surface after the gasification of: a) bio-oil; and b) slurry. After the slurry gasification, the surface seemed to be coated by melted ash components, whereas the surface after the bio-oil gasification was smooth, close to the fresh surface. Since the char in the slurry has a higher ash content than the bio-oil, it is suspected that the ash coats the surface of the bed material. This may happen on the catalyst surface leading to catalyst deactivation. However, the catalyst surface did not seem to be coated as much (Figure 3.10). Since the catalyst in the present study was not designed for fluidized bed reactors, the catalyst was subjected to attrition, which could keep the catalyst surface fresh, even in the presence of higher ash content. However, attrition leads to significant catalyst loss; it cannot be counted as a benefit for catalyst improvement.
Chapter 3. Steam Gasification of Bio-oil and Bio-oil/Char Slurry in a Fluidized Bed Reactor

Figure 3.10  a) SEM images of a) fresh catalyst; and b) fresh sand

Figure 3.11  SEM images of catalyst surface after a) bio-oil gasification; and b) slurry gasification

Figure 3.12  SEM images of sand surface after a) bio-oil gasification; and b) slurry gasification
Chapter 3. Steam Gasification of Bio-oil and Bio-oil/Char Slurry in a Fluidized Bed Reactor

3.4 Conclusions

Steam gasification of bio-oil and bio-oil/char slurry was conducted using a lab-scale fluidized bed reactor. The effect on the product gas yield of catalysis was studied, as well as the gasification temperature and feedstock effects under catalytic steam gasification; and the space velocity and the steam to carbon ratio effects under non-catalytic steam gasification. Catalysis of the water-gas shift reaction and steam gasification, significantly affected the product gas yields: larger H$_2$ yield and smaller CO and hydrocarbons yields. In addition, the carbon conversion to gas was higher under the catalytic steam gasification than for non-catalytic steam gasification. In addition, catalyst appeared to suppress generation of residual carbon during steam gasification, more effectively at higher temperature range of 755–815°C. Therefore, catalysis is necessary to yield the maximum amount of H$_2$, while high temperature is needed for high carbon conversion to gas. With increasing gasification temperature, CO and CO$_2$ yield increased for non-catalytic steam gasification. However, the gasification temperature did not show any clear effect on CO and CO$_2$ yield under the catalytic conditions. For both catalytic and non-catalytic steam gasification: 1) the carbon conversion to gas from the slurry steam gasification was lower than that from bio-oil, probably due to the initial char content; and 2) the hydrocarbon yield was not affected clearly by the gasification temperature. Limited effects of the space velocity and the steam-to-carbon ratio were shown under the non-catalytic steam gasification in the range of experimental setting in the present study. Since the carbon conversion is less than 100%, i.e., much lower in slurry steam gasification, the residual unconverted carbon must be removed from the bed to prevent accumulation. Using a dual-bed gasifier could reduce the external energy input to supply heat for the steam gasification reaction. The H$_2$ and CO yields obtained under the
catalytic steam gasification of both the bio-oil and slurry were close to the values predicted by the equilibrium model, in which the kinetic effects (existence of the unconverted carbon and hydrocarbons) were taken into account. Gas yield results appeared consistent with those from the literature. The product gas yield can be calculated reasonably using the parameters for the model determined empirically in the present study. Catalyst was subject to deactivation which caused decreases in CO and H₂ yields, and increases in CO₂ and CH₄ yields. The surfaces of the catalyst and the sand seemed to be coated by ash contents after the slurry gasification due to the slurry’s larger amount of ash content than bio-oil. Attrition of the catalyst was measureable in gasification runs of one-hour duration.
Chapter 3. Steam Gasification of Bio-oil and Bio-oil/Char Slurry in a Fluidized Bed Reactor

3.5 References


Sakaguchi, M., Watkinson, A. P. and Ellis, N. Partial oxidation of bio-oil and bio-oil/char slurry in a fluidized bed reactor. to be submitted

Sakaguchi, M. Watkinson, A. P. and Ellis, N. Steam gasification reactivity of char from rapid pyrolysis of bio-oil/char slurry. to be submitted
CHAPTER 4  Partial Oxidation of Bio-Oil and Bio-Oil/Char Slurry in a Fluidized Bed Reactor

4.1  Introduction

Increased interest in renewable resources from concerns about climate change caused by anthropogenic greenhouse gas, mainly CO$_2$ (IPCC, 2007), and demand for a secure supply of fuel, energy and chemicals have increased the interest in biomass as a renewable and sustainable resource candidate. Biomass-derived fuels or chemicals obtained from short rotation forestry and other energy crops can contribute to reducing net CO$_2$ emissions.

Biomass can be converted to transportation fuels and chemicals by thermochemical or biological processes. Synthesis gas production is a key first step in the thermochemical route for producing synthesized fuels and/or materials. Either solid primary biomass or secondary products derived from pyrolysis processes may be converted to gas by gasification technology. In fast pyrolysis processes, biomass is heated up to around 500°C in absence of oxygen within a few seconds and decomposed to gas, vapour and char. The condensed liquid product from the vapour, bio-oil is a dark brown-coloured liquid of similar elemental composition to the feedstock biomass material (Bridgwater et al., 2001). Due to its high density (typically 1200 kg/m$^3$) and its liquid form bio-oil can be readily stored, and pumped, leading to reduced storage and transportation cost compared to dry biomass. When mixed with the by-product char from the same process, a bio-oil/char slurry of density 1300 kg/m$^3$ can be prepared (at 80 wt% bio-oil/20

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3 A version of this chapter will be submitted for publication. Sakaguchi, M., Watkinson, A. P. and Ellis, N. Partial oxidation of bio-oil and bio-oil/char slurry in a fluidized bed reactor.
Chapter 4. Partial Oxidation of Bio-oil and Bio-oil/Char Slurry in a Fluidized Bed Reactor

wt% char). The slurry has an energy density 32% higher than the original biomass fed to the pyrolyzer.

Partial oxidation of the bio-oil or slurry with air produces a gas useful for fuel. With pure oxygen a synthesis gas is produced which can be converted to high-quality fuels and chemicals. As carbon content of the fuel controls the maximum yields of H₂ and CO which are important factors for the yields of synthetic liquid products, slurry of high carbon content is an attractive feedstock for synthesis gas production. van Rossum et al., (2007) studied bio-oil partial oxidation in a catalytic and non-catalytic fluidized bed reactor, and investigated the catalytic effect on syngas yield, hydrocarbon yield and carbon-to-gas conversion. Marda et al., (2009) studied non-catalytic partial oxidation of bio-oil in which bio-oil was atomized and gasified directly in an O₂/He atmosphere without a bed over a wide range of temperatures (625–850°C), and showed that the ratio of air to feedstock affected the conversion to gas more than temperature. Partial oxidation of bio-oil/char slurry is limited to studies of oxygen blown, pressurized, entrained-flow gasification at 1200-1600°C, to produce synthesis gas (Dinjus et al., 2004; Henrich, 2005). In the present study, the slurry and bio-oil were gasified by partial oxidation in a fluidized bed reactor at lower temperatures than in previous studies. Product gases from partial oxidation of the slurry and the bio-oil, in both catalytic and non-catalytic processes, and at varied air ratios and temperatures, were analyzed to determine the effect of gasification conditions.

4.2 Experimental details

Bio-oil and char, produced from wood in a commercial-scale fast pyrolysis plant, were provided by Dynamotive Energy Systems Corporation of Canada. Char was the by-product of
the bio-oil production, in which it is separated from hot pyrolyzed gas by a cyclone. Bio-oil and char were produced from the same feedstock at the same plant at yields of 60–75 wt%, and 15–20 wt%, respectively, with non-condensable gases (10-20 wt%). Proximate analysis of the char and the ultimate analysis of the char and bio-oil are shown in Tables 4.1 and 4.2, respectively. Water content of the bio-oil was 25.2 wt%. Bio-oil/char slurry was prepared by mixing 80 wt% bio-oil and 20 wt% char. Prior to mixing, char was crushed and sieved to a particle size below 38 μm. Particle size of the char was 5.9 μm (median), measured using the Mastersizer 2000 (Malvern Instruments).

<table>
<thead>
<tr>
<th>Table 4.1</th>
<th>Proximate analysis of Original Char in wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>Volatile Matter (dry basis)</td>
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<td>27.1</td>
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</tbody>
</table>

<table>
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<tr>
<th>Table 4.2</th>
<th>Ultimate analyses of bio-oil and Original Char in wt%; bio-oil is shown in the wet basis and char is shown in the dry ash free basis.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>C</td>
</tr>
<tr>
<td>Bio-oil</td>
<td>42.5</td>
</tr>
<tr>
<td>Char</td>
<td>76.5</td>
</tr>
</tbody>
</table>

*Ultimate analysis of bio-oils was done by Canadian Microanalytical Service Ltd., Delta, British Columbia*

4.2.1 Fluidized bed material

A commercial naphtha steam-reforming catalyst, RK-212 (composed of 12–15% Ni, 0–3% NiO, 25–30% MgO, 1–2% K₂O, 1–4% CaO and 60–65% Al₂O₃), from Haldor-Topsoe was used as bed material for catalytic partial oxidation. To understand better the catalytic effect, sand
was also used as a bed material for non-catalytic partial oxidation. Both catalyst and sand were crushed and sieved into the particle size between 180 and 355 μm.

4.2.2 Gasification setup

Partial oxidation experiments were carried out using a lab-scale fluidized bed reactor (Figure 4.1). The reactor was made of 310 stainless steel, and comprised of 3-inch diameter (nominal) pipe (I.D.=77.9 mm, h≈800 mm) with a distribution plate. It was surrounded by a 9 kW furnace. The reactor was charged with 0.6 L (bulk) of either the catalyst or the sand. The bed was fluidized by superheated steam, and air when partial oxidation was carried out. The bio-oil and slurry were fed from the side of the fluidized bed through an atomizer nozzle which is fully surrounded by a cooling jacket to keep the feedstock temperature below 80°C to avoid plugging by thermal decomposition. Excess steam in the product gas was condensed and separated by a condenser. Fine char and catalyst particles which were possibly generated in the reactor were captured by an internal cyclone in the reactor, and a filter after the condenser. Product gas flow was measured by a volumetric flow meter combined with a thermocouple and a pressure transducer with which the product mass flow rate was determined. The concentrations of \( \text{H}_2 \), \( \text{N}_2 \), \( \text{CO} \), \( \text{CO}_2 \) and \( \text{CH}_4 \) were measured by micro gas chromatograph CP-4900 (Varian, Inc.) with COX column and thermal conductivity detector, and \( \text{C}_2-\text{C}_4 \) components (acetylene, ethylene, ethane, propene, propane, iso-butane, 1-butene and butane) were measured by gas chromatograph/mass spectroscopy, GC-3800/MS-4000 (Varian, Inc.) with a capillary column, CP-PoraBOND Q fused silica, 25 m × 0.25 mm. Temperatures and product gas flow rates were recorded during experiments.
4.2.3 Experimental procedure

When the catalyst was used as a bed material, H₂/N₂ (~50% H₂, from 400°C for approximately 2 hours) was introduced from the bottom of the reactor for activation. To atomize the bio-oil and the slurry, a mixture of air and pure N₂, were injected as atomizing gases. When the sand was the bed material, the reactor was heated up to the gasification temperature with air injection. The bio-oil and the slurry were fed at 7.5 g/min and 6.6 g/min, respectively, and water was introduced to a steam generator at the feeding rates of 8.7 g/min and 8.2 g/min for bio-oil.
and slurry partial oxidation, respectively. Air was introduced from the bottom of the reactor to provide an air ratio of $\lambda=0.1–0.5$. ($\lambda$=1 corresponds to complete combustion of feedstock)

Typically the ratio of air used in atomization to that used for fluidization was 3 to 9. After each gasification experiment, methanol was introduced to the atomizer to clean the nozzle, and then an air/N$_2$ mixture was introduced to remove carbon residue in the reactor which could possibly accumulate during the experiment.

### 4.2.4 Definitions

In the present study, the hydrogen and carbon yields are described in mole% of elemental hydrogen and carbon in each component of the product gas produced from the feedstock without inherent water: 1) H$_2$, CH$_4$ and C$_2$–C$_4$ components shown above for the hydrogen yield; and 2) CO, CO$_2$, CH$_4$ and C$_2$–C$_4$ components for the carbon yield. The carbon conversion to gas is the sum of the carbon yield of each product gas component. The hydrogen yield larger than 100% can be possible due to steam gasification reaction in which water reacts with the feedstock yielding H$_2$ and CO followed by the water-gas shift reaction,

$$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{CO}_2 \quad (4.1)$$

which consumes CO yielding more H$_2$.

The air ratio ($\lambda$) is the fraction of oxygen introduced into the reactor compared to that required for complete combustion; $\lambda$=1 means that sufficient oxygen is supplied to yield carbon dioxide and water as described below,

$$\text{C}_x\text{H}_y\text{O}_z + \left( x + \frac{y}{4} - \frac{z}{2} \right) \text{O}_2 \rightarrow x\text{CO}_2 + \frac{y}{2}\text{H}_2\text{O} \quad (4.2)$$
where \( C_xH_yO_z \) represents the chemical formula of bio-oil or bio-oil/char slurry. For bio-oil, \( \lambda=1 \) corresponds to 4.1 L air/g bio-oil.

The steam to carbon ratio (\( H_2O/C \)) is the molar ratio of the steam plus the inherent water of the feedstock introduced to the reactor and the carbon in the feedstock.

The gas hourly space velocity, \( G_{C1HSV} \) is defined as the volume of methane, assuming 100\% of carbon in the feedstock is converted to methane, at standard temperature and pressure per unit bulk volume of catalyst per hour.

### 4.3 Results and discussion

Table 4.3 shows a typical product gas composition and heating value from partial oxidation of bio-oil and bio-oil/char slurry. The nitrogen concentration was 50–70\% which was from atomizing the feedstock, and the steam concentration was c.a. 40\%. The air ratio was set at values of 0.1, 0.3 and 0.5 for catalytic and non-catalytic partial oxidation. The temperature was in the range of 790–850°C. \( H_2O/C \) was set at 2.1 where \( H_2/CO \) mole ratio was estimated as 2 at equilibrium, optimum for Fischer-Tropsch synthesis and/or methanol synthesis. The \( GC_1HSV \) was set at 510–600 h\(^{-1}\).
Chapter 4. Partial Oxidation of Bio-oil and Bio-oil/Char Slurry in a Fluidized Bed Reactor

Table 4.3  Product gas composition (in mol%) and heating value from partial oxidation of the bio-oil and the slurry with the catalyst and the sand at T≈842–848°C, H2O/C=2.1, λ=0.5 and GC1HSV≈550–590 h⁻¹; wet with nitrogen and dry nitrogen free basis

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<th>CO₂</th>
<th>CH₄</th>
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<th>N₂</th>
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<td>-</td>
<td>-</td>
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<td>-</td>
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<td>-</td>
<td>-</td>
<td>5.7</td>
</tr>
</tbody>
</table>

*H₂O concentration was calculated by H elemental balance. Due to measurement errors and undetectable components of the micro-GC (i.e., water), the total concentration is < 100%.

4.3.1 Effect of air ratio

The hydrogen and carbon yields at different air ratios in the catalytic and the non-catalytic partial oxidation are shown in Figure 4.2 (catalytic) and Figure 4.3 (non-catalytic). With increasing air ratio, the CO₂ yield increased and the H₂ yield decreased. This was caused by increased amounts of oxygen which reacted with chemical species containing carbon and hydrogen yielding CO₂ and H₂O. As a large amount of air reduces the quality of the produced gas, a low air ratio is preferred for stronger fuel gas production. In the present apparatus, the furnace provides heat to permit operation at lower air ratios than would be otherwise possible. There were no clear tendencies in the air ratio effect (0.1 < λ < 0.5) on the carbon conversion. This is probably because oxygen in the system firstly reacts with gaseous species in the reactor (such as H₂ and CO), and residual carbon remains unconverted due to its low reactivity, unless
excess amount of oxygen is supplied. For continuous autothermal operation, this carbon residue should be removed either in a dual-bed gasifier, or by chemical looping combustion in which the carbon residue is transported to a separate combustion process with the bed material to be burnt and recycled back to the partial oxidation reactor. The heat of combustion of the carbon residue can thus be transported by the enthalpy of the bed material. This helps supply heat for the endothermic reactions required for the steam gasification reaction, especially at low air-ratio conditions.
Chapter 4. Partial Oxidation of Bio-oil and Bio-oil/Char Slurry in a Fluidized Bed Reactor

Figure 4.2  
(a) Carbon yield (mol% - atomic) as CO, CO\textsubscript{2}, CH\textsubscript{4} and hydrocarbons (C\textsubscript{2}-C\textsubscript{4}); and 
(b) hydrogen yield (mol% - atomic) as H\textsubscript{2}, CH\textsubscript{4} and hydrocarbons (C\textsubscript{2}-C\textsubscript{4}) on the dry feed stock basis at catalytic partial oxidation, H\textsubscript{2}O/C=2.1, G\textsubscript{C}\textsubscript{1}HSV=510–600 h\textsuperscript{-1}.

Figure 4.3  
(a) Carbon yield (mol% - atomic) as CO, CO\textsubscript{2}, CH\textsubscript{4} and hydrocarbons (C\textsubscript{2}-C\textsubscript{4}); and 
(b) hydrogen yield (mol% - atomic) as H\textsubscript{2}, CH\textsubscript{4} and hydrocarbons (C\textsubscript{2}-C\textsubscript{4}) on the dry feed stock basis at non-catalytic partial oxidation, H\textsubscript{2}O/C=2.1, G\textsubscript{C}\textsubscript{1}HSV=510–600 h\textsuperscript{-1}.
4.3.2 Effect of temperature

Figures 4.4 and 4.5 show the carbon and hydrogen yield at different partial oxidation temperatures. At the same air ratio, the H\textsubscript{2} yield was larger at higher temperature than at lower temperature under both catalytic and non-catalytic conditions. The total hydrogen yield (except for H\textsubscript{2}O) showed a similar tendency. In addition, decrease of the CO yield at higher temperature corresponded to the increase of H\textsubscript{2} in the catalytic conditions, while this did not happen under non-catalytic conditions. This indicates that the catalysis of the water-gas shift reaction, which produces H\textsubscript{2} and CO\textsubscript{2} from CO and H\textsubscript{2}O, increased the H\textsubscript{2} yield significantly, while CO was not well converted to H\textsubscript{2} and CO\textsubscript{2} by the water-gas shift reaction without catalysis. The carbon and hydrogen yields as hydrocarbons including CH\textsubscript{4} decreased at higher temperature under both catalytic and non-catalytic conditions. This indicates that hydrocarbons were decomposed and steam gasified yielding H\textsubscript{2} and CO to greater extents at higher temperature. Meanwhile, no clear tendencies were found in the effect of temperature on the total carbon conversion.
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Figure 4.4 The effect of temperature on: a) the carbon yield (mol% - atomic) as CO, CO₂, CH₄ and hydrocarbons (C₂-C₄); and b) the hydrogen yield (mol% - atomic) as H₂, CH₄ and hydrocarbons (C₂-C₄); with non-catalytic partial oxidation, H₂O/C=2.1, \( G_{C1HSV} = 510 - 600 \) h⁻¹; BO: bio-oil, SL: slurry
Figure 4.5 The effect of temperature on: a) the carbon yield (mol% - atomic) as CO, CO₂, CH₄ and hydrocarbons (C₂-C₄); and b) the hydrogen yield (mol% - atomic) as H₂, CH₄ and hydrocarbons (C₂-C₄) with catalytic partial oxidation, H₂O/C=2.1, G_CHSV=510–600 h⁻¹; BO: bio-oil, SL: slurry
### 4.3.3 Difference between bio-oil and slurry in the product gas yield

At the same air ratio, partial oxidation of the slurry yielded less CO and H\(_2\) than that of bio-oil except for \(\lambda=0.1\) in non-catalytic condition. As the slurry contains char which is close to solid carbon, initial amounts of vaporized or gasified components in the reactor should be limited, and less than for bio-oil. This would cause less carbon conversion, and lower CO and H\(_2\) yields in the slurry partial oxidation. In both catalytic and non-catalytic conditions, the carbon conversion of the slurry to gas was less than for bio-oil. The catalyst did not indicate a clear improvement on the carbon conversion in the partial oxidation. The exception at \(\lambda=0.1\) in non-catalytic condition can be caused by the relatively large temperature difference, i.e., the bio-oil was gasified at lower temperature than the slurry, reducing the H\(_2\) yield.

### 4.3.4 Effect of catalysis

At the same temperature, air ratio and feedstock, the carbon conversion to gas from the catalytic and the non-catalytic conditions were similar, except for the \(\lambda=0.1\) case, where the carbon conversion of the bio-oil catalytic partial oxidation was lower than for the slurry, and the difference was relatively large. A significant difference was observed in the hydrogen yield and the ratio of yields of CO to CO\(_2\). By catalysis of the water-gas shift reaction, CO reacts well with H\(_2\)O yielding CO\(_2\) and H\(_2\), while CO remains unreacted and the hydrogen yield was low under non-catalytic conditions. In addition, the yield of hydrocarbons under catalytic conditions was also significantly reduced by catalysis of the steam reforming reactions.
4.3.5 Comparison with thermodynamic equilibrium

The data were compared with values calculated assuming thermodynamic equilibrium. To predict the product gas composition, the modeling approach for gasification of carbonaceous materials by Li et al. (Li et al., 2001) was applied. In the model, the system which included C, H, O, N and S, was simplified to 42 gaseous species and two solid species. The model was solved by minimizing Gibbs free energy of the system using the RAND algorithm. Details of the methodology are provided in the literature (Li et al., 2001).

4.3.5.1 H₂ and CO yields

Figure 4.6 compares the H₂ and CO yields between obtained data and the model-predicted values at each experimental condition. The H₂ yield was close to equilibrium and the difference was small at different air ratios; while the non-catalytic partial oxidation yielded much less H₂ than equilibrium, and the difference from the equilibrium became larger with increasing air ratio. The CO yield was greater under non-catalytic conditions and less under catalytic conditions due to the catalysis of the water-gas shift, yielding H₂ and consuming CO. Increase of air ratio without catalysis did not result in a product gas composition being closer to equilibrium. Especially when H₂O is fed to increase H₂ yield, catalysis is necessary to achieve the expected product yield.
4.3.5.2 \( \text{H}_2/\text{CO} \) ratio

Figure 4.7 shows experimental \( \text{H}_2/\text{CO} \) molar ratios compared to values predicted from the model at each experimental condition. Despite the experimental conditions set in order to yield the product gas \( \text{H}_2/\text{CO} \) ratio around 2, the results for all conditions deviated from this ratio; i.e., the results from the catalytic and the non-catalytic conditions were significantly higher and lower, respectively, than the expected ratio. Under actual experimental conditions, the carbon conversion was 66–96% which indicates a smaller amount of carbon involved in actual reaction, and this caused reaction at a higher \( \text{H}_2\text{O}/\text{C} \) ratio than expected, while the carbon conversion was 100% for all the conditions in the equilibrium model. Therefore, the equilibrium shifted to the right in Equation 4.1 due to the excess amount of \( \text{H}_2\text{O} \) involved in the reaction. This resulted in high \( \text{H}_2/\text{CO} \) ratios under catalytic conditions which exceeded equilibrium.
Figure 4.7  H₂/CO ratio compared with modified equilibrium model; 790–850°C, H₂O/C=2.1, G_C1HSV=510–600 h⁻¹, ●: bio-oil – catalytic, ■: slurry – catalytic, ○: bio-oil – non-catalytic, □: slurry – non-catalytic
4.3.5.3 Modified model

To better estimate the product gas composition, elemental abundances in the partial oxidation system should be adjusted, as done by Li et al. (2004), i.e., taking kinetic effects, such as unconverted carbon and hydrocarbons, which influence real processes by kinetics and/or mass transfer, into account. In the modified model, unconverted carbon, and carbon and hydrogen in hydrocarbons in the product gas were initially withdrawn from elemental abundances for the equilibrium calculation. The hydrocarbons were subsequently added to the result of the equilibrium calculation. Figures 4.8 and 4.9 show H\textsubscript{2} and CO yields, and H\textsubscript{2}/CO ratio, respectively, between our data and the values from the modified model at each experimental condition. Under catalytic conditions, the H\textsubscript{2} and CO yields were very close to equilibrium for both the slurry and the bio-oil, while with non-catalytic conditions the H\textsubscript{2} yield was much less than at equilibrium, and the CO yield was much higher than at equilibrium. As a result, the H\textsubscript{2}/CO ratios under catalytic conditions were close to the values estimated by the modified model, while under non-catalytic conditions, the ratio was much less. In addition, the estimated H\textsubscript{2}/CO ratio shifted higher than the original setting due to the change in elemental abundance of carbon and hydrogen. Therefore, especially in catalytic partial oxidation, the product gas yields are reasonably predictable once the parameters for the kinetic modified model, carbon conversion and hydrocarbon yield, are determined empirically from the actual gasification system.
Chapter 4. Partial Oxidation of Bio-oil and Bio-oil/Char Slurry in a Fluidized Bed Reactor

Figure 4.8  a) Hydrogen yield as H₂, and b) carbon yield as CO compared with modified equilibrium model; 790–850°C, H₂O/C=2.1, G_C1HSV=510–600 h⁻¹, ●: bio-oil – catalytic, ■: slurry – catalytic, ○: bio-oil – non-catalytic, □: slurry – non-catalytic

Figure 4.9  H₂/CO ratio compared with modified equilibrium model; 790–850°C, H₂O/C=2.1, G_C1HSV=510–600 h⁻¹, ●: bio-oil – catalytic, ■: slurry – catalytic, ○: bio-oil – non-catalytic, □: slurry – non-catalytic
4.4 Conclusions

The effect of air ratio, temperature and catalysis on partial oxidation of bio-oil and bio-oil/char slurry was studied. Catalysis of the water-gas shift reaction and the steam gasification significantly affected the product gas yield, resulting in large H₂ yields and small CO and hydrocarbons yields. At higher temperatures, the H₂ yield increased and the hydrocarbon yield was decreased, due to successful decomposition of hydrocarbons. The air ratio controlled total synthesis gas yield (H₂ and CO) as increased air consumed synthesis gas species via combustion, yielding CO₂ and H₂O. Bio-oil carbon conversion to gas was greater than for slurry due to its absence of initial char content. The H₂ yield from the catalytic partial oxidation was close to that at equilibrium, while the non-catalytic partial oxidation yielded much less H₂. The H₂/CO ratio of the product gas greatly exceeded the equilibrium model prediction in catalytic partial oxidation, due to the carbon conversion being less than 100%. This reduced actual carbon elemental abundance, involved in the reaction system, caused greater effective H₂O/C ratios. As it shifted the equilibrium, consuming CO to yield additional H₂ with the help of the catalysis, the H₂/CO ratio increased. Using a kinetically-modified equilibrium model in which unconverted carbon and hydrocarbons were excluded, the product gas yield can be estimated reasonably for the catalytic partial oxidation, as catalysis makes the reaction system close to equilibrium. Once the parameters for the modified model, the carbon conversion to gas and the hydrocarbon yield, are determined empirically for real processes, reasonable prediction of product gas yield would be available. For continuous autothermal operation with either bio-oil or slurry, unconverted carbon should be removed from the gasification stage, and combusted separately in a dual-gasifier or chemical looping combustion mode.
4.5 References


CHAPTER 5  A Case Study of Steam Gasification in a Dual-Bed Gasifier

5.1 Introduction

Steam gasification and partial oxidation of bio-oil/char slurry are promising means to produce synthesis gas from biomass. However, under some conditions more than 30% of carbon remained unconverted, and accumulated in the reactor due to the low steam gasification reactivity of the slurry. In a real process, unconverted carbon would be removed from the gasifier for utilization as a heat source in a separate combustor such as is used in dual-bed gasifiers (Chapters 3–4). Corella et al. (2007) reviewed biomass gasification with pure steam in dual fluidized-bed gasifiers, describing units developed from 1979 to 2007 by research groups from different parts of the world. A dual-bed gasifier can provide heat for endothermic reaction from a separated combustor in which unconverted carbon from the gasifier is burnt and generating heat. By using a dual-bed gasifier, the product gas can be obtained without dilution of air or CO₂. From the combustor, CO₂ can be obtained at high concentration, that is suitable for CO₂ capture or recycle to the other processes. In the present work, steam gasification of bio-oil/char slurry with removal of unconverted carbon by a dual-bed gasifier system was examined in a mass and heat balance computation using the kinetically modified equilibrium model.

4 A version of this chapter will be submitted for publication. Sakaguchi, M., Watkinson, A. P. and Ellis, N. A case study of steam gasification in a dual-bed gasifier.
5.2 Model dual-bed gasifier system

Figure 5.1 shows the dual-bed gasifier system considered in the present study. The system consists of a fluidized bed gasifier for the slurry steam gasification and a combustor in which unconverted carbon transferred with bed material from the gasifier is burnt with air. If necessary, auxiliary fuel can be fed to the combustor. After going through the combustor, the hot bed material moves back to the gasifier. The assumed reactor type is circulating fluidized bed type reactor. The number of degrees of freedom of the system is 15 in a situation of: 9 species involved, excess air introduced to the combustor, and identical temperatures of flows after the condenser (see degrees of freedom analysis below). Thus, 15 specifications (constraints) are required to determine the process. Product gas composition from the gasifier was calculated using the kinetically modified equilibrium model (Li, 2004) taking unconverted carbon into account, as outlined in Chapters 3 and 4. To determine the process, the following conditions were set (parenthesized numbers are constraints, in total 15):

- Char content in the slurry: 10, 15, 20, 25 and 30 wt%.
- \( \text{H}_2\text{O}/\text{C} \): 3.0, 5.5 and 8.0 mol/mol. (1)
- The slurry is fed at 1 kg/hr directly to the gasifier kept at 850°C. (2)
- All the pressures are set to 100 kPa (absolute). (5)
- Temperatures of inlet water, slurry and air are 25°C. (3)
- Heat of product gas is used to preheat water (steam) by Heat Exchanger 1.
- Temperature of product gas after Heat Exchanger 1 is 300°C to prevent tar deposition in pipeline downstream until scrubber (Murakami et al., 2007). (1)
- Temperature of exhaust from the combustor after Heat Exchanger 2 is 150°C. (1)
Carbon conversion to gas: carbon amount attributed to char content. (1)

Hydrocarbon yield = 0% (for simplification).

The preheated steam is heated up to 850°C by a steam heater, if the preheated steam temperature is less than 850°C (in most cases).

Unconverted char is transported with the circulating bed material to the combustor in which the char is burnt with air to keep the combustor temperature at 950°C.

Stoichiometric air ratio in the combustor is 1.5. (1)

The heat capacity of the bed material is assumed to be 1.0 kJ/(kg·K) (alumina).

Heat losses from equipment are assumed negligible.

The feedstock composition used for the calculation is shown in Table 5.1. Those are the same materials used in Chapters 3–4. The Matlab program is given as Appendix J. The code can be readily modified for different assumed values from the cases calculated. The product gas composition is determined by the gasifier temperature, the slurry feed rate and composition, the carbon conversion in the steam gasification, and the steam feed rate. Since the combustor temperature, air ratio, and unconverted carbon circulation rate are specified, the bed material circulation rate is determined by the energy balance of the combustor. With the conditions shown above, these determine the process. At the condition of H₂O/C=1, exhaust temperature from Heat Exchanger 2 is higher than 150°C due to much less water being preheated. The material and energy balance sheets for all the conditions are shown in Tables B.1–B.9 in Appendix B.
Chapter 5  A case study of steam gasification in a dual-bed gasifier

Figure 5.1  Schematic of dual-bed gasifier for bio-oil/char slurry steam gasification

Table 5.1  Elemental analysis and water content of bio-oil and char in wt%, as-received.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
<th>O (by diff.)</th>
<th>Water content</th>
<th>Higher heating value (MJ/kg)</th>
<th>Lower heating value (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bio-oil</td>
<td>42.5</td>
<td>7.2</td>
<td>0.3</td>
<td>0.3</td>
<td>49.7</td>
<td>25.2</td>
<td>17.0</td>
<td>15.5</td>
</tr>
<tr>
<td>Char</td>
<td>76.5</td>
<td>3.7</td>
<td>0.3</td>
<td>0.3</td>
<td>19.2</td>
<td>2.3</td>
<td>28.6</td>
<td>27.8</td>
</tr>
<tr>
<td>Slurry (80 wt% Bio-oil/20 wt% Char)</td>
<td>49.3</td>
<td>6.5</td>
<td>0.3</td>
<td>0.3</td>
<td>43.6</td>
<td>20.6</td>
<td>19.3</td>
<td>17.9</td>
</tr>
</tbody>
</table>
5.3 Equilibrium model for gasifier product gas composition

Product gas composition from the gasifier was determined by an equilibrium model for gasification of carbonaceous materials (Li et al., 2001). In the model, the system which included C, H, O, N and S, was simplified to 42 gaseous species and two solid species. The model was solved by minimizing Gibbs free energy of the system using the RAND algorithm. To calculate unconverted carbon amount generated in the gasifier, elemental abundances in the steam gasification system were adjusted at the initial stage of free energy minimization, in a similar way to that of Li et al. (2004). Other material and energy balances were calculated by separate calculation sheets.

5.4 Results and discussion

5.4.1 Effect of char content in slurry

Figures 5.2 and 5.3 show 1) the effect of char content in the feed slurry on the total required process energy, total recycled energy, energy required for gasifier and energy transferred from the combustor to the gasifier by circulation of the bed material; and b) the effect of char content on the bed material circulation rate and required auxiliary fuel (slurry) amount, respectively, under the condition of H₂O/C=5.5. The required energy for the gasifier slightly decreases with increasing char content, while the recycled energy by circulation of the bed material increases. Total required energy (Figure 5.2) remained constant with increasing char content, while total recycled energy increased. This recycled energy increase is caused by increased char content which also increases bed material circulation rate, resulting in larger heat transfer from the combustor to the gasifier.
Under the conditions specified, auxiliary fuel has to be supplied to the combustor to sustain the process. The required auxiliary fuel amount increased with decreasing char content. Because slurry with high char content generates a large amount of unconverted carbon, and it is transported to combustor for energy recovery, a larger amount of energy can be recycled with high char content. This indicates that a large amount of unconverted carbon, resulting from high carbon content in the slurry in the gasifier, helps process operation by utilizing the heat of combustion of unconverted carbon.
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A case study of steam gasification in a dual-bed gasifier

Figure 5.2  Effect of char contents in slurry on energy requirements and recycles (H₂O/C=5.5)

Figure 5.3  Effect of char contents in slurry on bed material circulation rate and auxiliary fuel (slurry) amount (H₂O/C=5.5)
5.4.2 Effect of $\text{H}_2\text{O}/\text{C}$

Figures 5.4 and 5.5 show the effect of $\text{H}_2\text{O}/\text{C}$ on total required process energy, total recycled energy, energy required for gasifier and energy transferred from the combustor to the gasifier by circulation of the bed material, and the effect of $\text{H}_2\text{O}/\text{C}$ on the bed material circulation rate and required auxiliary fuel (slurry) amount, respectively, using 20 wt% char slurry. Note that the lowest $\text{H}_2\text{O}/\text{C}$ ratio considered here was 1.0 mol/mol which is lower than was studied experimentally. The total required energy increased steeply with increasing $\text{H}_2\text{O}/\text{C}$ because the energy requirement for steam generation increased. Recycle energy also increased, but not as much as did the total required energy. Because the product gas final temperature is $300^\circ\text{C}$ to prevent tar deposition in pipeline, the large amount of latent heat of water in the product gas cannot be recovered; the more $\text{H}_2\text{O}/\text{C}$ is used, the more energy is consumed. If tar content was eliminated by conditions in the gasifier, the product gas temperature could be lowered, leading to substantial reductions in auxiliary fuel requirements. The auxiliary fuel amount decreases significantly with decreasing $\text{H}_2\text{O}/\text{C}$ (Figure 5.5), due to less water having to be preheated. As the amount of auxiliary fuel is sensitive to $\text{H}_2\text{O}/\text{C}$ (for example, it exceeds 1 kg/h at $\text{H}_2\text{O}/\text{C}=4.5$), therefore the $\text{H}_2\text{O}/\text{C}$ ratio should be determined carefully not to consume much energy. As the unconverted carbon amount is constant at the experimental condition (char content in slurry is constant), the bed material circulation rate is not affected.
Figure 5.4  Effect of H$_2$O/C on energy requirements and recycles for 20% char in slurry

Figure 5.5  Effect of H$_2$O/C on bed material circulation rate and auxiliary fuel amount for 20% char in slurry
5.5 Conclusions

A case study of steam gasification of bio-oil/char slurry in a dual-bed gasifier system is conducted. From the material and energy balances, with product gas composition determined using the kinetically modified equilibrium model, the following conclusions may be drawn:

- The higher char content in slurry increases bed material circulation rate, and thus the heat transfer from the combustor to the gasifier for fixed air ratio in the combustor.
- Over the range of conditions covered, auxiliary fuel is required in all cases.
- The energy requirement is sensitive to the H₂O/C ratio since the latent heat of water cannot be recovered in this study. The produced gas exit temperature of 300°C, set to prevent tar deposition, limits heat recovery and contributes significantly to auxiliary fuel requirements. Lower water fractions lead to a more efficient process design due to savings in latent heat recovery. Additional effort should be made for heat integration to improve the process including heat recovery of latent heat of water in the product gas.
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5.6 References


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CHAPTER 6  Conclusions and Suggestions for Further Work

6.1 Conclusions

Bio-oil and bio-oil/char slurry are promising forms of biomass for transportation to centralized sites for conversion into useful products through gasification. Despite numerous works on steam gasification targeting bio-oil fractions as a feedstock, limited research is available where whole bio-oil was used, probably due to its complex polymerization and coking properties at high temperature gasification conditions. As well, gasification of bio-oil/char slurry has been limited to partial oxidation using oxygen in a high temperature and pressure process (Dinjus et al., 2004; Henrich, 2005). Therefore, in the present study, gasification of whole bio-oil and bio-oil/char slurry was investigated by both steam gasification and partial oxidation at rather lower temperature conditions. To investigate the role of char in steam gasification of bio-oil/char slurry injected into gasifiers, steam gasification reactivity of char made from rapid pyrolysis of bio-oil/char slurry was studied via thermogravimetry (Chapter 2). Secondly, gasification of straight bio-oil and bio-oil/char slurry was conducted in a lab-scale fluidized bed reactor system constructed for this work, in order to investigate actual gasification performance and produced gas properties (Chapters 3–4). Thirdly, the material and energy balance of steam gasification in a dual-bed gasifier was conducted to investigate its efficiency at various operating conditions (Chapter 5).

Kinetics of gasification of char originally produced with bio-oil, and char produced by pyrolysis of bio-oil/char slurry was studied in a thermogravimetric analyzer modified to accommodate steam. The rate of reaction increased with fractional conversion between 0.2 and
The reactivity of Slurry Char was very close to that of Original Char in the temperature range of 900–1200°C. At 900°C, as conversion increased, the reactivity of Slurry Char became less compared to that of Original Char. This deactivation was consistent with the change in the surface area by rapid pyrolysis. Heating rate of bio-oil/char slurry injected into a steam gasification reactor is an important factor for the gasifier system design; therefore, a range of heating rates was tested. The steam partial pressure was varied over the range 10 to 50 kPa. The kinetic parameters of steam gasification of Slurry Char and Original Char according to the $n$-th order kinetic model were determined at $X=0.5$: $E=235$ kJ/mol, $k_0=1.69\times10^6$ and $n=0.41$ for char made from bio-oil/char slurry, and $E=219$ kJ/mol, $k_0=7.38\times10^5$ and $n=0.34$ for Original Char. These activation energies over 200 kJ/mol and reaction orders below 0.6 are similar to values for wood char found in the literature. Discrepancies with the values in literature are probably due to uncertainty of model fitting, or origin of chars. From the reactivity work, it is suggested that gasifiers for the slurry can be designed as for char gasification to create fine droplets for rapid heating in the gasifier in order for the resulting char to be of high reactivity.

A fluidized bed suitable for the gasification of bio-oil and bio-oil/char slurry has been designed and fabricated (Appendix C). The atomizer inserted into the gasifier required careful design in order to ensure proper injection of the feed due to high viscosity and the polymerization property of the bio-oil under the high temperature environment. Using a nozzle for liquids of high viscosity with surrounding cooling jacket, stable injection was achieved. The gasification system was operated successfully at bio-oil feed rate of 0.16–0.32 kg/h for superficial gas velocities of $3U_{mf}$ to $12U_{mf}$. Bed material was sand or catalyst. On a dry N$_2$ free basis, gases contained typically 17–61% H$_2$, and 7–40% CO.
In both steam gasification and partial oxidation, the presence of catalyst strongly affected both product gas composition and yield. Specifically, the H₂/CO ratio was significantly higher in catalytic gasification (~4) than in non-catalytic gasification (~1) due to catalysis of the steam gasification and water-gas shift reactions. This resulted in approximately two times higher H₂ yields and half CO yields in catalytic gasification. Carbon conversion to gas was greater with bio-oil than bio-oil/char slurry due to the absence of char. In partial oxidation, the air ratio affected H₂ and CO yield significantly: large air ratios reduced the H₂ and CO yield and increased CO₂ yield because the increased amount of oxygen oxidized more of those components. In steam gasification, the carbon conversion of the slurry to gas was less than for bio-oil, probably because the steam gasification reactivity of char in the slurry was so small that the char remained unconverted. Thus, the unconverted carbon seemed to accumulate during the gasification. Gasification temperature also affected the carbon conversion to gas in the slurry steam gasification. At a temperature of 815°C, the carbon conversion to gas reached 70%. The unconverted carbon was equivalent to the amount of char in the slurry. The char apparently remained unconverted while the bio-oil fraction seemed to be gasified at a high degree of conversion. Steam conversion analysis revealed that catalyst is necessary for steam to become involved in the gasification and yield more H₂. Without catalyst, steam was hardly involved in the gasification reaction at the temperatures tested. H₂O/C and space velocity of feed did not clearly affect the product gas yields.

From the kinetic study in Chapter 2, the reactivity of char from bio-oil/char slurry was generally about 38% less than for Original Char. Considering the carbon conversion to gas hardly exceeds 70% which is equivalent to carbon amount of char in the slurry, steam
gasification of the slurry can be regarded as a combination of fast gasification of the reactive bio-oil with high conversion to gas, and low extent of reaction with the char. Char gasification controls the kinetics, and use of reaction kinetics for char is the key of the system design. Therefore, the gasifier system should be designed with more focus on use of solid carbon rather than gasifying only liquid and/or gas. The dual-bed gasifier/combustor system seems to be a useful configuration for this situation.

The experimental results were compared with the kinetically modified equilibrium model as done by Li (2002). The model took kinetic restriction from unconverted carbon and hydrocarbons in the reaction system into account. Product gas yields from catalytic gasification were very close to those predicted using the model, while product gas yields from non-catalytic gasification were lower in H\textsubscript{2} and higher in CO, and thus, did not agree with the model calculations. Therefore, the gasification of bio-oil and bio-oil/char slurry can be reasonably predicted by the model, once the kinetic parameter (carbon conversion, and hydrocarbon yields) are determined empirically.

Using the kinetically modified equilibrium model, a mass and energy balance were calculated for a dual-bed gasifier system with slurries of various char concentration and H\textsubscript{2}O/C ratios (Chapter 5). Heat of combustion from unconverted carbon in the separate combustor can be transferred to the gasifier and/or the steam generator. This can contribute to the operating energy requirements for endothermic steam gasification. The higher char content in slurry increases bed material circulation rate, and thus the heat transfer from the combustor to the gasifier for fixed air ratio in the combustor. Energy requirement is sensitive to H\textsubscript{2}O/C ratio since the latent heat of water cannot be recovered in this study. Conditions of lower water feed rate
lead to a more efficient process design because it saves latent heat recovery. Additional effort should be made for heat integration to improve the process including heat recovery of latent heat of water in the product gas.

6.2 Recommended future work

Further studies on important factors for continuous operation of the slurry gasifier should be done in the future.

(1) Effect of char content in bio-oil/char slurry on gasification properties

The char content in bio-oil/char slurry may be determined at the production stage by how much of the pyrolysis char is required for the slurry itself and the other purposes (i.e. soil improvement for agriculture (Spokas et al., 2009)). For flexible reactor design with varied char content in the slurry, the effect of Slurry Char content on gasification properties should be studied. Tar sampling should be incorporated into this work.

(2) Experimental study using dual-bed gasifier

In the present study, it is noted that unconverted carbon from the gasifier should be used to generate heat, for example in a dual-bed gasifier. Experimental gasification study with a dual-bed gasifier is necessary to establish the feasibility of the process.

(3) Slurry feeding system design

The present study utilized an atomizer surrounded by a cooling jacket. Atomization was adequate for short duration runs. However, a better feeding system is needed for long duration, stable feeding of the slurry. From the experience of the gasification experiment, the feed system should be equipped with a device which mechanically removes solid
carbon or high viscosity feedstock at the end of feed tube, because feedstock plugging was the main problem during the experiments. Even using a cooling jacket, plugging by carbon deposition occurred at the end of atomizer, resulting in a pressure increase in the feed line. Developing a better feeding device might have a positive impact on future work using slurry.
6.3 References


APPENDICES
APPENDIX A  Research Note – CO₂ Gasification Reactivity of Fast Pyrolysis Char

A.1  Introduction

In Chapter 2, the gasification reactivity of bio-oil/char slurry, applicable to a steam blown fluidized bed gasifier operating at temperatures of 800–1200°C has been investigated. A dual-bed gasifier system proposed in Chapters 3–5 has a combustor which burns unconverted char in the gasifier. Recycling CO₂ produced from the combustor back to itself or the gasifier may allow the CO₂ convert into CO reacting with carbon. For the case of using CO₂ as a reactant for char gasification, char reactivity in CO₂ gasification is analyzed. Thus, the temperature effect on CO₂ gasification rate is analyzed. The activation energy is determined and compared with values from the literature, while the reactivity is compared with steam gasification.

A.2  Experimental

The char used for the present work was made from biomass by fast pyrolysis at Dynamotive Energy Systems corporation. It is noted that the char used in this study was different from the one used in Chapters 2–4. Char samples are from different process and feedstock: the same property cannot be expected. Table A.1 shows the ultimate analysis of the char used for the present work. Char was crushed and sieved to a particle size < 150 μm.
The char was gasified with steam in a thermogravimetric analyzer (TGA) (TA instruments Q600), which consisted of a horizontal balance beam holding a sample pan with a thermocouple in contact with the pan. The char (ca. 5 mg) was placed on an alumina pan, dried at 110°C for 5 minutes in H₂, and then heated to the gasification temperature (750–900°C) at a heating rate of 50°C/min. The final temperature was maintained for 5-15 minutes while CO₂ was injected into the TGA furnace. CO₂ was mixed with H₂ in the furnace and reacted with the char. The CO₂ partial pressure during the gasification was 33 kPa under total pressure of 100 kPa. The total gas flow rate for each gasification temperature was set at 100 ml/min.

### A.3 Treatment of experimental results

In the present study, the char reactivity at a given time was defined as:

\[
r(t) = \frac{-1}{w(t) - w_f} \frac{d(w(t) - w_f)}{dt}
\]  

(A.1)

The degree of conversion, \(X(t)\) was obtained by:

\[
X(t) = 1 - \frac{w(t) - w_f}{w_a - w_f}
\]  

(A.2)

Combining Equations A.1 and A.2 gave reactivity as a function of degree of conversion:
Appendix A  
Research note – CO₂ gasification reactivity of fast pyrolysis char

\[ r(X) = \frac{1}{1-X} \frac{dX}{dt} \]  \hspace{1cm} \text{(A.3)}

In this study, steam gasification reactivity of chars was evaluated using Equation A.3.

Activation energy for CO₂ gasification reactivity of the char at \( X=0.5 \) was obtained according to a reaction model,

\[ r = k_0 \cdot \exp \left( -\frac{E}{RT} \right) \]  \hspace{1cm} \text{(A.4)}

A.4  Results and discussion

Figure A.1 shows the reactivity of the char at different gasification temperatures. The reactivity highly depends on the temperature. Figure A.2 shows the Arrhenius type plot of the reactivity at 50\% conversion for the temperature range of 750–900°C. Since the data were taken at one steam partial pressure, pressure dependency on the reactivity was not analyzed. Therefore, only activation energy \( E \) was determined and compared. Using Equation A.4, the activation energy was determined as \( E=186 \) kJ/mol. The activation energy is comparable but smaller than values from literature (Table A.2). This is probably due to the smaller flow rate of reactant gas in the TGA furnace causing insufficient dispersion of converted gas from the sample, thus inhibiting the gasification, especially at higher temperatures.
Appendix A  Research note – CO₂ gasification reactivity of fast pyrolysis char

Table A.2  Activation energy for CO₂ gasification: determined and literature value for comparison

<table>
<thead>
<tr>
<th>Source</th>
<th>Temperature range</th>
<th>Char origin</th>
<th>( E ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>(750–900°C)</td>
<td>Fast pyrolysis of wood</td>
<td>186</td>
</tr>
<tr>
<td>Risnes et al., (2000)</td>
<td>(700–1000°C)</td>
<td>Wheat straw</td>
<td>205.6</td>
</tr>
<tr>
<td></td>
<td>(700–1000°C)</td>
<td>Spruce</td>
<td>219.9</td>
</tr>
<tr>
<td>Groeneveld and van Swaaij, (1980)</td>
<td>(800–1000°C)</td>
<td>Deal</td>
<td>217.1</td>
</tr>
</tbody>
</table>

A.5  Comparison with steam gasification reactivity

The CO₂ gasification reactivity was compared to the steam gasification reactivity. The char was gasified in the same manner reported in Table A.3. CO₂ gasification reactivity 50% conversion \((X=0.5)\) was 0.0011 s\(^{-1}\), and the steam gasification reactivity at 900°C, 30 kPa steam and 50% conversion \((X=0.5)\) was 0.0021 s\(^{-1}\). The reactivity ratio of steam gasification to CO₂ gasification was 1.9. It can be expected that the reactivity of both steam and CO₂ gasification of char at the same gasification condition is of the same order of magnitude.

Table A.3  Gasification conditions for reactivity analysis in TGA (for comparison between steam and CO₂)

<table>
<thead>
<tr>
<th>Carrier gas</th>
<th>Temperature</th>
<th>Reactant gas pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ gasification</td>
<td>He</td>
<td>900°C</td>
</tr>
<tr>
<td>Steam gasification</td>
<td>N₂</td>
<td>900°C</td>
</tr>
</tbody>
</table>
A.6 Conclusion

Reactivity of char CO₂ gasification was studied and compared with that of steam gasification. The activation energy was also determined and compared. Since the reactivity ratio of steam and CO₂ gasification of the char was 1.9, general reactivities for both steam and CO₂ gasification are expected to be of the same order of magnitude.

Figure A.1  Effect of temperature on char reactivity in CO₂ gasification
Figure A.2  Arrhenius type plot of char reactivity in CO$_2$ gasification
A.7 References


APPENDIX B  Material and Energy Balance Sheet, and Degrees of Freedom Analysis

B.1 Calculation sheets for mass and energy balance for Chapter 5

Following tables are calculation sheets for mass and energy balance of a dual-bed gasifier discussed in Chapter 5.
Table B.1  Material and energy balance at H\textsubscript{2}O/C=5.5, char content=10 wt%, and carbon conversion of 83%

<table>
<thead>
<tr>
<th>Component</th>
<th>M</th>
<th>Stream</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kg/kmol</td>
<td>Flow (mol/h)</td>
</tr>
<tr>
<td>H\textsubscript{2}</td>
<td>2.016</td>
<td>0.0 0.0 0.0 0.0 0.0 59.0 0.0 0.0 59.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>CO</td>
<td>28.010</td>
<td>0.0 0.0 0.0 0.0 0.0 8.6 0.0 0.0 8.6 0.0 0.0 0.0</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>44.010</td>
<td>0.0 0.0 0.0 0.0 0.0 22.8 0.0 0.0 22.8 0.0 6.5 6.5</td>
</tr>
<tr>
<td>H\textsubscript{2}O gas</td>
<td>18.015</td>
<td>0.0 0.0 105.9 136.8 195.4 170.3 0.0 0.0 170.3 0.0 0.0 0.0</td>
</tr>
<tr>
<td>H\textsubscript{2}O liquid</td>
<td>18.015</td>
<td>0.0 195.4 89.5 58.5 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>Slurry (CH\textsubscript{1.2}O\textsubscript{0.47}·0.29H\textsubscript{2}O)</td>
<td>26.407</td>
<td>37.9 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>C (solid)</td>
<td>12.0107</td>
<td>0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>N\textsubscript{2} (Air)</td>
<td>28.0134</td>
<td>0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>O\textsubscript{2} (Air)</td>
<td>31.9988</td>
<td>0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>Bed material (Al\textsubscript{2}O\textsubscript{3})</td>
<td>102.00</td>
<td>0.0 0.0 0.0 0.0 0.0 0.0 0.0 117.7 117.7 0.0 0.0 0.0</td>
</tr>
<tr>
<td>Total</td>
<td>kg/h</td>
<td>1.00 3.52 3.52 3.52 4.43 12.08 12.00 4.43 1.33 1.41 1.41 1.41</td>
</tr>
<tr>
<td>Phase</td>
<td>L</td>
<td>L</td>
</tr>
<tr>
<td>Pressure</td>
<td>kPa(abs)</td>
<td>100 100 100 100 100 100 100 100 100 100 100 100 100</td>
</tr>
<tr>
<td>Temperature</td>
<td>°C</td>
<td>25 25 100 100 850 850 850 950 300 25 950 150</td>
</tr>
<tr>
<td>Temperature</td>
<td>K</td>
<td>298 298 373 373 1123 1123 1123 1223 573 298 1223 423</td>
</tr>
<tr>
<td>Volume</td>
<td>m\textsuperscript{3}/h</td>
<td>0.0 0.0 3.3 4.2 18.2 24.3 0.0 0.0 12.4 1.1 4.7 1.6</td>
</tr>
<tr>
<td>Enthalpy H-H\textsubscript{2}O</td>
<td>kJ/h</td>
<td>0 0 5436 6700 14675 15352 9993 11102 9916 0 1444 179</td>
</tr>
<tr>
<td>C\textsubscript{p} mean</td>
<td>kJ/kmol K</td>
<td>- 75.4 53.3 46.7 42.5 40.6 97.8 102.0 35.2 29.2 36.5 31.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Heat exchanger</th>
<th>A</th>
<th>B</th>
<th>Bed material circulation</th>
<th>Steam heater</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature IN</td>
<td>°C</td>
<td>850 25</td>
<td>950 100</td>
<td>850 950</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>1123 298</td>
<td>1223 373</td>
<td>1123 1223</td>
</tr>
<tr>
<td>Temperature OUT</td>
<td>°C</td>
<td>300 100</td>
<td>150 100</td>
<td>950 850</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>573 373</td>
<td>423 373</td>
<td>1223 1123</td>
</tr>
<tr>
<td>Heat transfer</td>
<td>kJ/h</td>
<td>-5437 5436</td>
<td>-1265 1264</td>
<td>1108 -1109</td>
</tr>
<tr>
<td></td>
<td>W</td>
<td>-1510 1510</td>
<td>-351 351</td>
<td>308 -308</td>
</tr>
</tbody>
</table>
### Appendix B

#### Material and Energy Balance Sheet, and Degrees of Freedom Analysis for Chapter 5

<table>
<thead>
<tr>
<th>Component</th>
<th>Stream</th>
<th>M</th>
<th>Flow (mol/h)</th>
<th>kg/kmol</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>M</td>
<td>2.016</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>CO</td>
<td>M</td>
<td>28.010</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>CO₂</td>
<td>M</td>
<td>44.010</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>H₂O gas</td>
<td>M</td>
<td>18.015</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>H₂O liquid</td>
<td>M</td>
<td>18.015</td>
<td>0.0</td>
<td>202.8</td>
</tr>
<tr>
<td>Slurry (CH₁.1295O₀.4370·₀.2841H₂O)</td>
<td>M</td>
<td>25.569</td>
<td>39.1</td>
<td>0.0</td>
</tr>
<tr>
<td>C (solid)</td>
<td>M</td>
<td>12.0107</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>N₂ (Air)</td>
<td>M</td>
<td>28.0134</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>O₂ (Air)</td>
<td>M</td>
<td>31.9988</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Bed material (Al₂O₃)</td>
<td>M</td>
<td>102.000</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

| Total     | kg/h   | 1.00 | 3.65 | 3.65 | 3.65 | 3.65 | 4.53 | 16.86 | 16.76 | 4.53 | 1.86 | 1.97 | 1.97 | 0.0 |
| Phase     |        | L    | L    | G+L  | G+L  | G    | G    | G     | S    | S    | G    | G    | G    |
| Pressure  | kPa(abs) | 100  | 100  | 100  | 100  | 100  | 100  | 100   | 100  | 100  | 100  | 100  | 100  |
| Temperature | °C  | 25   | 25   | 100  | 100  | 850  | 850  | 850   | 950  | 300  | 25   | 950  | 150  |
| Temperature | K    | 298  | 298  | 373  | 373  | 1123 | 1123 | 1123  | 1223 | 573  | 298  | 1223 | 423  |
| Volume    | m³/h  | 0.0  | 0.0  | 3.3  | 4.7  | 18.9 | 24.8 | 0.0   | 0.0  | 12.7 | 1.6  | 6.6  | 2.3  |
| Enthalpy H·H₂O | kJ/h | 0.0  | 5558 | 7322 | 15234 | 15890 | 13951 | 15499 | 10332 | 0.0  | 2015 | 250  |
| Cₚ mean  | kJ/kmol K | -    | 75.4 | 53.8 | 44.8 | 42.5 | 40.7 | 97.8  | 102.0 | 35.3 | 29.2 | 36.5 | 31.6 |

#### Heat exchanger

<table>
<thead>
<tr>
<th>Heat exchanger</th>
<th>A Product gas</th>
<th>Water</th>
<th>B Exhaust gas</th>
<th>Steam</th>
<th>Bed material circulation</th>
<th>Steam heater</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature IN</td>
<td>°C</td>
<td>850</td>
<td>25</td>
<td>950</td>
<td>100</td>
<td>850</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>1123</td>
<td>298</td>
<td>1223</td>
<td>373</td>
<td>1123</td>
</tr>
<tr>
<td>Temperature OUT</td>
<td>°C</td>
<td>300</td>
<td>100</td>
<td>150</td>
<td>100</td>
<td>950</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>573</td>
<td>373</td>
<td>423</td>
<td>373</td>
<td>1223</td>
</tr>
<tr>
<td>Heat transfer</td>
<td>kJ/h</td>
<td>-5558</td>
<td>5558</td>
<td>-1765</td>
<td>1764</td>
<td>1547</td>
</tr>
<tr>
<td></td>
<td>W</td>
<td>-1544</td>
<td>1544</td>
<td>-490</td>
<td>490</td>
<td>430</td>
</tr>
</tbody>
</table>
### Appendix B
Material and Energy Balance Sheet, and Degrees of Freedom Analysis for Chapter 5

#### Table B.3  Material and energy balance at H₂O/C=5.5, char content=20 wt%, and carbon conversion of 70%

<table>
<thead>
<tr>
<th>Component</th>
<th>M</th>
<th>Stream</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>kg/kmol</td>
<td>Flow (mol/h)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>2.016</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>CO</td>
<td>28.010</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>6.8</td>
<td>0.0</td>
<td>0.0</td>
<td>6.8</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>CO₂</td>
<td>44.010</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>21.4</td>
<td>0.0</td>
<td>0.0</td>
<td>21.4</td>
<td>0.0</td>
<td>12.1</td>
<td>12.1</td>
</tr>
<tr>
<td>H₂O gas</td>
<td>18.015</td>
<td>0.0</td>
<td>0.0</td>
<td>109.5</td>
<td>167.6</td>
<td>210.2</td>
<td>187.7</td>
<td>0.0</td>
<td>0.0</td>
<td>187.7</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>H₂O liquid</td>
<td>18.015</td>
<td>210.2</td>
<td>100.7</td>
<td>42.6</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Slurry (CH₁.₀₅1.₇O₀.₄₀₀₀·₀.₂₇₅₄H₂O)</td>
<td>24.783</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>C (solid)</td>
<td>12.0107</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>12.1</td>
<td>0.0</td>
<td>0.0</td>
<td>12.1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>N₂ (Air)</td>
<td>28.0134</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>68.5</td>
<td>68.5</td>
<td>68.5</td>
</tr>
<tr>
<td>O₂ (Air)</td>
<td>31.9988</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>18.2</td>
<td>6.1</td>
<td>6.1</td>
<td>6.1</td>
</tr>
<tr>
<td>Bed material (Al₂O₃)</td>
<td>102.00</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>220.8</td>
<td>220.8</td>
<td>220.8</td>
<td>2.65</td>
<td>2.65</td>
<td>2.65</td>
<td>2.65</td>
</tr>
<tr>
<td>Total</td>
<td>1.00</td>
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#### Heat exchanger

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<th>B</th>
<th>Exhaust gas</th>
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<th>Bed material circulation</th>
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Table B.4  Material and energy balance at H₂O/C=5.5, char content=25 wt%, and carbon conversion of 64%

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<th>Steam heater</th>
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Table B.5  Material and energy balance at H\textsubscript{2}O/C=5.5, char content=30 wt\%, and carbon conversion of 56%

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<th>Steam heater</th>
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### Material and energy balance at H₂O/C=1.0, char content=20 wt%, and carbon conversion of 70%

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<th>Bed material circulation</th>
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Table B.7  Material and energy balance at H$_2$O/C=3.0, char content=20 wt%, and carbon conversion of 70%

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Heat exchanger

| Temperature IN | °C | 850 | 25  | 950 | 100 | 850 | 950 |
|               | K  | 1123| 298 | 1223| 373 | 1123| 1223|
| Temperature OUT| °C | 300 | 100 | 150 | 296 | 950 | 850 |
|               | K  | 573 | 373 | 423 | 569 | 1223| 1123|
| Heat transfer  | kJ/h| -3475| 3475| -2374| 2372| 2080| -2081|
|               | W  | -965| 965 | -659| 659 | 578 | -578|

Appendix B
Material and Energy Balance Sheet and Degrees of Freedom Analysis for Chapter 5
Table B.8  Material and Energy Balance Sheet, and Degrees of Freedom Analysis for Chapter 5

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<th>Stream 3</th>
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<td>kJ/kmol K</td>
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<th>B Exhaust gas</th>
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<td>423</td>
<td>373</td>
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<td>-578</td>
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B.2 Degrees of freedom in the dual-bed gasifier system

Species: 9 species (H₂, CO, CO₂, H₂O, N₂, O₂, C(solid), Bed material, Slurry)

General constraints:

Excess amount of air for the combustor is introduced.

Temperatures of water and product gas after the condenser are the same.

**Entire process**

\[ N_v = 5(N_{sp} + 2) + 1 = 5(9 + 2) + 1 = 56 \]

(Number of flows \( \times (N_{sp} + T + P) +1 \) for energy balance)

\( N_r: \)

- Material balance (C, H, N, O) \( 4 \)
- Energy balance \( 1 \)

Specifications:

- Flow 1 (all 9 concentrations) \( 8 \)
- Flow 2 (all 9 concentrations) \( 8 \)
- Flow 9 (5 concentration) \( 5 \)
- Flow 10 (all 9 concentrations) \( 8 \)
- Flow 12 (6 concentrations) \( 6 \)

Product gas composition is a function of \( T \) \( 41 \)

\[ N_d = 56 - 41 = 15 \]
**Gasification reactor:**

\[ N_v = 5(N_{sp} + 2) + 1 = 5(9 + 2) + 1 = 56 \]

(Number of flows × (\(N_{sp} + T + P\)) +1 for energy balance)

\( N_r: \)

Material balances (C, H, N, O, BM) 5

Energy balance 1

Specifications:

Flow 1 (all 9 concentration) 8
Flow 5 (all 9 concentrations) 8
Flow 6 (Slurry, \(N_2\), \(O_2\), C and BM are determined) 5
Flow 7 (7 concentrations except C and BM) 7
Flow 8 (all 9 concentrations) 8

\[ T5 = T6 = T7 \]

2 44

\( N_d = 56 - 44 = 12 \)

**Combustor:**

\[ N_v = 4(N_{sp} + 2) + 1 = 4(9 + 2) + 1 = 45 \]

(Number of flows × (\(N_{sp} + T + P\)) +1 for energy balance)

\( N_r: \)

Material balances (C, H, N, O, BM) 5

Energy balance 1

Specifications:
Flow 7 (7 concentrations except C and BM) 7
Flow 8 (all 9 concentrations) 8
Flow 10 (concentration of \( \text{N}_2, \text{O}_2 \) and others) 8
Flow 11 (\( \text{H}_2=\text{CO}=\text{H}_2\text{O}=\text{BM}=\text{C}=\text{Slurry}=0 \)) 6

\[ T_8 = T_{11} \]

\[ N_d = 45 - 36 = 9 \]

**A: Heat exchanger 1**

\[ N_v = 4(N_{sp} + 2) + 1 = 4(9 + 2) + 1 = 45 \]

(Number of flows \( \times \) \( N_{sp} + T + P \) +1 for energy balance)

\[ N_r: \]

- Material balances (2 streams) 2
- Energy balance 1

Specifications:

- Composition of inlet and outlet streams the same \( 2(N_{sp}-1) \) 16
- Composition inlet Flow 9 (\( \text{N}_2=\text{O}_2=\text{C}=\text{BM}=\text{Slurry}=0 \)) 5
- Composition inlet Flow 2 (all 9 concentration) 8 32

\[ N_d = 45 - 32 = 13 \]

**B: Heat exchanger 2**

\[ N_v = 4(N_{sp} + 2) + 1 = 4(9 + 2) + 1 = 45 \]

(Number of flows \( \times \) \( N_{sp} + T + P \) +1 for energy balance)
Appendix B. Material and Energy Balance Sheet, and Degrees of Freedom Analysis for Chapter 5

\( N_r: \)

- Material balances (2 streams) \( 2 \)
- Energy balance \( 1 \)

Specifications:

- Composition of inlet and outlet streams the same \( 2(N_{sp}-1) \) \( 16 \)
- Composition inlet Flow 3 (all 9 concentration) \( 8 \)
- Composition inlet Flow 11 (6 concentration) \( 6 \) \( 33 \)

\( N_d = 45 - 33 = 12 \)

B.3 Nomenclature

- BM Bed material
- \( N_d \) Number of degrees of freedom
- \( N_r \) Number of independent constraints
- \( N_{sp} \) Number of chemical species
- \( N_v \) Number of variables
APPENDIX C  Details of Apparatus

Figure C.1  Locations of thermocouples and pressure transducers
Figure C.2  Detail of gasification reactor assembly
Appendix C  Details of apparatus

Figure C.3  Drawing of reactor top
Figure C.4  Drawing of reactor bottom
Figure C.5  Drawing of flange part
Appendix C  Details of apparatus

Figure C.6  Drawing of distribution plate
Figure C.7  Drawing of reactor lid for the bottom
Figure C.8  Drawing of reactor lid for the top
Figure C.9  Drawing of graphite gasket
Figure C.10  Drawing of internal cyclone
Appendix C  
Details of apparatus

Figure C.12  
Drawing of cooling jacket

Figure C.11  
Drawing of atomizer slot
Appendix C  Details of apparatus

Figure C.13  Drawing of spray nozzle adaptor

Figure C.14  Aircap and aircap body, assembled with spray nozzle adaptor with 1/8-inch-O.D. feedline

Figure C.15  Spray nozzle (former) assemble of Swagelok fittings with 1/16-inch-O.D. feed line
C.1 **Recommendations for atomizer design**

In this study, several atomizer designs and settings were evaluated to atomize the bio-oil/char slurry.

**Atomizer from the bottom of the reactor**

Atomizer was an assembly of Swagelok fittings having a 1/16-inch hole at the end. 1/16-inch-O.D. stainless steel tube was used for the slurry feedline, and a 1/4-inch-O.D. stainless steel tube was used for the outer tube in which N₂ or air was fed as atomizer gas. The atomizer line was placed from the bottom of the reactor go into the bed material through the distribution plate. Due to the limited space at the bottom of the reactor, no cooling devices were installed for the atomizer.

**Performance**

The feed line was plugged easily by:

- Bed material because atomizer outlet hole faces upward into the bed material
- Thermal degradation of bio-oil and slurry which yielded either high viscosity fluid or solid carbon
- Char from the slurry due to the small diameter of the feedline tube

**Atomizer from the side of the reactor with cooling jacket**

To solve the plugging problems, a new atomizer was designed with following features:

- An airbrush nozzle was used for atomizer nozzle in place of the single outlet hole.
- A cooling jacket was installed to cover the atomizer fully to prevent feedstock thermal degradation in the feedline.
1/8-inch-O.D. feedline tubing was used to replace the 1/16-inch tube and prevent plugging by slurry.

**Recommendation**

It is essential that the slurry be kept cool before it reaches the atomizer, to prevent plugging in the line or in the atomizer itself. If an atomizer style is chosen as feeding method, cooling device upstream of atomization is necessary. Feeding slurry, which is a high viscosity fluid, needs wide tubing of sufficient diameter. Thus, at least 1/8-inch-O.D. tubing is recommended for the feedline. If the reactor has enough room at the bottom, and enough purge at the atomizer, atomizer could be placed at the bottom of the reactor for reasons of symmetry.

A device which removes degraded feedstock and solid carbon in the feedline is also recommended for more stable feed.
APPENDIX D  Experimental Procedure

Before heating up

- Prepare ice trap
- Set up micro-GC and connect the gas line
- Turn on the micro-GC computer and open the controlling software (Galaxy)
- Set up the micro-GC acquisition sequence
- Check electronic breakers are ON
- Open N\textsubscript{2} and H\textsubscript{2} valves of pressure regulators on gas cylinders
- Open building air valve on the wall and set the pressure to 100 psi
- Open building water valve on the wall
- Open cooling water valve and set to reading of 30
- Make sure the 3 way valve after the condenser is open to the flow meter
- Make sure the stop valve before the afterburner is open
- Close the valve at the bottom of the liquid collector
- Turn on the recording computer
  - Open recording software (PDAQVIEW), and start recording
- Open N\textsubscript{2} valves for:
  - atomizer (purging and protect atomizer from heat), set at ~1.5 L/min
  - purging pressure transducers at 5 ml/min
  - purging rapture disc line at 10 ml/min

(when sand is used, air can be used for atomizer purging)
Preheating Steam generator

- Set steam generator final temperature to 800°C
- Wait for 1 hour

Turn on after burner

- Set final temperature to 700°C
- Open air valve for after burner and set the flow rate at 2 scfm

Heating up reactor

- Set final temperatures of top and bottom furnaces to gasification temperature

Catalyst activation (when catalyst is used)

- Before introducing H₂, introduce small amount of water to purge all oxygen from the steam generator and the reactor
- Open H₂ valve at 800 ml/min when the bed temperature reaches 400°C
- Leave 30 minutes, after the bed temperature reaches gasification temperature

Gasification of bio-oil or bio-oil/char slurry

- Close H₂ valve

Start feeding

- Start micro-GC acquisition sequence
- Turn on water pump
  - Make sure no bubbles are in the water feed line
  - Measure feeding rate by weighing the water, and adjust pump speed to achieve required feeding rate
Appendix D  Experimental procedure

- Open and adjust N\textsubscript{2} and/or air valve for the atomizer and reactor bottom to required flow rate
- Turn on feed pump
  - Feed pump is very stable and does not need adjustment
- Record feed rates of water and feedstock by weighing them periodically
- Record flow rates of atomizer gases and gas introduced from the reactor bottom periodically
- Adjust flow meter pressure around 3 psi-g by adjusting the valve before the afterburner to make steady flow to the micro-GC

After each gasification condition

- Feed methanol to wash the feed line
- Stop feed pump

(Keep the atomizer gas flow on)

- Open air valve to burn residual carbons

(note that keep an eye on the reactor temperature, not to exceed 900°C)

(once the residual carbons completely burnt out, the temperature drops rapidly)

Repeat “Start feeding” with next setting

Shutdown

- Turn off micro-GC
- Stop feed pump
- Stop water pump
- Switch atomizer gas to air and keep the atomizer gas flow on
Appendix D  Experimental procedure

- Keep cooling water flow on
- Stop all the gases and cooling water when all the monitoring temperatures reach ambient temperature
- Turn off recording and shutdown the computer

**Emergency shutdown**

- Press emergency shutdown button (that shutdown all furnaces and pumps)
- Evacuate the room
APPENDIX E  Flow Meter Calibrations

Figure E.1  Calibration of the water pump at 50% stroke (IWAKI metering pump, adjustable stroke, model#: EWB15F1-PC)

\[ y = 0.4292x + 0.8968 \]

\[ R^2 = 0.9993 \]
Figure E.2  Calibration of the pump for bio-oil or bio-oil/char slurry (CHEM-TECH peristaltic pump, model#: CTPD2HS1-PAP1-XXXXX)
Figure E.3 Calibration of Air/N\textsubscript{2} flow controller for atomizer (air for partial oxidation; N\textsubscript{2} for steam gasification)
Figure E.4   Calibration of the flow controller for air introduced at the bottom of the reactor
Figure E.5  Calibration of N₂ flow controller for atomizer in partial oxidation
#1, N₂ purge for pressure transducer (PT3), reactor bed bottom

![Graph showing the calibration of N₂ flow controller for purging pressure transducer line at the bottom of the reactor.](image)

Figure E.6 Calibration of N₂ flow controller for purging pressure transducer line at the bottom of the reactor
Figure E.7  Calibration of N₂ flow controller for purging pressure transducer line at the top of the reactor

$$y = 1.29 	imes 10^{-5}x^3 - 9.07 	imes 10^{-4}x^2 + 2.34 	imes 10^{-1}x + 2.20 	imes 10^0$$

$$R^2 = 9.98 	imes 10^{-1}$$
Figure E.8  Calibration of N\textsubscript{2} flow controller for purging rupture disc line

The equation is given as:

\[ y = 3.45\times 10^{-5}x^3 + 4.74\times 10^{-3}x^2 + 2.68\times 10^{-1}x + 2.03\times 10^0 \]

with \( R^2 = 1.00\times 10^0 \)
Figure E.9  Calibration of N$_2$ flow controller for H$_2$/N$_2$ mix from the reactor bottom for activating catalyst

\[ y = -1.57E-03x^3 + 1.44E-01x^2 + 1.34E+01x - 2.78E+01 \]

\[ R^2 = 9.99E-01 \]
Figure E.10  Calibration of H$_2$ flow controller for H$_2$/N$_2$ mix from the reactor bottom for activating catalyst

\[
y = 1.27E+01x \\
R^2 = 1.00E+00
\]
Figure E.11  Calibration of \( \text{N}_2 \) flow controller for purging outside the reactor inside the furnaces.

\[
y = 7.29 \times 10^{-5}x^3 + 1.49 \times 10^{-2}x^2 + 9.04 \times 10^{-1}x + 8.07 \times 10^0
\]

\[
R^2 = 9.98 \times 10^{-1}
\]
# APPENDIX F Location of Thermocouples and Pressure Transducers

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All pressure transducers and thermocouples are from OMEGA

Flow meter is from Cole-Parmer
APPENDIX G  Experimental Data
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<td>2.1</td>
<td>3.8</td>
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<td>N2 from the bottom (measured)</td>
<td>L/min</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
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<td>Slurry or Bio-oil feeding rate</td>
<td>g/min</td>
<td>6.47</td>
<td>6.40</td>
<td>6.82</td>
<td>6.42</td>
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<td>H % in Slurry or Bio-oil</td>
<td>%</td>
<td>64.8</td>
<td>6.48</td>
<td>6.48</td>
<td>6.48</td>
<td>7.22</td>
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<td>C % in Slurry or Bio-oil</td>
<td>%</td>
<td>48.39</td>
<td>48.39</td>
<td>48.39</td>
<td>48.39</td>
<td>42.47</td>
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<td>N % in Slurry or Bio-oil</td>
<td>%</td>
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<td>0.30</td>
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<td>O % in Slurry or Bio-oil</td>
<td>%</td>
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<td>43.37</td>
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<td>43.37</td>
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<td>49.71</td>
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<td>Water content of Slurry or Bio-oil</td>
<td>% wt</td>
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<td>20.00</td>
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<td>Product Gas Temperature (T at flow meter) (°C)</td>
<td>28.5</td>
<td>30.1</td>
<td>28.9</td>
<td>29.9</td>
<td>26.5</td>
<td>27.2</td>
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<td>Pressure at Flow meter</td>
<td>kPa-g</td>
<td>3.38</td>
<td>3.47</td>
<td>2.41</td>
<td>2.43</td>
<td>2.75</td>
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<td>%</td>
<td>154.2</td>
<td>22.02</td>
<td>12.96</td>
<td>18.90</td>
<td>23.01</td>
<td>24.39</td>
<td>17.82</td>
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<td>%</td>
<td>58.88</td>
<td>52.53</td>
<td>61.47</td>
<td>56.62</td>
<td>50.33</td>
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<td>CO in Product gas (N2 included)</td>
<td>%</td>
<td>3.19</td>
<td>6.89</td>
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<td>4.67</td>
<td>4.98</td>
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<td>0.83</td>
<td>0.55</td>
<td>1.03</td>
<td>0.98</td>
<td>0.49</td>
<td>0.90</td>
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<td>CO2 in Product gas (N2 included)</td>
<td>%</td>
<td>19.42</td>
<td>15.27</td>
<td>19.06</td>
<td>16.09</td>
<td>18.78</td>
<td>14.77</td>
<td>18.53</td>
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<tr>
<td>Acetylene C2H2 in Product gas (N2 included)</td>
<td>%</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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<td>0.00</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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<td>Ethane C2H6 in Product gas (N2 included)</td>
<td>%</td>
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<td>0.00</td>
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<td>0.00</td>
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<td>Propene C3H6 in Product gas (N2 included)</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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<td>Propane C3H8 in Product gas (N2 included)</td>
<td>%</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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<tr>
<td>Isobutane C4H10 in Product gas (N2 included)</td>
<td>%</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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<tr>
<td>1-Butene C4H8 in Product gas (N2 included)</td>
<td>%</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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<td>Butane C4H10 in Product gas (N2 included)</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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<td>PO_SE15-3</td>
<td>PO_SE15-4</td>
<td>PO_SE15-5</td>
<td>PO_SE09-1</td>
<td>PO_SE09-2</td>
<td>PO_SE09-3</td>
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<tr>
<td>Feed</td>
<td>Slurry</td>
<td>Slurry</td>
<td>Slurry</td>
<td>Slurry</td>
<td>Slurry</td>
<td>Bio-oil</td>
<td>Bio-oil</td>
<td>Bio-oil</td>
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<tr>
<td>Bed material</td>
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<td>Gasification temperature (Bed temperature) (°C)</td>
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<td>839</td>
<td>744</td>
<td>744</td>
<td>843</td>
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<td>λ, air ratio</td>
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<td>0.5</td>
<td>0.5</td>
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<td>Bed pressure (kPa-g)</td>
<td>21.8</td>
<td>23.3</td>
<td>24.6</td>
<td>35.1</td>
<td>44.4</td>
<td>16.3</td>
<td>16.3</td>
<td>17.7</td>
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<td>Water feed capacity (g/min)</td>
<td>8.80</td>
<td>8.93</td>
<td>8.67</td>
<td>8.63</td>
<td>8.64</td>
<td>8.47</td>
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<td>8.25</td>
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<td>Air Atomizer (measured) (L/min)</td>
<td>12.1</td>
<td>9.0</td>
<td>12.3</td>
<td>10.5</td>
<td>16.0</td>
<td>12.0</td>
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<td>12.0</td>
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<td>N2 Atomizer (measured) (L/min)</td>
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<td>6.3</td>
<td>3.2</td>
<td>6.6</td>
<td>0.0</td>
<td>0.0</td>
<td>5.1</td>
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<td>Air from the bottom (measured) (L/min)</td>
<td>4.4</td>
<td>2.1</td>
<td>4.5</td>
<td>2.3</td>
<td>4.7</td>
<td>4.0</td>
<td>2.0</td>
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<tr>
<td>N2 from the bottom (measured) (L/min)</td>
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<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
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<td>Slurry or Bio-oil feeding rate (g/min)</td>
<td>5.39</td>
<td>6.39</td>
<td>6.39</td>
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<td>6.39</td>
<td>7.80</td>
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<td>Water content of Slurry or Bio-oil (%)</td>
<td>6.48</td>
<td>6.48</td>
<td>6.48</td>
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<td>6.48</td>
<td>7.22</td>
<td>7.22</td>
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<td>Product Gas Temperature (T at flow meter) (°C)</td>
<td>31.5</td>
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<td>37.0</td>
<td>47.2</td>
<td>42.3</td>
<td>27.1</td>
<td>29.5</td>
<td>32.1</td>
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<td>Product gas flow rate (measured) (L/min in N2)</td>
<td>18.59</td>
<td>22.05</td>
<td>22.95</td>
<td>25.16</td>
<td>22.89</td>
<td>22.06</td>
<td>22.57</td>
<td>23.24</td>
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<tr>
<td>Pressure at Flow meter (kPa-g)</td>
<td>5.23</td>
<td>5.55</td>
<td>5.53</td>
<td>6.26</td>
<td>6.54</td>
<td>2.09</td>
<td>2.15</td>
<td>2.35</td>
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<tr>
<td>H2 in Product gas (N2 included) (%)</td>
<td>6.60</td>
<td>8.02</td>
<td>5.58</td>
<td>7.01</td>
<td>6.78</td>
<td>8.95</td>
<td>10.28</td>
<td>6.82</td>
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<tr>
<td>N2 in Product gas (N2 included) (%)</td>
<td>68.08</td>
<td>67.40</td>
<td>68.33</td>
<td>70.46</td>
<td>67.05</td>
<td>59.34</td>
<td>59.69</td>
<td>61.21</td>
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<tr>
<td>CO in Product gas (N2 included) (%)</td>
<td>7.02</td>
<td>10.29</td>
<td>8.16</td>
<td>8.22</td>
<td>7.71</td>
<td>11.36</td>
<td>12.78</td>
<td>14.37</td>
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<tr>
<td>CH4 in Product gas (N2 included) (%)</td>
<td>1.36</td>
<td>1.91</td>
<td>1.18</td>
<td>1.76</td>
<td>1.12</td>
<td>1.75</td>
<td>2.60</td>
<td>1.76</td>
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<tr>
<td>CO2 in Product gas (N2 included) (%)</td>
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<td>9.47</td>
<td>14.57</td>
<td>10.39</td>
<td>14.93</td>
<td>13.37</td>
<td>9.17</td>
<td>11.01</td>
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<tr>
<td>Acetylene C2H2 in Product gas (N2 included) (%)</td>
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<td>0.00</td>
<td>0.00</td>
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<td>0.00</td>
<td>0.00</td>
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<td>Ethylene C2H4 in Product gas (N2 included) (%)</td>
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<td>0.48</td>
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<td>0.00</td>
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<tr>
<td>Propane C3H8 in Product gas (N2 included) (%)</td>
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<td>0.01</td>
<td>0.01</td>
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<td>0.00</td>
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<tr>
<td>Isobutane C4H10 in Product gas (N2 included) (%)</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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<td>1-Butene C4H8 in Product gas (N2 included) (%)</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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<td>Butane C4H10 in Product gas (N2 included) (%)</td>
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<td>PO_NO26-1</td>
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</tr>
<tr>
<td>Bed material</td>
<td>Sand</td>
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<td>Sand</td>
<td>Sand</td>
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<td>Sand</td>
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<td>Gasification temperature (Bed temperature) (°C)</td>
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<td>843</td>
<td>841</td>
<td>814</td>
<td>790</td>
<td>790</td>
<td>818</td>
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<td>0.1</td>
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<tr>
<td>Bed pressure</td>
<td>kPa</td>
<td>g/min</td>
<td>L/min</td>
<td>L/min</td>
<td>L/min</td>
<td>g/min</td>
<td>L/min</td>
<td>L/min</td>
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<tr>
<td>Water content of Slurry or Bio-oil</td>
<td>5.1</td>
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<td>0.0</td>
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<td>1.7</td>
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<td>Slurry or Bio-oil feeding rate</td>
<td>L/min</td>
<td>L/min</td>
<td>L/min</td>
<td>L/min</td>
<td>L/min</td>
<td>g/min</td>
<td>g/min</td>
<td>g/min</td>
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<td>H % in Slurry or Bio-oil</td>
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<td>7.22</td>
<td>7.22</td>
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<td>7.22</td>
<td>7.22</td>
<td>6.48</td>
<td>7.22</td>
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<tr>
<td>C % in Slurry or Bio-oil</td>
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<td>42.47</td>
<td>42.47</td>
<td>48.39</td>
<td>42.47</td>
<td>42.47</td>
<td>48.39</td>
<td>42.47</td>
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<td>N % in Slurry or Bio-oil</td>
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<td>0.30</td>
<td>0.30</td>
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<td>0.30</td>
<td>0.30</td>
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</tr>
<tr>
<td>O % in Slurry or Bio-oil</td>
<td>49.71</td>
<td>49.71</td>
<td>49.71</td>
<td>43.37</td>
<td>49.71</td>
<td>49.71</td>
<td>43.37</td>
<td>49.71</td>
</tr>
<tr>
<td>Water content of Slurry or Bio-oil</td>
<td>25.22</td>
<td>25.22</td>
<td>25.22</td>
<td>20.18</td>
<td>25.22</td>
<td>25.22</td>
<td>20.18</td>
<td>25.00</td>
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<tr>
<td>Product Gas Temperature (T at flow meter) (°C)</td>
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<td>27.4</td>
<td>25.2</td>
<td>39.7</td>
<td>30.0</td>
<td>27.7</td>
<td>27.2</td>
<td>26.1</td>
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<tr>
<td>Product gas Flow rate (measured)</td>
<td>20.05</td>
<td>21.06</td>
<td>19.56</td>
<td>25.64</td>
<td>21.85</td>
<td>27.69</td>
<td>24.83</td>
<td>22.40</td>
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<tr>
<td>Pressure at Flow meter</td>
<td>kPa</td>
<td>g/min</td>
<td>L/min in N2</td>
<td>L/min</td>
<td>g/min</td>
<td>kPa</td>
<td>g/min</td>
<td>L/min</td>
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<tr>
<td>H2 in Product gas (N2 included)</td>
<td>%</td>
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<td>6.20</td>
<td>6.89</td>
<td>9.10</td>
<td>8.93</td>
<td>27.99</td>
<td>22.37</td>
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<tr>
<td>N2 in Product gas (N2 included)</td>
<td>%</td>
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<td>60.20</td>
<td>58.71</td>
<td>71.61</td>
<td>67.90</td>
<td>48.91</td>
<td>57.59</td>
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<tr>
<td>CO in Product gas (N2 included)</td>
<td>%</td>
<td>13.48</td>
<td>15.50</td>
<td>11.91</td>
<td>8.43</td>
<td>11.40</td>
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Table G.4  Experimental data of steam gasification #1

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APPENDIX H  Sample Calculations

A sample calculation sheet is provided here.

Table H.1  Sample calculation for run ID: PO_OC14-2

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<td>N2bottom</td>
<td>L/min</td>
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<td>g/min</td>
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<td>O % in Slurry or Bio-oil</td>
<td>[Ofeed]</td>
<td>%</td>
</tr>
<tr>
<td>Water content of Slurry or Bio-oil</td>
<td>[Wfeed]</td>
<td>%-wt</td>
</tr>
<tr>
<td>Product Gas</td>
<td>Tpc</td>
<td>(°C)</td>
</tr>
<tr>
<td>Temperature</td>
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<td></td>
</tr>
<tr>
<td>Product gas Flow</td>
<td>Vpmeasured</td>
<td>L/min in</td>
</tr>
<tr>
<td>rate (measured)</td>
<td></td>
<td>N2</td>
</tr>
<tr>
<td>Pressure at Flow</td>
<td>Pfm</td>
<td>kPa-g</td>
</tr>
<tr>
<td>meter</td>
<td></td>
<td></td>
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### Appendix H  Sample calculations

<table>
<thead>
<tr>
<th>Component</th>
<th>Formula</th>
<th>Unit</th>
<th>Value</th>
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<tbody>
<tr>
<td>H₂ in Product gas (N₂ included)</td>
<td>[H₂p]</td>
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<tr>
<td>N₂ in Product gas (N₂ included)</td>
<td>[N₂p]</td>
<td>%</td>
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<td>[COp]</td>
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<td>CO₂ in Product gas (N₂ included)</td>
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<tr>
<td>Ethylene C₂H₄ in Product gas (N₂ included)</td>
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<td>%</td>
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<td>Ethane C₂H₆ in Product gas (N₂ included)</td>
<td>[C₂H₆p]</td>
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<td>Propane C₃H₈ in Product gas (N₂ included)</td>
<td>[C₃H₈p]</td>
<td>%</td>
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<tr>
<td>Isobutane C₄H₁₀ in Product gas (N₂ included)</td>
<td>[iC₄H₁₀p]</td>
<td>%</td>
<td>0.00</td>
</tr>
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<td>1-Butene C₄H₈ in Product gas (N₂ included)</td>
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</tr>
<tr>
<td>Butane C₄H₁₀ in Product gas (N₂ included)</td>
<td>[nC₄H₁₀p]</td>
<td>%</td>
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<tr>
<td>Catalyst or sand weight</td>
<td>Wbed</td>
<td>g</td>
<td>780</td>
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<td>Catalyst or sand bulk density</td>
<td>Dbed</td>
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<tr>
<td>Bed volume</td>
<td>Vbed</td>
<td>cm³</td>
<td>=Wbed/Dbed</td>
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### Constants

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<td>Atomic weight of H</td>
<td>AWH</td>
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<tr>
<td>Atomic weight of C</td>
<td>AWC</td>
<td>g/mol</td>
<td>12.0107</td>
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<tr>
<td>Atomic weight of N</td>
<td>AWN</td>
<td>g/mol</td>
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<tr>
<td>Atomic weight of O</td>
<td>AWO</td>
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<tr>
<td>Gas constant</td>
<td>R</td>
<td>J/mol K</td>
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### Feed

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<tr>
<th>Component</th>
<th>Symbol</th>
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<tr>
<td>Water feed</td>
<td>nWf</td>
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<td>=Wf/18.01528</td>
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<tr>
<td>Water in Slurry or Bio-oil</td>
<td>wfeed</td>
<td>g/min</td>
<td>=F*[Wfeed]/100</td>
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</table>

1.79
<table>
<thead>
<tr>
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<th>Symbol</th>
<th>Unit</th>
<th>Formula</th>
<th>Value</th>
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</thead>
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<tr>
<td>Water in Slurry or Bio-oil</td>
<td>nWfeed</td>
<td>mol/min</td>
<td>nWfeed/18.01528</td>
<td>0.07</td>
</tr>
<tr>
<td>Air Atomizer (measured)</td>
<td>nAatomizer</td>
<td>mol/min</td>
<td>101300<em>nAatomizer/1000/(R</em>Troomk)</td>
<td>0.36</td>
</tr>
<tr>
<td>N2 Atomizer (measured)</td>
<td>nN2atomizer</td>
<td>mol/min</td>
<td>101300<em>nN2atomizer/1000/(R</em>Troomk)</td>
<td>0.16</td>
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<tr>
<td>N2 Atomizer (Total)</td>
<td>vTotN2atomizer</td>
<td>L/min</td>
<td>101300<em>vTotN2atomizer/1000/(R</em>Troomk)</td>
<td>10.71</td>
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<tr>
<td>N2 Atomizer (Total)</td>
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<td>mol/min</td>
<td>101300<em>vTotN2atomizer/1000/(R</em>Troomk)</td>
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</tr>
<tr>
<td>O2 Atomizer (Total)</td>
<td>nTotO2atomizer</td>
<td>mol/min</td>
<td>101300<em>vTotO2atomizer/1000/(R</em>Troomk)</td>
<td>0.07</td>
</tr>
<tr>
<td>Air from the bottom (measured)</td>
<td>nAbottom</td>
<td>mol/min</td>
<td>101300<em>nAbottom/1000/(R</em>Troomk)</td>
<td>0.09</td>
</tr>
<tr>
<td>N2 from the bottom (measured)</td>
<td>nN2bottom</td>
<td>mol/min</td>
<td>101300<em>nN2bottom/1000/(R</em>Troomk)</td>
<td>0.00</td>
</tr>
<tr>
<td>N2 from the bottom (total)</td>
<td>vTotN2bottom</td>
<td>L/min</td>
<td>101300*N2atomizer/0.790524+N2bottom</td>
<td>1.62</td>
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<tr>
<td>N2 from the bottom (total)</td>
<td>nTotN2bottom</td>
<td>mol/min</td>
<td>101300<em>vTotN2bottom/1000/(R</em>Troomk)</td>
<td>0.07</td>
</tr>
<tr>
<td>O2 from the bottom (total)</td>
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<tr>
<td>O2 from the bottom (total)</td>
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<td>mol/min</td>
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<tr>
<td>N2 in feed</td>
<td>nN2feed</td>
<td>L/min</td>
<td>vTotN2atomizer+vTotN2bottom</td>
<td>12.33</td>
</tr>
<tr>
<td>O2 in feed</td>
<td>nO2feed</td>
<td>L/min</td>
<td>vTotN2atomizer+vTotO2bottom</td>
<td>2.22</td>
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<tr>
<td>Total gas</td>
<td>nTotfeed</td>
<td>mol/min</td>
<td>nWf+nN2feed+nO2feed</td>
<td>1.11</td>
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<tr>
<td>H in Slurry or Bio-oil (Dry)</td>
<td>nHfeeddry</td>
<td>g/min</td>
<td>F*[Hfeed]/100-F*[Wfeed]/100/(AWH*2+AWO)<em>2</em>AWH</td>
<td>0.272</td>
</tr>
<tr>
<td>C in Slurry or Bio-oil (Dry)</td>
<td>nCfeeddry</td>
<td>g/min</td>
<td>F*[Cfeed]/100</td>
<td>0.416</td>
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<tr>
<td>N in Slurry or Bio-oil (Dry)</td>
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<td>g/min</td>
<td>F*[Nfeed]/100</td>
<td>3.107</td>
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<tr>
<td>O in Slurry or Bio-oil (Dry)</td>
<td>nOfeeddry</td>
<td>g/min</td>
<td>F*[Ofeed]/100</td>
<td>2.785</td>
</tr>
<tr>
<td>H in Slurry or Bio-oil (Dry)</td>
<td>nHfeeddry</td>
<td>mol/min</td>
<td>mHfeed/AWH</td>
<td>0.413</td>
</tr>
<tr>
<td>C in Slurry or Bio-oil (Dry)</td>
<td>nCfeeddry</td>
<td>mol/min</td>
<td>mCfeed/AWC</td>
<td>0.259</td>
</tr>
<tr>
<td>N in Slurry or Bio-oil (Dry)</td>
<td>nNfeeddry</td>
<td>mol/min</td>
<td>mNfeed/AWN</td>
<td>0.001</td>
</tr>
<tr>
<td>O in Slurry or Bio-oil (Dry)</td>
<td>nOfeeddry</td>
<td>mol/min</td>
<td>mOfeed/AWO</td>
<td>0.174</td>
</tr>
<tr>
<td>H in Slurry or Bio-oil (Dry)</td>
<td>nHfeeddry</td>
<td>g/min</td>
<td>F*[Hfeed]/100-F*[Wfeed]/100/(AWH*2+AWO)<em>2</em>AWH</td>
<td>0.272</td>
</tr>
<tr>
<td>Product Gas</td>
<td>nHfeeddry</td>
<td>mol/min</td>
<td>mHfeeddry/AWH</td>
<td>0.270</td>
</tr>
</tbody>
</table>

Temperature (T at flow meter)  

Tpk = Tpc+273.15  

K = Tpc+273.15
## N2 Viscosity (calculated)

| \( \mu_{N_2} \) | Pa·s | \(-0.00000065592\times T_{pk}^{0.6081}/(1+5.714/T_{pk}+0.714/T_{pk}^2) \) | 1.79E-05 |

## Viscosity (calculated)

| \( \mu_{\text{product}} \) | Pa·s | Viscosity of mixed gas was calculated by correlation below. \( \mu_{\text{mix}}=\sum_{i=1}^{n}(x_i\mu_i/\sum_{j=1}^{n}x_j) \frac{\phi_i}{8\left(1+\frac{\mu_i}{\mu_j}\right)^{1/4}\left(\frac{M_j}{M_i}\right)^{1/4}} \) | 1.71E-05 |

## Product gas Flow rate (calculated)

| Product gas Flow rate (calculated) | \( V_{p\text{compensated}} \) | L/min | \( =V_{p\text{measured}}\times \mu_{N_2}/\mu_{\text{product}} \) | 22.45 |

| H2 in Product gas (N2 included) | \( V_{H_2p} \) | L/min | \( =V_{p\text{compensated}}\times [H_2p]/100 \) | 4.24 |

| N2 in Product gas (N2 included) | \( V_{N_2p} \) | L/min | \( =V_{p\text{compensated}}\times [N_2p]/100 \) | 12.71 |

| CO in Product gas (N2 included) | \( V_{COp} \) | L/min | \( =V_{p\text{compensated}}\times [COp]/100 \) | 1.05 |

| CH4 in Product gas (N2 included) | \( V_{C_4H_4p} \) | L/min | \( =V_{p\text{compensated}}\times [CH_4p]/100 \) | 0.23 |

| CO2 in Product gas (N2 included) | \( V_{C_2H_2p} \) | L/min | \( =V_{p\text{compensated}}\times [C_2H_2p]/100 \) | 0.00 |

| Ethylene C2H4 in Product gas (N2 included) | \( V_{C_2H_4p} \) | L/min | \( =V_{p\text{compensated}}\times [C_2H_4p]/100 \) | 0.00 |

| Ethane C2H6 in Product gas (N2 included) | \( V_{C_2H_6p} \) | L/min | \( =V_{p\text{compensated}}\times [C_2H_6p]/100 \) | 0.00 |

| Propene C3H6 in Product gas (N2 included) | \( V_{C_3H_6p} \) | L/min | \( =V_{p\text{compensated}}\times [C_3H_6p]/100 \) | 0.00 |

| Propane C3H8 in Product gas (N2 included) | \( V_{C_3H_8p} \) | L/min | \( =V_{p\text{compensated}}\times [C_3H_8p]/100 \) | 0.00 |

| Isobutane C4H10 in Product gas (N2 included) | \( V_{iC_4H_10p} \) | L/min | \( =V_{p\text{compensated}}\times [iC_4H_10p]/100 \) | 0.00 |

| 1-Butene C4H8 in Product gas (N2 included) | \( V_{1C_4H_8p} \) | L/min | \( =V_{p\text{compensated}}\times [1C_4H_8p]/100 \) | 0.00 |

| Butane C4H10 in Product gas (N2 included) | \( V_{nC_4H_10p} \) | L/min | \( =V_{p\text{compensated}}\times [nC_4H_10p]/100 \) | 0.00 |

| H2 in Product gas (N2 included) | \( n_{H_2p} \) | mol/min | \( =(101300+pfm\times 1000)\times V_{H_2p}/1000/(R\times T_{pk}) \) | 0.17 |

| N2 in Product gas (N2 included) | \( n_{N_2p} \) | mol/min | \( =(101300+pfm\times 1000)\times V_{N_2p}/1000/(R\times T_{pk}) \) | 0.52 |

| CO in Product gas (N2 included) | \( n_{COp} \) | mol/min | \( =(101300+pfm\times 1000)\times V_{COp}/1000/(R\times T_{pk}) \) | 0.04 |

| CH4 in Product gas (N2 included) | \( n_{CH_4p} \) | mol/min | \( =(101300+pfm\times 1000)\times V_{CH_4p}/1000/(R\times T_{pk}) \) | 0.01 |
### Appendix H  
Sample calculations

<table>
<thead>
<tr>
<th>Component (Product gas)</th>
<th>Chemical Formula</th>
<th>Concentration Unit</th>
<th>Concentration Calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ in Product gas (N₂ included)</td>
<td>nCO₂p</td>
<td>mol/min</td>
<td>((101300 + pfm \times 1000) \times VCO₂p / 1000 / (R \times Tpk))</td>
</tr>
<tr>
<td>Acetylene C₂H₂ in Product gas (N₂ included)</td>
<td>nC₂H₂p</td>
<td>mol/min</td>
<td>((101300 + pfm \times 1000) \times VC₂H₂p / 1000 / (R \times Tpk))</td>
</tr>
<tr>
<td>Ethylene C₂H₄ in Product gas (N₂ included)</td>
<td>nC₂H₄p</td>
<td>mol/min</td>
<td>((101300 + pfm \times 1000) \times VC₂H₄p / 1000 / (R \times Tpk))</td>
</tr>
<tr>
<td>Ethane C₂H₆ in Product gas (N₂ included)</td>
<td>nC₂H₆p</td>
<td>mol/min</td>
<td>((101300 + pfm \times 1000) \times VC₂H₆p / 1000 / (R \times Tpk))</td>
</tr>
<tr>
<td>Propene C₃H₆ in Product gas (N₂ included)</td>
<td>nC₃H₆p</td>
<td>mol/min</td>
<td>((101300 + pfm \times 1000) \times VC₃H₆p / 1000 / (R \times Tpk))</td>
</tr>
<tr>
<td>Propane C₃H₈ in Product gas (N₂ included)</td>
<td>nC₃H₈p</td>
<td>mol/min</td>
<td>((101300 + pfm \times 1000) \times VC₃H₈p / 1000 / (R \times Tpk))</td>
</tr>
<tr>
<td>Isobutane C₄H₁₀ in Product gas (N₂ included)</td>
<td>niC₄H₁₀p</td>
<td>mol/min</td>
<td>((101300 + pfm \times 1000) \times VïC₄H₁₀p / 1000 / (R \times Tpk))</td>
</tr>
<tr>
<td>1-Butene C₄H₈ in Product gas (N₂ included)</td>
<td>n₁C₄H₈p</td>
<td>mol/min</td>
<td>((101300 + pfm \times 1000) \times V₁C₄H₈p / 1000 / (R \times Tpk))</td>
</tr>
<tr>
<td>Butane C₄H₁₀ in Product gas (N₂ included)</td>
<td>nₙC₄H₁₀p</td>
<td>mol/min</td>
<td>((101300 + pfm \times 1000) \times VnC₄H₁₀p / 1000 / (R \times Tpk))</td>
</tr>
<tr>
<td>H in Product gas (N₂ included)</td>
<td>mHp</td>
<td>g/min</td>
<td>((nH₂p \times 2 + nCH₄p \times 4 + nC₂H₂p \times 2 + nC₂H₄p \times 4 + nC₂H₆p \times 6 + nC₃H₆p \times 6 + nC₃H₈p \times 8 + niC₄H₁₀p \times 10 + n₁C₄H₈p \times 8 + nₙC₄H₁₀p \times 10) \times AWH)</td>
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<tr>
<td>C in Product gas (N₂ included)</td>
<td>mCp</td>
<td>g/min</td>
<td>((nCOp + nCH₄p + nCO₂p + (nC₂H₂p + nC₂H₄p + nC₂H₆p + nC₃H₆p + nC₃H₈p \times 3 + n₁C₄H₁₀p + nₙC₄H₁₀p + nₙC₄H₁₀p) \times 4) \times AWC)</td>
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<td>N in Product gas (N₂ included)</td>
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<td>(nN₂p \times 2 \times AWN)</td>
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<td>O in Product gas (N₂ included)</td>
<td>mOp</td>
<td>g/min</td>
<td>((nCOp + nCO₂p \times 2) \times AWO)</td>
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**Summary**

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<tr>
<th>Parameter (Actual)</th>
<th>Value</th>
</tr>
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<tbody>
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<td>(\lambda) (Actual)</td>
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<tr>
<td>H₂O/C (Actual)</td>
<td>StoCactual</td>
</tr>
<tr>
<td>GC₁HSV (Actual)</td>
<td>GC₁HSVactual</td>
</tr>
<tr>
<td>Bed pressure</td>
<td>Pabs</td>
</tr>
<tr>
<td>Feeding rate in g/ml-cat</td>
<td>FperVbed</td>
</tr>
<tr>
<td>Steam in feed</td>
<td>[Steaminfeed]</td>
</tr>
<tr>
<td>N₂ in feed</td>
<td>[N₂infeed]</td>
</tr>
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### Appendix H Sample calculations

<table>
<thead>
<tr>
<th>Calculation</th>
<th>Formula</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>O₂ in feed</td>
<td>[O₂\text{in feed}] %-%-mol = \frac{nO₂feed}{n\text{Totfeed}} \times 100</td>
<td>8</td>
</tr>
<tr>
<td>O from steam and air (Product gas)</td>
<td>[O\text{from steamair}] % = \frac{(mO-p-mOfeed)}{mO*100}</td>
<td>49</td>
</tr>
<tr>
<td>H from steam (Product gas)</td>
<td>[H\text{from steam}] % = \frac{(mH-p-mHfeed)}{mH*100}</td>
<td>-6</td>
</tr>
<tr>
<td>C conversion (Carbon to gas)</td>
<td>[C_{\text{conv}}] % = \frac{mCp}{mCfeed} \times 100</td>
<td>78</td>
</tr>
<tr>
<td>H₂ yield (stoichiometric)</td>
<td>[H₂\text{stoic}] %-%-mol = \frac{nH₂p}{n\text{StoicH₂}} \times 100</td>
<td>32</td>
</tr>
<tr>
<td>H₂ yield from 1 kg feed</td>
<td>[H₂\text{perkgfeed}] kg/kg = \frac{nH₂p \times AWH*2/F}{mP}</td>
<td>0.055</td>
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<tr>
<td>H₂/CO in product gas</td>
<td>[H₂\text{toCO}] mol/mol = \frac{nH₂p}{nCOp}</td>
<td>4.0</td>
</tr>
<tr>
<td>N₂ closure</td>
<td>[N₂\text{clos}] %-%-vol = \frac{VN₂p}{vN₂\text{feed}} \times 100</td>
<td>103</td>
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<tr>
<td>H₂ in Product gas (N₂ free)</td>
<td>[H₂\text{pN₂free}] % = \frac{[H₂p]}{100-[N₂p]} \times 100</td>
<td>43.6</td>
</tr>
<tr>
<td>CO in Product gas (N₂ free)</td>
<td>[CO\text{pN₂free}] % = \frac{[COp]}{100-[N₂p]} \times 100</td>
<td>10.8</td>
</tr>
<tr>
<td>CH₄ in Product gas (N₂ free)</td>
<td>[CH₄\text{pN₂free}] % = \frac{[CH₄p]}{100-[N₂p]} \times 100</td>
<td>2.4</td>
</tr>
<tr>
<td>CO₂ in Product gas (N₂ free)</td>
<td>[CO₂\text{pN₂free}] % = \frac{[CO₂p]}{100-[N₂p]} \times 100</td>
<td>37.1</td>
</tr>
<tr>
<td>Acetylene C₂H₂ in Product gas (N₂ free)</td>
<td>[C₂H₂\text{pN₂free}] % = \frac{[C₂H₂p]}{100-[N₂p]} \times 100</td>
<td>0.0</td>
</tr>
<tr>
<td>Ethylene C₂H₄ in Product gas (N₂ free)</td>
<td>[C₂H₄\text{pN₂free}] % = \frac{[C₂H₄p]}{100-[N₂p]} \times 100</td>
<td>0.0</td>
</tr>
<tr>
<td>Ethane C₂H₆ in Product gas (N₂ free)</td>
<td>[C₂H₆\text{pN₂free}] % = \frac{[C₂H₆p]}{100-[N₂p]} \times 100</td>
<td>0.0</td>
</tr>
<tr>
<td>Propene C₃H₆ in Product gas (N₂ free)</td>
<td>[C₃H₆\text{pN₂free}] % = \frac{[C₃H₆p]}{100-[N₂p]} \times 100</td>
<td>0.0</td>
</tr>
<tr>
<td>Propane C₃H₈ in Product gas (N₂ free)</td>
<td>[C₃H₈\text{pN₂free}] % = \frac{[C₃H₈p]}{100-[N₂p]} \times 100</td>
<td>0.0</td>
</tr>
<tr>
<td>Isobutane C₄H₁₀ in Product gas (N₂ free)</td>
<td>[C₄H₁₀\text{pN₂free}] % = \frac{[C₄H₁₀p]}{100-[N₂p]} \times 100</td>
<td>0.0</td>
</tr>
<tr>
<td>₁-Butene C₄H₈ in Product gas (N₂ free)</td>
<td>[₁C₄H₈\text{pN₂free}] % = \frac{[₁C₄H₈p]}{100-[N₂p]} \times 100</td>
<td>0.0</td>
</tr>
<tr>
<td>Butane C₄H₁₀ in Product gas (N₂ free)</td>
<td>[nC₄H₁₀\text{pN₂free}] % = \frac{[nC₄H₁₀p]}{100-[N₂p]} \times 100</td>
<td>0.0</td>
</tr>
<tr>
<td>Carbon yield as CO</td>
<td>[Y\text{CasCO}] %-%mol/mol feed = \frac{nCOp}{nCfeed} \times 100</td>
<td>16.7</td>
</tr>
<tr>
<td>Carbon yield as CO₂</td>
<td>[Y\text{CasCO₂}] %-%mol/mol feed = \frac{nCO₂p}{nCfeed} \times 100</td>
<td>57.5</td>
</tr>
<tr>
<td>Carbon yield as CH₄</td>
<td>[Y\text{CasCH₄}] %-%mol/mol feed = \frac{nCH₄p}{nCfeed} \times 100</td>
<td>3.7</td>
</tr>
<tr>
<td>Carbon yield as C₂-C₄</td>
<td>[Y\text{CasC₂to₄}] %-%mol/mol feed = \frac{(nC₂H₂p+nC₂H₄p+nC₂H₆p)*2+(nC₃H₆p+nC₃H₈p)*3+(nC₄H₁₀p+nC₄H₁₀p)*4}{nCfeed} \times 100</td>
<td>0.0</td>
</tr>
<tr>
<td>Hydrogen yield as H₂ (Based on dry feed)</td>
<td>[Y\text{HasH₂dry}] %-%mol/mol feed = \frac{nH₂p*2}{nHfeeddry} \times 100</td>
<td>129.4</td>
</tr>
<tr>
<td>Hydrogen yield as CH₄ (Based on dry feed)</td>
<td>[Y\text{HasCH₄dry}] %-%mol/mol feed = \frac{nCH₄p*4}{nHfeeddry} \times 100</td>
<td>14.1</td>
</tr>
<tr>
<td>Hydrogen yield as C2-C4 (Based on dry feed)</td>
<td>( Y_{HasC2to4dry} )</td>
<td>( % \text{mol/mol dry feed} )</td>
</tr>
<tr>
<td>Steam conversion</td>
<td>( % \text{dry feed base} )</td>
<td>( \frac{\text{mH}_p - \text{mHfeeddry}}{(\text{W}_f + \text{mWfeed}) \cdot 2 \cdot \text{AWH}/(2 \cdot \text{AWH} + \text{AWO})} \cdot 100 )</td>
</tr>
<tr>
<td>Superficial velocity of steam at 700°C</td>
<td>( \text{m/s} )</td>
<td>( \frac{\text{nW}<em>f \cdot \text{R} \cdot \text{T}</em>{rk}/100000/\left(0.0779^2/4\cdot\pi\right)}{60} )</td>
</tr>
</tbody>
</table>
APPENDIX I  Heat of Reactions of Steam Gasification, Steam Gasification Followed by the Water-Gas Shift Reaction, and Partial Oxidation of Bio-Oil

I.1  Heat of reaction: steam gasification, steam gasification followed by the water-gas shift reaction and partial oxidation of bio-oil

Combustion of bio-oil,

\[
\text{CH}_{1.31}\text{O}_{0.47} + 1.0925 \text{ O}_2 \rightarrow \text{CO}_2 + 0.655 \text{ H}_2\text{O} \,(g) \quad \Delta H_{298}^0 = -462 \text{ kJ/(mol-carbon)} \quad (I.1)
\]

Combustion of hydrogen,

\[
\text{H}_2 + 0.5 \text{ O}_2 \rightarrow \text{H}_2\text{O} \,(g) \quad \Delta H_{298}^0 = -242 \text{ kJ/mol} \quad (I.2)
\]

Combustion of carbon mono oxide,

\[
\text{CO} + 0.5 \text{ O}_2 \rightarrow \text{CO}_2 \quad \Delta H_{298}^0 = -283 \text{ kJ/mol} \quad (I.3)
\]

Steam gasification of bio-oil, steam gasification of bio-oil followed by water-gas-shift reaction and partial oxidation gasification of bio-oil can be described by linear combination of reactions (I-1-3). Subsequently, the heat of reactions can be obtained as followings,

Steam gasification of bio-oil,

\[
\text{CH}_{1.31}\text{O}_{0.47} + 0.53\text{H}_2\text{O} \,(g) \rightarrow \text{CO} + 1.185\text{H}_2 = (I-1) - 1.185(I-2) - (I-3) \quad (I.4)
\]
Appendix I  Heat of reactions of steam gasification, steam gasification followed by the water-gas shift reaction, and partial oxidation of bio-oil Sample calculations

\[ \Delta H_{298}^{0} = (-462) - 1.185(-242) - (-283) = +108 \text{ kJ/(mol-carbon)} \]

Steam gasification of bio-oil followed by water-gas-shift reaction,

\[ \text{CH}_{1.31}\text{O}_{0.47} + 1.53\text{H}_{2}\text{O} (g) \rightarrow \text{CO}_2 + 2.185\text{H}_{2} = (\text{I-1}) - 2.185(\text{I-2}) \]

\[ \Delta H_{298}^{0} = (-462) - 2.185(-242) = +67 \text{ kJ/(mol-carbon)} \] (I.5)

Partial oxidation gasification of bio-oil,

\[ \text{CH}_{1.31}\text{O}_{0.47} + 0.265\text{O}_{2} \rightarrow \text{CO} + 0.655\text{H}_{2} = (\text{I-1}) - 0.655(\text{I-2}) - (\text{I-3}) \]

\[ \Delta H_{298}^{0} = (-462) - 0.655(-242) - (-283) = -20 \text{ kJ/(mol-carbon)} \] (I.6)

Heat of combustion of bio-oil is calculated based on,

\[ \text{HHV} = 0.341 \text{C} + 1.322 \text{H} - 0.12 (\text{O} + \text{N}) - 0.0153 \text{ A} + 0.0686 \text{ S} \text{ kJ/g} \] (I.7)

where C, H, O, N, S, and A are the weight percents of carbon, hydrogen, oxygen, nitrogen, sulfur, and ash respectively. N, S, and A are regarded as negligible (Domalski et al., 1987).

I.2  Reference

APPENDIX J Matlab Code for Thermodynamic Equilibrium Calculation

J.1 Main program for free energy minimization (FEM) model RAND algorithm

The program code originates from Li, X. (2002). It was modified for the present study as in the following:

- Empirical equations in the original code to estimate unconverted carbon and methane concentration were deleted. For the present study, the code was modified to input unconverted carbon and yield of hydrocarbons as a kinetically modified model (J1).
- To calculate the initial elemental abundance from bio-oil/char slurry with different char content, the code was modified in order to input char concentration (J1 and J3).
- S/C ratio to be input in molar ratio.

File name: sdgas.m
Function: Main program of equilibrium model

```
% Version 1.0 [ Standard Version for C-H-O-N-S Systems ]
% (C) Masakazu Sakaguchi (Jan 3, 2010) modified Xiantian Li's code
% (1) Input Model Parameters
% Bio-oil and slurry gasification share the same database: coaldat.m
% All calculations are made based on 1 kg of feedstock (dry basis)

prompt = {'Enter minimum temperature, deg C', 'Enter number of T intervals', 'Enter T increment, K', 'Enter system pressure, bar', 'Enter initial Oxygen ratio, stoichiometric', 'Enter Ca/S molar ratio', 'Enter fuel type index (1:Bio-oil WL)', 'Enter number of air ratio changes', 'H2O/C, mol/mol', 'Char content, wt%', 'Feeding water temperature (C)', 'Nitrogen purge (L/min)', 'Fuel feeding rate (g/min)', 'Kinetic modification? (y=1,n=0)', 'Carbon conversion (%)', 'C yield as hydrocarbons (%)', 'H yield as hydrocarbons (%-dry basis)'};
defAns = {'850', '1', '50', '1.013', '0', '0', '1', '1', '2.1', '0', '20', '0', '6.59', '0', '100', '100', '100'};
title = 'Inputs for equilibrium model'
lineNo = 1;
answer = inputdlg(prompt, title, lineNo, defAns);
[S1, S2, S3, S4, S5, S6, S7, S8, S9, S10, S11, S12, S13, S14, S15, S16, S17] = deal(answer(:));
Ti = str2num(S1); % Minimum operating temperature (C)
```

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Appendix J  
Matlab code for thermodynamic equilibrium calculation

```matlab
T0 = Ti + 273;  \% Operating temperature (K)
NT = str2num(S2);  \% Number of T intervals (-)
DT = str2num(S3);  \% Temperature increment (K)
p = str2num(S4);  \% System pressure (bar)
alpha = str2num(S5);  \% Initial air ratio (-)
Ca = str2num(S6);  \% Ca/S molar ratio (-)
NF = str2num(S7);  \% Fuel type: 1 = Bio-oil; 2 = Char, etc.
rH2O = str2num(S9);  \% H2O/C (mol/mol)
Charcont = str2num(S10)/100;  \% Char content (wt. fraction kg/kg)
tstem = str2num(S11);  \% Feeding water temperature (C)
N2purge = str2num(S12);  \% N2 purge (L/min)
feedrate = str2num(S13);  \% Fuel feeding rate (g/min)
NFIT = str2num(S14);  \%: 100% C conversion, 1: Kinetic modification
TotalCyield = str2num(S15);  \% C conversion in %
YChydroc = str2num(S16);  \% C yield as hydrocarbons in %
YHhydroc = str2num(S17);  \% H yield as hydrocarbons in %  
% The total weight (kg) of moisture added to 1 kg of dry-basis sawdust:

dalfa = 0.05;  \% The increment of air ratio
rfuel = 1;  \% Fuel feed rate (kg/hr): bio-oil incl.H2O
NE0 = 0;  \% EA0: 0 = Direct input, 1 = From database
NE = 5;  \% Number of elements
NANA = 2;  \% Base, fuel analysis: 1: ar, 2: ad, 3: daf
NO = 1;  \% Oxidant: 1 = air, 2 = pure oxygen
NREF = 3;  \% Print: 1 = short, 2 = 6 species, 3 = long
dissip = 0;  \% Dissipation from the reactor surface
err = 0.00000001;  \% Maximum error for convergence test
NCP = 1;  \% Calculate fuel Cp(T) and enthalpy using: 1 = Coimbra and Queiroz (1995); 2 = Richardson (1993)
Iguess = 0;  \% 0: simple method, 1: linear programming

%--------------------------------------------------------
[Dat1, Dat11, Dat2, Dat3, Dath, Dath1] = coaldat(NE);

disp(' ')
disp(['
   Current Date: ' date ' '])
disp(' ')

%previous_flops = flops;

% (2) Calculate number of independent reactions in the system

SEM = Dat2(:, [2:(1+NE)]);  \% Load speacies-element matrix (SEM)
[N,M] = size(SEM);  \%Size of species-element matrix
NC = M;  \% Number of components
nr = rank(SEM);  \% Rank of SEM
mr = N - rank(SEM);  \% Model parameter
T = T0;  \% Initial temperature (K)
R = 8.31448;  \% Thermodynamic constant, J/mol-K

for i=1:N
    SI(i)=Dat1(i,2);  \% Si = State info
end

% Count the respective numbers of gas, liquid and solid species

ngas = 0;  \% Initialization
nliq = 0;
```

Appendix J  
Matlab code for thermodynamic equilibrium calculation

```
nsol = 0;
for i = 1:N
    if SI(i) == 1
        ngas = ngas + 1;
    elseif SI(i) == 2
        nliq = nliq + 1;
    elseif SI(i) == 3
        nsol = nsol + 1;
    end
end

% Count the number of phases
NP = 1; % Gas phase as an ideal solution
if nliq >= 1
    NP = NP + 1; % Liquid species from another ideal solution
end
NP = NP + nsol; % Each solid species is an individual phase

NZ = 0; % Number of inert species
N1 = N - NZ; % Number of reactive species
N2 = M + 1; % An index that will be used later
N3 = M + NP; % An index that will be used later

disp(')
disp(['Number of elements considered = ' num2str(M)])
disp(['Number of species considered = ' num2str(N)])
disp(['Number of gaseous species = ' num2str(ngas)])
disp(['Number of liquid species = ' num2str(nliq)])
disp(['Number of solid species = ' num2str(nsol)])
disp(['Number of components = ' num2str(NC)])
disp(['Number of phases involved = ' num2str(NP)])
disp(')

% (3) Calculate initial element abundance (moles)
alfa = alpha; % Initialization of z

if NREP == 1
    report = zeros(NT,1+IZ);
end

% -----------Start outer-layer iteration-------------
for iz = 1:IZ % outer-layer iteration of AR or P
    EA0 = zeros(M,1); % Clear memory and re-initialize EA0
    alfa = alpha + (iz-1)*dalfa; % Current air ratio

    % Call abundsd3.m to calculate an element abundance vector (EAV):
    [EA0, CEA, V0, Vair, mair, Uwat, Hfuel, N2purge, HHV, Conv, Tm0, tfuel, tnitro] =
        abundsd(NE, Dat3, rfuel, rH2O, NF, NO, NANA, NFIT, alfa, Ca, Charcont, tstm, N2purge, feedrate, TotalCyield, YChydroc, YHydroc);

    UC = EA0(1);
    UN = EA0(2);
    UO = EA0(3);
    if M >= 4
        UN = EA0(4);
    end
    if M >= 5
```
Appendix J  Matlab code for thermodynamic equilibrium calculation

US = EA0(5);
end

e0 = [UC, UH, UO];

if M == 3
    mfeed = UC*12.011 + UH*1.00794 + UO*15.994;
elseif M == 4
    mfeed = UC*12.011 + UH*1.00794 + UO*15.994 + UN*14.0067;
elseif M == 5
    mfeed = UC*12.011 + UH*1.00794 + UO*15.994 + UN*14.0067 + US*32.066;
end
totmol = 0.0; % The total moles of all feed elements
for j = 1:M
    totmol = totmol + EA0(j);
end
CEA = EA0;

% (4) Estimate the initial guess of gas composition (y and x vectors)
A0 = [
    % Components
    1 0 1 0 0 0 0 0  % CO = 14 (Species ID number)
    0 2 0 0 0 0 0 0  % H2 = 11
    1 0 2 0 0 0 0 0  % CO2 = 15
    0 0 0 2 0 0 0 0  % N2 = 22
    0 0 0 1 0 0 0 0  % S(g) = 33
    0 0 0 0 0 1 0 0  % Cl(g) = 43
    0 0 0 0 0 0 1 0  % Na(g) = 46
    0 0 0 0 0 0 0 1 ];  % Ca(g) = 50

% (4.1) a0 is the coefficient matrix to estimate the moles of components.
% Row = species; Col = element
a0 = A0(1:M, 1:M);

if M == 3
    anonc = [SEM(1:10,:); SEM(12:13,:); SEM(16:21,:)];
elseif M == 4
    anonc = [SEM(1:10,:); SEM(12:13,:); SEM(16:21,:); SEM(23:32,:)];
elseif M == 5
    anonc = [SEM(1:10,:); SEM(12:13,:); SEM(16:21,:); SEM(23:32,:); SEM(34:44,:)];
elseif M == 6
    anonc = [SEM(1:10,:); SEM(12:13,:); SEM(16:21,:); SEM(23:32,:); SEM(34:42,:);
              SEM(44:47,:)];
elseif M == 7
    anonc = [SEM(1:10,:); SEM(12:13,:); SEM(16:21,:); SEM(23:32,:); SEM(34:42,:);
              SEM(44:45,:); SEM(47:64,:)];
elseif M == 8
    anonc = [SEM(1:10,:); SEM(12:13,:); SEM(16:21,:); SEM(23:32,:); SEM(34:42,:);
              SEM(44:45,:); SEM(47:49,:); SEM(51:77,:)];
end

% ---------------------------------------

if Iguess == 0
% (4.2) Make an initial guess by a hand-estimation device
small = min(EA0);  % Smallest component in EA0
stoi = [UC, UH, UO/1.5];  % A device to evaluate C-H-O stoichiometry
Appendix J  
Matlab code for thermodynamic equilibrium calculation

smaller = min(stoi);  % smallest element in UC, UH and UO/1.5
ynonc = small * ones(N-M, 1)/10000;

% This logical variable modifies the initial guess for H2O to keep all component moles positive.
% The following block is valid only for M >= 3:
if smaller == stoi(1)  % C-lean
  ynonc(10) = UH - UC;  % Deduce H as H(g)
  ynonc(11) = UO - 1.5 * UC;  % Deduce O as O(g)
elseif smaller == stoi(2)  % H-lean
  ynonc(1) = UC - UH;  % Deduce C as C(g)
  ynonc(11) = UO - 1.5 * UH;  % Deduce O as O(g)
elseif smaller == stoi(3)  % O-lean
  ynonc(1) = UC - UO/1.5;  % Deduce C as C(g)
  ynonc(10) = UH - UO/1.5;  % Deduce H as H(g)
end

% End of the block

lens = length(ynonc);
if lens ~= (N-NC)
disp(' Length of the non-component vector is wrong.')
pause
end

% Calculate b0 the right-hand side vector
db0 = zeros(M,1);
b0 = zeros(M,1);
for k = 1:M
  for i = 1:(N-M)
    db0(k) = db0(k) + anonc(i,k)*ynonc(i);
  end
  b0(k) = EA0(k) - db0(k);
end

% Solve for initial guess
yc0 = a0\b0;  % Use transpose of b0.
if M == 3
  y0 = [ynonc(1:10); yc0(2); ynonc(11:12); yc0(1); yc0(3); ynonc(13:18)];
elseif M == 4
  y0 = [ynonc(1:10); yc0(2); ynonc(11:12); yc0(1); yc0(3); ynonc(13:18); ynonc(19:29)];
elseif M == 5
  y0 = [ynonc(1:10); yc0(2); ynonc(11:12); yc0(1); yc0(3); ynonc(13:18); ynonc(19:28); ynonc(29:59)];
elseif M == 6
  y0 = [ynonc(1:10); yc0(2); ynonc(11:12); yc0(1); yc0(3); ynonc(13:18); ynonc(19:28); yc0(5); ynonc(29:59)];
elseif M == 7
  y0 = [ynonc(1:10); yc0(2); ynonc(11:12); yc0(1); yc0(3); ynonc(13:18); ynonc(19:28); yc0(5); ynonc(29:37); yc0(6); ynonc(38:47)];
elseif M == 8
  y0 = [ynonc(1:10); yc0(2); ynonc(11:12); yc0(1); yc0(3); ynonc(13:18); ynonc(19:28); yc0(5); ynonc(29:37); yc0(6); ynonc(38:41); yc0(7); ynonc(42:57)];
end

[h,H] = enth(Dath,Dath1,T,y0);  % Calculate enthalpy
[cy0,ys0,x0,xg0,xs0,EA,CEA0] = calcc(SI, SEM, y0, EA0);
(4.3) Check the non-negativity constraint

\[
\text{ymin} = \min(yc0)
\]

if ymin < 0
  \[\text{NT} = 1;\]
  \[\text{NIT} = 1;\]
  disp(' Non-negativity requirements not met. '');
  disp(' Use linear programming to make another initial guess. ');
end

(6) Solve for a new set of \(y(i)\) by iteration using RAND algorithm

\[
\text{m} = 1; \quad \text{% Mark the first iteration}
\]
\[
\text{Ind} = 0; \quad \% \text{If Ind = 0, go ahead to next iteration.}
\]

% The following sentences are for initialization
\[
\text{al} = \text{zeros(N3, N3)} + \text{eps};
\]
\[
\text{y} = y0; \quad \text{summit} = \text{zeros(NT,1)};
\]
\[
\text{xt} = \text{zeros(NT,N)}; \quad \text{yt} = \text{zeros(NT,N)};
\]
\[
\text{xtdry} = \text{zeros(NT,N)}; \quad \text{dqt} = \text{zeros(NT,1)};
\]
\[
\text{Cwat} = \text{zeros(NT,1)}; \quad \text{hhvgas} = \text{zeros(NT,1)};
\]
\[
\text{HHVgas} = \text{zeros(NT,1)}; \quad \text{hhvdry} = \text{zeros(NT,1)};
\]
\[
\text{vgdry} = \text{zeros(NT,1)}; \quad \text{vgwet} = \text{zeros(NT,1)};
\]
\[
\text{E1} = \text{zeros(NT,1)}; \quad \text{E2} = \text{zeros(NT,1)};
\]
\[
\text{spc} = \text{zeros(NT,2)}; \quad \text{sph} = \text{zeros(NT,2)};
\]
\[
\text{spo} = \text{zeros(NT,2)}; \quad \text{spn} = \text{zeros(NT,2)};
\]
\[
\text{sps} = \text{zeros(NT,2)}; \quad \text{gama} = \text{zeros(NT,1)};
\]
\[
\text{mathane} = \text{zeros(NT,1)};
\]
% End of matrix initialization.

\[
\text{if NREP} = 1
\]
\[
\text{\quad report} = [ ]; \quad \text{report1} = [ ]; \quad \text{report2} = [ ];
\]
end

(6.1) Start temperature iteration

\[
\text{for it = 1:NT} \quad \% \text{Starts temperature iteration}
\]
\[
\text{\quad if it == 1}
\]
\[
\text{\quad \quad \text{NIT} = 100;}
\]
\[
\text{\quad else}
\]
\[
\text{\quad \quad \text{NIT} = 40; \quad \% \text{Maximum number of iterations}}
\]
\[
\text{\quad \quad \text{for i = 1:N}}
\]
\[
\text{\quad \quad \quad \text{y(i)} = \text{yt(it-i,i)};}
\]
\[
\text{\quad \quad \end}
\]
\[
\text{\quad \end}
\]
\[
\text{\quad TT(it) = T0 + (it-1)*DT;}
\]
\[
\text{\quad T = TT(it);}
\]

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% Initialization for each T iteration:

[cy,ys,x,xg,xs,EA,CEA] = calcc(SI,SEM,y,EA0);
[smu,smustar] = mut(T,p,Dat1,Dat11);
[h,H] = enth(Dath,Dath1,T,y);
% End of initialization.

% Calculate chemical potential of each species
for i = 1:N
    if SI(i) == 1
        smutp(i) = smustar(i) + R*T*log(xg(i)+1e-200)/1000.0;  % Gases
    elseif SI(i) == 2
        smutp(i) = smustar(i);  % Liquids
    elseif SI(i) == 3
        smutp(i) = smustar(i);  % Solids
    end
end

% Calculate the total enthalpy and total free energy

toth = 0.0;
totg = 0.0;
for i = 1:N
    toth = toth + H(i);  % Total enthalpy of reaction system
    totg = totg + smutp(i);  % Total Gibbs free energy of system
end

Ind = 0;
% Continue iteration until a new value is given to Ind.
while Ind == 0
% (7) Calculate the chemical potential of species i at T and p.

itm = mod(it,30);
imm = mod(m,30);
[a1,b1,ra1,ra2] = abzuc(SI,SEM,EA,CEA,EA0,smutp,T,p,y,imm);
x1 = a1\b1;
% (7.1) Calculate new species mole numbers.

bir = zeros(N,1);
f = zeros(N,1);
dy = zeros(N,1);
% Calculate dy(i)

for i = 1:N
    for j = 1:M
        bir(i) = bir(i) + SEM(i,j) * x1(j);
    end
% Do not alter anything in this line.
Appendix J  Matlab code for thermodynamic equilibrium calculation

if SI(i) == 1
    f(i) = bir(i) + x1(N2) - smutp(i)*1000/(R*T);
end

if M == 3
    f(21) = x1(N2+1); % C(s)
elseif M == 4
    f(33) = x1(N2+1); % C(s)
elseif M == 5
    f(43) = x1(N2+1); % C(s)
    f(44) = x1(N2+2); % S(s)
elseif M == 6
    f(46) = x1(N2+1); % C(s)
    f(47) = x1(N2+2); % S(s)
end

% Add other single-species phases HERE in future versions.

end

for i = 1:N
    dy(i) = f(i)*y(i); % Increase in each species moles
end

[ynew] = forcer(dy,y); % Call the convergence forcer
y = ynew;
maxdy = max(abs(dy));

% (7.2) Update system data, prepare for next temperature iteration.

[cy,ys,xg,ys,xs,EA,CEA] = calc(SI,SEM,y,EA0);
[dq,totdh,totdgh,toth,totph,totgh,totsh] = heatcoal(T,alfa,Dath,Dat2,Dat3,NF,H,y,Uwat,Ca,dissip,Hfeed,hff,tstm);
dqt(it) = dq;
totdht(it) = totdh;
totht(it) = toth;
totph(it) = totph;
totgh(it) = totgh;
totsh(it) = totsh;
Ttoth(it) = toth;

% disp({' Net heat output to maintain current T = ' num2str(dq) ' kJ/hr ' })

for i = 1:N
    if SI(i) == 1
        smutp(i) = smustar(i) + R*T*log(xg(i)+1e-200)/1000.0;
    elseif SI(i) == 3
        smutp(i) = smustar(i);
    end
end

% (7.3) Calculate the species split of each element

for i = 1:N
    Cy(it,i) = cy(i,1);
    Hy(it,i) = cy(i,2);
    Oy(it,i) = cy(i,3);
    if M > 4
        Ny(it,i) = cy(i,4);
    end
end
Appendix J
Matlab code for thermodynamic equilibrium calculation

% (7.4) Set condition for termination of iteration

if m > NIT
    Ind = 2;
elseif max(abs(dy)) <= err % Never write it as: abs(max(dy)) !!
    Ind = 1;
else
    Ind = 0;
end

m = m + 1;

end % Terminate temperature iteration (while end)

% Record the Ind value

if itm == 1
    if Ind == 1
        disp('  ')
        disp([' Convergence is attained at the ' num2str(m) '-th iteration.'])
        disp('  ')
    elseif Ind == 2
        disp([' Convergence not attained after ' num2str(NIT) ' iteration.'])
    end
end

Ind = 0; % Reset Ind. Very important sentence.
m = 1; % Reset m.

for i = 1:N
    yt(it,i) = y(i);
    xt(it,i) = x(i);
    xtg(it,i) = xg(i);
    dqt(it) = dq;
end

for i = 1:N
    xtdry(it,i) = xtg(it,i) / (1 - xtg(it,17)); % Species content in dry gas
    summit(it) = summit(it) + yt(it,i);
end

% (7.5) Calculate equilibrium composition to be reported

if M == 5 % This function designed for sawdust
    for i = 1:N
        % Overall molar composition
        xt(it,i) = yt(it,i) / summit(it);
        % Wet gas composition, excluding C(s) and S(s)
        xtg(it,i) = yt(it,i) / (summit(it) - yt(it,43) - yt(it,44));
        % Dry gas composition, excluding water, C(s) and S(s)
        xtdry(it,i) = yt(it,i) / (summit(it) - yt(it,17) - yt(it,43) - yt(it,44));
        % N2 free dry gas composition, excluding Nitrogen, water, C(s) and S(s)
        xtdryNN(it,i) = yt(it,i) / (summit(it) - yt(it,17) - yt(it,22) - yt(it,43) - yt(it,44));
    end
    xtg(it,43) = 0;
    xtg(it,44) = 0;
    xtdry(it,17) = 0;
Appendix J  Matlab code for thermodynamic equilibrium calculation

```matlab
% Preparing output report

if M == 3
    Cconv = 100.0 * (1 - yt(:,21)/UC);  % Carbon conversion
    vgdry = (summit - yt(:,17) - yt(:,9) - yt(:,N)) * 8.31448 * 298.15 / 100000;
    vgwet = (summit - yt(:,N)) * 8.31448 * 298.15 / 100000;
    E1 = 100 * (vgdry(:) * hhv dry(:) * 1000 + (dqt(:) <= 0) .* dqt(:))/(HHV * rfuel);
    E1 = Gasif. Eff. E1 (%) excluding condensables
    E2 = 100 * (vgwet(:) * hhv gas(:) * 1000 + (dqt(:) <= 0) .* dqt(:))/(HHV * rfuel);
    E2 = Gasif. Eff. E1 (%) including condensables
elseif M == 4
    Cconv = 100.0 * (1 - yt(:,33)/UC);
    vgdry = (summit - yt(:,17) - yt(:,9) - yt(:,N)) * 8.31448 * 298.15 / (1.01325*100000);
    vgwet = (summit - yt(:,N)) * 8.31448 * 298.15 / (1.01325*100000);
```

end
```
Appendix J  Matlab code for thermodynamic equilibrium calculation

E1 = 100 * (vgdry(:).*hhvdry(:)*1000 + (dqt(:) <= 0).*dqt(:))/(HHV*rfuel);
E2 = 100 * (vgwet(:).*hhvgas(:)*1000 + (dqt(:) <= 0).*dqt(:))/(HHV*rfuel);

elseif M == 5
Cconv = 100.0 * (1 - y(:,43)/UC);
vgdry = (sumit - y(:,17) - y(:,9) - y(:,43)) * 8.31448 * 298.15 / (1.01325*100000);
vgwet = (sumit - y(:,43)) * 8.31448 * 298.15 / (1.01325*100000);
E1 = 100 * (vgdry(:).*hhvdry(:)*1000 + (dqt(:) <= 0).*dqt(:))/(HHV*rfuel);
E2 = 100 * (vgwet(:).*hhvgas(:)*1000 + (dqt(:) <= 0).*dqt(:))/(HHV*rfuel);
wt = zeros(Nt,N);
vgeach = zeros(Nt,N);
for i=1:N
  wt(:,i) = Dat2(i,10)*y(:,i)/1000;
  vgeach(:,i) = y(:,i) * 8.31448 * 298.15 / 100000;
end

% (8.1) Major species statistics
if M == 3
  format long e
  report = 100*[TT(:)/100, xtdry(:,11), xtdry(:,14), xtdry(:,5), xtdry(:,15), xtdry(:,16) + xtdry(:,8) + xtdry(:,9), xtdry(:,21), xtdry(:,17)];
  disp('T, C(s), CH4, CO, CO2, H2, H2O')
  report = 100*[TT(:)/100, xt(:,21), xt(:,5), xt(:,14), xt(:,15), xt(:,11), xt(:,17)];
  report
elseif M == 4
  ytc = [y(:,5), y(:,7), y(:,14:15), y(:,11), y(:,17), y(:,23), y(:,22), y(:,26), y(:,33)];
  % CH4, C2H4, CO, CO2, H2, H2O, HCN, N2, NH3, C(s)
  if NREP == 1
    report(:,1) = TT(:);
    report(:,(1+iz)) = 100 * xt(:,33);
  elseif NREP == 2
    report = 100 * [TT(:)/100, xtdry(:,14:15), xtdry(:,11), xtdry(:,5), ytc(:,17)*2/(100*UH)];
  end
else M == 5
  if NREP == 1
    report = 100*[TT(:)/100, xt(:,43)];
  elseif NREP == 2
    report1 = 100 * [TT(:)/100, xtdry(:,14:15), xtdry(:,11), xtdry(:,5)];
  elseif NREP == 3
    % (8.2) Fate of elements - Elemental split
    spc(:,1) = y(:,43)*1/EA0(1);  % C(s)
    spc(:,2) = spc(:,1) + y(:,5) /EA0(1);  % CH4
    spc(:,3) = spc(:,2) + y(:,14)*1/EA0(1);  % CO
    spc(:,4) = spc(:,3) + y(:,15)*1/EA0(1);  % CO2
    spc(:,5) = spc(:,4) + y(:,30)*1/EA0(1);  % HCN
    sph(:,1) = y(:,5)*4/EA0(2);  % CH4
    sph(:,2) = sph(:,1) + y(:,7)*4/EA0(2);  % C2H4
    sph(:,3) = sph(:,2) + y(:,11)*2/EA0(2);  % H2
    sph(:,4) = sph(:,3) + y(:,17)*2/EA0(2);  % H2O
    sph(:,4) = sph(:,4) + y(:,31)*1/EA0(2);  % H
    sph(:,4) = sph(:,4) + y(:,31)*1/EA0(2);  % HCN
    sph(:,4) = sph(:,4) + y(:,26)*3/EA0(2);  % NH3

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Appendix J  Matlab code for thermodynamic equilibrium calculation

```matlab
spo(:,1) = + yt(:,14)*1/EA0(3);  % CO
spo(:,2) = spo(:,1) + yt(:,15)*2/EA0(3);  % CO2
spo(:,3) = spo(:,2) + yt(:,17)*1/EA0(3);  % H2O
spo(:,4) = spo(:,3) + yt(:,13)*2/EA0(3);  % O2

spn(:,1) = (yt(:,30) + yt(:,31))*1/EA0(4);  % HCN
spn(:,2) = spn(:,1) + yt(:,22)*2/EA0(4);  % N2
spn(:,3) = spn(:,2) + yt(:,26)*1/EA0(4);  % NH3
sps(:,1) = (yt(:,36) + yt(:,37))*1/EA0(5);  % SO2 + SO3
sps(:,2) = sps(:,1) + yt(:,38)*1/EA0(5);  % COS
sps(:,3) = sps(:,2) + yt(:,41)*1/EA0(5);  % HS
sps(:,4) = sps(:,3) + yt(:,42)*1/EA0(5);  % H2S

% Molar fraction of hydrogen that stays in H2O in the product.
gama(:) = 100*yt(:,17)*2/UH;

%-----------------------------------------
report0a = [TT(:) - 273, TT(:), E1(:), hhvdry(:,1).*vgdry(:,1).*1000, Hcondenserw(:), Hauserheat(:)];
report0b = [TT(:) - 273, TT(:), E1(:), hhvdry(:,1).*vgdry(:,1).*1000.*feedrate/1000/60, Hcondenserw(:)*feedrate/1000/60, Hauserheat(:)*feedrate/1000/60, dqt(:)*feedrate/1000/60];

% Major speceis
report1 = [TT(:) - 273, TT(:), xtdry(:,11), xtdry(:,14), xtdry(:,15), xtdry(:,5), xtdry(:,6) + xtdry(:,7) + xtdry(:,8) + xtdry(:,9), xtdry(:,22), xtdry(:,38), xtdry(:,35), xtdry(:,36), xtdry(:,37), xtdry(:,27), xtdry(:,28), xtdry(:,29), xtdry(:,31), xtdry(:,35)*xtdry(:,36)*xtdry(:,37), xtdry(:,27)*xtdry(:,28)*xtdry(:,29)];
report2 = [TT(:) - 273, TT(:,11), xtg(:,11), xtg(:,14), xtg(:,15), xtg(:,5), xtg(:,6) + xtg(:,7) + xtg(:,8) + xtg(:,9), xtg(:,22), xtg(:,42), xtg(:,17), xtg(:,43), xtg(:,38), xtg(:,35), xtg(:,36), xtg(:,37), xtg(:,27), xtg(:,28), xtg(:,29), xtg(:,31), xtg(:,35)*xtg(:,36)*xtg(:,37), xtg(:,27)*xtg(:,28)*xtg(:,29)];
report3 = [TT(:) - 273, TT(:,11), xt(:,11), xt(:,14), xt(:,15), xt(:,5), xt(:,6) + xt(:,7) + xt(:,8) + xt(:,9), xt(:,22), xt(:,42), xt(:,17), xt(:,43), xt(:,38), xt(:,35), xt(:,36), xt(:,37), xt(:,27), xt(:,28), xt(:,29), xt(:,31), xt(:,35)*xt(:,36)*xt(:,37), xt(:,27)*xt(:,28)*xt(:,29)];
report4 = [TT(:) - 273, TT(:,11), xtdryNN(:,11), xtdryNN(:,14), xtdryNN(:,15), xtdryNN(:,5), xtdryNN(:,6) + xtdryNN(:,7) + xtdryNN(:,8) + xtdryNN(:,9), xtdryNN(:,22), xtdryNN(:,38), xtdryNN(:,35), xtdryNN(:,36), xtdryNN(:,37), xtdryNN(:,27), xtdryNN(:,28), xtdryNN(:,29), xtdryNN(:,31), xtdryNN(:,35)*xtdryNN(:,36)*xtdryNN(:,37), xtdryNN(:,27)*xtdryNN(:,28)*xtdryNN(:,29)];
report5 = [TT(:,273), TT(:,11), yt(:,11), yt(:,14), yt(:,15), yt(:,5), yt(:,6) + yt(:,7) + yt(:,8) + yt(:,9), yt(:,22), yt(:,42), yt(:,17), yt(:,43), yt(:,38), yt(:,35), yt(:,36), yt(:,37), yt(:,27), yt(:,28), yt(:,29), yt(:,31), yt(:,35)*yt(:,36)*yt(:,37), yt(:,27)*yt(:,28)*yt(:,29)];
report6 = [TT(:,273), TT(:,11), wt(:,11), wt(:,14), wt(:,15), wt(:,5), wt(:,6) + wt(:,7) + wt(:,8) + wt(:,9), wt(:,22), wt(:,42), wt(:,17), wt(:,43), wt(:,38), wt(:,35), wt(:,36), wt(:,37), wt(:,27), wt(:,28), wt(:,29), wt(:,31), wt(:,35)*wt(:,36)*wt(:,37), wt(:,27)*wt(:,28)*wt(:,29)];
report8 = [TT(:,273), TT(:,11), xtdryNN(:,11)];
report9 = [TT(:,273), TT(:,11), xtg(:,11)];
report10 = [TT(:,273), TT(:,11)];
report11 = [TT(:,273), TT(:,11), xtdryNN(:,11)];
report12 = [TT(:,273), TT(:,11)];
```

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Appendix J  Matlab code for thermodynamic equilibrium calculation

report13 = [TT(:,2)-273, TT(:,1), wt(:,1:1)];
report14 = [TT(:,2)-273, TT(:,1), vgeach(:,1:1)];

% Conversion and efficiency
report15 = [xtdry(:,26), xtdry(:,40), Cconv(:,1), gama(:,1), hhvdry(:,1), vgdry(:,1),
100000*hhvdry(:,1).*vgdry(:,1)/HHV, dqt(:,1)];

% Minor species
report16 = 100000*[ xtdry(:,5:9), xtdry(:,26:31), xtdry(:,36:38), xtdry(:,42:42)];

% (ppm) CH4-C3H8 NH3-HCN SO2,SO3 COS H2S
% The smallest species is not reported, but calculated by difference.
report17 = [TT(:,1:1), spc(:,1:4), sph(:,1:3), spo(:,1:3), spn(:,1:2), sps(:,1:3)];

% C split H split O split N split S split

current_alfa = alfa;

EA0' Uwat

report1 report2
report3
report4
%File output format

datenow=datenow(datevec(now),21);
fileid1='F';
fileid2=num2str(NF,'%03.0f'); %Fuel type
fileid3='F';
fileid4=num2str(p*10,'%03.0f'); %Pressure [Bar*10]
fileid5='S';
fileid6=num2str(rH2O,'%03.0f'); %S/C [mol%]
fileid7='C';
fileid8=num2str(Charcont*100,'%03.0f'); %Char ratio [wt% (100*kg/kg-biooil-wet)]
fileid9='O';
fileid10=num2str(alpha*100,'%03.0f'); %Oxygen ratio [stoi. ratio mol%]
fileid11='NP';
fileid12=num2str(N2purge*10,'%03.0f'); %N2 purge rate [Nm3/min]
fileid13='FR';
fileid14=num2str(feedrate*10,'%03.0f'); %Fuel feeding rate [g/min]

filename=strcat(fileid,expansion);

fid = fopen(uiputfile(filename),'w');
fprintf(fid,'%s
',datenow);
fprintf(fid,'Condition_ID: %s
',fileid);
fprintf(fid,'Fuel_type: %1.0f
',NF);
fprintf(fid,'Fuel_feed_rate: %15.9f kg/hr
',rfuel);
fprintf(fid,'Pressure: %7.3f bar
', p);
fprintf(fid,'H2O/C: %7.3f mol/mol
', rH2O);
fprintf(fid,'Water-add/fuel: %7.3f kg/kg
', 18.015/12.011*Dat3(5,NF)/100*(1-
18.015/12.011*Dat3(14,NF)/100));
fprintf(fid,'Water-addition(steam): %7.3f kg/kg-fuel
', Uwatadd*18.015/1000);
fprintf(fid,'Actual_water_addition: %7.3f g/min
', Uwatadd*18.015*feedrate/1000);
fprintf(fid,'Char_ratio: %7.3f kg/kg
', Charcont);
fprintf(fid,'Oxygen_ratio: %7.3f mol/mol stoic.-ratio
', alpha);
Appendix J  Matlab code for thermodynamic equilibrium calculation

```matlab
fprintf(fid,'%6.0f %6.0f %15.9f %15.9f %15.9f %15.9f %15.9f %15.9f %15.9f %15.9f %15.9f %15.9f %15.9f %15.9f %15.9f %15.9f %15.9f %15.9f %15.9f %15.9f
');
fprintf(fid,'Each_species_mol_fraction_in_dry-N2free-gas_((xtdryNNn)\n');
fprintf(fid,'T[C] T[K] H2 CO CO2 CH4
');
fprintf(fid,'N2 H2S H2O C(s) COS
');
fprintf(fid,'SO SOX N2O NO NO2
');
fprintf(fid,'NH3 SO2 SO3
');
fprintf(fid,'N2O NO NO2
');
fprintf(fid,'Each_gas_species_amount_in_mol/hr__((yt)\n');
fprintf(fid,'\n');
fprintf(fid,'Total_water_in_fuel %15.9f
');
fprintf(fid,'Water_added_to_bio-oil %15.9f
');
fprintf(fid,'\n');
fprintf(fid,'Each_gas_species_amount_in_kg/hr__((wt)\n');
fprintf(fid,'\n');
fprintf(fid,'Total_water_in_fuel %15.9f
');
fprintf(fid,'Water_added_to_bio-oil %15.9f
');
fprintf(fid,'\n');
fprintf(fid,'Each_gas_species_volume_in_Nm3/hr__((vgeach)\n');
fprintf(fid,'\n');
fprintf(fid,'\n');
fprintf(fid,'\n');
fprintf(fid,'\n');
fprintf(fid,'\n');
fprintf(fid,'\n');
```

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Appendix J  Matlab code for thermodynamic equilibrium calculation

fprintf(fid,'%6.0f %6.0f %15.9f %15.9f %15.9f %15.9f %15.9f %15.9f %15.9f %15.9f %15.9f %15.9f %15.9f %15.9f
',report9.');
fprintf(fid,'n');

fprintf(fid,'xtdryNN\n');
fprintf(fid,'Species number - 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44\n');
fprintf(fid,'\n');

fprintf(fid,'vgeteach\n');
fprintf(fid,'Species number - 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44\n');
fprintf(fid,'\n');

fclose(fid);
Appendix J  Matlab code for thermodynamic equilibrium calculation

end
end
%
---------------------------------------------
end  % End of outer-layer pressure/alpha/iz iteration
%
End of the FEM equilibrium model program.
Appendix J  
Matlab code for thermodynamic equilibrium calculation

J.2 Thermodynamic database

File name: coaldat.m

Function: Thermodynamic, chemical and fuel property database for the equilibrium model. The database is designed for a maximum of 8 elements, 77 species

function [Dat1, Dat11, Dat2, Dat3, Dath, Dath1] = coaldat(NE)
% COALDAT chooses species and generates data for FEM algorithm based on the number of elements.

disp(' ')
disp(' DATA FOR COAL AND BIOMASS COMBUSTION / GASIFICATION MODEL ')
disp(' ')
disp(' Version 1.0 Masakazu Sakaguchi modified Xiantial Li's code (Jan. 3, 2010) ')
disp(' ')

% (1) Thermodynamic data
% Dat1 - Thermodynamic data. Source: JANAF (1985). Unit: kJ/mol, P = 1 bar
% col 1 - species index
% col 2 - phase index (1 = gas, 2 = liquid, 3 = solid)
% col 3-7 - 5 correlation factors of DGfo(T)
% col 8 - cut-off temperature above which alternative correlations are used
% col 9 - species identification

% Form of correlations
% dGfo(T,i) = Dat1(i,3) + Dat1(i,4)*T*log(T) + Dat1(i,5)*T^2 + Dat1(i,6)/T + Dat1(i,7)*T;

dat1 =
% Gaseous species - the first ideal solution

% NP a b c d e T Species
1 1 718.7355 -0.0031881 1.9694E-06 -349.8554 -0.137650 3000 % C-g
2 1 598.0953 0.0043862 -1.9285E-07 -343.7758 -0.110660 3000 % CH
3 1 389.5788 0.0077494 -6.6767E-07 -349.8554 -0.137650 3000 % CH2
4 1 149.0231 0.014182 -2.9054E-06 41.6868 -0.084363 3000 % CH3
5 1 -71.8931 0.02432 -6.5597E-06 362.4270 -0.070448 3000 % CH4
6 1 237.5202 0.033256 1.0033E-06 -100.2833 -0.152990 3000 % CH2
7 1 54.1895 0.01689 -5.6205E-06 449.8686 -0.079724 3000 % CH2
8 1 54.1895 0.01689 -5.6205E-06 449.8686 -0.079724 3000 % CH2
9 1 350.4716 0.66056 -2.6670E-04 -46636.1389 -4.40930 1600 % CH4
10 1 215.7586 0.0037896 9.1095E-07 10.6162 -0.00162 3000 % H
11 1 0 0 0 0 0 3000 % H2
12 1 248.3877 0.0052751 8.6902E-07 -86.4689 -0.025042 3000 % O
13 1 0 0 0 0 0 3000 % O2
14 1 -106.8226 0.0033849 1.2143E-06 -326.6449 -0.117690 3000 % CO
15 1 -392.9600 0.0012695 3.3456E-07 -11.6092 -0.012005 3000 % CO2
16 1 40.3471 0.0020491 -1.2972E-07 -99.8727 -0.030869 3000 % CH
17 1 -239.0906 0.010852 -2.2307E-06 18.3029 0.026247 3000 % H2O
18 1 45.1098 0.030933 -1.6060E-05 -333.1775 -0.117240 3000 % H2O
19 1 45.1098 0.030933 -1.6060E-05 -333.1775 -0.117240 3000 % H2O
20 1 2.4359 0.0054918 -1.5372E-06 135.5294 0.007803 3000 % NO2

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### Appendix J: Matlab code for thermodynamic equilibrium calculation

<table>
<thead>
<tr>
<th>% Solids - single-species phases</th>
</tr>
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<tbody>
<tr>
<td>63</td>
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<tr>
<td>64</td>
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</table>

<table>
<thead>
<tr>
<th>% Liquid species - the second ideal solution</th>
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</tbody>
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<table>
<thead>
<tr>
<th>% Solids - single-species phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>63</td>
</tr>
<tr>
<td>64</td>
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</tbody>
</table>

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<thead>
<tr>
<th>% Solids - single-species phases</th>
</tr>
</thead>
<tbody>
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<td>73</td>
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<td>74</td>
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<td>75</td>
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</tbody>
</table>

Matlab code for thermodynamic equilibrium calculation
### Appendix J

**Matlab code for thermodynamic equilibrium calculation**

```matlab
76 3 -1412.6200 0.050125 -1.1297e-06 -312.6500 0.024180 2000 % CaSO4
77 3 -818.1100 -0.0857846 2.8497e-05 -178.0300 0.741505 1112 % CaCl2
```
Appendix J  Matlab code for thermodynamic equilibrium calculation

53 1 -135.1063 -0.0052293 -2.6241E-06 -380.4109 0.091046 3000 % CaS-g

% Liquid species - the second ideal solution

54 2 -102.0722 0.00027844 -3.8527E-06 31.9057 0.089756 1600 % Na-l
55 2 -603.1522 -0.0483350 9.7810E-07 641.5320 0.642100 3000 % Na2O-l
56 2 -532.4731 -0.0368850 3.8832E-06 307.9617 0.486990 2500 % NaOH-l
57 2 -1357.4400 -0.0777160 2.8704E-06 -126.2168 1.012900 2500 % Na2CO3
58 2 -615.2298 -0.0331660 7.0543E-07 -50.4397 0.521040 3000 % NaS-l
59 2 -1664.5100 -0.0717650 2.9858E-06 -181.8829 1.147800 3000 % Na2SO4
60 2 -505.1877 -0.0281640 3.1939E-07 -70.9886 0.368450 2500 % NaCl-l
61 2 -195.1217 -0.0377100 5.8557E-06 -256.3111 0.382540 2500 % Ca-l
62 2 -725.6541 -0.0173170 -5.6041E-07 -991.9894 0.318130 3000 % CoO-l

% Solids - single-species phases

63 3 0 0 0 0 0 3000 % C-s
64 3 0 0 0 0 0 3000 % S-s
65 3 -713.7362 -0.1176400 2.1687E-05 4547.5904 1.192000 2000 % Na2O-s
66 3 2469.6893 4.8916000 -1.8881E-03 125735.7140 -34.769600 1500 % NaOH-s
67 3 -1387.7580 -0.0645030 -9.0077E-06 -198.6146 0.960480 2000 % Na2CO3
68 3 -769.4582 -0.1608900 2.5916E-05 1662.5306 1.519800 2000 % Na2S-s
69 3 -1590.6950 0.0073529 -4.5470E-05 0 0.632690 1500 % Na2SO4
70 3 -2490.9921 4.9294000 -1.9042E-03 126100.0000 -35.077000 1500 % NaCl-s
71 3 0 0 0 0 0 3000 % Ca-s
72 3 -799.9182 -0.0168030 -3.0821E-07 -309.0810 0.337110 3000 % CaO-s
73 3 -996.2730 -0.0223540 4.4400E-06 596.7389 0.447650 1000 % Ca(OH)2
74 3 -1241.8400 -0.0710110 3.4234E-05 2447.3300 0.745000 1200 % CaCO3
75 3 -700.9383 -0.0146900 -4.0703E-07 -158.3563 0.313420 3000 % CaS-s
76 3 -1412.6200 0.0501250 -1.1297E-06 -312.6500 0.024180 2000 % CaSO4
77 3 -818.1100 -0.0857846 2.8497E-05 -178.0300 0.741505 1112 % CaCl2

% Dath - Heat of formation and correlation factors for enthalpy.
% Ref. pressure: 1 atm (1.013 bar) for 38 species given in Pankratz's books,
% 1 bar for all other species (JANAF data).
% Water occurs as H2O (g), otherwise wrong.
% col 1  - species index
% col 2  - phase index
% col 3-6 - correlation factors for enthalpy
% col 7  - heat of formation of the species (kJ/mol)
% col 8  - temperature range of application
% col 9  - species identification
% Ho(T)=Ho(Z)+aT/1000 + bT^2/1000000 + cT^-1 + d

dathah = [

% Gaseous species
% NP a b c d DHfo(298) T Species
1 1 20.7192 0.037656 -9.7864 -6.15048 716.670 2000 % C-g
2 1 27.6313 2.7448 41.0016 -8.8832 594.128 3000 % CH
3 1 38.6452 3.7555 408.7690 -14.0607 386.392 3000 % CH2
4 1 47.3888 6.2452 784.6346 -18.7179 145.687 3000 % CH3
5 1 52.9240 9.9567 1405.2934 -24.1768 -74.873 3000 % CH4
6 1 57.6040 5.8194 1046.3957 -22.4273 226.731 3000 % C2H2
7 1 73.3320 10.869 2132.0253 -33.4348 52.467 3000 % C2H4

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### Appendix J

**Matlab code for thermodynamic equilibrium calculation**

- **Solids** - the second ideal solution
- **Liquid species** - single-species phases

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Liquid</th>
<th>Solid</th>
<th>% NaOH</th>
<th>% Na2O</th>
<th>% NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Na2O</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>NaOH</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

% Liquid species - the second ideal solution

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Liquid</th>
<th>Solid</th>
<th>% NaOH</th>
<th>% Na2O</th>
<th>% NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Na2O</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>NaOH</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

% Solids - single-species phases
### Appendix J  
Matlab code for thermodynamic equilibrium calculation

```matlab
% Gaseous species

datah1 = [
3  14.7193 3.204944 720.9032 -7.09188 0 2000 % C-s
4  31.8890 -2.1803 -1884.7120 -3.0467 0 882 % S-s
5  55.9694 20.572728 -78.2408 -18.25479 -417.982 1300 % Na2O-a
6  108.4800 -8.7382 1892.2624 -38.4824 -425.931 1500 % NaOH-s
7  126.2500 28.23 1673.3871 -46.939 -1130.770 2000 % Na2CO3
8  74.8308 9.9286 -182.4224 -22.5810 -336.100 1100 % Na2S-a
9  87.4047 58.426 -4393.8200 -16.7088 -1379.290 1500 % Na2SO4
10 42.0032 11.196384 -161.9208 -12.97458 -411.120 1074 % NaCl-s
11 30.8253 6.845 530.9676 -12.8472 0 1773 % Ca-s
12 48.9970 2.514 547.2851 -16.8339 -365.089 2100 % CaO-s
13 91.6459 14.7372 91.6648 -31.6522 -986.085 1000 % Ca(OH)2
14 97.9350 14.198 1855.4379 -36.8346 -1207.600 1200 % CaCO3
15 49.9402 2.117104 334.3016 -16.20045 -473.210 2000 % CaS-s
16 32.8630 61.278 -6316.0380 4.5425 -1434.110 2000 % CaSO4
17 69.8393 7.949376 159.4104 -22.04131 -795.400 1045 % CaCl2
];
```

% Simulation

datah1 = [
3  14.7193 3.204944 720.9032 -7.09188 0 2000 % C-s
4  31.8890 -2.1803 -1884.7120 -3.0467 0 882 % S-s
5  55.9694 20.572728 -78.2408 -18.25479 -417.982 1300 % Na2O-a
6  108.4800 -8.7382 1892.2624 -38.4824 -425.931 1500 % NaOH-s
7  126.2500 28.23 1673.3871 -46.939 -1130.770 2000 % Na2CO3
8  74.8308 9.9286 -182.4224 -22.5810 -336.100 1100 % Na2S-a
9  87.4047 58.426 -4393.8200 -16.7088 -1379.290 1500 % Na2SO4
10 42.0032 11.196384 -161.9208 -12.97458 -411.120 1074 % NaCl-s
11 30.8253 6.845 530.9676 -12.8472 0 1773 % Ca-s
12 48.9970 2.514 547.2851 -16.8339 -365.089 2100 % CaO-s
13 91.6459 14.7372 91.6648 -31.6522 -986.085 1000 % Ca(OH)2
14 97.9350 14.198 1855.4379 -36.8346 -1207.600 1200 % CaCO3
15 49.9402 2.117104 334.3016 -16.20045 -473.210 2000 % CaS-s
16 32.8630 61.278 -6316.0380 4.5425 -1434.110 2000 % CaSO4
17 69.8393 7.949376 159.4104 -22.04131 -795.400 1045 % CaCl2
];
```
### Appendix J

#### Matlab code for thermodynamic equilibrium calculation

```matlab
39 1 33.4302 0.995792 375.7232 -11.31772 280.328 3000 % CS
40 1 56.3815 1.5756 714.1594 -20.0176 116.943 3000 % CS2
41 1 28.6646 1.916272 -234.7224 -7.92868 139.327 2500 % HS
42 1 31.5515 6.71532 121.3360 -10.40979 -20.502 2000 % H2S
43 1 23.0915 -0.326352 1771.9240 -8.25503 121.302 3000 % Cl
44 1 36.9322 0.368192 285.7672 -12.0039 0 3000 % Cl2
45 1 34.2460 0.598312 4134.6288 -17.99358 -92.312 3000 % HCl
46 1 20.7652 0.016736 -1.2552 -6.18814 107.300 3000 % Na-g
47 1 51.9505 1.6391 346.7762 -16.9438 -197.757 3000 % NaOH-g
48 1 14.4120 2.915 2366.9623 -53.1502 -1033.620 3000 % Na2SO4
49 1 37.2358 0.3858 118.9968 -11.5661 -181.418 3000 % NaCl-g
50 1 19.8067 0.3758 -571.4430 -5.6241 177.800 3000 % Ca-g
51 1 23.0042 6.5738 -410.8451 -5.0186 43.932 3000 % CaO-g
52 1 85.9217 3.571 991.8630 -29.7821 -610.764 3000 %Ca(OH)2
53 1 24.3673 7.2837 -331.7881 -6.0861 123.595 3000 % CaS-g

% Liquid species - the second ideal solution

54 2 29.3047 -0.38493 -380.3256 -5.03754 0 1171 % Na-l
55 2 104.6000 0 0 -31.186 -372.843 3000 % Na2O-l
56 2 88.5501 -2.5713 -180.4221 -25.6167 -416.878 2500 % NaOH-l
57 2 209.0100 -4.1645 12222.2540 -102.5933 -1108.520 2500 % Na2CO3
58 2 92.0480 0 0 -11.7989 -323.940 2000 % Na2S-l
59 2 21.1740 -3.3885 8801.9448 90.8069 -356.390 3000 % Na2SO4
60 2 68.4502 0 0 0 -3.30354 -385.923 1800 % NaCl-l
61 2 35.0000 0 0 0 -2.648 0 2500 % Ca-l
62 2 62.7600 0 0 0 -28.193 -557.335 3000 % CaO-l

% Solids - single-species phases

63 3 23.6019 0.560656 3012.4800 -15.42641 0 3000 % C-s
64 3 31.8890 -2.1803 -1884.7120 -3.0467 0 882 % S-s
65 3 55.9694 20.5728 -78.2408 0 0 1800 % Ca2O-s
66 3 108.4800 -8.7382 1892.2624 -38.4824 0 2500 % NaOH-s
67 3 126.2500 28.23 1673.3871 -46.939 0 2000 % Na2CO3
68 3 -582.2747 310.5239 0 336.3476 -336.100 1276 % Na2S-s
69 3 87.4047 58.426 -4393.8200 -16.7088 -1379.290 1500 % Na2SO4
70 3 68.4502 0 0 0 0 1800 % NaCl-s
71 3 5.2567 3.407 -2705.4100 212.0632 0 3000 % Ca-s
72 3 51.2990 1.9775 1301.6968 -13.8306 -635.089 3000 % CaO-s
73 3 91.6459 14.7372 941.6648 -31.6522 -986.085 1000 % Ca(OH)2
74 3 97.9350 14.198 1855.4379 -36.8346 -1207.600 1200 % CaCO3
75 3 49.9402 2.117104 334.3016 -16.20045 -473.210 2000 % CaS-s
76 3 32.8630 61.278 -6316.0380 4.5425 -1434.110 2000 % CaSO4
77 3 122.2690 -7.451704 -70.2912 -31.91137 -795.400 1600 % CaCl2
```

% (2) Species-element matrix (SEM)
%
% Data2 - Basic chemical data
% col 1 = species index
% col 2-9 = species-element matrix
% col 10 = molecular weight of a species

data2 = [

% Group 1 - gases
% C H O N S Cl Na Ca M. wt Species
```
Appendix J  
Matlab code for thermodynamic equilibrium calculation

```
1 1 0 0 0 0 0 0 0 12.011 % C-g
2 1 1 0 0 0 0 0 0 13.0189 % CH
3 1 2 0 0 0 0 0 0 14.0269 % CH2
4 1 3 0 0 0 0 0 0 15.0348 % CH3
5 1 4 0 0 0 0 0 0 16.0428 % CH4
6 2 2 0 0 0 0 0 0 26.0379 % C2H2
7 2 4 0 0 0 0 0 0 28.0538 % C2H4
8 2 6 0 0 0 0 0 0 30.0696 % C2H6
9 3 8 0 0 0 0 0 0 44.6565 % C3H8
10 1 1 0 0 0 0 0 0 1.00794 % H
11 2 0 0 0 0 0 0 0 2.01588 % H2
12 0 1 0 0 0 0 0 0 15.9994 % O
13 0 2 0 0 0 0 0 0 31.9988 % O2
14 1 0 1 0 0 0 0 0 28.0104 % CO
15 1 0 2 0 0 0 0 0 44.0098 % CO2
16 0 1 1 0 0 0 0 0 17.0073 % OH
17 0 2 1 0 0 0 0 0 18.0153 % H2O
18 0 2 2 0 0 0 0 0 34.0147 % H2O2
19 1 1 1 0 0 0 0 0 29.0183 % HCO
20 0 1 2 0 0 0 0 0 33.0067 % HO2
21 0 0 1 0 0 0 0 0 14.0067 % N
22 0 0 2 0 0 0 0 0 39.0116 % N2
23 0 1 0 1 0 0 0 0 53.9964 % N2O
24 0 1 1 0 0 0 0 0 78.0191 % N2O2
25 2 0 1 0 0 0 0 0 60.0763 % NO
26 1 3 0 1 0 0 0 0 84.0817 % NO2
27 0 1 1 0 0 0 0 0 42.0171 % NO3
28 0 1 1 1 0 0 0 0 36.0386 % NO2
29 0 2 1 0 0 0 0 0 35.0378 % N2O3
30 1 0 1 0 0 0 0 0 60.0763 % N2O4
31 1 1 0 1 0 0 0 0 70.0005 % N2O5
32 1 1 1 1 0 0 0 0 43.0251 % HN
33 0 0 0 0 1 0 0 0 32.066 % S-g
34 0 0 0 0 2 0 0 0 64.132 % S2-g
35 0 0 1 0 1 0 0 0 48.0654 % SO
36 0 0 2 0 1 0 0 0 64.0648 % SO2
37 0 0 3 0 1 0 0 0 80.0642 % SO3
38 0 1 0 1 0 0 0 0 60.0763 % COS
39 0 1 0 0 1 0 0 0 44.077 % CS
40 1 0 0 2 1 0 0 0 76.143 % CS2
41 0 1 0 0 0 1 0 0 33.0739 % HC
42 0 2 0 1 0 0 0 0 34.0819 % H2C
43 0 0 0 0 0 1 0 0 35.4527 % Cl
44 0 0 0 0 2 0 0 0 70.9054 % Cl2
45 0 1 0 0 0 1 0 0 36.4606 % HCl
46 0 0 0 0 0 1 0 0 22.9898 % Na-g
47 0 1 1 0 0 0 1 0 39.9971 % NaOH-g
48 0 0 4 0 1 0 2 0 142.043 % Na2SO4-g
49 0 0 0 0 1 1 0 0 58.4452 % NaCl-g
50 0 0 0 0 0 0 0 1 40.078 % Ca-g
51 0 0 1 0 0 0 0 0 56.0774 % CaO-g
52 0 2 2 0 0 0 0 1 74.0927 % Ca(OH)2-g
53 0 0 0 0 0 1 0 0 72.144 % CaS-g

% Group 2 - liquids

54 0 0 0 0 0 0 1 0 22.9898 % Na-l
55 0 0 1 0 0 0 2 0 61.9789 % Na2O-l
56 0 1 1 0 0 0 1 0 39.9971 % NaOH-l
57 1 0 3 0 0 0 2 0 105.989 % Na2CO3-l
58 0 0 0 0 1 0 2 0 78.0455 % Na2S-l
```
Matlab code for thermodynamic equilibrium calculation

59 0 0 4 0 1 0 2 0 142.043 % NaSO4-l
60 0 0 0 0 0 1 1 0 58.4425 % NaCl-l
61 0 0 0 0 0 0 0 0 1 40.078 % Ca-l
62 0 1 0 0 0 0 0 0 1 56.0774 % CaO-l

% Group 3 - solids
63 1 0 0 0 0 0 0 0 12.011 % C-s
64 0 0 0 0 1 0 0 0 32.066 % S-s
65 0 0 1 0 0 0 2 0 61.9789 % Na2O-s
66 0 1 1 0 0 0 1 0 39.971 % NaOH-s
67 1 0 3 0 0 0 2 0 105.989 % Na2CO3
68 0 0 0 0 1 0 2 0 78.0455 % Na2S-s
69 0 0 4 0 1 0 2 0 142.043 % NaSO4-s
70 0 0 0 0 0 1 1 0 58.4425 % NaCl-s
71 0 0 0 0 0 0 0 1 40.078 % Ca-s
72 0 0 1 0 0 0 0 1 56.0774 % CaO-s
73 0 2 2 0 0 0 0 0 1 74.0927 % Ca(OH)2-s
74 1 0 3 0 0 0 0 1 100.087 % CaCO3-s
75 0 0 0 0 1 0 0 1 72.144 % CaS-s
76 0 0 4 0 1 0 0 1 136.142 % CaSO4-s
77 0 0 0 0 2 0 1 110.983 % CaCl2-s

];

% (3) Fuel analyses
% -----------------------------------------
% Data3 - Fuel data
data3 = [
% Sawdust species
% Proximate analysis (as received basis, wt %) - 10 species maximum.
% 1 2 3 4 5 6 7 8 9
% Highv Cypr SPF Heml SPF Ced/H PBS Mix-1 Mix-2
0 27.1 0 0 0 0 0 0 0 0 % Volatile matter
0 67.1 0 0 0 0 0 0 0 0 % Fixed carbon
0 5.8 0 0 0 0 0 0 0 0 % Ash
0 2.3 0 0 0 0 0 0 0 0 % Moisture

% Ultimate analysis (dry base, wt % - (Bio-oil is also on the dry basis))
% Bio-oil on the wet basis: C 42.47; H 6.89; O 50.04; N 0.3; S 0.3
% 1 2 3 4 5 6 7 8 9
% Biooil(WL) Char(WL) ModC ModC1 ModC2
56.7933 78.442 99.96 99.96 0.0 0.0 0.0 0.0 0.0 % C
5.88115 3.5284 0.01 0.01 0.0 0.0 0.0 0.0 0.0 % H
36.523 17.396 0.01 0.01 0.0 0.0 0.0 0.0 0.0 % O
0.40118 0.32644 0.01 0.01 0.0 0.0 0.0 0.0 0.0 % N
0.40118 0.32644 0.01 0.01 0.0 0.0 0.0 0.0 0.0 % S
0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 % Cl
0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 % Na
0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 % Ca
0.0 5.8 0.0 0.0 0.0 0.0 0.0 0.0 0.0 % Moisture
25.22 2.3 0.0 50.0 0.0 0.0 0.0 0.0 0.0 % HHV (MJ/kg)

];
% Select species to be considered in the sub-set with NE elements

Dat1 = []; % Initialization
Dat11 = [];
Dat2 = [];
Dat3 = [];
Datn = [];
Dat1n = [];

if NE == 1 % C
    Dat1 = [ data1(1,:); data1(63,:)];
    Dat11 = [data11(1,:); data11(63,:)];
    Dat2 = [ data2(1,:); data2(63,:)];
    Datn = [ datah(1,:); datah(63,:)];
    Dat1n = [data1n(1,:); data1n(63,:)];
elseif NE == 2 % C-H
    Dat1 = [ data(1:11,:); data(63,:)];
    Dat11 = [data11(1:11,:); data11(63,:)];
    Dat2 = [ data2(1:11,:); data2(63,:)];
    Datn = [ datah(1:11,:); datah(63,:)];
    Dat1n = [data1n(1:11,:); data1n(63,:)];
elseif NE == 3 % C-H-O
    Dat1 = [ data(1:20,:); data(63,:)];
    Dat11 = [data11(1:20,:); data11(63,:)];
    Dat2 = [ data2(1:20,:); data2(63,:)];
    Datn = [ datah(1:20,:); datah(63,:)];
    Dat1n = [data1n(1:20,:); data1n(63,:)];
elseif NE == 4 % C-H-O-N
    Dat1 = [ data(1:32,:); data(63,:)];
    Dat11 = [data11(1:32,:); data11(63,:)];
    Dat2 = [ data2(1:32,:); data2(63,:)];
    Datn = [ datah(1:32,:); datah(63,:)];
    Dat1n = [data1n(1:32,:); data1n(63,:)];
elseif NE == 5 % C-H-O-N=S
    Dat1 = [ data(1:42,:); data(63:64,:)];
    Dat11 = [data11(1:42,:); data11(63:64,:)];
    Dat2 = [ data2(1:42,:); data2(63:64,:)];
    Datn = [ datah(1:42,:); datah(63:64,:)];
    Dat1n = [data1n(1:42,:); data1n(63:64,:)];
elseif NE == 6 % C-H-O-N=S-Cl
    Dat1 = [ data(1:45,:); data(63:64,:)];
    Dat11 = [data11(1:45,:); data11(63:64,:)];
    Dat2 = [ data2(1:45,:); data2(63:64,:)];
    Datn = [ datah(1:45,:); datah(63:64,:)];
    Dat1n = [data1n(1:45,:); data1n(63:64,:)];
elseif NE == 7 % C-H-O-N=S-Cl-Na
    Dat1 = [ data(1:49,:); data(54:60,:); data(63:70,:)];
    Dat11 = [data11(1:49,:); data11(54:60,:); data11(63:70,:)];
    Dat2 = [ data2(1:49,:); data2(54:60,:); data2(63:70,:)];
    Datn = [ datah(1:49,:); datah(54:60,:); datah(63:70,:)];
    Dat1n = [data1n(1:49,:); data1n(54:60,:); data1n(63:70,:)];
elseif NE == 8
    Dat1 = data1;
    Dat11 = data11;
    Dat2 = data2;
    Datn = datah;
    Dat1n = data1n;
end

Dat3 = data3;
disp(' Chemical, thermodynamic and fuel analysis data')
disp(' for coal and biomass combustion/gasification is successfully loaded.')
disp(' ')
Appendix J  
Matlab code for thermodynamic equilibrium calculation

J.3  Elemental abundance

File name: abundsd.m

Function: To calculate the abundance of each element present in the system

function [EA0,CEA,V0,Vair,mair,Uwat,Uwatadd,Hfeed,hfuel,hN2purge,HHV,hff,Conv,Tm0,tfuel,tnitro] = abundsd(NE,Dat3,rfuel,rH2O,NF,NO,NANA,NFIT,alfa,Ca,Charcont,tstm,N2purge,feedrate,TotalCyield,YChydroc,YHhydroc)

% ABUNDSD calculates element abundance from sawdust, oxidant, and steam data
% Last update: Jan 2, 2010 Version 1.0 Masakazu Sakaguchi modified Xiantial Li’s code (Jan. 3, 2010) % Hydrocarbon modified version 1.0
% The total abundance of an element is the sum of its abundances in main fuel, auxiliary fuel, air, steam, and sorbent % All calculations are based on 1kg of feedstock (dry basis).
% Make sure that all ultimate analyses of feedstocks are on dry basis
Moistoil=Dat3(14,NF)/100;
Moistchar=Dat3(14,NF+1)/100;
Car = (1-Charcont)*Dat3(5,NF)*(1-Moistoil)+ Charcont*(1-Moistchar)*Dat3(5,NF+1);
Har = (1-Charcont)*(Dat3(6,NF)*(1-Moistoil)) + Charcont*((1-Moistchar)*Dat3(6,NF+1));
Nar = (1-Charcont)*Dat3(8,NF)*(1-Moistoil)+ Charcont*(1-Moistchar)*Dat3(8,NF+1);
Sar = (1-Charcont)*Dat3(9,NF)*(1-Moistoil)+ Charcont*(1-Moistchar)*Dat3(9,NF+1);
Clar = (1-Charcont)*Dat3(10,NF)*(1-Moistoil)+ Charcont*(1-Moistchar)*Dat3(10,NF+1);
Naar = (1-Charcont)*Dat3(11,NF)*(1-Moistoil)+ Charcont*(1-Moistchar)*Dat3(11,NF+1);
Caar = (1-Charcont)*Dat3(12,NF)*(1-Moistoil)+ Charcont*(1-Moistchar)*Dat3(12,NF+1);
UCasor = 0;
% (1) Calculate moles of each element
Conv1 = 100;
Conv2 = 0; % Initialization
UCint = Car*rfuel*1000/(12.011*100);
if NFIT == 0
  Conv = 100;
else
  if NFIT == 1 % An experimental carbon conversion, (%)
    Conv1 = TotalCyield;
    Conv2 = YChydroc;
    Conv = Conv1 - Conv2;
  end
  UC = UCint*Conv/100; % Moles of C entering equilibrium
  UHInt = Har*rfuel*1000/(1.00794*100);
  UH0 = 2*UCint*rH2O; % Each mol H2O contains 2 mol H
  UHext = UH0;
if NFIT == 1 % The actual moles of H that enters the equilibrium system
  Conv3 = YHhydroc;
  DUHhydro = UHInt*Conv3/100; % Moles of carbon deducted as CH4
  UH = UH0 + UHInt - DUHhydro;
end

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else
    UH = UH0 + UHint;
end

Uwat = UCint*rH2O; %totmoist*1000/18.0153;
Uwatadd = Uwat - ((1-Charcont)*Moistoil+Charcont*Moistchar)*rfuel*1000/(18.0153);
% Uwat denotes external moisture added to the dry base, mol/kg_dryfuel
if Uwat <= 0.000001
    Uwat = 0.000001;
end

UOint = Oar*rfuel*1000/(15.9994*100);
% UOint does not include O from the ash-bound oxygen

if NE < 5
    Tm0 = Car/12.011+ (Har/1.00794)/4.0 - (Oar/15.9994)/2.0;
else
    Tm0 = Car/12.011+ (Har/1.00794)/4.0 - (Oar/15.9994)/2.0 + Sar/32.066;
end
% Tm0 is the total moles of O2 (not O) required to burn 100g of fuel

if NO == 1
    % Stoichiometric air @ 298K, 1.013 bar (Nm3/kg_dry sawdust):
    V0 = (Tm0/100*1000*8.314472*298.15/101325.027*100/20.9476;  
% Stoichiometric pure oxygen (Nm3/kg_dry fuel):
    V0 = (Tm0/100*1000*8.314472*298.15/101325.027*100/99.992;
else
    Vair = V0*rfuel*alfa;  % Nm3/hr @ 1atm, 298 K
% mair = (Tm0/0.209476) * 28.964 * 10 * rfuel * alfa;  % (gram/hr)
% mair includes the weight of minor species (Ar, Ne, etc.) in air.
% So mair can be calculated with another formula:
    mair = (Tm0*31.9988 + Tm0*(0.78084/0.209476)*28.0135 + Tm0*(0.000314/0.209476)*44.0098)*rfuel*10*alfa;  % (gram/hr)
if NO == 1
    UOair = 2 * Tm0 * alfa *(10* rfuel) * (1 + 0.000314/0.209476);  
% One mole of O2 contains 2 moles of O atoms
% One mole of air also contains 0.000314 mole of CO2
else
    UOair = 2 * Tm0 * (rfuel*1000/100)*alfa;  
% One mole of O2 contains 2 moles of O atoms
end

UNext = UNext/2.0;  % Oxygen that comes from total moisture
UOsor = 0.0;
Umoist = rfuel*1000/(15.9994*100)*((1-Charcont)*(Moistoil+Charcont*Moistchar)+(15.9994/18.0153));
UO = UOint + UOair + UNext + UOsor;  % + Umoist;
% UOint must be added because it has been subtracted from UOair.
% If the oxidant is air, modify the C abundance due to CO2 in air.
if NO == 1
    UC = UC + 0.000314*Tm0*(rfuel*1000/100)*alfa;
end

UNint = Nar*rfuel*1000/(14.0067*100);  % mol/hr
UNext = 2*(N2purge*60/1000)*101300/(8.314472*298.15)*rfuel*1000/(feedrate*60));  % mol/hr
if NO == 1
    UNAir = (78.084/20.9476)*UOair;  % The N/O molar ratio in air
else
    UNAir = UOair*0.008/99.992;  % Ind. grade oxygen has 0.008% N2
end
Appendix J  Matlab code for thermodynamic equilibrium calculation

end

UN = UNint + UNair + UNext;

if NE >= 5
    US = Sar * rfuel * 1000 / (32.066*100);
    UCasor = Ca * US;  % Sorvent for sulfur retention
end

if NE >= 6
    UCl = Clar * rfuel * 1000 / (35.4527*100);
end

if NE >= 7
    UNa = Naar * rfuel * 1000 / (22.9898*100);
end

if NE >= 8
    UCa = Caar * rfuel * 1000 / (40.078*100);
end

UCaint = Caar * rfuel * 1000 / (40.078*100);
UCatot = Ca*(US + UCl);  % Moles of Ca needed to remove S and Cl
UCasor = UCatot - UCa;  % Total externally added Ca (sorbent)
purity = 96.5 / 100;  % Purity of sorbent
rsorb = UCasor * 56.0774 / (purity*1000);  % Sorbent feed rate (kg/hr)
Caconv = 1.0/Ca;  % Ca conversion
UCa = UCatot * Caconv;  % The actual mol of Ca entering equilibrium

% *-----------------------------------------------------------------
EA0 = zeros(NE,1);  % Initialization of EA0

if NE == 2
    EA0 = [UC; UH];
elseif NE == 3
    EA0 = [UC; UH; UO];
elseif NE == 4
    EA0 = [UC; UH; UO; UN];
elseif NE == 5
    EA0 = [UC; UH; UO; UN; US];
elseif NE == 6
    EA0 = [UC; UH; UO; UN; US; UCl];
elseif NE == 7
    EA0 = [UC; UH; UO; UN; US; UCl; UNa];
elseif NE == 8
    EA0 = [UC; UH; UO; UN; US; UCl; UNa; UCa];
end

% *-----------------------------------------------------------------
if NF >= 10
    EA0 = zeros(NE,1);
end

CEA = EA0;

% (2) Calculate enthalpy of feedstock

tfuel = 60;  % fuel temperature(deg C)
tmoist = tfuel;
tsorb = 25;
toxy = 150;
tsurr = 25;
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Matlab code for thermodynamic equilibrium calculation

% The heat of formation of the fuel
% Assume the molecular weight of the fuel is 100.
% The chemical formula of the fuel is C_a1 H_a2 O_a3 N_a4 S_a5

af = zeros(8,1);
ar2db = 100/(100-Dat3(14,NF));   % ar2db > 1
ar2daf = 100/(100-Dat3(13,NF)-Dat3(14,NF));   % ar2daf > 1. Conversion factor from ar base to daf base

af(1) = Dat3(5,NF)/12.011;   % C
af(2) = Dat3(6,NF)/1.00794;   % H
af(3) = Dat3(7,NF)/15.9994;   % O
af(4) = Dat3(8,NF)/14.0067;   % N
af(5) = Dat3(9,NF)/32.066;    % S
af(6) = Dat3(10,NF)/35.453;   % Cl
af(7) = Dat3(11,NF)/22.9898;  % Na
af(8) = Dat3(12,NF)/40.078;   % Ca

HHVdaf in kJ/kg, dry ash free base
%hhvdaf = HHV * ar2daf;        % Don't remove this line! Daf base (kJ/kg)
HHVdb   = 341*Dat3(5,NF) + 1322*Dat3(6,NF) - 120*(Dat3(7,NF)+Dat3(8,NF)) - 15.3*Dat3(9,NF) + 68.6*Dat3(9,NF);   % kJ/kg dry Thermodynamic data for biomass materials and waste components/sponsored by the ASME research committee on industrial and municipal wastes; edited by E.S.Domalski, T.L.Jobe,Jr., T.A.Milne, pp339
HHV = HHVdb/ar2db;

% Now calculate the heat of formation of the fuel (H2O in liq. state)
% a1   C   + a1   O2  = a1   CO2     a1 *   (-393.522) kJ/mol
% a2/2 H2  + a2/4 O2   = a2/2 H2O     a2/2 * (-285.840) kJ/mol
% a5   S   + a5   O2  = a5   SO2     a5 *   (-286.842) kJ/mol
% a1   CO2 + a2/2 H2O  = a4/2 N2 + ... = Fuel + Tm0 O2 + 79/21* Tm0 N2
% The heat of formation of the fuel is:


hfuel = (tfuel-25)*3.2;   %kJ/kg-fuel(any types))

if NO == 1   % air
    cpoxy = 8.31448*(3.355 + 0.575*(toxy + 273.15)/1000 - 0.016 * (1/(toxy +273.15)^2)*100000)/1000;   % kJ/mol.K
    cpsorb = 8.31448*(6.104 + 0.443*(tsorb + 273.15)/1000 - 1.047 * (1/(tsorb +273.15)^2)*100000)/1000;   % kJ/mol.K
    cpstm = 8.31448*(3.470 + 1.450*(tstm + 273.15)/1000 + 0.121 * (1/(tstm +273.15)^2)*100000)/1000;   % kJ/mol.K
    cpstmliq= 8.31448*(8.712 + 1.25*(tstm + 273.15)/1000 - 0.18 * ((tstm +273.15)^2)/1000000)/1000;   % kJ/mol.K
    cpnitro= 8.31448*(3.280 + 0.593*(tnitro + 273.15)/1000 + 0.04 * (1/(tnitro +273.15)^2)*100000)/1000;   % kJ/mol.K
else   % Oxygen
    cpoxy = 8.31448*(3.639 + 0.506*(toxy + 273.15)/1000 - 0.227 * (1/(toxy +273.15)^2)*100000)/1000;   % kJ/mol.K
end
cpstmliq= 8.31448*(8.712 + 1.25*(tstm + 273.15)/1000 - 0.18 * ((tstm +273.15)^2)/1000000)/1000;   % kJ/mol.K

if NO == 1   % moles of air
    moxy = (Tm0/0.209476)*alfa*rfuel;
end
else
    moxy = (Tm0/0.99992) * alfa*rfuel;
end

hN2purge=cpnitro * UNext*(tnitro-25); % kJ
hoxymoxy = cpoxy * moxy *(toxy-25); % kJ
hsorb = cpsorb* UCasor*(tsorb-25); % kJ
if tstm >= 100
    hstm = cpstm * UOext *(tstm-25); % kJ
else
    hstm = cpstmliq * UOext *(tstm-25) - 2442.5 * UOext * 18.015/1000; %kJ
end
% This line implies that water and steam are added at the same T.

Hfeed = hfuel + hN2purge + hoxymoxy + hstm + hsorb;

disp('  
disp(['' Stoichiometric moles of O2 = ' num2str(Tm0) ' (mole/100g dry fuel) '')
disp(['' Stoichiometric air of fuel = ' num2str(V0) ' (Nm3/kg_dry fuel) ')]
disp(['' Total air supply = ' num2str(Vair) ' (Nm3/hr) ')]
disp(['' Higher heating value of fuel= ' num2str(HHV) ' (kJ/kg dry fuel) '])
disp(['' Enthalpy of feed = ' num2str(Hfeed) ' (kJ/kg fuel) '])
disp('  

J.4 Molar fraction of each species

File name: calcc.m

Function: To calculate the current molar fraction of each species

```
function [cy,ys,x,xg,xs,EA,CEA] = calcc(SI,SEM,y,EA0)

% CALCC updates the current molar fractions and element abundance vector with new y results.
% Version 1.0  Masakazu Sakaguchi modified Xiantial Li’s code (Jan. 3, 2010)

[N,M] = size(SEM);
NP = 1;  % One homogeneous phase
ytot = 0;
ytot1 = 0;
ytot2 = 0;
x = zeros(N,1);  % Overall molar fraction of species i
xg = zeros(N,1);  % Molar fraction of species i in gas phase
xl = zeros(N,1);   % Molar fraction of species i in liquid phase
cy = zeros(N,M);   % Element distribution in each species
EA = zeros(M,1);   % Overall element abundance
ns = zeros(N,1);

% Count the number of single-species phases
m = 0;
nliq = 0;
for i = 1:N
    if SI(i) == 1
        m = m + 1;
        ns(i) = m;
    end
    if SI(i) == 2
        nliq = nliq + 1;
    end
end
ys = zeros(m,1);
xs = ones(m,1);
NP = NP + m;
CEA = zeros(M,NP);
for k = 1:m
    for i=1:N
        if ns(i) == k
            ys(k) = y(i);
        end
    end
end
% Compute the species split of each element, cy
for i = 1:N
    for j = 1:M
        cy(i,j) = y(i)*SEM(i,j)/EA0(j);
    end
end
```

```
Appendix J  
Matlab code for thermodynamic equilibrium calculation

```matlab
ytot = ytot + y(i);
ytot1 = ytot1 + (SI(i) == 1) * y(i); % Gas phase
ytot2 = ytot2 + (SI(i) == 2) * y(i); % Liquid phase
end

x = y/ytot; % Overall reduced molar fraction
for i = 1:N
    if SI(i) == 1
        xg(i) = y(i)/ytot1; % Reduced molar fraction in gas phase
    elseif SI(i) == 2
        xl(i) = y(i)/ytot2; % Reduced molar fraction in liquid phase
    end
end

% Calculate a new EA and CEA for iteration
for j = 1:M
    for i = 1:N
        EA(j) = EA(j) + y(i)*SEM(i,j);
        if SI(i) == 1
            dirac = 1.0;
        else
            dirac = 0.0;
        end
        CEA(j,1) = CEA(j,1) + y(i)*dirac*SEM(i,j); % Gas
        if nliq >= 1
            CEA(j,2) = CEA(j,2) + y(i)*(SI(i) == 2)*SEM(i,j); % Liquid phase
            % M == 7 or 8
            % CEA(j,3) = C(s)
            % CEA(j,4) = S(s), ...
        else
            if M == 3
                CEA(j,2) = y(N)*SEM(N,j); % Solid phases 1 = C(s)
            elseif M == 4
                CEA(j,2) = y(N)*SEM(N,j); % Solid phases 1 = C(s)
            elseif M == 5
                CEA(j,2) = y(43)*SEM(43,j); % Solid phases 1 = C(s)
                CEA(j,3) = y(44)*SEM(44,j); % Solid phases 2 = S(s)
            elseif M == 6
                CEA(j,2) = y(46)*SEM(46,j); % Solid phases 1 = C(s)
                CEA(j,3) = y(47)*SEM(47,j); % Solid phases 2 = S(s)
            end
        end
    end
end
```
Appendix J
Matlab code for thermodynamic equilibrium calculation

J.5 Standard chemical potential

File name: mut.m
Function: To compute the standard chemical potential of each species

```matlab
function [smu, smustar] = mut(T, p, Dat1, Dat11)
% Mut calculates the standard chemical potential mu* at (T, p)
% smu, smustar: kJ/mol

[N, NN] = size(Dat1); % NN is useless but recorded here.
R = 8.31448;
smustar = zeros(N, 1);
for i = 1:N
    Tcut(i) = Dat1(i, 8);
    if T > 1177.00
        Dat1(44, 2) = 2; % Na becomes vapour at this temperature
    end
    smu(i) = Dat1(i, 3) + Dat1(i, 4)*T*log(T) + Dat1(i, 5)*T^2 + Dat1(i, 6)/T + Dat1(i, 7)*T;
    if T > Tcut(i) % Alternative correlations for DGfo(T)
        smu(i) = Dat11(i, 3) + Dat11(i, 4)*T*log(T) + Dat11(i, 5)*T^2 + Dat11(i, 6)/T + Dat11(i, 7)*T;
    end
    if Dat1(i, 2) == 2 % For condensed phase
        smustar(i) = smu(i); % mu* = DGfo(T), ignoring vapour term
    elseif Dat1(i, 2) == 1 % For gas phase
        smustar(i) = smu(i) + R * T * log(p) / 1000;
    end
end
```
J.6 Species enthalpy

File name: enth.m
Function: To compute the enthalpy of each species

function [h,H] = enth(Dath,Dathl,T,y)
    % ENTH computes the enthalpy of each species, unit in kJ/mol
    [N,M] = size(Dath);
    H = zeros(N,1);
    for i = 1:N
        if T <= Dath(i,8)
            h(i) = Dath(i,3)*T/1000 + Dath(i,4)*T^2/1000000 + Dath(i,5)/T + Dath(i,6);
        else
            h(i) = Dathl(i,3)*T/1000 + Dathl(i,4)*T^2/1000000 + Dathl(i,5)/T + Dathl(i,6);
        end
        H(i) = h(i).*y(i);
    end
Appendix J  
Matlab code for thermodynamic equilibrium calculation

J.7  
Elements in the RAND matrix

File name: abzuc.m
Function: To compute the RAND matrix A and vector B

function [a1,b1,ra1,ra2] = abzuc(SI,SEM,EA,CEA,EA0,smutp,T,p,y,imm)
% ABZUC calculates the RAND matrix elements a1(N3,N3)
% In RAND algorithm, the Lagrange multipliers are solved from a1.x = b1

[N,M] = size(SEM);
%
% (1) Count the number of gas, liquid and solid species

ngas = 0;
nliq = 0;
nsol = 0;

for i = 1:N
    if SI(i) == 1
        ngas = ngas + 1;
    elseif SI(i) == 2
        nliq = nliq + 1;
    elseif SI(i) == 3
        nsol = nsol + 1;
    end
end
%
% Count the number of phases

NP = 1;  % Gas phase as an ideal solution
if nliq > 0
    NP = NP + 1; % Liquid phase as another ideal solution
end
NP = NP + nsol; % Each solid as a single-species phase

if nliq > 0
    NP = nsol + 2;
else
    NP = nsol + 1;
end

NZ = 0;  % Number of inert species
N1 = N - NZ;  % Number of reactive species
N2 = M + 1;
N3 = M + NP;
R = 8.31448;

if min(EA0) > 0.0001
    yz = 0.005*min(EA0);
else
    yz = 0.0000005;
end

a1 = zeros(N3,N3);
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Matlab code for thermodynamic equilibrium calculation

\[ \text{b1} = \text{zeros(N3,1)}; \]
\[
\text{for } j = 1:M \\
\text{for } k = j:M \\
\text{for } i = 1:N1 \\
\quad a1(j,k) = a1(j,k) + SEM(i,j) \times SEM(i,k) \times y(i); \\
\text{end} \\
\text{end} \\
\text{end} \\
\]
\[
\text{Zone I} - [j \leq M, k \leq M] \\
\text{Zone II} - [j \leq M, k > M] \\
\text{Zone III} - [j > M, k \leq M] \\
\text{Zone IV} - [j > M, k > M] \\
\]
\[
\text{ra1} = \text{rank(a1)}; \\
\text{ra2} = \text{cond(a1)}; \\
\]
\[
\text{for } j = 1:M \\
\text{for } k = j:M \\
\text{for } i = 1:N1 \\
\quad a1(j,k) = a1(j,k) + SEM(i,j) \times SEM(i,k) \times y(i); \\
\text{end} \\
\text{end} \\
\text{end} \\
\]
\[
\text{EA0(j)}: \text{the initial element abundance vector estimated from feed data.} \\
\text{EA(j)}: \text{the element abundance of the current iteration.} \\
\]
% The incorporation of EA0(j)-EA(j) on the right side is believed to help prevent error accumulation.

% Zone II - [j > M]
for j = N2:N3
    if j == N2
        % Gas phase
        for i = 1:N
            b1(N2) = b1(j) + y(i) * (SI(i) == 1) * smutp(i) * 1000/(R*T);
            % RT is timed by 1000 because the unit of smutp is kJ/mol
        end
    elseif j >= N2 + 1
        if nliq > 0 % or M >= 7
            for i = 1:N
                b1(N2+1) = b1(j) + y(i) * (SI(i) == 2) * smutp(i) * 1000/(R*T);
                % RT is timed by 1000 because the unit of smutp is kJ/mol
            end
        else
            if M == 3
                b1(N2+1) = y(N) * smutp(N) * 1000/(R*T); % SSP-1: C(s)
            elseif M == 4
                b1(N2+1) = y(N) * smutp(N) * 1000/(R*T); % SSP-1: C(s)
            elseif M == 5
                b1(N2+1) = y(43) * smutp(43) * 1000/(R*T); % SSP-1: C(s)
                b1(N2+2) = y(44) * smutp(44) * 1000/(R*T); % SSP-1: S(s)
            end
        end
    end
end

if imm == 1
    if ra1 ~= M + NP
        disp('')
        disp([' Rank of RAND coefficient matrix = ' num2str(ra1)])
        disp([' Condition number of RAND matrix = ' num2str(ra2)])
        disp('')
    elseif ra2 > 50000000
        disp('')
        disp([' Condition number of RAND matrix = ' num2str(ra2)])
        disp('')
    end
end
J.8 Convergence forcer

File name: forcer.m
Function: To speed up convergence by ensuring non-negativity of each species

```matlab
function [ynew] = forcer(dy,y)
% FORCER computes new mole numbers and guarantee their non-negativity.
% Do not modify anything in this function.

n = length(dy);
par = 0.5;
ynew = zeros(n,1);

for i = 1:n
    if par < -dy(i)/y(i)
        par = -dy(i)/y(i);
    end
end

par = 1/par;
if par > 0 & par <= 1
    if par < 0.1
        par = par * 0.999;
    else
        par = par * 0.99;
    end
else
    par = 1.0;
end

for i = 1:n
    ynew(i) = y(i) + dy(i) * par;
    if ynew(i) <= 1e-200  % minimum value control
        ynew(i) = 1e-200;
    end
end
```
J.9   Energy balance

File name: heatcoal.m  
Function: Energy balance modulus

function [dq,totdh,totdgh,totth,totgh,totsh] = 
    heatcoal(T,alfa,Dath,Dat2,Dat3,NF,H,y,Uwat,Ca,dissip,Hfeed,hff,tstm)

% HEATCOAL does energy balance for coal and biomass gasification.  
% All results are per 1 kg of biomass (dry basis)
% Version 1.0 Masakazu Sakaguchi modified Xiantian Li's code (Jan. 3, 2010)

% Initialization
[N,M] = size(Dath);
totth = 0;
totdh = 0;
totdgh = 0;
totdlh = 0;
totdsh = 0;
totph = 0;
totgh = 0;
totsh = 0;
%totdh25 = 0;
htrans = 0;
dq = 0;
calcin = 0;
sure = 0;
sure0 = 0;
dhsure = 0;
tfactor = 0;	afactor = 0;
uncal = 0;
sulfate = 0;
spentlime = 0;
ttt = 0;
hcal = 0;
huncal = 0;
huncal = 0;
hsulfate = 0;
heptlime = 0;
calcium = 0;

% End of initialization

% (1) Enthalpy of feedstock: Hfeed
hfeed = Hfeed;  % kJ (sensible heat)

% (2) Total product heat of formation @298K and enthalpy at T
for i = 1:N
    totdh = totdh + Dath(i,7) * y(i);  % Total heat of formation, kJ
    toth = toth + H(i);  % System total enthalpy, kJ
end
if Dath(i,2) == 1
Appendix J  Matlab code for thermodynamic equilibrium calculation

totdgh = totdgh + H(i);
elseif Dath(i,2) == 2
totdlh = totdlh + H(i);
elseif Dath(i,2) == 3
totdsh = totdsh + H(i);
end

end

end % Calculate fractional calcination and sulfur retention

if Ca >= 0.1 % If sorbent is added for sulfur removal
    [sure, calcin] = sulfre(T, alfa, Ca);
end

% Sulfur retention products (basis: 1 kg of fuel)
sulfur = (Dat3(9,NF)/100)*1000/32.066; % Moles of sulfur in 1 kg fuel
calcium = sulfur*Ca; % Moles of Ca added
hcal = calcium*calcin*(-178.989); % Heat effect of calcination
uncal = calcium*(1-calcin); % Moles of uncalcined CaCO3
sulfate = sulfur*sure; % Moles of CaSO4 formed
haulf = sulfate*502.179; % Heat effect of sulfation
spentlime = (calcium - uncal)-sulfate; % Moles of spent lime
dhsure = hcal + hsulf; % Net heat effect of sulf-re

% Sensible heat (enthalpy) of sulfur retention products
huncal = uncal* (97.935*T/1000 + 14.198*T^2/1000000 + 1855.4379/T - 36.8346); % CaCO3
hsulfate = sulfate* (32.863*T/1000 + 61.278*T^2/1000000 - 6316.038/T + 4.5425); % CaSO4
hsptlime = spentlime* (48.997*T/1000 + 2.5140*T^2/1000000 + 573.2851/T - 16.8339); % CaO

% Old ash in fuel
oldash = Dat3(3,NF)/100; % kg/kg_fuel (Note: not mol/kg_fuel)
holdash = oldash*(1.15e-4*T^2 + 0.82709*T - 239.38); % kJ/kg_fuel

% New ash from sulfur retention
newash = uncal + sulfate + spentlime; % mol/kg_fuel
hnewash = huncal + hsulfate + hsptlime; % kJ/kg_fuel
htotash = holdash + hnewash; % kJ/kg_fuel

% Modification of gas and solid enthalpy
totgh = toth;
for i=1:N
    if Dath(i,2) == 1
        totgh = totgh - H(i); % Total gas enthalpy, kJ/kg_fuel
    end
    if Dath(i,2) == 3
        totsh = totsh + H(i); % Total solid enthalpy, kJ/kg_fuel
    end
end

totsh = totsh + htotash;
totph = totgh + totsh; % Total product enthalpy, kJ/kg_fuel

% (3) Heat of formation of the feed: From Dath
hf1 = hff; % Fuel, kJ/kg_fuel
hf2 = Uwat*Dath(17,7); % DMf0(298) for H2O (vapour), kJ/kg_fuel
hf3 = -1207.6*calcium; % Heat of formation of limestone
hfeed = hf1 + hf2 + hf3; % kJ/kg_fuel
Appendix J  

Matlab code for thermodynamic equilibrium calculation

% (4) Reactor surface heat transfer in this time interval (preset as 1 hr)
htrans = dissip; %dissipation from reactor surface

% (5) Heat required to maintain the current temperature (kJ/kg_fuel)
dq = (totdh + toth + htrans) - (hfeed + hfeed + dhsure);

% HHV already considered in hff, kJ/kg_fuel (as received)
Appendix J  Matlab code for thermodynamic equilibrium calculation

J.10  Reference