UNIVERSITÉ DU QUÉBEC À TROIS-RIVIÈRES

CONCEPTION ET ANALYSE TECHNICO-ÉCONOMIQUE DE LA PRODUCTION DE MÉTHANOL À PARTIR DE LA GAZÉFICATION DES PRODUITS DE LA PYROLYSE

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Foreword

My previous discipline being organic chemistry, when I first learned that my topic was about biomass, I found it to be a real challenge due to the limited knowledge I had on the topic.

The basis for this research originates from the BioÉnergie La Tuque (BELT) refinery project objective of my thesis was to find ways to produce syngas from a slurry consisting of a mixture of biochar and pyrolysis oil. The gasification experiment was supposed to be done at CanmetENERGY research center in Ottawa. Unfortunately, the planning of these experiments had to be abandoned for various reasons, essentially for lack of funding. Therefore, the thesis had to be redirected to a more fundamental, yet practical approach based on various simulations of the gasification with an extensive use of the Aspen Plus software to analyse new ways to optimise these processes. Consequently, various parameters were tested by the model design during the first part of my PhD work. The results obtained could then be compared with experimental data collected in the literature, making it possible to validate our model and approaches. The results of the simulated experiments on syngas properties at an industrial scale allowed us to highlight the advantages and limitations of the gasification technology. These findings are extremely relevant for any future practical syngas application and constitute the main contribution of my thesis work. In addition to syngas synthesis, I also have extended my study to its application to synthetic biofuels. On this basis, I also achieved a techno-economic analysis to explore the feasibility of methanol production.

As part of my future research, I am planning to continue to explore this topic further and use what I have learned to contribute more to transforming our society in a more sustainable society.

Acknowledgments

I would like to thank my professor Patrice J. Mangin, for trusting me to complete this project. Thanks are due to him for his numerous advices, as well as for the great freedom he gave me to realize my project. Not only did he make me aware of the importance of this discipline for society, but he also made me understand that scientific research is not just about piling up publications in high-quality scientific journals, but above all about using the scientific knowledge gained to make a contribution to our society. This philosophy has greatly improved my view of science and taught me to think from different angles.

This research would have been impossible to complete without the help and encouragement of my two post-doctoral colleagues, Benoit Delcroix and Olivier Rezazgui. Benoit in particular has always encouraged me to continue to think and learn even in difficult times, when I felt somehow helpless. Whether in designing my model or writing my thesis, he helped me a lot and always in a very selfless way. Sincere gratitude to you Benoît.

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Finally, thanks to each member of my family for your unconditional financial support, love and care.

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Summary

Among the major economic and ecological challenges of the 21st century, climate change and sustainable development are the most publicised but also the most crucial. Thus, renewable and sustainable energy sources such as solar, wind, and biomass have been recently considered as an elegant solution to the energy crisis, and biofuels as an alternative to fossil ones. Indeed, fuels produced from biomass are renewable and reduce oil dependency while diversifying the energy supply. In addition, because biofuels are produced from biomass, the use of biofuels potentially has a zero or even negative carbon impact on the environment.

Canada has an abundance of renewable biomass, both forestry and agricultural that can be used to provide clean energy and materials. Canada is the second largest country in the world with 9.985 million km^2; it alone holds 9% of the world's forest area (347 million hectares). The use of the huge Canadian "forest and agricultural reservoir" produces many wastes and non-recovered co-products, such as sawdust and other forest residues, corn stalks for the food industry, but also municipal wastes (*e.g.* school canteens, road services…). All these unused wastes could be recovered and converted into biofuels. Using these leftover residues to produce green fuels could help Canada to reduce its waste generation, while providing a solution to climate change as well as a new circular and sustainable economy form.

Pyrolysis oil, as liquid energy carrier, is produced from lignocellulosic biomass by fast pyrolysis at high temperature. Pyrolysis oil has attracted extensive attention due to its high volumetric energy density and its ease of transport and storage. It is worth noting that pyrolysis oil contains only a small amount, sometimes even undetectable depending on the biomass source, of sulfur, nitrogen, metals and ash. As a result, the syngas produced by gasification of pyrolysis contains less harmful gas emissions and can be directly used in downstream applications.

The purpose of this thesis is to explore the application of pyrolysis oil. Firstly, a model for syngas production from pyrolysis oil gasification was developed to predict the effect of gasifier operating conditions on syngas properties. Two syngas application are

assumed: (1) direct use in fuel cells and (2) biofuel synthesis. The actual experimental parameters such as gasifier agent, temperature, and moisture content in pyrolysis oil were investigated. Secondly, a novel process model simulating methanol synthesis *via* pyrolysis oil gasification was developed to predict the effect of operating conditions on methanol production yield. Rectisol® unit acted as syngas purifier that not only remove impurities, but also changed the syngas composition and improved methanol yield. The main parameter, *i.e.* the gasifying temperature, pyrolysis oil moisture content, Rectisol® temperature/pressure, and methanol synthesis reactor temperature/pressure, were explored then discussed to highlight the impacts of various operating conditions on methanol yield. Although methanol produced from natural gas is commercially available, there is currently no production based on pyrolysis oil. Therefore, we decided to conduct a technical and economic analysis of methanol production from pyrolysis oil. This study was based on current technologies such as gasification, syngas post-treatment, and methanol synthesis, and at different scales of plants, in order to test its potential feasibility. Then, in order to estimate the competitiveness of this new technology, two other sources of raw materials were also studied: biochar and pine biomass.

In order to carry out this study, initially a dual theoretical and experimental approach was envisaged. However, due to unforeseen circumstances beyond our control, only the theoretical part could be explored. Theoretical study was based on Aspen plus software, and results obtained with the designed model were validated by experimental data from the literature. Therefore, this study provides guidance for potential future applications of pyrolysis oil.

Firstly, a model simulating syngas production from pyrolysis oil is studied. Aspen plus software is used to simulate gasification that includes drying, decomposition, combustion, and gasification processes. The syngas composition obtained from simulation are 55.9 mol% H_2, 24.0 mol% CO, 19.8 mol% CO_2, and 0.3 mol% CH_4. The simulated syngas results are in good agreement with the experimental results. Two syngas applications are assumed, fuel cell and methanol synthesis. Studies have shown that the syngas produced from pyrolysis oil at high temperature with low moisture content in pyrolysis oil is beneficial for fuel cell applications. Oxygen and air should not be used in gasification that

will decrease syngas enthalpy value. On the other hand, the syngas produced at an appropriate temperature around 1000°C with the moisture content in pyrolysis oil selected at 40% is beneficial for fuel production. Secondly, based on the results of previous study, we extend the syngas application in biofuel synthesis. An Aspen plus model is developed to simulate the production of methanol. The model comprises gasification, syngas cleaning, and methanol synthesis. It is concluded from the simulation that the maximum methanol yield is around 8.04 kmol/1000kg (methanol/pyrolysis oil). The entire process includes gasification, Rectisol®, and methanol synthesis processes. The simulations of gasification, Rectisol® and methanol synthesis were all validated by experimental results from literature. Research shows that an increase in gasification temperature from 400 °C to 600 °C resulted in a higher syngas stoichiometric number (SN) value. Moisture content in pyrolysis oil increases from 10% to 30% leads to an increase in SN value. Rectisol® operated at -20 °C and 40 bar leads to an appropriate SN value and a higher methanol yield. Methanol synthesis reactor operating at 250 °C and 50 bars can be an optimal choice. Finally, a model simulating methanol production from different bioresources is investigated by using simulation software Aspen plus. The model process consists of gasification, syngas post-treatment, methanol synthesis with recycle system and methanol purification. This simulation is similar to the actual methanol synthesis process. As this research project is intended to provide guidance on potential industrial applications, we extended the scope of the study to two additional feedstocks, namely pine biomass and biochar, and conducted a techno-economic analysis of these three (the original plus the extended two) feedstocks to explore whether the use of pyrolysis oil to produce methanol is commercially competitive. The syngas composition produced by gasification as well as methanol yield are obtained from the model results. The methanol yields from biomass, biochar, and pyrolysis oil are 507.3kg, 578.2kg, and 283.1kg, respectively. The study has demonstrated that the methanol produced from biochar seems to be the most promising option. In contrast, pyrolysis oil appears to be the most expensive solution. Regardless of the feedstock used in any project, biomass, biochar, or pyrolysis oil, it is difficult to reach economic benefits when the plant scale is below 1000 tons per day (TPD). The sensitivity analysis has shown that bio-methanol price is the most significant factor. For biochar, when the bio-methanol price is 1100$/ton, the economic benefits can be realized at the minimum plant scale of 1000 TPD.

Résumé

Parmi les grands défis économiques et écologiques du XXIe siècle, le changement climatique et le développement durable sont les plus médiatisés mais aussi les plus cruciaux. Ainsi, les sources d'énergies renouvelables et durables telles que le solaire, l'éolien et la biomasse ont récemment été considérées comme une solution prometteuse à la crise énergétique, et les biocarburants comme une alternative aux combustibles fossiles. En effet, les carburants produits à partir de la biomasse sont renouvelables et permettent de diminuer la dépendance au pétrole tout en diversifiant l'approvisionnement énergétique. De plus, parce qu'ils sont produits à partir de la biomasse, ils ont potentiellement un impact carbone zéro ou même négatif sur l'environnement.

Le Canada dispose d'une abondance de biomasse renouvelable, tant forestière qu'agricole, qui peut être utilisée pour fournir de l'énergie et des matériaux propres. Deuxième plus grand pays du monde avec 9,985 millions de km^2, il détient à lui seul 9 % de la superficie forestière mondiale (347 millions d'hectares). L'utilisation de cet immense réservoir végétal produit de nombreux déchets et coproduits non valorisés, tels que la sciure et autres résidus forestiers, les tiges de maïs pour l'industrie alimentaire mais aussi les déchets municipaux (par exemple, les cantines scolaires, les services de voirie...). Tous ces déchets non utilisés pourraient être récupérés et transformés en biocarburants. L'utilisation de ces biomasses résiduelles pour produire des carburants verts pourrait aider le Canada à réduire sa production de déchets, tout en apportant une solution au changement climatique ainsi qu'une nouvelle forme d'économie circulaire et durable.

L'huile de pyrolyse, en tant que vecteur d'énergie liquide, est produite à partir de biomasse lignocellulosique par pyrolyse rapide à haute température. L'huile de pyrolyse a suscité un grand intérêt en raison de sa densité énergétique volumétrique élevée et de sa facilité de transport et de stockage. Il convient de noter que l'huile de pyrolyse ne contient qu'une faible quantité, parfois indétectable selon le type de biomasse, de soufre, d'azote, de métaux et de cendres. Par conséquent, le gaz de synthèse produit par la gazéification de la pyrolyse contient moins d'émissions de gaz nocifs et peut être directement utilisé dans des applications en aval.

L'objectif de notre projet de thèse est d'explorer l'application de l'huile de pyrolyse. Premièrement, un modèle de production de gaz de synthèse à partir de la gazéification des huiles pyrolytiques a été développé. Ce dernier avait pour but de prédire l'effet des conditions de fonctionnement du gazéifieur sur les propriétés finales du gaz. Deux applications du gaz de synthèse sont considérées : (1) utilisation directe dans les piles à combustible ; (2) la synthèse de biocarburants. Les paramètres expérimentaux tels que l'agent de gazéification, la température du gazéifieur et la teneur en humidité de la biohuile pyrolytique ont été étudiés. Ensuite, un nouveau modèle simulant le procédé de synthèse du méthanol suite à la gazéification d'huiles pyrolytiques a été mis au point pour prédire l'effet des conditions de fonctionnement sur le rendement en méthanol. La technologie Rectisol® a été choisie comme purificateur du gaz de synthèse, qui non seulement élimine les impuretés mais également modifie la composition du gaz et ainsi améliore le rendement en méthanol. Les principaux paramètres ont été examinés afin de mettre en lumière l'influence des diverses conditions de fonctionnement sur le rendement en méthanol: température de gazéification, teneur en humidité de l'huile de pyrolyse, température/pression du Rectisol® ou encore la température/pression du réacteur de synthèse du méthanol.

Bien que le méthanol issu du gaz naturel soit disponible commercialement, il n'existe actuellement aucune production de méthanol à partir d'huile pyrolytique. C'est pourquoi nous avons décidé de réaliser une analyse technico-économique de la production de méthanol à partir d'huile de pyrolyse. Cette étude a été basée sur la technologie actuelle de gazéification, post-traitement du gaz de synthèse et synthèse du méthanol, et à différentes échelles d'usines, afin d'en tester la faisabilité technico-économique potentielle. Ensuite, afin d'estimer la compétitivité de cette nouvelle technologie, deux autres sources de matières premières ont également été étudiées, soit du biochar, un sous-produit de la pyrolyse, et de la biomasse.

Pour mener à bien cette étude, une double approche théorique et expérimentale a été envisagée. Cependant, en raison de circonstances imprévues et indépendantes de notre volonté, seule la partie théorique a pu être explorée. L'étude théorique était basée sur une utilisation *ad hoc* du logiciel Aspen plus, et les résultats obtenus avec le modèle ont été

validés par des données expérimentales provenant de la littérature. Par conséquent, cette étude a fourni des orientations pour les futures applications potentielles de l'huile de pyrolyse.

Tout d'abord, un modèle simulant la production de gaz de synthèse à partir d'huile de pyrolyse est étudié. Le logiciel Aspen plus est ici utilisé pour simuler la gazéification qui comprend les processus de séchage, de décomposition, de combustion et de gazéification. La composition du gaz de synthèse obtenue par simulation est de 55,9 % en moles de H_2, 24,0 % en moles de CO, 19,8 % en moles de CO_2 et 0,3 % en moles de CH_4. Les résultats du gaz de synthèse simulé sont en bon accord avec les résultats expérimentaux. Deux applications de gaz de synthèse sont considérées, l'alimentation de piles à combustible et la synthèse de méthanol. Des études ont montré que le gaz de synthèse produit à partir d'huile de pyrolyse à haute température avec une faible teneur en humidité dans l'huile de pyrolyse est bénéfique pour les applications de piles à combustible. L'oxygène et l'air ne devraient pas être utilisés dans la gazéification, ce qui diminuerait la valeur d'enthalpie du gaz de synthèse. D'autre part, le gaz de synthèse produit à une température appropriée d'environ 1000°C avec une teneur en humidité de l'huile de pyrolyse sélectionnée à 40% est bénéfique pour la production de combustible. Deuxièmement, sur la base des résultats d'une étude précédente, nous avons élargi l'application du gaz de synthèse dans la synthèse des biocarburants. Un modèle Aspen plus a été développé pour simuler la production de méthanol. Le modèle comprend la gazéification, l'épuration du gaz de synthèse et la synthèse du méthanol. À partir de la simulation, nous avons trouvé que le rendement maximum de méthanol est d'approximativement 8,04 kmol/1000kg (méthanol/huile de pyrolyse). L'ensemble du processus comprend la gazéification, le procédé Rectisol® et la synthèse du méthanol. Les simulations de la gazéification, du Rectisol® et de la synthèse du méthanol ont toutes été validées par des résultats expérimentaux provenant de la littérature. Nos travaux montrent que l'augmentation de la température de gazéification de 400 ℃ à 600 ℃ entraîne une valeur stoechiométrique (SN, de l'acronyme anglais stoichiometric number) plus élevée du gaz de synthèse. L'augmentation de la teneur en humidité de l'huile de pyrolyse de 10 à 30 % entraîne une augmentation de la valeur SN. Le Rectisol® opéré à -20 ℃ et 40 bar conduit à une valeur SN appropriée et à un rendement en méthanol plus élevé. Le réacteur de synthèse du méthanol fonctionnant à 250 °C et 50 bars représente un choix potentiel optimal. Enfin, un modèle simulant la production de méthanol par différentes ressources de biomasse est étudié à l'aide du logiciel de simulation Aspen plus. Le modèle inclut la gazéification, le post-traitement du gaz de synthèse, la synthèse du méthanol avec un système de recyclage et la purification du méthanol. Cette simulation est similaire au processus réel de synthèse du méthanol. Comme ce projet de recherche est destiné à fournir des indications sur les applications industrielles potentielles, nous avons étendu la portée de l'étude à deux matières premières supplémentaires : biomasse de pin et biochar. Nous avons effectué une analyse technico-économique de ces trois (la biomasse initiale plus les deux supplémentaires) matières premières afin de déterminer si l'utilisation de l'huile de pyrolyse pour produire du méthanol est commercialement compétitive. La composition du gaz de synthèse produit par gazéification ainsi que le rendement en méthanol sont obtenus à partir des résultats du modèle. Les rendements en méthanol de la biomasse, du biochar et de l'huile de pyrolyse sont respectivement de 507,3 kg, 578,2 kg et 283,1 kg. L'étude a démontré que le méthanol produit à partir de biochar semble être l'option la plus prometteuse. En revanche, l'huile de pyrolyse est difficilement envisageable. Quel que soit le projet basé sur la biomasse, le biochar et l'huile de pyrolyse, il est difficile de réaliser des bénéfices économiques lorsque la capacité de l'usine est inférieure à 1000 tonnes par jour (TPD). L'analyse de sensibilité a montré que le prix du bio-méthanol demeure le facteur le plus important. Pour le biochar, lorsque le prix du bio-méthanol est de 1100$/tonne, les bénéfices économiques peuvent être réalisés à l'échelle minimale d'une usine de 1000 TPD.

Keywords

Biomass; Biochar; Pyrolysis oil; Bio-methanol; Aspen plus; Techno-economic analysis; Thermochemical pathway; Biofuel synthesis; Beechwood chips

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$$R_{CH_3OH}(\mathrm{kmol/kgcat\cdot s}) = (k_{MeOH}p_{CO_2}p_{H_2})\frac{[1-\frac{1}{K_{E1}}(\frac{p_{H_2O}p_{CH_3OH}}{p_{CO_2}p_{H_2}^3})]}{[1+k_3\left(\frac{p_{H_2O}}{p_{H_2}}\right)+k_1\sqrt{p_{H_2}}+k_2p_{H_2O}]^3}$$

Equation 6.3 **Erreur ! Signet non défini.**

$$R_{WGS}(\mathrm{kmol\,/\,kgcat\cdot s}) = (k_{WGS}p_{CO_2})\frac{[1-\frac{1}{K_{E2}}(\frac{p_{H_2O}p_{CO}}{p_{CO_2}p_{H_2}})]}{[1+k_3\left(\frac{p_{H_2O}}{p_{H_2}}\right)+k_1\sqrt{p_{H_2}}+k_2p_{H_2O}]}$$

Equation 6.4 **Erreur ! Signet non défini.**

$$CO + 2H_2 = CH_3OH \quad (\Delta H_{300K} = -90.77\ \mathrm{kJ/mol})$$

Equation 7.1 **Erreur ! Signet non défini.**

$$CO_2 + 3H_2 = CH_3OH + H_2O\ (\Delta H_{300K} = -49.16\ \mathrm{kJ/mol})$$

Equation 7.2 **Erreur ! Signet non défini.**

$$\mathrm{Cost}_1 = \mathrm{Cost}_0\left[\frac{\mathrm{size}_1}{\mathrm{size}_0}\right]^n$$

Equation 7.3 **Erreur ! Signet non défini.**

TCI = Fixed Capital Cost (FC) + Working Capital (WC)

Equation 7.4 **Erreur ! Signet non défini.**

FC = Direct Cost + Indirect Cost

Equation 7.5 **Erreur ! Signet non défini.**

$TPC = C_R + C_U + C_{OM} + C_{PR} + C_D + C_{LI} + C_P + C_G$

Equation 7.6 **Erreur ! Signet non défini.**

$$\text{Annual depreciation} = \frac{(\text{fixed capital investment } - \text{salvage value})}{\text{service life}}$$

Equation 7.7 **Erreur ! Signet non défini.**

$$\mathrm{NPV} = \sum_{t=1}^{n} \frac{C_t}{(1+i)^t} - C_0$$

Equation 7.8 **Erreur ! Signet non défini.**

$$\mathrm{NPV} = \sum_{t=1}^{n} \frac{C_t}{(1+\mathrm{IRR})^t} - C_0 = 0$$

Equation 7.9 **Erreur ! Signet non défini.**

$$\mathrm{DPBP} = A + \frac{B}{C}$$

Equation 7.10 **Erreur ! Signet non défini.**

Aspen Plus blocks description

RStoic	Drying
Sep	Separation
RYield	Decomposition
RGibbs	Combustion
RGibbs	Gasification
Radfrac	Rectisol®
Heater	Heat up or cool down syngas
MCompr	Compress syngas
RPlug	Methanol synthesis

REquil	Methanol synthesis
Flash 2	Separation
Radfrac	Methanol distillation

List of abbreviations

CEPCI	Chemical Engineering Plant Cost Index
CHP	Combined Heat and Power
DPBP	Discounted Payback Period
FC	Fixed Capital Cost
FT	Fischer-Tropsch
GHG	Greenhouse Gases
HES	Hybrid Energy System
HHV	Higher Heating Value
IGCC	Integrated Gasification Combined Cycle
IGFC	Integrated Gasification Fuel Cell
IRES	Integrated Renewable Energy Systems
IRR	Internal Rate of Return
LHHW	Langmuir-Hinshelwood-Hougen-Watson
LHV	Lower Heating Value
MDEA	N-Methyldiethanolamine
MEA	Monoethanolamine
Mt	Million tons (metric)
MTBE	Methyl *Tert*-Butyl Ether
Mtoe	Million Tons of Oil Equivalent

MWth	Megawatt Thermal
NC	Nonconventional
NREL	National Renewable Energy Laboratory
NPV	Net Present Value
PFD	Process Flow Diagram
ppb	part per billion
ppmv	parts per million by volume
PR-BM	Boston-Mathias alpha function
PSA	Pressure Swing Adsorption
RNG	Renewable Natural Gas
SMR	Steam Methane Reforming
SN	Stoichiometric Number
SOFC	Solid Oxide Fuel Cell
TCI	Total Capital Investment
TEA	Techno-Economic Analysis
TPC	Total Product Cost
TPD	Tons Per Day
WC	Working Capital
WGS	Water Gas Shift

Chapter 1 - Introduction

Nowadays, energy consumption increases drastically in the world, especially in developing countries, such as China, India, and Cuba. The annual energy consumption is about 14000 Mtoe (Million tons of oil equivalent), 80-85% of which is supplied by fossil fuels [1]. Thus, the renewable resources only account for a small proportion of global energy consumption. The term renewable energy is used to refer to energy that, at least on a human timeline, is naturally renewed to the point of being considered as practically inexhaustible and also available in large quantities. There are five main types of renewable energy: solar, wind, hydro, biomass, and geothermal. Their common characteristic is that they produce little or no polluting emissions during the exploitation phase, thus helping to combat the greenhouse effect and global warming [2]. In contrast, gasoline, coal, natural gas, diesel, plastics, and other products that come from fossil fuels are not renewable and emit several pollutants into the atmosphere [3]. The increase in the global energy consumption has led to an alarming rise in emissions of CO_2, NO_x and SO_x into the environment [4]. The greenhouse gases (GHG) emissions from fossil fuels have a dominant influence on the atmospheric CO_2 concentration that results in rising global temperatures and sea levels. Furthermore, CO_2 emissions from fuel combustion grew rapidly in the past decades. According to the International Energy Outlook, world energy-related CO_2 emissions will increase from 30.2 billion metric tons in 2008 to 43.2 billion metric tons in 2035 [5].

In Canada, Bliss Baker, president of the Global Renewable Fuels Alliance (GRFA), called for a climate agreement at the 21st Conference of the Parties (COP 21) to take action to significantly reduce carbon emissions from the transportation sector and incorporate increased percentages of biofuels blending as part of their national plans. Baker noted that the transportation sector produces about 25-30% of the world's greenhouse gas (GHG) emissions. Therefore, low-carbon transport fuel alternatives to crude oil, such as ethanol, are a cost-effective and immediately available option for countries to adopt. Biofuels represent a significant step in the right direction that governments can take substantial actions to address climate change coming out of COP 21 [6].

In order to meet the rapidly increasing global energy demand while respecting new environmental challenges, the use of renewable and sustainable energies (*e.g.* solar, wind and biomass) appear to be an elegant, economic, and viable solution.

Renewable energy sources, such as photovoltaic, wind, solar or small-scale hydro energy, provide an alternative to electricity generation in remote areas [7]. It creates a new pathway of energy system for remote communities, where the cost of grid extension is expensive and the price for fuel transportation increases drastically with the remoteness of the location. The widely used term "Hybrid Energy System" (HES) describes an energy system, which combines renewable and conventional energy sources. The systems are known as Integrated Renewable Energy Systems (IRES) [8]. Numerous hybrid energy systems have been installed in many countries over the last two decades, resulting in the development of systems that can compete with conventional, fuel-based remote area power supplies. Hoicka and Rowlands [9] have indicated that the complementary nature of solar and wind resources is a potential advanced option for the integration of renewable energy into Ontario power system. Thomaidis et al [10] have shown that the complementarity of solar and wind resources can improve the reliability of the power system in the Iberian Peninsula. However, the IRES shortcomings limit them from being widely used in all regions of the world. The initial cost of purchasing an IRES system is fairly high, the IRES system is influenced by weather and terrain, and cloudy and rainy days have a noticeable effect on this energy system. Besides that, the energy produced by an IRES system should be used immediately or it needs to be stored in a large battery, which also increases the cost and limits IRES applications [11].

Thus, biofuels are now seen as a credible alternative to fossil fuels. Biofuels are liquid or gaseous fuels produced from biomass. Two of the most common biofuels are ethanol and biodiesel. Indeed, biofuels can be considered as a renewable energy source since they are derived from biomass which is renewable. Moreover, their carbon balance is neutral and sometimes even negative, as the CO_2 emissions caused by their combustion are offset by the CO_2 absorbed upstream by the cultivated biomass [3]. Biofuels are often also called renewable biofuels of simply renewable fuels. For practical reasons, we will use "biofuels" as it is the most common term.

There is a worldwide interest for using biomass as a friendly method for hydrogen-rich gas production, which also has a potential to decrease CO_2 emissions [12]. Using biomass can mitigate the carbon dioxide concentration in the atmosphere, meaning that the amount of carbon dioxide released by biomass combustion is the same as the one absorbed through plant photosynthesis. However, about 95% of worldwide hydrogen production comes from catalytic Steam Methane Reforming (SMR) of natural gas. Using natural gas generates roughly 30 million tons per year of carbon dioxide [13]. Natural gas remains a cheap source of hydrogen. There is an increasing interest in replacing it with renewable sources of hydrogen to reduce greenhouse gases emissions and mitigate the environmental impacts. Therefore, the industry is trying to explore renewable sources of hydrogen. Producing hydrogen-rich gases from biomass is currently one of the other potentially effective methods that would greatly reduce the amount of CO_2 release since the carbon is absorbed from the atmosphere and recycled by growing into biomass through photosynthetic reactions [14, 15].

Even though hydrogen is considered as a clean and efficient fuel, it needs nevertheless costly high-pressure infrastructures for its storage and transportation since it is a volatile gas. Moreover, hydrogen is an inflammable gas, which involves security risks during use, storage and transportation. Besides, a large amount of energy is consumed to produce hydrogen [16]. On the contrary, methanol is an energy-dense and reasonably stable liquid under normal conditions. It is considered as a potential alternative fuel that can be used as a gasoline blend for combustion engines or fuel cell vehicles. In addition, methanol serves a variety of functions as a feedstock for many chemicals in the chemical industry, such as methylamines, methyl halides and methyl ethers [17]. Several advantages of methanol, such as higher boiling points, lower production and improved safety make it can be widely utilized in the engines and fuel cells [18].

From a green energy transition perspective, Canada is an excellent candidate. Indeed, as shown in **Figure 1.1**, this country has significant natural resources and the second largest forest area in the world with 347 million hectares (9% of the world's forest). Considering only the province of Quebec, we arrive at an area of 76 million hectares (*i.e.* 18.92% of the Canadian forest and 2% of the world's forest area) [19].

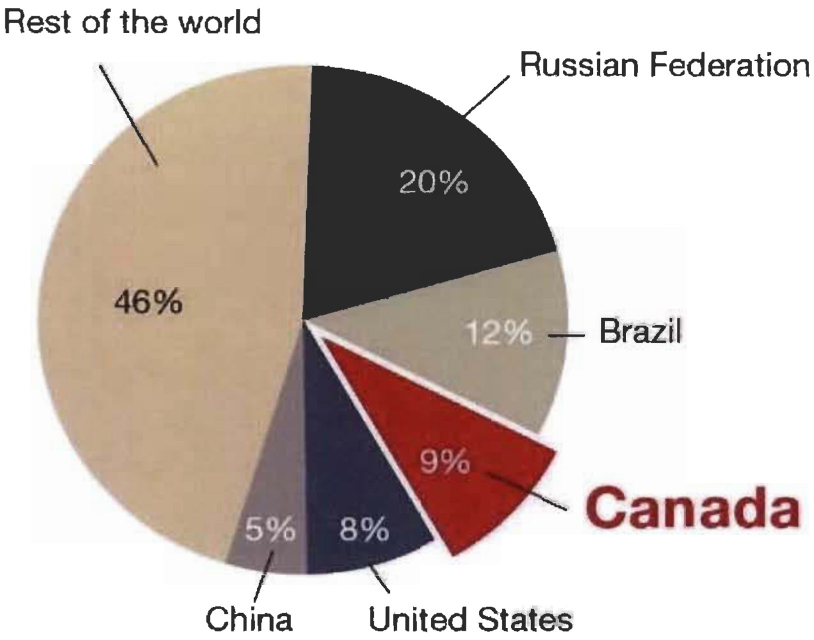


Figure 1.1 Global forest distribution [20]

Chapter 2 -Literature review

Lignocellulosic biomass is the most abundant organic material on earth and has the greatest potential as renewable feedstock to produce fuel, heat, and electricity [21]. Biomass consists mainly of cellulose, hemicellulose, and lignin polymers, other components are minerals, proteins, starch, nucleic acids, oils, and resins [22]. The content of cellulose in biomass ranges from 40 to 60 wt.%; lignin being the second largest component of biomass, accounting for 18 to 40 wt.%. Hemicellulose accounts for 20 to 40 wt.% of the biomass [23]. In recent years, due to the steady depletion of traditional fossil fuels but mainly due to growing concerns about environmental pollution and climate change, lignocellulosic biomass is becoming popular as an alternative solution [24]. In a biorefinery, almost all the types of biomass feedstocks can be converted into energy through applied specific conversion technologies. Through biological, chemical or thermochemical processes, the biomass is converted to its elementary components, which will then be used to produce molecules with high added value. Compared to biological processes, thermochemical treatments present several advantages in terms of treatment time and product yields. Among the thermochemical processes, gasification and pyrolysis have been extensively studied because these technologies have reached a certain level of maturity and are deployed in several sectors of industry, which allows today lignocellulosic biomass to be considered to be used on a large industrial scale.

2.1 Biorefinery concept

A biorefinery is a facility with integrated processes that aim at converting in an efficient, sustainable and flexible manner, biomass feedstock into multiple marketable bioproducts, biofuels, and energy (heat and power) [25]. The biorefinery (see **Figure 2.1)** includes a wide range of processes that convert biomass into products, which can then be used as value-added products, *e.g.* biofuels and chemicals.

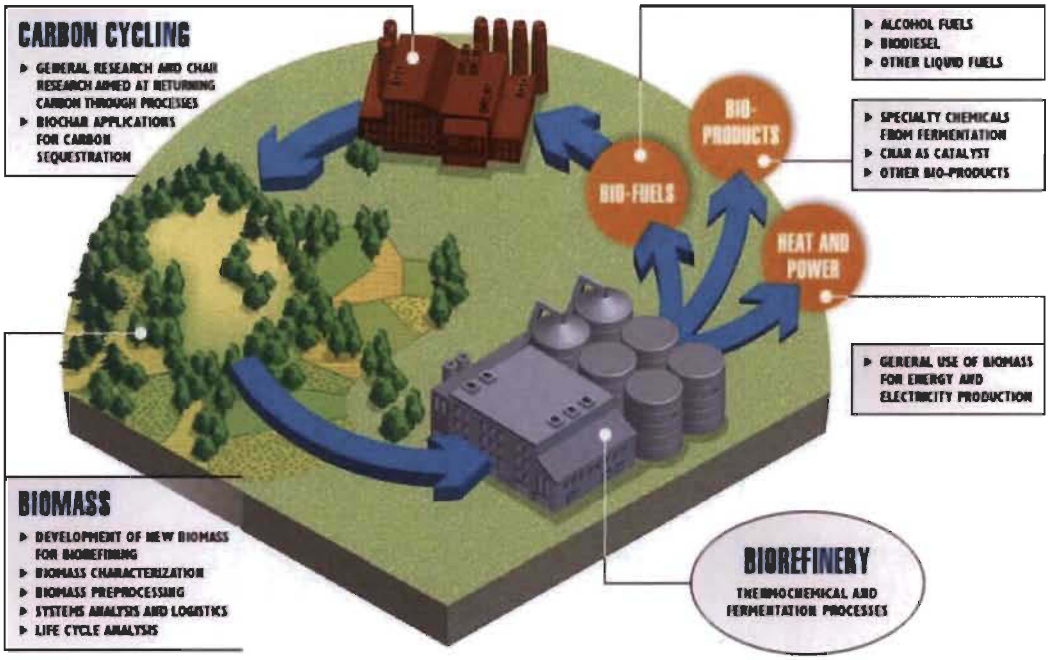


Figure 2.1 Scheme of biorefinery concept [26]

Several different biorefinery pathways exist, including thermochemical, biochemical, physical, and chemical processes [27] , as shown in **Figure 2.2**.

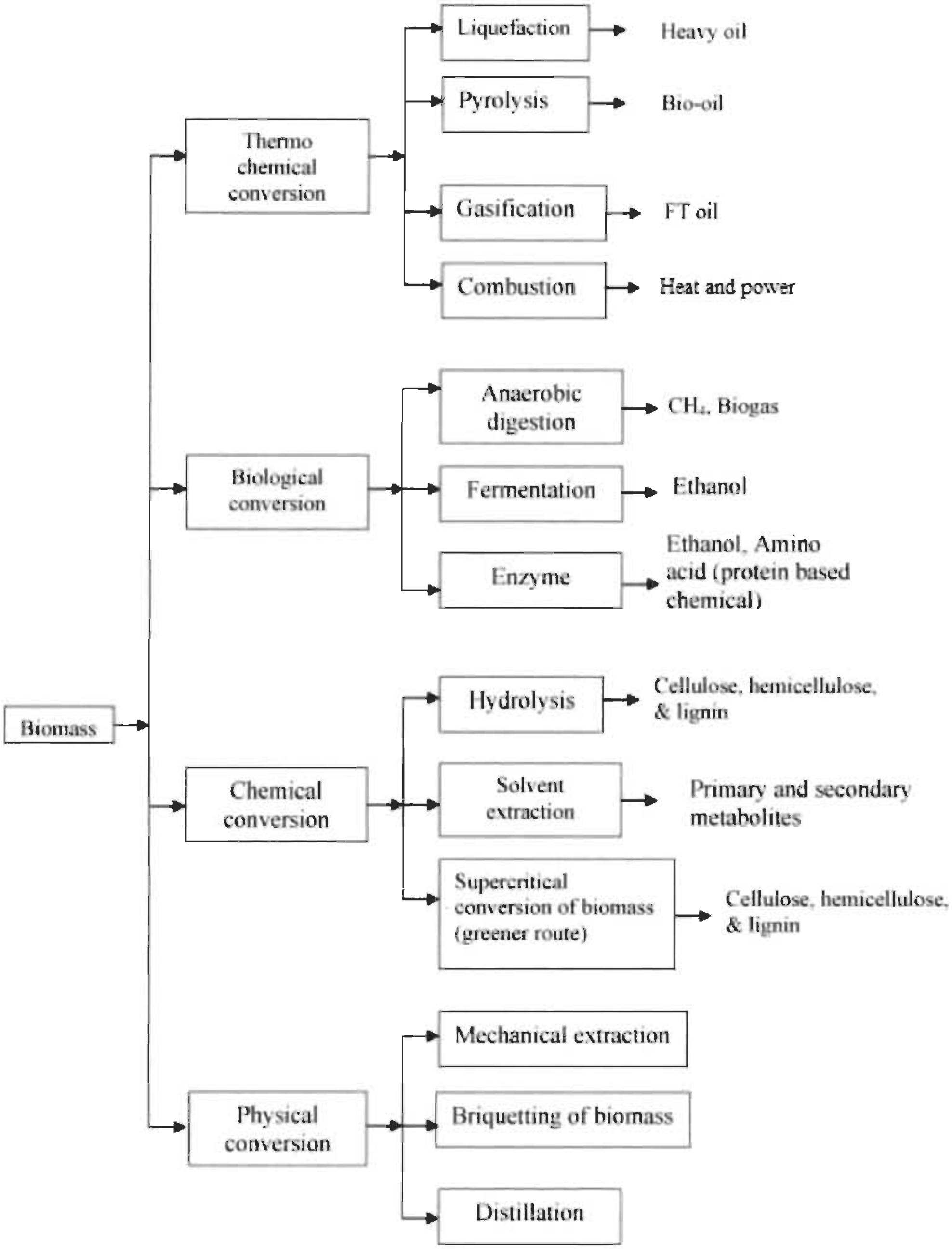


Figure 2.2 Scheme of biomass conversion processes [28]

Chemical processes in a biorefinery aim at producing high added-value products from reactants. The typical chemical pathway in biomass conversion is hydrolysis. Hydrolysis uses dilute or concentrated acid, alkaline or enzymes to depolymerize the raw biomass into sugars or other biomass derived chemicals [29]. Acid hydrolysis with dilute or concentrated acids could be used to generate sugar monomers from lignocellulosic biomass [30]. The highest glucose yields from concentrated acid hydrolysis reach up to 90% [31]. Another kind of hydrolysis is the alkaline hydrolysis, even though it is a fast reaction process, it can lead to degradation and formation of lactic acid [32]. For this reason, alkaline hydrolysis has been considered more suitable as a pre-treatment for biomass to perform subsequent enzymatic hydrolysis.

Biochemical processes operate commonly at lower temperatures and slower reaction rates than thermochemical processes. The common types of biochemical processes are fermentation and anaerobic digestion. The fermentation uses microorganisms and enzymes to convert biomass into recoverable products, usually alcohols or organic acids, including ethanol which are the main products obtained from fermentation [33]. The enzymatic hydrolysis requires pre-treatment to separate the lignocellulosic biomass into cellulose, hemicellulose, and lignin [14]. Several pre-treatment processes are used to remove the inhibitory substances, such as acid-based, hydrothermal, mild alkaline, oxidative, and chemical pulping processes [34]. Cellulose crystallinity, lignin and hemicellulose contribute to the resistance of biomass to enzymatic hydrolysis. So, biomass pre-treatment such as hot water and ammonia fibre expansion have proven necessary [35, 36]. Unfortunately, the cost of the enzyme remains currently an important bottleneck for such processes. Other concerns include slow reaction rates and low thermal stability of enzymes, which drastically reduces profitability on an industrial scale.

Anaerobic digestion involves the bacterial breakdown of biodegradable organic materials in the absence of oxygen over a temperature range from about 30 to 65°C. The main product of this process is biogas (methane, CO_2 and other impurities), which can be upgraded up to above 97% methane content and used as renewable natural gas (RNG) [37]. But the anaerobic digestion needs a pre-processing of the input material in order to ensure smooth process operations.

Compared to other processes, thermochemical processes are characterized by higher temperatures and faster conversion rates. They use high temperature, reactants and pressure to break biomass down into smaller parts which can be converted into biofuels, chemicals, heat and power. The kind of products generated by thermochemical processes depend on parameters such as temperature, pressure, feed rate, residence time, biomass particle size, and any quenching processes [38]. The low requirement of physical and chemical properties of the feedstock is the reason for the popularity of the thermochemical pathway. Other advantage of using a thermochemical process compared to other processes is that it is easier to break down the lignocellulosic material in a controlled manner to produce high concentrations of the desired intermediate products. In addition, thermochemical processes can be allowed to be carried out on a large scale [39]. Considering that Canada has abundant biomass resources [19], the thermochemical process becomes, for Canada, a most interesting pathway to produce biofuels.

2.2 Thermochemical processes

Thermochemical processing is the use of heat to facilitate the chemical conversion of biomass into energy and chemical products. The thermochemical conversion process is complex. The components, configurations and operating conditions used are somehow typical and comparable to petroleum refining processes [40]. Biomass can be converted into syngas by thermochemical conversion. Thermochemical processes consist typically of three main processes for converting biomass into energy and chemicals, *i.e.* combustion (complete oxidation), gasification (partial oxidation), and pyrolysis (thermal degradation without oxygen) [41]. Other thermochemical conversions are the torrefaction and hydrothermal liquefaction. These categories are classified according to the product and temperature range. The main pathways for the thermochemical conversion are represented in **Figure 2.3**.

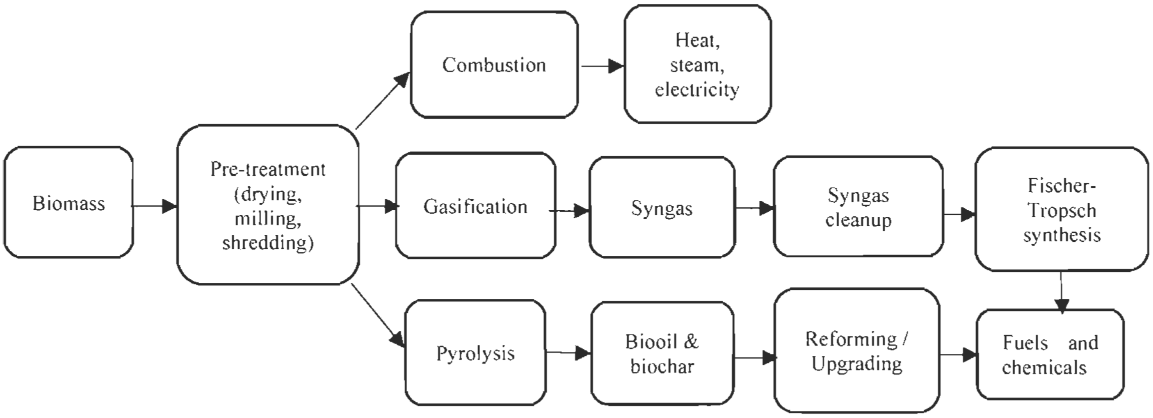
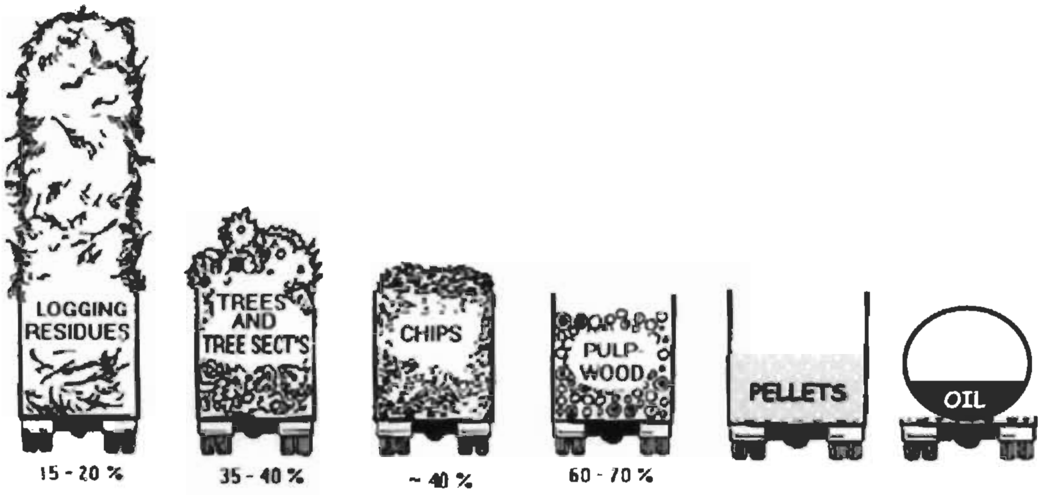


Figure 2.3 The overall scheme of the thermochemical conversion process [38]

The gasification converts biomass at high temperature with low oxygen content to produce syngas, which is a mixture of H_2, CO, CO_2 and CH_4 [42]. Through post-treatment, the syngas then can be directly used as biofuels or as a chemical platform to produce fuels such as Fischer-Tropsch (FT) fuels, dimethyl ether, ethanol, isobutane... or chemicals such as alcohols, organic acids, ammonia, and so on. Another thermochemical method is pyrolysis, which utilizes intermediate temperatures (300~600°C) without oxygen to convert the solid feedstock into liquid pyrolysis oil (or bio-oil), solid biochar and gases [43]. Combustion is the most common pathway for biomass conversion, which involves burning biomass in an oxygen-rich environment, mainly for heat and power applications [44].

2.2.1 Pyrolysis

Pyrolysis is the thermal decomposition of organic matter occurring in the absence of oxygen. It is an endothermic process that can be balanced energetically when a small percentage of oxygen is used. Biomass is thus transformed into liquid oil (bio-oil), pyrolysis char (biochar) and non-condensable gas [45-47]. Pyrolysis of organics is a complex process since it consists of simultaneous and successive reactions. In the process, the thermal decomposition starts at 350 °C ~ 550 °C and goes up to 700 °C ~ 800 °C in the absence of oxygen [48]. The macromolecules are cracked into smaller molecules, *e.g.* gases, condensable vapours (tars and oils) and solid biochar. Pyrolysis concentrates most of the chemicals and energy into a denser liquid oil or biochar [19, 20, 23, 24]. Although the liquids are not "oils" *per se*, there are commonly referred as bio-oil or pyrolysis oil that can be considered as highly oxygenated "crude oils". Pyrolysis has the advantage of converting biomass into an intermediate energy carrier that can be stored and transported economically. Pyrolysis oil has some advantages, compared to solid biomass. First (1), in comparison with the solid fuels, the pyrolysis oil contains a small amount of sulfur, nitrogen and ash. Therefore, its combustion produces less harmful gas emissions such as nitrogen oxides (NOx) and sulfur dioxide (SO_2), compared to conventional fossil fuels [49]. Second (2), the volumetric energy density is increased about 5 times more than the "bulk" biomass [49], as shown in **Figure 2.4**. It makes pyrolysis oil cheaper to transport over long distances. Third (3), pyrolysis oil can be stored in tanks, resists well against biodegradation and cannot be ignited at ambient temperature. Fourth (4), liquids are easier to process especially when pressurized processes are considered. This method gives the opportunity to take advantage of the biomass when large-scale plant is considered.



Proportion of solids in forest fuels. All loads have the same solid content. (Modified after Nilsson 1983).

Figure 2.4 Volumetric energy density depending on the forest biomass condition [50]

2.2.1.1 Pyrolysis process

Pyrolysis can be described as the thermal decomposition of an organic compound to produce solid, liquid (from vapour condensation), and gas products. Typically, the outcome and yield of products from biomass pyrolysis depend on the operating conditions: biochar production is favored by low temperatures, slow heating rates, and long residence time; pyrolysis oil production is favored by low or moderate temperatures, high heating rates, and short gas residence times; gas production is favored by high-temperatures, low heating rates, and long gas residence times [51]. Examples of product distributions obtained from fast and slow pyrolysis processes are summarized in the following **Table 2.1** [46] [52].

Table 2.1 Typical product yields obtained from fast and slow pyrolysis of wood

Process	Conditions	Product yield (%)		
		Liquid	Char	Gas
Fast pyrolysis	Moderate temperature and short residence time (< 5 sec)	75	12	13
Slow pyrolysis	Low temperature and long residence time (5-30 min)	30	35	35

(1) Slow pyrolysis is the most common way to produce biochar at slow heating rate, relatively low temperatures (from 300 to 600 °C), and long residence times. Slow pyrolysis is recommended for solid production (20~40% of charcoal). **Figure 2.5** presents a slow pyrolysis reactor for biochar product.

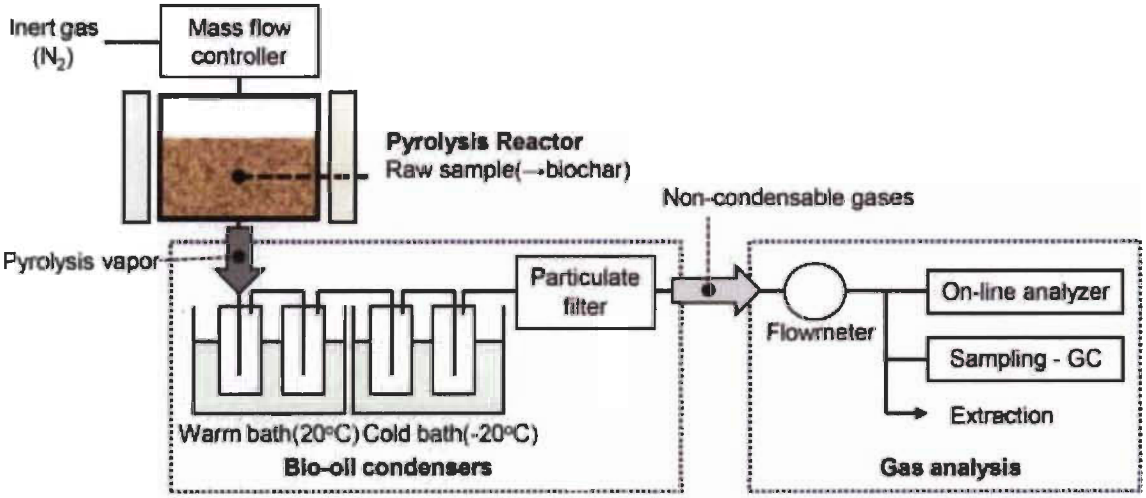


Figure 2.5 Schematic diagram of a slow pyrolysis reactor [53]

(2) Fast pyrolysis is the thermal decomposition of biomass to liquid oil as the main product. The process involves faster heating rates and much shorter residence times than

slow pyrolysis. Under proper conditions, the pyrolysis oil yield can reach as much as 75% [23]. A fluidized bed reactor for pyrolysis oil production is presented in **Figure 2.6**.

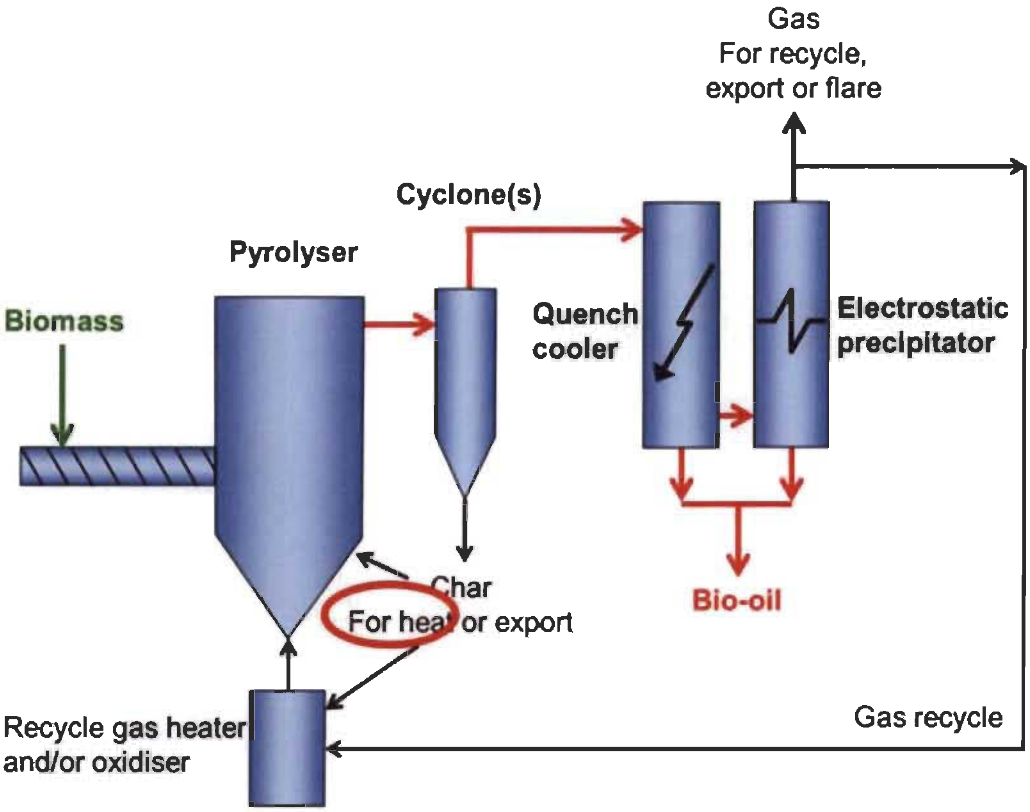


Figure 2.6 Schematic diagram of a fast pyrolysis fluidized-bed reactor [46]

2.2.1.2 Pyrolysis products properties

(a) Pyrolysis oil

Pyrolysis oil is a complex compound of numerous oxygenated hydrocarbons produced, for example, from lignocellulosic biomass. It includes carboxylic acids, sugars, alcohols, aldehydes, ketones, esters, furans, and aromatics, and the water content of pyrolysis oil generally ranges between 15 and 25 wt.% (the moisture content varies depending on the processes used to produce the pyrolysis oil) [54, 55]. Example of the chemical composition of pyrolysis oil is shown in **Figure 2.7** [56]. The composition of pyrolysis oil depends on the type of biomass feedstock, alkali content, reactor type, pyrolysis temperature, residence time, efficiency of char removal, etc. [45, 57, 58]. The pyrolysis oil can be separated into water-insoluble and aqueous fractions by water addition [59].

The water-insoluble fraction is deemed as more suitable for upgrading because it contains less oxygenated molecules and is compatible with crude oil. It is also considered as a high-value fraction due to its higher energy content compared to other fractions of the pyrolysis oil [60]. The aqueous fraction is a light brown liquid composed of water and mostly hydrophilic low molecular weight oxygenated compounds such as carboxylic acids, carbohydrates, aldehydes, ketones, and alcohols.

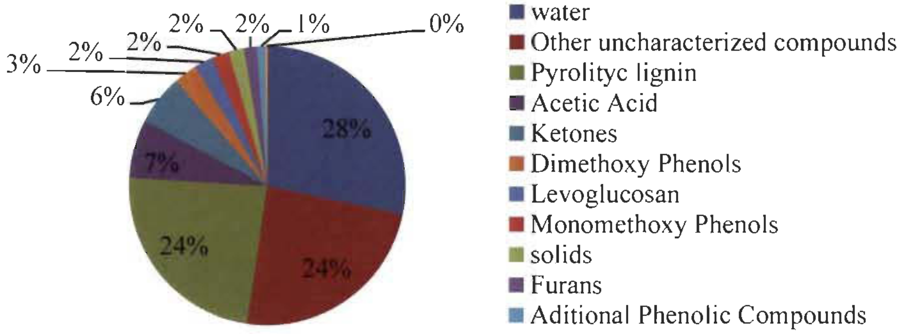


Figure 2.7 Chemical compounds detected in pyrolysis oil [56]

Pyrolysis oil has a similar appearance to heavy oil and is also considered as energy and as a hydrogen carrier. However, its properties (**Table 2.2**), such as the lower heating value, high oxygen content, volatility, high viscosity, acidity, chemical instability, and incompatibility with respect to standard petroleum fuels, limit the pyrolysis oil potential applications. Due to its chemical instability, the pyrolysis oil is subjected to aging, which leads to a decrease in hydrogen content when stored for a long time [61]. During storage, the pyrolysis oil becomes more viscous due to chemical and physical changes: many polymerization reactions occur, and volatiles are emitted with aging. Some studies found that the reactions and aging effects occur quite quickly, especially at higher temperatures but the effects are lessened if the pyrolysis oil is stored at low temperature [62]. To address the barriers of using bio-oil as a fuel, several approaches, *e.g.* increasing pH, filtration, and/or solvent addition, to modify and improve its quality have been explored [63]. The pyrolytic oil characteristics seriously limit its applications [64]. The high level of oxygenation of pyrolysis oil makes them more reactive when compared to traditional feedstock [65, 66]. Some of the main limitations of pyrolysis oil utilization include: high production cost, incompatibility with conventional fuels, and the lack of defined standards (quality, transportation and handling) [45, 67]. However, pyrolysis oil is still being considered for use as energy carrier due to its high enthalpy value. Canadian "fast pyrolysis" companies are in a stage of using biomass through a biorefinery approach. The pyrolysis oil can be directly used as an energy source. Even so, commercial production is still in its infancy. However, pyrolysis oil has a significant advantage over some other biomass fuels in that, once it is produced, it can be exploited to extract value-added products or even transport the liquid to a central processing plant for conversion into energy [68].

Table 2.2 Typical properties of wood pyrolysis oil, heavy fuel oil, diesel and gasoline [69-71]

Physical property	Pyrolysis oil	Heavy fuel oil	Diesel	Gasoline
Moisture content (wt.%)	15-30	0.1	-	-
pH	2.5	-	-	-
Elemental composition (wt.%)				
C	54-58	85	86	85
H	5.5-7.0	11.0	12.9	15.0
O	35-40	1.0	-	-
N	0-0.2	0.3	0.1	-
Ash	0-0.2	0.1	-	-
LHV(MJ/kg)	16-19	40	42	42
Viscosity at 50°C (cP)	17-100 (medium bio-oil) 100-600 (heavy bio-oil)	180	2.9	0.4
Solids (wt.%)	0.2-1	1	-	-
Distillation residue (wt.%)	Up to 50	1	-	-

(b) Biochar

In parallel with oil, charcoal-rich material is also produced by pyrolysis. This material is often named "biochar" and have a high ash content and porosity [72, 73]. Biochar produced from slow pyrolysis treatment of waste biomass is used for solid fuel applications [74]. However, biochar poses some difficulties, such as incompatibility with automobile engines and higher ash pollutants [37–39]. Nevertheless, biochar has several merits, including high carbon content, high stability, high porosity, and high surface area, which makes it an important product of pyrolysis [75]. The reaction temperature and raw materials are two main factors affecting the properties of biochar [76]. The increase of pyrolysis temperatures will lead to the increase of surface area of biochar, which facilitates higher sorption of chemicals such as pesticides [77]. The biochar elemental distribution has been studied in some research studies (**Table 2.3**). Approximately 70 percent of its composition is carbon, the remaining percentage consists of nitrogen, hydrogen and oxygen, among other elements. The biochar properties depend on several parameters, such as feedstock, process, residence time, heating rate, etc. [78].

Table 2.3 Biochar characteristics based on biomass source

Biomass source	**C (wt.%)**	**H (wt.%)**	**N (wt.%)**	**O (wt.%)**	**Ash (wt.%)**	**Calorific value (MJ/kg)**
Switchgrass [79]	60.7	4.0	0.8	8.7	25.9	19.4
Wheat straw [80]	71.1	3.0	0.3	25.6	-	28.1
Pine wood [81]	83.5	3.0	0.3	8.3	2.3	31.7
Mixed sawdust [82]	83.1	3.7	0.2	13.0	-	30.8

(c) Pyrolysis gas

In general, pyrolysis gas is not a desired product. Nevertheless, it is an inevitable product during the pyrolysis process. The pyrolysis gas, also named "syngas", is composed of CO_2, CO and a small amount of NOX, SO_X, H_2S, H_2, aldehydes, ketones, volatile carboxylic acids, and gaseous hydrocarbons. The major gas components are CO_2 and CO [83]. Pyrolysis gases have relatively low average calorific values, which are about 1.3 MJ/kg [84] and are produced in small volumes, difficulty to valorize.

2.2.1.3 Pyrolysis product applications

As described above, pyrolysis oil, biochar and syngas are produced from biomass through pyrolysis. Due to their specific properties, these three products can be used for many different applications, ranging from the synthesis of chemical reagents to soil improvement and energy production.

(a) Pyrolysis oil

Pyrolysis oil is composed of a complex mixture of more than 300 oxygenate compounds. However, numerous compounds and properties are close to crude oil, which makes pyrolysis oil useable in chemical and thermal applications [85]. Considering pyrolysis oil properties, multiple utilizations may be envisaged such as shown in **Figure 2.7**. In terms of thermal applications, pyrolysis oil can be used as a substitute to fossil fuels to generate heat, electricity, and chemicals, which can then be used in boiler, furnace, turbine, diesel engine, or power stations. In terms of chemical applications, upgrading pyrolysis oil to a transportation fuel is feasible. Transportation fuels such as methanol or Fischer-Tropsch products can be derived from pyrolysis oil by gasification and synthesis gas processes. Moreover, a wide range of chemicals can be extracted from pyrolysis oil, such as aldehydes, phenols, and L- (-)-glucose.

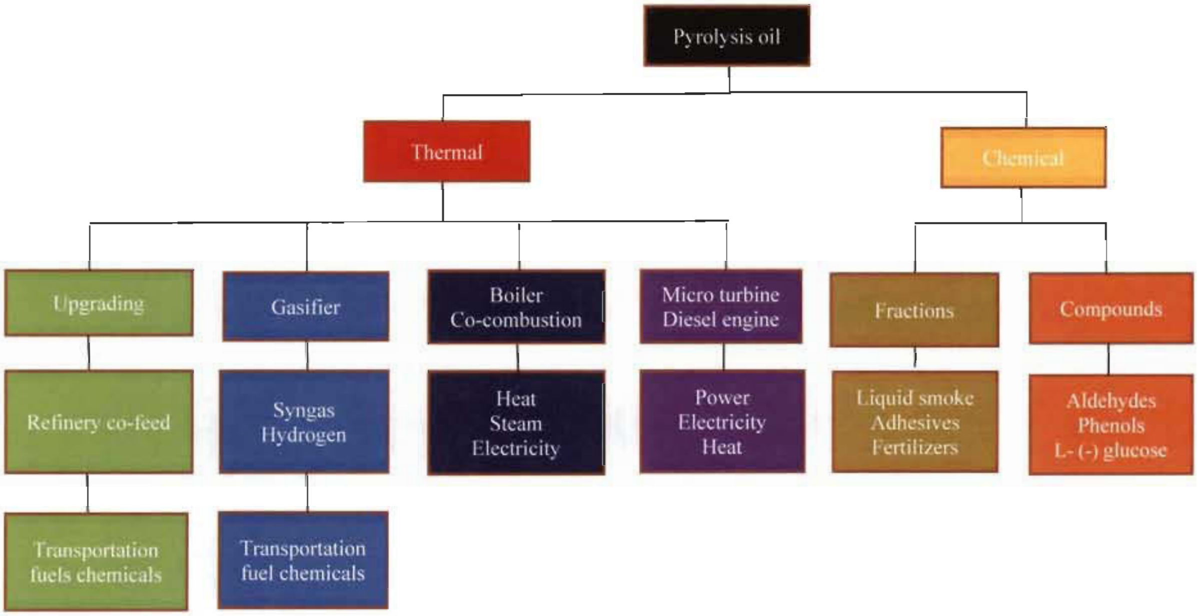


Figure 2.8 Various applications of pyrolysis oil [86]

(b) Biochar

The applications of biochar **(Figure 2.8)** include, for example, soil enhancer, bulking agent for composting, activated carbon, remediation of water and soil, energy, and carbon sequestration [87-90]. Biochar can also be used as an efficient sorbent for various organic and inorganic contaminants, due to its significant specific surface area and special structure [88]. Biochar has also positive effects on overall plant growth, since its basic physical and chemical characteristics such as pH, porosity and metal adsorption property, enable the slow release of nutrients and improve the soil quality. Such an application can potentially reduce the requirements of conventional dosage of fertilizers [91]. It is worth noting that the higher heating value of biochar produced from pine wood reach up to 31.7 MJ/kg, which makes that biochar can be used as a fuel (see **Table 2.3**).

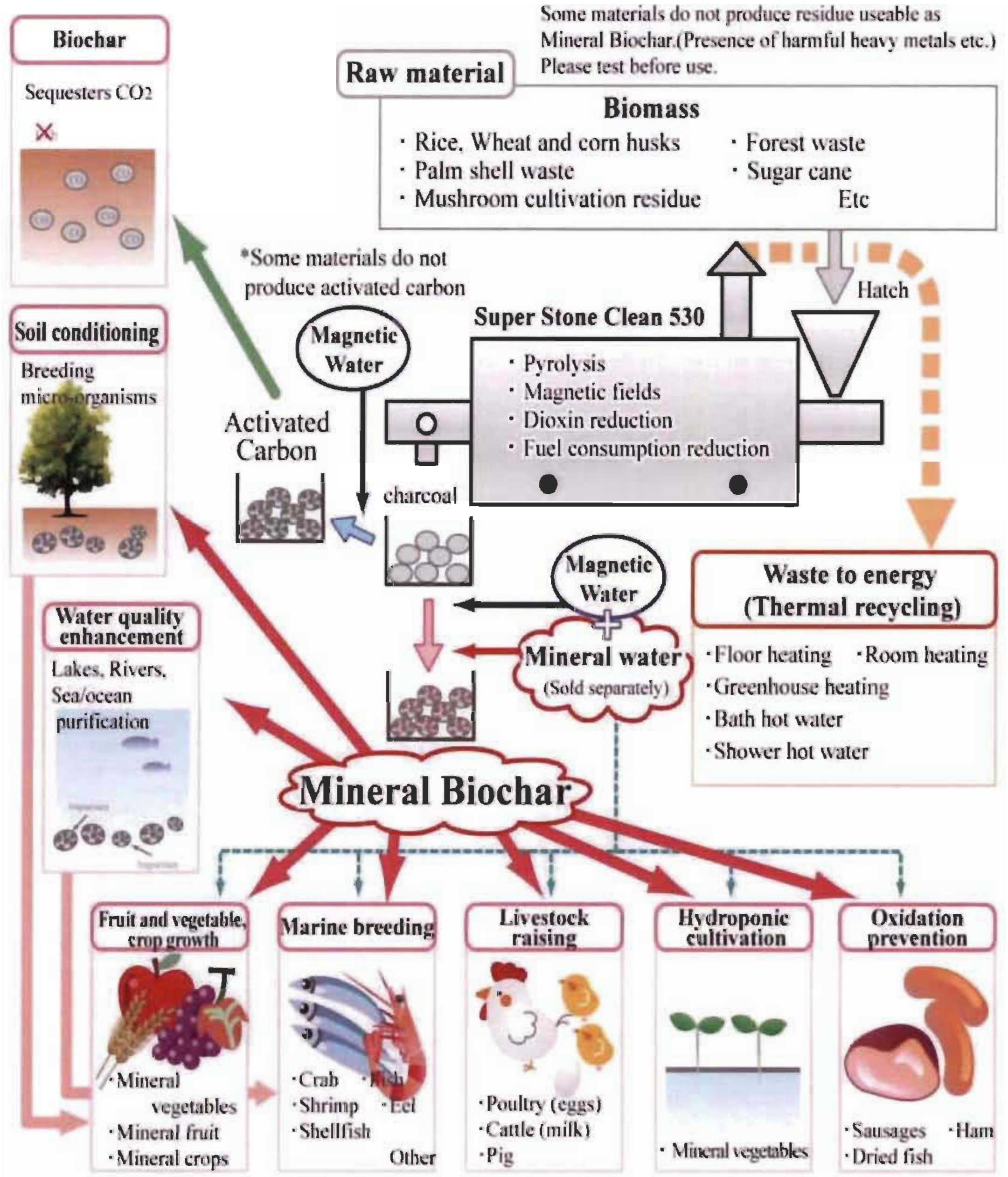


Figure 2.9 Applications of biochar [92]

(c) Biogas

Most of the time, pyrolysis gases are recycled in the pyrolysis process in order to provide heat [46]. The residual heat coming from the flue gas (burned syngas) can be used to preheat the biomass and decreases consequently the energy needs for biomass drying.

2.2.2 Gasification

Gasification is the process of converting carbonaceous materials into carbon monoxide, hydrogen, and carbon dioxide. That is achieved by making the feedstock react with a controlled amount of oxygen and/or steam at high temperature without combustion. During the gasification process, high temperatures break down feedstock into small molecules including H_2, CO, CO_2, CH_4 and water along with ashes, char, tars, as well as some amount of H_2S [93]. By this way, gasification process is able to separate pollutants and inorganic contents from the clean gas. The operating temperatures of gasification units generally range from 750 °C to 1100 °C [94], and sometimes even higher like in plasma gasification.

Figure 2.9 shows a schematic diagram of the gasification process reactions in a fixed bed gasifier (Updraft gasifier: air/stream is fed from bottom to top, while produced syngas leaves from gasifier top). Initially, feedstock, for example coal, is fed into gasifier top where coal is dried and heated up (zone 4). After that, the coal is devolatilized in a separate zone (zone 1). The first reaction, which occurs in zone 1, is carbon combustion to produce carbon dioxide and thus provide the necessary heat for the endothermic gasification reaction that occurs in the upper zones 2 and 3. In this section, charcoal is burned and transformed into ashes. Combustion gases and steam flow to the next zones 2 and 3, providing char to the lower combustion zone where syngas, such as H_2, CO and CO_2, is produced.

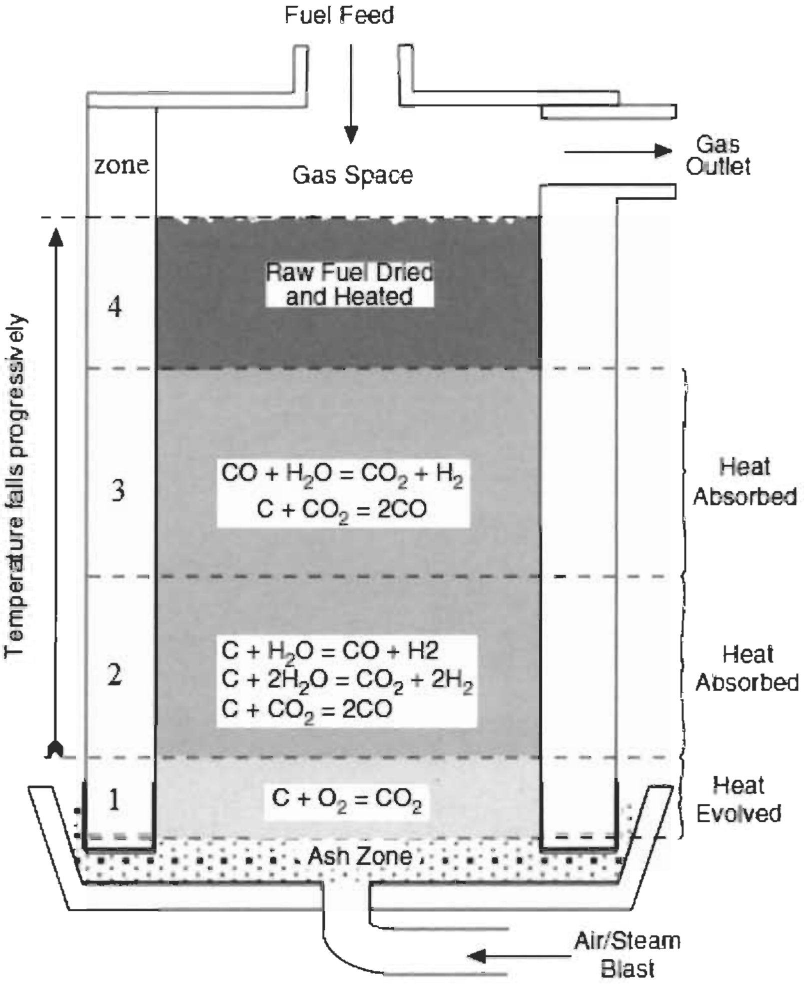


Figure 2.10 Schematic reaction of a gasification in a fixed bed [95]

During gasification, several physicochemical processes take place at different temperature ranges [95] (see **Table 2.4**).

Table 2.4 Physicochemical processes at each temperature range

Process	Reaction	Temperature
1	Drying	>150 °C
2	Pyrolysis	150~700 °C
3	Combustion	700~1500 °C
4	Reduction	800~1100 °C

Processes 1, 2 and 4 are endothermic reactions that absorb heat provided by the exothermic combustion and often by an external heating system. In the drying process, the moisture and the light fraction compounds are evaporated at low temperature (above 150 °C). The water vapour, organic liquids and non-condensable gases (such as CO, CO_2, H_2, and CH_4)

are formed and separated from the solid carbon or oil in the pyrolysis process part of the gasification. The combustion process, an exothermic reaction, oxidizes fuel constituents while the gasification process reducing them to combustible gases is an endothermic reaction. In reduction processes, carbon deposition (char) is formed at high temperatures.

Hydrogen-rich gas production through gasification from biomass resource such as industrial, agricultural, forestry waste have received much attention [96]. Considering the objectives of decrease in green house gases (GHG) emissions from fossil fuels consumption, biomass gasification for energy and fuels production is considered as one of the potential options to tackle this issue.

2.2.3 Combustion

Combustion is the simple method to convert fuel into heat with oxygen in air. Since biomass are primarily composed of carbon, hydrogen and oxygen, the main products from combustion are carbon dioxide and water. Biomass combustion systems, based on furnace type and operation conditions can produce hot gas, air and steam very efficiently, typically recovering 65~90% of the energy contained in the fuel [97].

2.3 Gas cleaning up and conditioning

As described above, gasification is a process dedicated to the production of syngas (mainly H_2, CO, CO_2 and CH_4). However, depending on biomass used, the mixture may contain impurities that will need to be removed in order to allow downstream operations, often using catalysts that can be poisoned by such impurities, and obtain high purity gases. These impurities can be solid particles (char and tars), organic molecules (sulfur, hydrocarbons, ammonia, halide, CO_2) and even metals [98].

Raw syngas cleanup is an essential process prior to syngas downstream application. In order to satisfy the operating conditions of downstream processes such as Fischer-Tropsch, methanol synthesis and fuel cell (see **Table 2.5**), a series of cleaning steps are applied to ensure the syngas quality. On the other hand, in order to enlarge the syngas application in the biofuel synthesis, its composition must be adjusted to obtain the appropriate H_2/CO molar ratio, for example using a Water Gas Shift (WGS) process. To ensure a deep removal of impurities, a series of gas post-treatment processes based on chemical and physical methods are applied.

Table 2.5 Contaminant specifications for Fischer-Tropsch, methanol synthesis and fuel cell [99, 100]

Process	Contaminants	Requirements
Fischer-Tropsch synthesis	Sulfur	< 60 ppb
	Halides	< 10 ppb
	Nitrogen	< 10 ppmv NH_3 < 0.2 ppmv NOx < 10 ppb HCN
Methanol synthesis	Sulfur (not COS)	<0.5 ppmv
	Halides	< 0.001 ppmv
	Fe and Ni	< 0.005 ppmv
Solid oxide fuel cell	Sulfur	< 1 ppmv
	Nitrogen	-
	Chlorine	< 10 ppmv

*ppb part per billion
*ppmv parts per million by volume

2.3.1 Particulates removal

The removal of solid particles and char contained in the syngas stream is regarded as the primary gas cleaning step. This first purification is typically performed by cyclones or filters at the outlet of the gasifier. This type of technology is widely applied in industry due to its low cost and significant level of performance for removing solid particles. Additionally, ceramic or candle filters can be used to improve the particulate removal from syngas [101].

2.3.2 Tar removal

The impurities include large molecular weight hydrocarbons, which are known as tars [102]. Tar deposits are accumulated in filters, pipes, engines, and other surfaces where they reduce the performance of downstream reactions. The content of these undesirable contaminants can be reduced by controlling the operating conditions such as temperature, biomass heating rate, reaction time, etc., appropriate reactor equipment design, and suitable gas conditioning systems [103]. For operation conditions, higher temperatures can reduce the generation of tar during the gasification process. Recently, catalytic removal has been widely used due to its high removal efficiency and good selectivity. Two types of catalysts are designed for tar removal: (1) natural mineral catalyst, such as dolomite, olivine, clay mineral, and iron ore, (2) synthetic catalysts, such as char, alkali metal carbonate, activated alumina, and transition metal-based catalyst [104]. For gas conditioning systems, tars can be destroyed by addition of steam and oxygen. For appropriate reactor equipment, some gas cleaning systems may be used to drastically reduce the tar and particulate components of the product stream. It is usually carried out by filtration and scrubbing of the output gas [105].

2.3.3 Sulfur removal

Sulfur is a know poison for the majority of catalysts and should therefore be eliminated. It is present in syngas as hydrogen sulfide (H_2S) or sulfur dioxide (SO_2). Hydrogen sulfide content in raw biomass-derived syngas depends on the type of feedstocks, ranging from 100 ~ 200 ppmv [106]. H_2S and SO_2 contents in the syngas can be high, especially when the syngas is derived from coal, heavy oil, biomass or waste materials. Hydrogen sulfide is a reactive compound and a high concentration in the natural gas could poison downstream catalysts and thus limit the syngas applications [107]. Therefore, the removal of sulfur is necessary to protect catalysts from poisoning and protect the turbines and pipes used in electricity generation from corrosion.

To avoid the sulfur poisoning in downstream, conventional plants are equipped with desulfurizer units that remove H_2S, SO_2 and COS (usually below 1 ppm) [108]. Conventional sulfur removal processes such as water scrubbing, amines scrubbing or zinc oxide sorption occur at low temperatures [109].

Amine scrubbing method is best suited for large-scale operations, with a decrease in H_2S content below to 10 ppmv and 30 ppmv total sulfur [110]. As described by Lien and *al.*, a simple water scrubbing column can be used to reduce the H_2S content [111]. Their results demonstrated that the concentration of H_2S in syngas decreased significantly with water level and increased with syngas flow rate, but the water scrubbing process can only be used on a small scale [111]. Research in the last few decades have also been focused on binary and ternary oxides of zinc [112], calcium [113], manganese [114], and ceria [115]. For example, ZnO beds are used as a polishing step to reduce the sulfur concentration down to a level lower than 0.01 ppm to meet the requirements for methanol and FT synthesis [116].

2.3.4 CO_2 removal.

The syngas coming from the gasifier can contain a considerable amount of CO_2. The oil, gas and chemical industries have been separating CO_2 from gas streams for decades. In most cases the CO_2 is removed in order to meet the downstream product requirements [117]. CO_2 removal can be achieved through different processes such as chemical (amine) or physical (Selexol® or Rectisol®) absorption.

The leading process for CO_2 capture is a chemical absorption, in which the solvent such as monoethanolamine (MEA), methyldiethanolamine (MDEA), and others amines or hot potassium carbonate can be considered as chemical absorption solvents [118]. The chemical solvents in such applications are less expensive than the physical method. However, the shortcomings of chemical processes cannot be ignored. First (1), high energy consumption during the solvent regeneration; second (2), the need to use of inhibitors and resistant materials to prevent corrosion; third (3), a limitation due to the minimum size of actual plant being 800 t/day; fourth (4), the degradation of solvents in the presence of O_2, SO_x and other impurities such as particles and other chemicals (HCl, HF and Hg, ...) [119].

Physical absorption such as the Selexol® process is a mature technology which has been used in the refinery industry, natural gas sweetening (removal of hydrogen sulphide) and syngas processing since the 1960s. The Selexol® process uses a mixture of different dimethyl ethers and polyethylene glycol, which provides a selective absorption of H_2S, COS, mercaptans and CO_2 from a variety of natural and synthesis gas streams [119]. The disadvantage of the Selexol® process is that it requires high operating pressure when absorbing gas. Nowadays, the Rectisol® process is a better method for CO_2 removal. Indeed, compared to Selexol®, Rectisol® can operate at 10 °C and at pressures up to 0.5 MPa which appears more advantageous for industrial applications [120]. Moreover, more than 98% of CO_2 and sulfur in the gas are removed. Methanol is used as a solvent in the Rectisol® process, since it's a better solvent to solubilize CO_2 than water, especially at low temperatures. The solubility of CO_2 in methanol is approximately four times higher than in water at ambient temperature, and more than eight times higher at temperatures below 273 K [121, 122]. Therefore, methanol has been industrially used as a physical absorbent of CO_2 in the Rectisol® method at 213~223 K [123].

2.3.5 Water gas shift

Gasification of natural gas does not allow syngas composition to reach the H_2/CO molar ratio of 2, as required for FT and methanol synthesis [124]. In order to reach a H_2/CO molar ratio of 2, a Water Gas Shift (WGS) unit is usually required to increase the H_2 fraction in syngas [125]. The WGS reaction (**Equation 2.1**) is an industrial process typically coupled with steam methane reforming, which has been extensively studied [126-128]. It consists of converting the CO in the syngas into CO_2 and H_2 by consuming steam (**Equation 2.1**), which is particularly interesting to counterbalance the H_2/CO imbalance resulting from biomass gasification. The WGS reaction is typically performed by using two units, a high temperature shift reactor (350~450 °C), and a low temperature reactor (200~215 °C) [129].

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad (\Delta H_{300K} = 41.21\ \mathrm{kJ/mol}) \qquad \textbf{Equation 2.1}$$

In the low temperature shift reactor, the typical composition of commercial catalysts has been defined as 32–33 % CuO, 34–53 % ZnO, and 15–33 % Al_2O_3. The active catalytic species is CuO, while the ZnO and Al_2O_3 structural supports have the key roles to prevent copper poisoning by sulfur and dispersion/pellet shrinkage, respectively. Low reaction temperatures must be maintained due to the susceptibility of copper to thermal sintering. These low temperatures also reduce the occurrence of side reactions [130].

In the high temperature shift reactor, the typical composition of commercial catalyst consists of a mixture of Fe_2O_3, Cr_2O_3 and MgO. Here, the active catalytic species is Fe_2O_3, while chromium and MgO are used both to stabilize iron oxide and prevent sintering [131]. Other more noble metals such as Pt supported on ceria have been widely studied, however they remain very expensive, which strongly limits their use on an industrial scale [132].

In the WGS process, the reactants must be desulfurized before they reach the catalyst reactor because most of the catalysts (*e.g.* CuO) are easily contaminated by sulfur. To circumvent this difficulty, much research has been carried out to develop new catalysts that are less sensitive to such type of poisoning and/or remain active when the reaction gas contains sulfur (*e.g.* H_2S). Without being exhaustive, we can refer to products such as iron cerium (Fe-Ce)-based [133-135] as well as nickel molybdenum (Ni-Mo)-based catalysts [136]. Moreover, these catalysts and especially the Mo-based can be used over a wide range of temperatures [137].

2.4 Methanol synthesis

Methanol is considered as an alternative energy carrier (*e.g.* rocket fuel), a medium for the storage and transportation of hydrogen, and a starting building block for many chemicals (*e.g.* lacquers, paints, inks, antifreeze, dyes, plastics). In addition to its traditional use as solvent, methanol is used as a raw material for the synthesis of many chemical platform molecules. For example, its conversion into formaldehyde (about 35% of the world's methanol production) is used to manufacture plastics, synthetic resins, explosives and certain crease-resistant fabrics. It is also one of the precursors for the manufacture of acetic acid (9%), methyl *tert*-butyl ether (MTBE) (25%) or simply the manufacture of alcohols [138]. The remainder is used in the fuel and energy sector. For example, it can be blended with different grades of gasoline for existing automobiles and hybrid flexible vehicles [139]. However, the last use remains limited because it can react with the aluminium in the tanks, forming methoxides capable of corroding the metal.

Commercially, methanol is produced from natural gas or coal steam reforming, mainly containing CO and H_2 along with a small amount of CO_2 [140]. The methanol synthesis process can be described by following equilibrium reactions:

$$\mathrm{CO} + 2\mathrm{H_2} \leftrightarrows \mathrm{CH_3OH} \quad (\Delta \mathrm{H_{300K}} = -90.77\ \mathrm{kJ/mol}) \qquad \textbf{Equation 2.2}$$

$$\mathrm{CO_2} + 3\mathrm{H_2} \leftrightarrows \mathrm{CH_3OH} + \mathrm{H_2O}\ (\Delta \mathrm{H_{300K}} = -49.16\ \mathrm{kJ/mol}) \qquad \textbf{Equation 2.3}$$

It is necessary to take into account carbon dioxide, because the synthesis of methanol can occur through two different reactions (**Equation 2.2**) and (**Equation 2.3**). Carbon dioxide appears in one reaction (**Equation 2.3**) as one of the reactants. Moreover, carbon dioxide acts as a promoter of reaction and helps to maintain the activity of the catalyst [141]. In this research, Rozovsky used labelled CO, and then concluded that the CO_2 is a precursor of methanol [142]. This is confirmed by Chinchen *et al.* who also used labelled CO_2 [143]. The ideal gaseous composition for methanol synthesis reactor is expressed based on a stoichiometric number M [139], which is defined in the following **Equation 2.4**. The stoichiometric number M should ideally be equal to 2.1 [144].

$$M = \frac{n(H_2)-n(CO_2)}{n(CO)_{CO}+n(CO_2)} \qquad \textbf{Equation 2.4}$$

Where n means molar fraction.

At the industrial scale, the purified syngas produced by SMR units usually contains the appropriate molar ratio of hydrogen to carbon monoxide. This mixture is then fed into a methanol synthesis reactor using a $Cu/ZnO/Al_2O_3$ catalyst at temperatures in the range of 200~400 °C [139, 145]. The exothermic reaction implies that a sufficiently high pressure is desired to shift the equilibrium towards methanol production. Wang *et al.* [146] indicated that the incorporation of ZnO enhances the activities of Cu-based catalysts due to the improved synergic effect. Using alumina in the catalyst produces two unique properties: first, it delays and protects the active catalyst particles from agglomeration; secondly, it enhances carbon monoxide adsorption and activation [147]. In addition to alumina, oxides of Mn and Zr have been reported as good promoters for the Cu-based catalysts [148]. Nobel Pd/CeO_2 catalyst allows a better syngas conversion and methanol selectivity, which has been reported as stable for 100 hours [149]. Deactivation of Pd/CeO_2 catalysts during methanol synthesis reactions under 30 ppm of hydrogen sulfide gas was studied by Ma *et al.* Syngas conversion was performed at 240 °C, using a feed H_2/CO molar ratio of syngas at a space velocity of 1000 h^{-1} and a 3.0 MPa pressure. The catalyst used by Ma *et al.* showed a high sulfur tolerance [150].

2.5 Fuel cells

Fuel cells directly convert the chemical energy of fuels into electricity and thermal energy, without any combustion. They require continuous flow of fuel, H_2 being the most common, and oxygen to operate steadily. Due to their high efficiency and low environmental impact, fuel cells have been extensively explored as a promising technology for clean and efficient power generation for stationary and mobile applications. They provide an opportunity to develop thermodynamic systems that generate electricity on the basis of electrochemical reactions by consumption of reactants from external sources [151].

The power cycle based on gasification and Solid Oxide Fuel Cells (SOFC) is called the Integrated Gasification Fuel Cell (IGFC) cycle. The IGFC cycle is similar to an integrated gasification combined cycle power plant, but the gas turbine power generation unit is replaced by a fuel cell power generation unit. SOFCs in the IGFC cycle can be operated to isolate a carbon dioxide-rich anodic exhaust stream, which efficiently captures carbon to address greenhouse gas emissions [152].

2.6 Aspen plus

Aspen Plus is a well-known process software that integrates optimization, sensitivity analysis and economic evaluation tools. It is highly appreciated by researchers and industrialists for its ability to simulate chemical reactions and processes, from unit operations to complete chemical plants. Aspen plus is also able to perform many of the core calculations of chemical engineering, such as mass balance, energy balance, vapor-liquid equilibrium, heat transfer, mass transfer, chemical kinetics, fractionation and pressure drop [153].

The advantage of Aspen Plus precise modeling of thermodynamic properties has led to its widespread use in the chemical and petroleum industries for steady-state and dynamic simulation, process design, performance modelling and optimization.

The process model is the complete layout of the engineering system and includes the following steps: flowsheet, chemical composition, operating conditions, and techno-economic analysis (TEA).

2.6.1 Flowsheet

A process model flowsheet encompasses the entire system. The flowsheet shows one or more inlet streams into the units (*i.e.* heat exchanger, compressor, reactor, distillation column, etc.) and throughout the process. The flowsheet also defines the flow rate and pathways of the various streams.

2.6.2 Chemical Composition

The process model specifies all the chemical components used in the system, from reactants to products.

2.6.3 Operating conditions

All unit operations in the process model are set under specific operating conditions (*i.e.* temperature, pressure, etc.). They are usually designed by the manager, since it is the operating conditions of the process that affect the outcome of the system.

Due to its ability to define each variable and depending on the validity of initial hypotheses and description of the process to be calculated, the Aspen software allows to make calculations which are as close as possible to reality, allowing to obtain results easily transposable experimentally.

2.7 Techno-economic analysis

Techno-economic analysis (TEA) is a methodological framework for analyzing the techno-economic performance of a process, product or service. TEA typically combines process modeling, engineering design and economic evaluation.

The purpose of TEA is to enable engineers in research and technical development to conduct TEA work in a consistent and transparent manner. In principle, TEA is a cost-benefit comparison using different methods. These assessment methods are used for following tasks: (1) evaluate the economic viability of a specific project; (2) investigate cash flows (*e.g.* financing issues) over the lifetime; (3) evaluate the scale and application possibilities of different technologies; (4) compare the economic quality of different technology applications providing the same service [154].

The internal rate of return (IRR) and net present value (NPV) are two of the most important indicators in the TEA. The IRR is a measure used in capital budgeting to estimate the rate of return on a potential investment. IRR is the interest rate at which the net present value of all cash flows from a project or investment equals zero. NPV is used in capital budgeting and investment planning to analyze the profitability of a projected investments or projects. DPBP is a measurement that allows a company or investor know when their investment will pay off, i.e. when the cash flow generated by the project will cover the cost of the project. The NPV and IRR calculation are shown in the following Equations.

$$NPV = \sum_{t=1}^{n} \frac{C_t}{(1+i)^t} - C_0$$ **Equation 2.5**

$$NPV = \sum_{t=1}^{n} \frac{C_t}{(1+IRR)^t} - C_0 = 0$$ **Equation 2.6**

$$\mathrm{DPBP} = \mathrm{A} + \frac{\mathrm{B}}{\mathrm{C}}$$ **Equation 2.7**

Chapter 3 – Objectives

3.1 Objectives

The goal of this study is to investigate the use of pyrolysis products as material for production of energy and power in fuel cells or the synthesis of biofuels.

Based on the literature review, pyrolysis oil as an alternative to biomass is seldom reported. Some researches demonstrated that pyrolysis oil can be used as an additive in engines, but its application is limited to large less efficient engines (e.g. ships) because of the pyrolysis oil high viscosity, oxygen content and instability at high temperature. Pyrolysis oil exhibits many advantages over biomass as it constitutes a first conversion of biomass. Therefore, it is clean (low ash, sulfur, and nitrogen content), has higher volumetric energy density and easier to process, which can then be considered for biofuel production. Consequently, in our work, pyrolysis oil is used as a feedstock to produce gases for use in fuel cell and biofuel synthesis. Once the pyrolysis oil is used to produce biofuels, the issue is to conduct a techno-economic analysis of the entire process for different feedstocks (biomass and biochar), so that it can be determined whether the use of pyrolysis oil to produce biofuel is economically competitive. The final challenge is to conduct sensitive analysis to minimize uncertainty in the techno-economic analysis.

To achieve the thesis global objective, several specific objectives must be completed:

a) Study of the conversion of the pyrolysis products into syngas through gasification using Aspen Plus simulations. Characterization of the syngas is achieved to know if it matches the specifications needed for direct use in fuel cells or for fuel synthesis (methanol synthesis). Several practical parameters such as gasification agent, gasification temperature, and moisture content in pyrolysis oil are tested.

b) Methanol synthesis from pyrolysis oil gasification by Aspen plus simulations. Firstly, gasification is used to convert pyrolysis oil into syngas. Syngas must then be cleaned and conditioned to reduce as low as possible pollutants such as HCl, NH_3, CH_4, H_2S in order to match the syngas specifications for further applications and to avoid specific issues like catalysts poisoning during methanol synthesis.

Moreover, the content of CO_2 in the syngas needs to be adjusted, which has an effect on methanol synthesis. Depending on the syngas content, the methanol yield will be significantly decreased. Finally, the operating conditions of methanol synthesis also needs to be explored and optimized.

c) Synthesis of methanol from different lignocellulosic bioresources (pine biomass, biochar, and pyrolysis oil) by using process simulation software Aspen plus. The whole process includes gasification, syngas post-treatment, and methanol synthesis with recycling system. For each raw material considered, a complete evaluation of the optimal parameters and maximum theoretical yields is carried out. Afterwards, techno-economic analysis of the production of methanol from biomass, biochar and pyrolysis oil at different plant scales is conducted to assess the competitiveness of pyrolysis oil in fuel production. Finally, a sensitivity analysis is conducted to identity the most important factors.

Chapter 4 – Materials and methods

4.1 Materials

In this project, we compared three feedstocks for methanol production: pyrolytic oil, biochar, and biomass. In order to best describe the properties of the different materials in simulations conducted using Aspen Plus software, experimental data from the literature were used. Pyrolysis oil was produced from beech wood chips in the pilot plant (200 kg/h) at BTG, the Netherlands [155]. Biochar was produced from rapeseed grown in Germany and processed by pyrolysis using a Pyroformer at the University of Aston [156]. For the biomass, pine trees from the region of Castilla La Mancha (Spain) were used [157]. **Table 4.1** describes the properties of each of the raw materials considered (elemental analysis and calorific value).

Table 4.1 Elemental and calorific analysis of pyrolysis oil, biochar and biomass

Element contents	**Pyrolysis oil [155]**	**Biochar [156]**	**Biomass [157]**
Carbon (wt.%)	30.4 ~ 37.7	60.3	52.7
Hydrogen (wt.%)	7.6 ~ 7.9	4.0	5.5
Oxygen (wt.%)	54.4 ~ 61.7	27.2	41.7
Nitrogen (wt.%)	< 0.01	4.20	0.01
Sulfur (wt.%)	< 0.01	0.01	0.08
Ash (wt.%)	-	4.2	2.7
Gross calorific value (MJ/kg)	17	24	20

4.2 Methods

The main purpose of this research is to design a comprehensive process model for methanol synthesis via pyrolysis oil. Aspen Plus process engineering software is applied to design the detailed process model and identify the influence of the operation conditions on syngas properties and methanol yield. After that, techno-economic analysis is performed based on the output of process models and literature data.

4.2.1 Modelling methodology

The use of biomass-based resource to produce methanol in a plant can be broken down into three steps. In the first step, feedstocks are gasified in a gasification plant to be converted into syngas. The syngas produced is assumed to be used in biofuel synthesis and fuel cells, which must therefore comply with very precise specifications. That is the reason why in the second step, it is treated in a syngas post-treatment unit (Rectisol® and water scrubber), after what the syngas will be suitable for biofuel synthesis. The treated syngas is thus compressed and introduced into a methanol plant to produce the desired biofuel.

4.2.1.1 Gasification

The gasification process is composed of four parts, namely drying, decomposition, combustion, and gasification. The RStoic (drying) unit is simulated as a drying process to extract moisture from feedstock. Then, the RYield (decomposition) unit is simulated as a decomposition process to convert feedstock into its elemental composition. The combustion process is simulated by the RGibbs (combustion) unit to complete chemical equilibrium. Finally, another RGibbs unit is used to simulate gasification where the syngas composition is calculated by minimizing Gibbs-free energy.

4.2.1.2 Syngas post-treatment

The syngas post-treatment is composed of four units, namely, a cyclone, a cooler, a water scrubber or Rectisol®, and a multistage compressor. A SSplit (separation) unit is used to simulate a cyclone to remove condensable materials such as char and tar. Then, high temperature syngas is cooled down by a Heater unit. Afterward, syngas is feed into a water scrubber or Rectisol® (RadFrac unit) to remove impurities such as particulates, ammonia, halides, and tars. In Rectisol® process, methanol is used as solvent that can remove part of CO_2 at appropriate operating condition. After quenching and removing impurities, the syngas is compressed to high pressure by using a multistage compressor (MCompr unit).

4.2.1.3 Methanol synthesis

After syngas post-treatment, the purified syngas is introduced into the methanol synthesis plant where hydrogenation of CO_2 and CO occurs. The methanol synthesis process is modelled by a REquil (RGibbs reactor) and RPlug unit (Kinetic reactor).

4.2.2 Economic analysis methodology

Economic analysis is a process of analyzing the strengths and weaknesses of a system or process economy. Present study takes into account the opportunity costs of resources employed and attempts to measure in financial terms both private and social costs and benefits of a project. It can also provide the project developer with a method to understand the key parameters impacting a project so that he is in a position to optimize the allocation of resources.

4.2.2.1 Total capital investment

The total capital investment refers to the purchase of equipment, materials, installation, instruments, electrical systems, buildings, service facilities, supervision, contractor's fee, etc. Total capital investment always makes a significant impact on the economic analysis. Indeed, when companies make large investments in capital goods, revenues do not increase immediately, and it takes a long time for company to become profitable. That is either evaluated as cumulative cash flow which includes all financial parameters (e.g. taxes, amortizing, credits, etc.) along the years as soon as initial investment is made or by the discounted payback period (DPBP).

4.2.2.2 Product cost estimation

The product cost estimation comprises raw materials cost, utilities cost, operating & maintenance cost, patents & royalties cost, depreciation cost, and local taxes & insurance cost. The cost of the product determines how much profit the company makes each year, the lower the cost of product, the more profit the company makes.

4.2.2.3 Profitability indicators

Three indicators were chosen to assess the project profitability: Net Present Value (NPV), Internal Rate of Return (IRR), and discounted payback period (DPBP). NPV is the value of all future cash flows discounted to the present over the entire life of an investment. The IRR calculates the rate of return provided by the project, DPBP calculates a period within which the initial investment of the project is recovered. Those indicators are used to estimate the profitability of potential investments.

4.3 Publication of work - approach

Based on the literature review and methodological discussion, we explored the potential use of pyrolysis oil in fuel cells and biofuel synthesis (bio-methanol). First, pyrolysis has been considered to produce gas for application in fuel cell or biofuel synthesis. The operating conditions of gasification and the properties of pyrolysis oil have been discussed. Then, our work has extended the application of syngas in biofuel synthesis by testing the effect of the operating conditions and properties of pyrolysis oil on methanol yield. Finally, a techno-economic analysis of the competitiveness of the pyrolysis oil route to biofuel synthesis compared to other feedstocks (biomass or biochar) has been carried out.

Following such an approach to our thesis work, we carried out our research and decided to present a thesis based on publications. Consequently, the core of the thesis work has been published in:

Article 1 (Chapter 5): “Simulation of Syngas Production via Pyrolysis-oil Gasification – Impacts of Operating Conditions on Syngas Properties”, BioResources journal; 2020; 15(1), 729-745.

Article 2 (Chapter 6): Methanol production from pyrolysis oil gasification- Model development and impacts of operating conditions, Zhihai Zhang, Benoit Delcroix, Olivier Rezazgui, Patrice Mangin. Accepted by Applied Sciences journal. Issue: Biorefineries and

Sustainable Biomass Conversion: Recent Advances - Section: Applied Biosciences and Bioengineering.

Article 3 (Chapter 7): "Simulation and Techno-Economic Assessment of Bio-methanol from Biomass, Biochar and Pyrolysis Oil", Zhihai Zhang, Benoit Delcroix, Olivier Rezazgui, Patrice Mangin, submitted to "Sustainable and energy technologies and assessments" August 12,2020. Under review.

Chapter 5 - Article 1: Simulation of Syngas Production via Pyrolysis-oil Gasification – Impacts of Operating Conditions on Syngas Properties

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5.1 Foreword

Preliminary potential applications of pyrolysis oil are published. The purpose of this part of the work was to explore potential applications of pyrolysis oils in fuel cells and fuel synthesis. In this section, a model simulating syngas production through pyrolysis oil gasification was established to predict the properties of syngas by changing the operating conditions such as agent, gasification temperature and moisture content in pyrolysis oil. The results are presented and discussed, focusing on the analysis of the effects of syngas composition, Lower Heating Value (LHV), H_2:CO molar ratio, etc.

5.2 Abstract

In this paper, a model simulating syngas production from pyrolysis oil gasification was developed, validated and used to predict the effect of operating conditions on syngas properties. The model consists of a process line that included units for pyrolysis oil drying, decomposition, combustion, and gasification. The model was validated using experimental data from literature, showing a good agreement between the model's results and the reference. Sensitivity analysis are carried out to evaluate the impacts of gasifying agent, temperature and pyrolysis oil moisture content on syngas composition, lower heating value (LHV) and H_2:CO molar ratio. Gasifying with air leads to a significant decrease in syngas LHV. Rising the temperatures from 200 to 600 °C, leads to higher

LHV and H_2:CO molar ratio. Above 600 °C, the LHV still increases, but the H_2:CO ratio slightly decreases. Moisture content in pyrolysis oil also has a major effect on the syngas composition. A high moisture content leads to high hydrogen content and low syngas LHV. Potential syngas applications are also discussed, *e.g.* for direct use in fuel cells and fuel production.

5.2.1 Keywords

Renewable resources; Syngas composition; H_2:CO molar ratio; Lower heating value; Aspen Plus model;

5.3 Introduction

The annual energy consumption is about 14000 Mtoe (Million tons of oil equivalent), 80-85% of which is supplied by fossil fuels [1]. The steady increase in global energy consumption has led to an alarming rise in emissions of CO_2, NOx, and SOx pollutions into the environment. The greenhouse gases (GHG) emissions from fossil fuels have a dominant influence on increasing atmospheric CO_2 concentration that translates into rising global temperatures and sea levels. Considering the rapidly increasing global energy demand and the growing concerns about the environmental challenges, renewable and sustainable energy (*e.g.* solar, wind, and biomass) is being viewed as a key solution to solve the energy crisis. Biofuels are regarded as a promising alternative to fossil fuels. Biofuels are considered as a renewable energy source since CO_2 emissions caused by their combustion are reabsorbed by the newly grown biomass [2].

Pyrolysis oil, also called bio-oil, is a complex blend of numerous oxygenated hydrocarbons produced from lignocellulosic biomass by fast pyrolysis process in the temperature range from 400 °C to 600 °C in the absence of oxygen [3]. This liquid contains carboxylic acids, alcohols, aldehydes, ketones, esters, furans, and aromatics [4]. The water content of pyrolysis oil generally ranges from 15 wt.% to 25 wt.% [5, 6]. Up to 70 wt.% of original dry biomass can be converted into pyrolysis oil [7]. The composition of pyrolysis oil depends on such factors as the type of biomass feedstock, alkali content, reactor type, pyrolysis temperature, residence time, efficiency of char removal, etc. [8-

10].

Pyrolysis oil offers several advantages over primary biomass sources, which means that there is potential to expand the scope of biomass feedstock application. The volumetric energy density is increased about 5 times over that of "bulk" biomass, making transportation economically more attractive, especially over long distances [11]. When large-scale remote biomass collection is considered, pyrolysis oil can first be produced locally and then transported to a central processing area to synthesize liquid hydrocarbons [12]. Second, pyrolysis oil being a liquid, makes its storage, transportation, processing, and pressurization easier. Pyrolysis oil can also be stored in tanks that resist well against degradation and cannot be ignited at ambient temperature. Third, pyrolysis oil contains only a small amount of sulfur, nitrogen and ash. Therefore, its combustion produces less harmful gas emissions such as nitrogen oxides (NOx) and sulfur dioxide (SO_2), compared to conventional fossil fuels [11]. Furthermore, as pyrolysis oil is produced through a low-temperature process, minerals and metals remain in the solid char.

Pyrolysis oil can be upgraded to liquid fuels and considered as an energy carrier. However, the drawbacks of pyrolysis oil are numerous and limit its applications. The use of pyrolysis oil offers some challenges due to its properties, such as the low LHV, high oxygen content, volatility, high viscosity, acidity, chemical instability, and incompatibility with respect to standard petroleum fuels [13]. Therefore, research is being conducted to upgrade pyrolysis oil and enlarge its scope of application. For example, Elliott *et al.* [14] investigated catalytic hydrocarbons as a way to convert pyrolysis oil into hydrocarbons, alkanes, and aromatics. Pyrolysis oil was being used to produce syngas through gasification [15, 16]. Bleeker *et al.* suggested using pyrolysis oil to produce pure hydrogen. The research showed that hydrogen can be produced through the oxidation of pyrolysis oil with a yield of 0.84 Nm^3/kg dry pyrolysis oil (LHV H_2/LHV oil = 0.4) [17].

During gasification, several thermochemical reactions take place at various temperature ranges: drying (>150 °C), decomposition (250 °C to 700 °C), combustion (700~1500 °C), and gasification (800~1000 °C). During drying stage, the moisture content is extracted from pyrolysis oil. The decomposition stage is initiated at about 250 °C when the labile bonds between the aromatic clusters are cleaved, generating light molecular weight fragments. This stage generates gaseous molecules such as H_2, CO, and CH_4, as well as light char and tar. After decomposition, pyrolysis oil undergoes combustion, which practically provides all the thermal energy required to sustain the endothermic reactions. This stage generates gaseous molecules such as CO_2 and H_2O. A series of endothermic reactions, including water gas, Boudouard, water gas shift, and steam methane reforming reactions occur at this stage [18]. Useful combustible gases, such as H_2 and CO, are produced at the gasification stage. At the end, the whole gasification process generates a syngas composed mainly of CO, CO_2, H_2, and CH_4. The production of CO, CO_2, CH_4, H_2, and steam in the whole process can be explained by the reactions given in (R-1 to R-8), which occur at various stages [19].

$C + 1/2\ O_2 \rightarrow CO$	- 111 MJ/kmol	Combustion reaction (R-1)
$C + O_2 \rightarrow CO_2$	- 283 MJ/kmol	Combustion reaction (R-2)
$H_2 + 1/2\ O_2 \rightarrow H_2O$	- 286 MJ/kmol	Combustion reaction (R-3)
$C + CO_2 \leftrightarrow 2CO$	+ 172 MJ/kmol	Boudouard reaction (R-4)
$C + 2H_2 \leftrightarrow CH_4$	- 75 MJ/kmol	Methanation reaction (R-5)
$C + H_2O \leftrightarrow CO + H_2$	+131 MJ/kmol	Water gas reaction (R-6)
$CO + H_2O \leftrightarrow CO_2 + H_2$	- 41 MJ/kmol	Water gas shift reaction (R-7)
$CH_4 + H_2O \leftrightarrow CO + 3H_2$	+ 206 MJ/kmol	Steam methane reforming reaction (R-8)

Clean ash free syngas is an important intermediate product for many processes, like those aimed at producing ammonia, hydrogen, methanol, and Fischer-Tropsch fuels. The syngas can also be used directly into fuel cells to generate heat and power [20]. Pröll *et al.* investigated the use of syngas produced from gasification and successfully fed into a combined heat and electrical power (CHP) unit rated at 8 MWth. Results demonstrated that CHP concepts based on biomass steam gasification can reach high electric efficiencies and high fuel utilization rates [21].

In this study, a model simulating syngas production via pyrolysis oil gasification was developed, validated and used to predict the effect of varying operating conditions on syngas properties. First, the modeling methodology is discussed, *i.e.* the assumptions, the description, and the validation of the model. Thereafter, results are presented and discussed, highlighting the impacts of various operating conditions on syngas properties, *i.e.*, syngas composition, LHV, and H_2:CO molar ratio. Lastly, the results are presented and discussed, highlighting the impacts of various operating conditions on syngas properties such as syngas composition, LHV, and H_2:CO molar ratio.

5.4 Modeling methodology

The main purpose was to design a comprehensive process model for pyrolysis oil gasification. Then, the model could be used as a predictive tool for optimization of the gasifier performance. Operating parameters such as gasifying agent type (steam, oxygen, and air), temperature, and pyrolysis oil moisture content were varied over wide ranges. The resulting syngas composition, LHV and H_2:CO molar ratio were investigated. Although gasifying pressure is also an important parameter that affects syngas composition, it was set to atmospheric pressure in this research for the purpose of avoiding the need more costly equipment that would be required for higher pressures.

5.4.1 Assumption

The whole model is based on the following assumptions:

(1) Gasification is assumed to be at steady state, isothermal, and thermodynamic equilibrium conditions [22].

(2) Pyrolysis oil devolatilization takes place instantaneously, and volatile products mainly consist of H_2, CO, CO_2, CH_4, H_2S, NH_3 and H_2O molecules.

(3) All gases are ideal gases and are uniformly distributed in the gas phase.

5.4.2 Model description

Based on the recommendation of the Aspen Plus User Guide version 10.2 [23], the Peng-Robinson equation of state with Boston-Mathias alpha function (PR-BM) was chosen to estimate all physical properties of the conventional components in the gasification process. The parameter alpha in PR-BM in the property package is a temperature dependent variable [23]. The Peng-Robinson property method is suitable for non-polar and weakly polar mixtures, applicable to all temperature and pressure ranges. Therefore, this function is recommended for gas processing, refinery, and petrochemical applications. The enthalpy and density model selected for both pyrolysis oil, are non-conventional components, HCOALGEN and DCOALIGT [22].

The Process Flow Diagram (PFD) in **Figure 5.1** shows the Aspen Plus blocks used to simulate the gasification process. The model consists of four stages in the modelling: drying (RStoic), decomposition (RYield), combustion (RGibbs), and gasification (RGibbs) [24]. The description of Aspen Plus block is presented in **Table 5.1**. The pyrolysis oil is specified as a non-conventional component in Aspen Plus and defined in the simulation model by using the ultimate and proximate analysis of pyrolysis oil. The NC (nonconventional) definition of pyrolysis oil is shown in Appendix A. The data for pyrolysis oil is given in **Table 5.2** and was extracted from previous work presented in the literature [12].

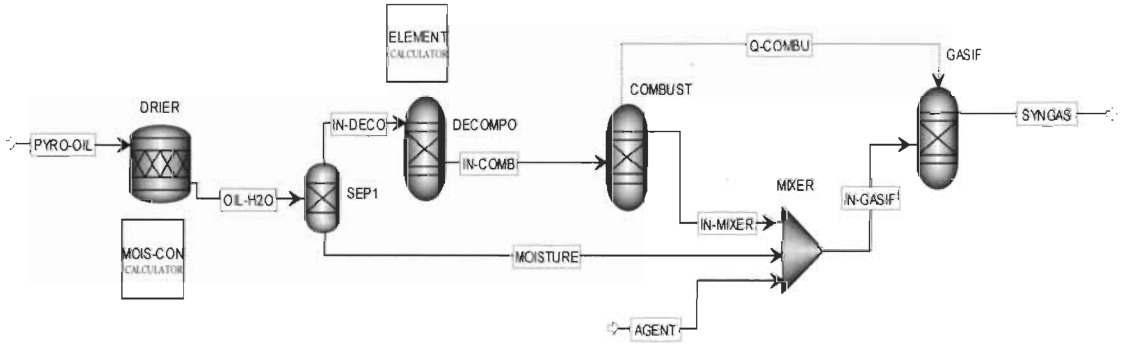

Figure 5.1 Aspen Plus simulation of pyrolysis oil gasification Process Flow Diagram

Table 5.1 Description of blocks used in the gasification model

Aspen Plus block ID	**Flowsheet Block ID**	**Description**
RStoic	DRIER	Reactor with known conversion rate - used to extract moisture from pyrolysis oil. Operation at 150 °C.
Sep	SEP1	Used to separate moisture from the pyrolysis oil.
RYield	DECOMPO	Yield reactor- used to decompose non-conventional pyrolysis oil into its components by FORTRAN statement. Operation at 500 °C.
RGibbs	COMBUST	Gibbs free energy reactor- used to complete chemical equilibrium by minimizing Gibbs free energy. Operation at 800 °C.
Mixer	MIXER	Used to mix pyrolysis oil and moisture
RGibbs	GASIF	Gibbs free energy reactor- used to calculate syngas composition by minimizing Gibbs

		free energy. Operation in the temperature range from 200 °C to 1200 °C.

*Drying Constant: 0.325 of pyrolysis-oil

Table 5.2 Pyrolysis oil composition defined in Aspen Plus

Proximate analysis (wt.%)	
Moisture content	32.5 ~ 43.7
Ultimate analysis (wt.%)	
Carbon	30.4 - 37.7
Hydrogen	7.6 - 7.9
Nitrogen	< 0.01-0.27
Oxygen	54.4 - 61.7
Sulfur	< 0.01

A kinetic free equilibrium model was developed in Aspen Plus to simulate the gasification process through the four stages. Aspen Plus simulation calculation method and syngas potential application are presented in Figure 2. Firstly, the moisture was extracted from pyrolysis oil, pyrolysis oil was fed into the RStoic block to model the drying process controlled by the FORTRAN statement in the calculator block that calculated moisture content. Secondly, dry pyrolysis oil was fed into a decomposition reactor where pyrolysis oil decomposes into its elemental components (C, H, O, N, S, etc.), the distribution of which was specified using a FORTRAN statement in a calculator block according to the pyrolysis oil ultimate analysis. RYield block is used to convert non-conventional pyrolysis oil into conventional components by using FORTRAN statements in the calculator block. Thirdly, combustion of pyrolysis oil is modeled by a Gibbs reactor. The RGibbs block handles the complete chemical equilibrium by minimizing the Gibbs free energy at an elevated temperature. The decomposed pyrolysis oil enters the RGibbs block where partial oxidation and combustion reactions occur. After combustion, the produced syngas was mixed with steam originating from pyrolysis oil moisture in a MIXER block. The mixture was fed into the gasification unit. Lastly, gasification is also modeled using a Gibbs reactor. The RGibbs block handles the calculation of the syngas composition by minimizing Gibbs free energy [25]. Afterward, the produced syngas will be applied in fuel cell or fuel production.

5.5 Results and discussion

The validated model is used alone with a sensitivity analysis to identify the effect of varying operating conditions on syngas properties. The key parameters investigated in this analysis are the type of medium (gasifying agent), gasification temperature, and moisture content in pyrolysis oil. The key syngas properties affected by the operating conditions and analyzed in this work are the syngas composition (given in mole fraction), the LHV and the H_2:CO molar ratio.

The LHV parameter represents the amount of heat released when a substance undergoes complete combustion with oxygen under standard conditions prior to condensation of water vapor produced. This parameter is meaningful when the generated syngas is used for energy applications, *e.g.* as a feedstock for fuel cells to generate electricity and heat (combined heat and power unit). The LHV can be calculated as a function of the molar fraction of molecules in the gaseous mixture as follow **Equation 5.1** [19]:

$$\text{LHV (MJ/Nm}^3) = (CO * 126.36 + H_2 * 107.98 + CH_4 * 358.18 + C_2H_2 * 56)/1000 \qquad \textbf{Equation 5.1}$$

If fuel synthesis applications are targeted, the main concern is the syngas composition (mole fraction of each element), with a particular focus on the H_2:CO molar ratio. For example, methanol synthesis and Fischer-Tropsch synthesis require a value of 2 for this ratio as follow **Equation 5.2** [26, 27].

$$H_2\text{:CO molar ratio} = n(H_2)\text{: } n(CO) \approx 2 \qquad \textbf{Equation 5.2}$$

5.5.1 Validation of results

The flowsheet in Aspen Plus is presented in Appendix B. The simulation model was validated by using experimental data from a study achieved by Van Rossum *et al.* [12] on the gasification of pyrolysis oil. The comparison between the reference experimental data and our simulation results is presented in **Table 5.3**. In the reference research, pyrolysis oil was used to produce syngas through gasification in a fluidized bed with nickel-based catalysts at 800 °C. The modeled syngas concentration is in good agreement with the experimental results, except for the concentration of carbon monoxide and methane. The most significant discrepancy is the high amount of methane (5.1 mol%)

obtained in the experimentations, compared to the amount predicted by the model (0.3 mol%). This trend of excess methane with respect to thermodynamics is well known. The methane reforming reaction (R-8) is limited due to slow kinetics at low temperature [28]. For the same reason, the actual amount of carbon monoxide found in the gas phase is smaller than that simulated by the kinetic-free model (see R-8). Nearly 90% carbon converted into syngas, the remaining carbon was converted into tar in Van Rossum research. In this research, tar was not defined in Aspen Plus, carbon was 100% converted into syngas. **Table 5.4** also presented the energy consumption of pyrolysis oil gasification based on a flow rate of 100 kg/h. As we can see that during the combustion stage, it releases 415.85 kW heat, which can be used for the gasification stage. The entire gasification process requires a total of 324.70 kW.

Table 5.3 Comparison between experimental and simulated results

Syngas composition (mole %)	Experiment [12]	Model	Difference (model - experiment)
H_2	55.5	55.9	0.4
CO	19.3	24.0	4.7
CO_2	19.0	19.8	0.8
CH_4	5.4	0.3	-5.1
C_2H_6	1.0	trace	-
H_2S	-	trace	-
NH_3	-	trace	-

Table 5.4 Energy Consumption for Each Stage

Case	Drying (150 °C)	Decomposition (500 °C)	Combustion (800 °C)	Gasification (800 °C)	Total
Energy Consumption (kW)	24.50	643.74	- 415.85	72.31	324.70

5.6 Effect of operating conditions

5.6.1.1 Effect of gasifying agents

The equivalence ratio is defined as the ratio of the actual fuel/air ratio to the stoichiometric fuel/air ratio required for complete combustion. In this research, the equivalence ratio of agent to pyrolysis oil was set at 0.2. Runs were conducted with three gasifying agents, *i.e.*

oxygen, steam, and air. **Figure 5.2** presents the syngas composition for each gasifying agent used in the process. **Figure 5.3** presents the LHV and H_2:CO molar ratio for each gasifying agent. Syngas produced with steam had the highest content in hydrogen (53.3 mol%) and carbon monoxide (33.0 mol%). As a result, the syngas LHV is also highest (9.89 MJ/Nm^3) in this configuration. Gasifying with oxygen leads to a smaller LHV because oxygen reacts with hydrogen and carbon monoxide within the mixture. However, the H_2:CO molar ratio was higher when gasifying with oxygen (1.85) compared to gasifying with steam (1.61). The higher ratio is favorable for fuel synthesis. Finally, gasifying with air leads the lowest LHV, because oxygen is diluted to 21% in this agent, the balance being mostly inert nitrogen. This trend of LHV variation as a function of gasifying agent is in good agreement with experiment with experimental results from Gil *et al.* [29], where three types of gasifying agents were used in biomass gasification and syngas distribution were tested. The H_2-content in the syngas was highest when steam was used as gasifying agent. Gasifying with air led to the lowest syngas LHV.

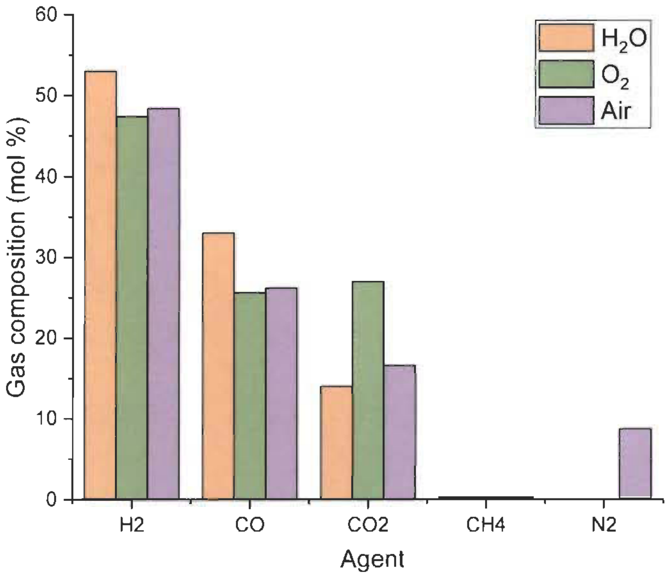

Figure 5.2 Effect of gasifying agent on syngas composition (at 800 °C).

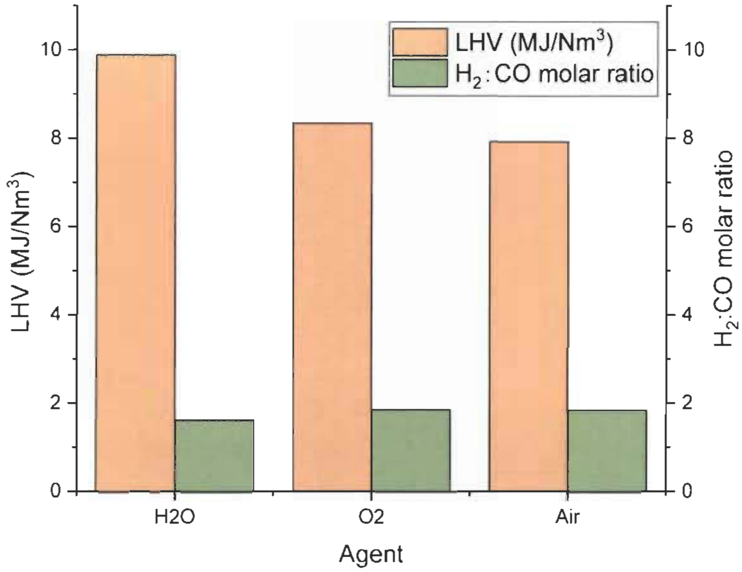

Figure 5.3 Effect of gasifying agent on syngas LHV and H_2:CO molar ratio (at 800°C).

5.6.1.2 Effect of gasifier temperature

The gasification temperature is an influential parameter in syngas production. **Figure 5.4** and **Figure 5.5** show the effect of temperature on syngas composition, LHV, and H_2:CO ratio. The gasifier temperature ranged from 200 °C to 1200 °C. At low temperatures, the syngas is composed mainly of methane and CO_2. The concentration of methane decreases with increasing gasifier temperatures from 200 °C to 600 °C. This decrease is due to the steam methane reforming reaction (R-8), which converts methane into hydrogen and CO. The carbon and hydrogen in pyrolysis oil are not completely converted into syngas at low temperatures. However, when the temperature increases from 200 °C to 800 °C, the content in carbon monoxide and hydrogen greatly increases. This trend is consistent with Boudouard (R-4) and water gas (R-6) reactions, *i.e.* the carbon in pyrolysis oil reacts with water and carbon dioxide to generate hydrogen and carbon monoxide. The carbon dioxide content thus decreases with temperature increase. High operating temperatures favor the production of hydrogen and carbon monoxide. The H_2:CO molar ratio reaches a maximum of 2.41 at 600 °C, and then gradually decreases with increasing temperature within this range. At high temperatures (above 800 °C), the concentrations of hydrogen and carbon dioxide slightly decrease, while the concentration of carbon monoxide slightly increases. This trend is attributed to the water gas shift reaction (R-7) becoming thermodynamically unfavorable. Due to its exothermic nature, this reaction is thermodynamically favoured at lower temperatures. Syngas LHV continuously increases (first rapidly, the more slightly) as the gasifier temperature rises, leading to higher production of carbon monoxide and to a syngas LHV of 9.51 MJ/Nm^3 at 1200 °C. The trend of H_2 and CO concentration, syngas LHV value and H_2:CO molar ratio was in good agreement with Dai study [30]. In his research, the H_2 concentration increases with increasing temperature and then decreases slightly. Syngas LHV value increases as the gasifying temperature increase. Syngas producing from high temperature is beneficial to fuel cells applications and harmful to fuel synthesis.

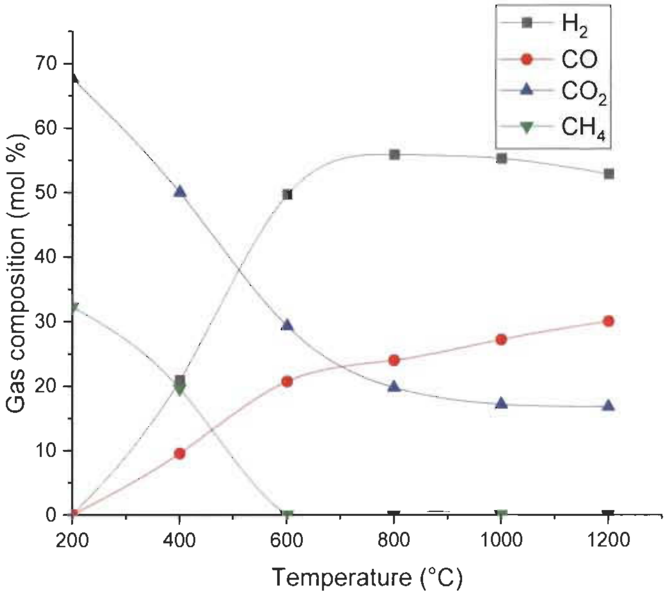

Figure 5.4 Effect of gasifier temperature on syngas composition.

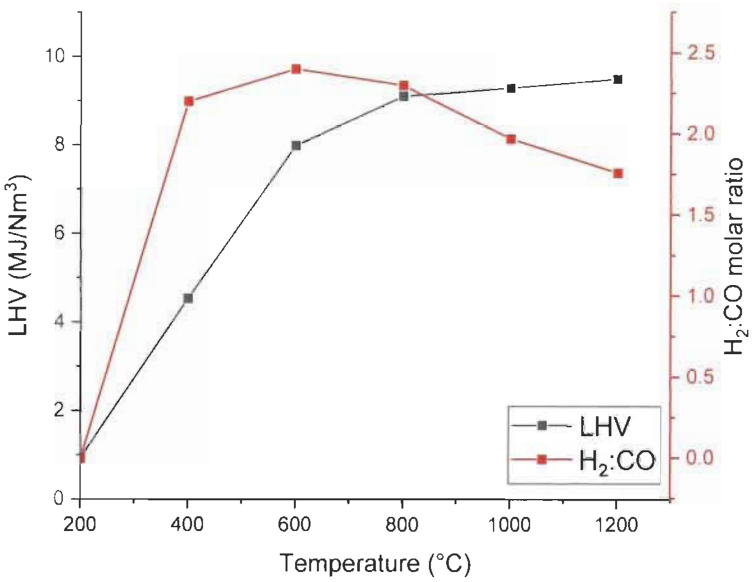

Figure 5.5 Effect of gasifier temperature on syngas LHV and H_2:CO molar ratio.

5.6.1.3 Effect of pyrolysis oil moisture content

Figures 5.6 and **5.7** present the effects of a pyrolysis oil moisture content ranges from 10 to 50 wt.% on syngas composition, H_2:CO molar ratio, and LHV. According to the water gas shift (R-7) and water gas reactions (R-6), an increasing moisture content leads to an increase in the mole fractions of hydrogen and carbon dioxide, and a decrease in the amount of carbon monoxide. As a result, the H_2:CO molar ratio gradually increases from a minimum of 1.5 to a maximum of 2.24 at 50 wt.% moisture content. However, the LHV decreases from 10.1 to 9.2 MJ/Nm^3 over the same range, due to the decrease in carbon monoxide content. Therefore, if energy applications are targeted (heat and power generation), the moisture content in pyrolysis oil should be kept low. If fuel synthesis (*e.g.* methanol or Fischer-Tropsch fuels) is targeted, the moisture content can be optimized at 40% to adjust the syngas composition, especially the H_2:CO molar ratio.

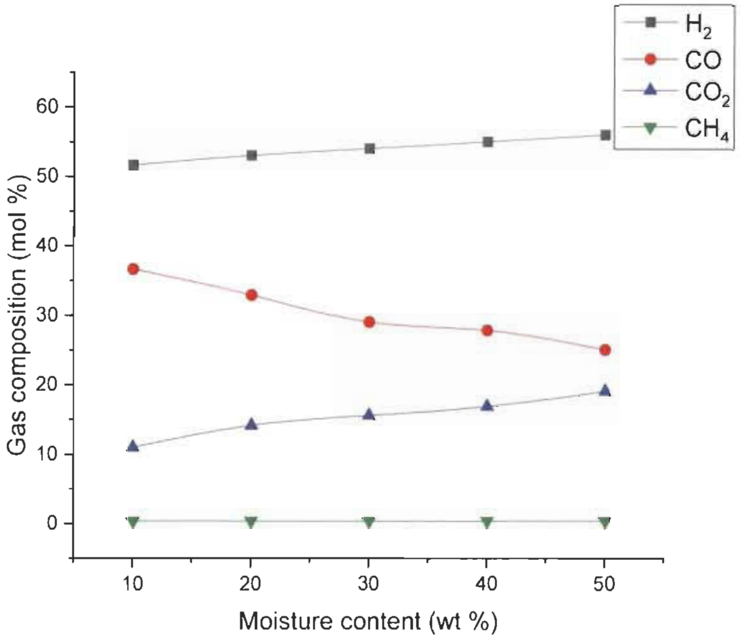

Figure 5.6 Effect of pyrolysis oil moisture content on syngas composition (at 800 °C).

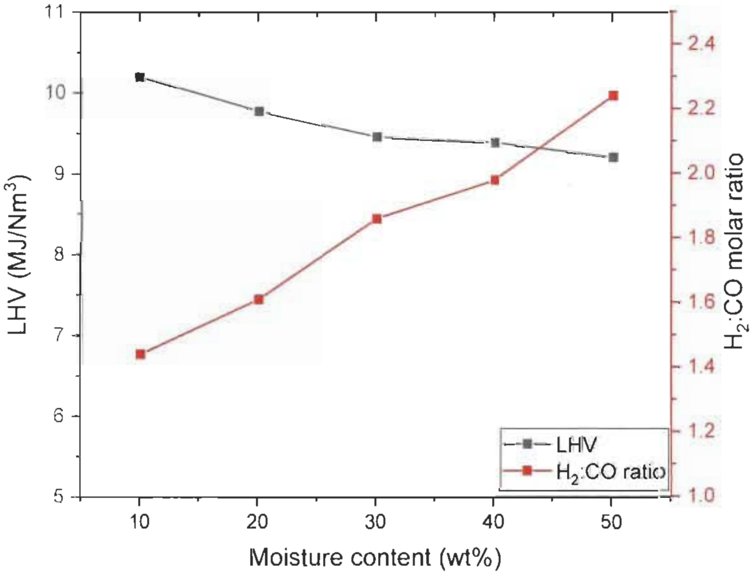

Figure 5.7 Effect of pyrolysis oil moisture content on syngas LHV and H_2:CO molar ratio (at 800 °C).

5.7 Conclusions

The objective of this study was to develop a model, simulate and predict the steady state performance of a pyrolysis oil gasification process. The results obtained from simulation are in good agreement with experimental data from literature. Therefore, the model can predict gasification performance over a wide range of operating conditions. The influence of various gasification agents was investigated by using a fixed equivalence ratio at 800°C. At these conditions, the syngas LHV was maximized at 9.89 MJ/Nm^3 by using steam as agent. High temperature favours to the production of carbon monoxide, which results in high syngas LHV (9.51 MJ/Nm^3). High moisture content in pyrolysis oil leads to a syngas that is rich in hydrogen, but poor in carbon monoxide content. As a result, the syngas LHV decreases with increasing moisture content in pyrolysis oil, but the H_2: CO molar ratio increases to 2.24 at 50 wt.% moisture content in pyrolysis oil.

If the syngas is applied to fuel cells to generate heat and electricity, then the O2 and air cannot be used as agent, which can reduce the LHV value of the syngas. Moisture content in pyrolysis-oil should be minimized. The syngas should also be produced at a high temperature for this application since it then has a higher enthalpy value that can potentially generate more electricity and heat.

If the syngas is used for methanol synthesis or Fischer-Tropsch fuel production, then a small amount of O_2 can be used to adjust the H_2:CO molar ratio. The syngas should be produced at 1000°C where H_2:CO molar ratio equal to 2. An appropriate amount of moisture content in pyrolysis oil should be selected at 40%.

Syngas produced from pyrolysis oil contains less nitrogen oxides and sulfur dioxide, making the syngas more suitable to fuel cells or fuel production processes. Therefore, pyrolysis oil provides a sustainable energy pathway from forest resources to a biofuel that can be used in the fuel cells, which can be deployed in the remote and off-grid communities to provide heat and electricity. Besides that, the use of pyrolysis oil generated from forest resources would help reducing our dependency on fossil fuels and cutting down greenhouse -gases emissions.

5.8 References

1. Mirandola, A. and E. Lorenzini, *Energy, environment and climate: From the past to the future.* International Journal of Heat and Technology, 2016. **34**(2): p. 159-164.

2. McKendry, P., *Energy production from biomass (part 1): overview of biomass.* Bioresource technology, 2002. **83**(1): p. 37-46.

3. Alvarez, J., *et al.*, *Bio-oil production from rice husk fast pyrolysis in a conical spouted bed reactor.* Fuel, 2014. **128**: p. 162-169.

4. Staš, M., *et al.*, *Overview of analytical methods used for chemical characterization of pyrolysis bio-oil.* Energy & Fuels, 2014. **28**(1): p. 385-402.

5. Bridgwater, A. and M. Cottam, *Opportunities for biomass pyrolysis liquids production and upgrading.* Energy & Fuels, 1992. **6**(2): p. 113-120.

6. Radlein, D., *The production of chemicals from fast pyrolysis bio-oils.* Vol. 1. 1999: CPL Press: Newbury, UK.

7. Chang, S., *et al.*, *Effect of hydrothermal pretreatment on properties of bio-oil produced from fast pyrolysis of eucalyptus wood in a fluidized bed reactor.* Bioresource technology, 2013. **138**: p. 321-328.

8. Huber, G.W., S. Iborra, and A. Corma, *Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering.* Chemical reviews, 2006. **106**(9): p. 4044-4098.

9. Demirbas, A., *The influence of temperature on the yields of compounds existing in bio-oils obtained from biomass samples via pyrolysis.* Fuel Processing Technology, 2007. **88**(6): p. 591-597.

10. Brown, R.C., D. Radlein, and J. Piskorz. *Pretreatment processes to increase pyrolytic yield of levoglucosan from herbaceous feedstocks.* in *ACS Symposium Series*. 2001. Washington, DC; American Chemical Society; 1999.

11. Rossum, G., *Steam reforming and gasification of pyrolysis oil.* 2009: University of Twente.

12. Van Rossum, G., S.R. Kersten, and W.P. van Swaaij, *Catalytic and noncatalytic gasification of pyrolysis oil.* Industrial & engineering chemistry research, 2007. **46**(12): p. 3959-3967.

13. Oasmaa, A. and S. Czernik, *Fuel Oil Quality of Biomass Pyrolysis OilsState of the Art for the End Users.* Energy & Fuels, 1999. **13**(4): p. 914-921.

14. Elliott, D.C., *et al.*, *Catalytic hydroprocessing of biomass fast pyrolysis bio-oil to produce hydrocarbon products.* Environmental Progress & Sustainable Energy: An Official Publication of the American Institute of Chemical Engineers, 2009. **28**(3): p. 441-449.

15. Postma, R.S., S.R. Kersten, and G. van Rossum, *Potassium-salt-catalyzed tar reduction during pyrolysis oil gasification.* Industrial & Engineering Chemistry Research, 2016. **55**(26): p. 7226-7230.

16. van Rossum, G., S.R. Kersten, and W.P. van Swaaij, *Staged catalytic gasification/steam reforming of pyrolysis oil.* Industrial & Engineering Chemistry Research, 2009. **48**(12): p. 5857-5866.

17. Bleeker, M., S.R. Kersten, and H. Veringa, *Pure hydrogen from pyrolysis oil using the steam-iron process.* Catalysis Today, 2007. **127**(1-4): p. 278-290.

18. Doherty, W., A. Reynolds, and D. Kennedy, *The effect of air preheating in a biomass CFB gasifier using ASPEN Plus simulation.* Biomass and bioenergy, 2009. **33**(9): p. 1158-1167.

19. Moghadam, R.A., *et al.*, *Investigation on syngas production via biomass conversion through the integration of pyrolysis and air–steam gasification processes.* Energy conversion and management, 2014. **87**: p. 670-675.

20. Tomasi, C., *et al.*, *Process analysis of a molten carbonate fuel cell power plant fed with a biomass syngas.* Journal of Power Sources, 2006. **157**(2): p. 765-774.

21. Pröll, T., *et al.*, *Fluidized bed steam gasification of solid biomass-Performance characteristics of an 8 MWth combined heat and power plant.* International Journal of Chemical Reactor Engineering, 2007. **5**(1).

22. Ramzan, N., *et al.*, *Simulation of hybrid biomass gasification using Aspen plus: A comparative performance analysis for food, municipal solid and poultry waste.* Biomass and Bioenergy, 2011. **35**(9): p. 3962-3969.

23. Elan, G., *Aspen plus user guide version 10.2 [M].* California: Aspen Technology, 1998.

24. Andrianopoulos, E., A. Korre, and S. Durucan, *Chemical process modelling of underground coal gasification and evaluation of produced gas quality for end use.* Energy Procedia, 2015. **76**: p. 444-453.

25. Begum, S., M. Rasul, and D. Akbar, *A numerical investigation of municipal solid waste gasification using aspen plus.* Procedia engineering, 2014. **90**: p. 710-717.

26. Ma, T., *et al.*, *Synthesis of hydrocarbons from H 2-deficient syngas in Fischer-Tropsch synthesis over Co-based catalyst coupled with Fe-based catalyst as water-gas shift reaction.* Journal of Nanomaterials, 2015. **2015**: p. 2.

27. Erena, J., *et al.*, *Direct synthesis of dimethyl ether from (H2+ CO) and (H2+ CO2) feeds. Effect of feed composition.* International journal of chemical reactor engineering, 2005. **3**(1).

28. Zhang, Y., J. Xiao, and L. Shen, *Simulation of methanol production from biomass gasification in interconnected fluidized beds.* Industrial & Engineering Chemistry Research, 2009. **48**(11): p. 5351-5359.

29. Gil, J., *et al.*, *Biomass gasification in atmospheric and bubbling fluidized bed: effect of the type of gasifying agent on the product distribution.* Biomass and Bioenergy, 1999. **17**(5): p. 389-403.

30. Dai, B., *et al.*, *Effect of the composition of biomass on the quality of syngas produced from thermochemical conversion based on thermochemical data prediction.* Energy & Fuels, 2019. **33**(6): p. 5253-5262.

5.9 Supplementary information

Appendix A

Table 5.5 Pyrolysis-oil NC definition

Attribute ID:			
PROXANAL		SULFANAL	
MOISTURE	32.5	PYRITIC	0.001
FC		SULFATE	
VM		ORGANIC	
ASH			

Appendix B

Table 5.6 Flowsheet in Aspen Plus

Component Mass flow (kg/hr)	**Pyro-oil**	**Oil-H_2O**	**IN-DECO**	**MOISTURE**	**IN-COMB**	**IN-MIXER**	**IN-GASIF**	**SYNGAS**
Pyrolysis oil	100							
Oil		67.5	67.5					
H_2O		32.5		32.5			32.5	
*H_2					4.15			
*O_2					32.82			
*C					30.40			
*N_2					0.27			
*S					0.001			
H_2O						trace	trace	4.27
H_2						4.09	4.09	6.42
CO						57.01	57.01	38.60
CO_2						trace	trace	50.04
CH_4						0.29	0.29	0.28
C						5.97	5.97	
H_2S						0.001	0.001	trace
H_3N						0.38	0.38	0.33
C_2H_6						trace	trace	trace

*Elemental distribution

Appendix C

Table 5.7 Effect of gasifying agents (800 °C)

Component Mass flow (kg/hr)	Pyro-oil	Oil-H2O	IN-DECO	MOISTURE	IN-COMB	IN-MIXER	AGENT			SYNGAS		
							Steam	Air	O_2	Steam	Air	O_2
Pyrolysis oil (20% moisture content)	84.4											
Oil		67.5	67.5									
H_2O		16.9		16.9			13.5					
H_2					4.15							
O_2					32.82			2.8	13.5			
C					30.40							
N_2					0.27			10.7				
S					0.001							
H_2O						trace				9.46	trace	2.08
H_2						4.09				5.64	5.21	4.50
CO						57.01				49.46	43.07	34.3
CO_2						trace				32.96	38.88	56.87
CH_4						0.29				0.253	0.009	trace
C (Pure Solid)						5.957						
H_2S						0.001				trace	trace	trace
H_3N						0.38				0.32	0.32	0.32
C_2H_6						trace				trace	trace	trace
N_2												10.7

Chapter 6 - Article 2: Methanol production from pyrolysis oil gasification- Model development and impacts of operating conditions

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6.1 Foreword

This paper published an application of pyrolysis oil. The purpose of this part of the work was to explore the application of pyrolysis oils in fuel synthesis. In this paper, a model was developed to simulate the production of methanol by pyrolysis oil gasification, methanol gasification, Rectisol® and methanol synthesis. The model was validated by previous studies. The model was then used to predict methanol production under different operating conditions such as gasification temperature, pyrolysis oil gasification temperature, moisture content in pyrolysis oil Rectisol® temperature/pressure, and methanol synthesis reactor temperature/ pressure.

6.2 Abstract

A novel process model simulating methanol production through pyrolysis oil gasification was developed, validated then used to predict the effect of operating conditions on methanol production yield. The model comprised gasification, syngas post-treatment, and methanol synthesis units. The model was validated using experimental data from the literature, and the results obtained by the model were consistent with reference data. The simulation results revealed that gasification temperature has a significant impact on syngas composition. Indeed, rising temperature from 400 °C to 600 °C leads to higher syngas stoichiometric number (SN) value. Conversely, SN value decreases when the gasifier temperature is above 1000 °C.

Moisture content in pyrolysis oil also affects both syngas composition and SN value; an increase in the first (from 10 to 30%) leads to an increase in SN value. The Rectisol® unit deeply influences the syngas SN value and methanol yield, the best results being obtained with operating conditions of -20 °C and 40 bar. Increasing the operating temperature of the methanol synthesis unit from 150 °C to 250 °C leads to an increase in the yield of methanol production; the yield decreases beyond 250 °C. Although high pressures favor the methanol production yield, the operating pressure in the synthesis unit is limited at 50 bar for practical considerations (*e.g.* equipment price, equipment requirements, or operational risks).

6.2.1 Keywords

Renewable resources; Aspen simulation; methanol synthesis; Rectisol®; sensitivity analysis; beechwood chips.

6.3 Introduction

The increase in global energy depletion and the massive utilization of fossil fuels have led to an alarming increase in CO_2 emissions into the environment and to potential energy supply issues. World energy-related CO_2 emissions will increase from 30.2 billion metric tons in 2008 to 43.2 billion metric tons in 2035 [1]. The greenhouse gases (GHG) emissions from fossil fuels have a dominant influence on the atmospheric CO_2 concentrations, leading to global temperature and sea level rise [2]. With the rapidly increasing global energy demand and the growing concerns about the environmental challenges, renewable and sustainable energy (*e.g.* solar, wind, and biomass) has been considered as key resources to solve the coming energy crisis. Among all the possible alternatives, biofuels have been regarded as the most promising substitute to fossil fuels. Indeed, bioresources (such as biomass, biochar, and pyrolysis oil) are an attractive feedstock to produce fuels because its utilization emits less greenhouse gases (GHG) if we consider that the newly grown biomass absorbs CO_2 emissions [3]. However, the bioresources only account for a small proportion of energy consumption.

Gasification is the most common thermochemical process to convert bioresources into a gaseous fuel in high temperature, partially oxidized atmosphere [4]. The syngas produced by gasification can be burned directly or used as fuel for turbines. It is also one of the key building blocks to produce fuels for transportation and chemicals. For example, the current usage of synthesis gas is for the production of ammonia (50%) and hydrogen (25%). The rest is dedicated to the production of methanol, Fischer–Tropsch (FT) products and other purposes [5].

Gasification is a process dedicated to the production of syngas, mainly composed of gases such as H_2, CO, CO_2 and CH_4. However, syngas contains impurities, including char, tars, high molecular weight hydrocarbons, sulfur, or CO_2; but also trace contaminants (*e.g.* ammonia, metals, halides…) [6]. All these impurities must be removed before the downstream operations. In addition to this purification step, the syngas composition must also be modified to meet the requirements of methanol synthesis, especially the content of H_2, CO, and CO_2. The most frequently applied technology for syngas cleaning up and CO_2 removal is the absorption process by means of chemical solvents, such as alkanolamines and Monoethanolamine (MEA) [7]. However, those processes are expensive, and a large scale is needed to be cost-effective [8]. Nowadays, Rectisol® is a better method for its removal, given that more than 98% of CO2 and sulfur in the gas can be removed [9]. Rectisol® uses methanol as CO_2 solvent since it is much more effective than water, especially at low temperatures. The solubility of CO_2 in methanol is about y four times of water at room temperature and more than eight times higher than of water at temperatures below 0 °C [10,11]. Therefore, methanol has been industrially used in the Rectisol® process as a physical absorber of CO_2 [12].

Nowadays, methanol is gaining more attention as a possible future fuel that can be used in fuel cells and engines [13,14]. Methanol is of interest for large-scale transportation applications because it has a significant positive environmental impact over fossil fuels, particularly when used in fuel-cell vehicles [15]. The technology to produce methanol from biomass is similar to that used to produce methanol from coal. [16]. The process flow chart is mainly composed of commercially established technologies such as gasification, syngas cleaning and conditioning, and methanol synthesis.

Pyrolysis oil, also called bio-oil, is a complex blend of numerous oxygenated compounds produced from lignocellulosic biomass through a thermochemical process (*i.e.*, pyrolysis) in the intermediate temperature ranges from 400 °C to 600 °C in the absence of oxygen [17]. Pyrolysis oil contains organic compounds such as carboxylic acids, alcohols, aldehydes, ketones, esters, furans, and aromatics [18]. The water content of pyrolysis oil generally ranges from 15 wt.% to 25 wt.% [19,20]. Up to 70 wt.% of the original dry biomass can be converted into pyrolysis oil [21]. The properties of pyrolysis oil depend on multiple factors such as the type of biomass feedstock, alkaline compounds content, reactor type, reaction temperature, residence time, char removal, etc. [22-24]. For example, the pyrolysis oil produced from pyrolysis of beech wood chips consist mainly of aldehydes, acids, esters, alcohols, ketones, benzene derivatives, phenol and alkanes, due to the different reaction conditions, the product content varies considerably [25].Compared to the primary biomass, pyrolysis oil presents several advantages. First, its volumetric energy density is increased about 5 times more than the "bulk" biomass, making transport economically more attractive, especially over long distances [26]. When large-scale remote biomass collection is considered, pyrolysis oil can firstly be produced locally and then transported to the central processing area [21]. Second, pyrolysis oil is a liquid, which makes storage, transport, processing and pressurization easier. It can also be stored in tanks that resist well against biodegradation and cannot be ignited at ambient temperature [26]. Third, compared to conventional fossil fuels, pyrolysis oil contains a small quantity of sulfur, nitrogen and ash. As a result, its combustion releases less harmful gas emissions such as nitrogen oxides (NOx) and sulfur dioxide (SO_2) [26]. Furthermore, as the pyrolysis oil is produced through a low temperature process, minerals and metals remain in the solid char residue. However, the drawbacks of pyrolysis oil should not be ignored, the pyrolysis oil properties limiting its applications. This phenomenon is caused by high oxygen content, volatility, high viscosity, acidity, low heating value and incompatibility with petroleum and other bio-based fuels [28]. Despite these constraints, pyrolysis oil has plentiful advantages to be used to produce syngas by gasification.

In this paper, a new model is dedicated to simulating the methanol production via a set of processes including pyrolysis oil gasification, Rectisol® and methanol synthesis. The model is then validated by experimental and industrial results and used in a sensitivity analysis to identify the effects of varying operating conditions on the methanol production yield. Firstly, the modeling methodology is discussed, *i.e.* assumptions, model's description and its validation. Thereafter, the main results of the sensitivity analysis are presented and discussed, highlighting the impacts of various operating conditions on methanol yield, *i.e.*, the gasifying temperature, pyrolysis oil moisture content, Rectisol® temperature/pressure, and methanol synthesis reactor temperature/pressure.

6.4 Materials and methods

6.4.1 Pyrolysis oil characteristics

The pyrolysis oil in this study has characteristics mentioned in reference [21]. It is produced by a company named BTG located in the Netherlands, processing beech wood chips in a pilot plant facility. The proximate and ultimate analysis provided the properties of this pyrolysis oil, which are presented in **Table 6.1**.

Table 6.1 Beech wood pyrolysis-oil composition

Proximate analysis (wt.%)	
Moisture content	32.5 - 43.7
Ultimate analysis (%)	
Carbon	30.4 - 37.7
Hydrogen	7.6 -7.9
Nitrogen	< 0.27
Oxygen	54.4 - 61.7
Sulfur	< 0.01

6.4.2 Modeling methodology

The main purpose was to design a comprehensive process model for methanol synthesis from pyrolysis oil gasification. The model was then used as a tool to identify the influence of the operating conditions on the methanol synthesis yield. Operating parameters such as gasification temperature, moisture content in pyrolysis oil, Rectisol® pressure and temperature, but also methanol synthesis reactor conditions (temperature and pressure) were varied over wide ranges.

Pyrolysis oil gasification was applied to produce syngas. In many cases, syngas produced from biomass through gasification is CO_2 rich or H_2 deficient. However, it can be adjusted using processes like water gas shift reaction, methane reforming, or CO_2 removal [29]. Supplying external H_2 is also a solution to adjust its composition before feeding into the fuel synthesis loop [30]. In this study, Rectisol® process was applied to clean up syngas and adjust syngas composition to satisfy the methanol synthesis requirements. Then post-treatment syngas was compressed at high pressure and introduced into the methanol synthesis reactor to produce the desired compound. The process flow diagram in **Figure 6.1** shows the Aspen Plus blocks illustrating the model used to simulate the methanol synthesis production from pyrolysis oil. The model consists of three main parts: gasification, syngas post-treatment, and methanol synthesis. The pyrolysis oil is specified as a non-conventional ingredient in Aspen Plus and defined in the block by properties presented in **Table 6.1**.

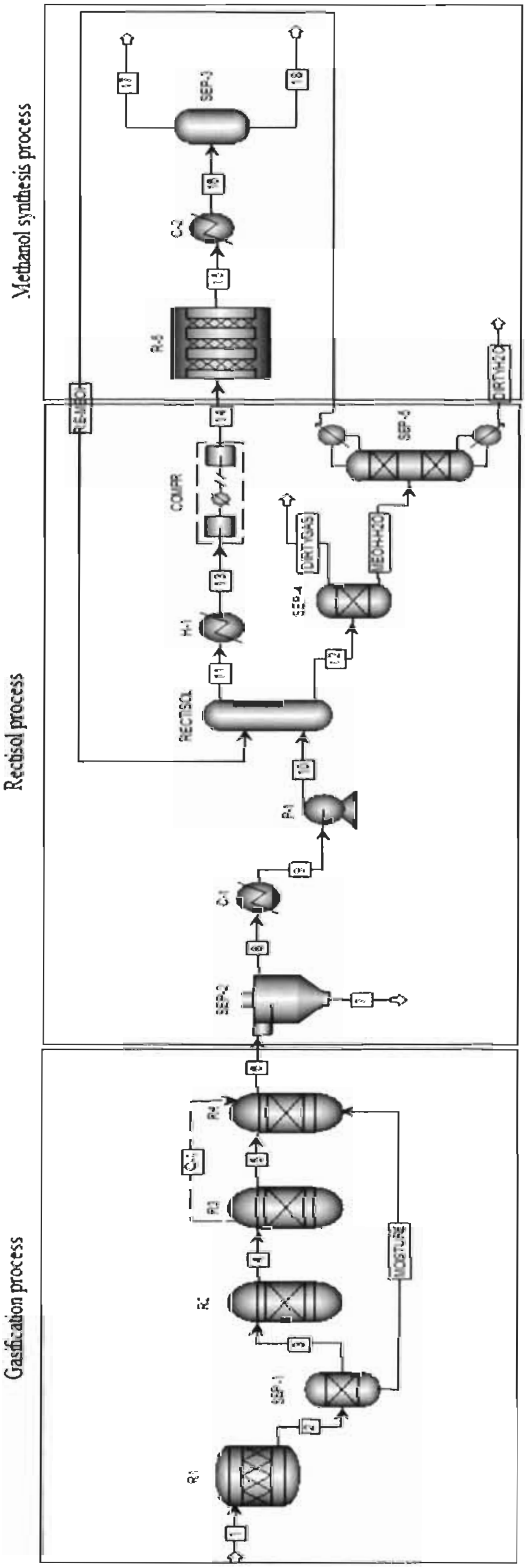

Figure 6.1 Process flow diagram of the Aspen Plus model for methanol synthesis via pyrolysis oil gasification

6.4.3 Gasification process

Several thermochemical reactions occur during gasification at different temperature zones: drying zone (> 150 °C), decomposition zone (250°C to 700 °C), combustion zone (700 °C to 1500 °C) and gasification zone (800 °C to 1200 °C) [30]. At drying stage, the moisture content is removed from pyrolysis oil. The decomposition stage is initiated at about 250 °C when the labile bonds between the aromatic clusters are cracked, generating light molecular weight fragments. This stage generates gaseous molecules such as H_2, CO, CH_4, as well as light char and tar. After decomposition, pyrolysis oil undergoes combustion, which practically provides the thermal energy required to sustain the endothermic reactions. This stage generates gaseous molecules such as CO_2 and H_2O [31]. A series of endothermic reactions, such as water gas, Boudouard, water gas shift, and steam methane reforming reactions occur at this stage [14]. Useful combustible gases such as H_2 and CO are produced at gasification stage. At the end, the whole gasification process generates a syngas composed mainly of CO, CO_2, H_2 and CH_4. The production of CO, CO_2, CH_4, H_2, and steam in the whole process can be explained by the reactions given in ((R-1) - (R-8)), which occur at various stages [15].

$C + 1/2O_2 \rightarrow CO$	- 111 MJ/kmol	Combustion reaction (R-1)
$C + O_2 \rightarrow CO_2$	- 283 MJ/kmol	Combustion reaction (R-2)
$H_2 + 1/2O_2 \rightarrow H_2O$	- 286 MJ/kmol	Combustion reaction (R-3)
$C + CO_2 \leftrightarrow 2CO$	+ 172 MJ/kmol	Boudouard reaction (R-4)
$C + 2H_2 \leftrightarrow CH_4$	- 75 MJ/kmol	Methanation reaction (R-5)
$C + H_2O \leftrightarrow CO + H_2$	+ 131 MJ/kmol	Water gas reaction (R-6)
$CO + H_2O \leftrightarrow CO_2 + H_2$	- 41 MJ/kmol	Water gas shift reaction (R-7)
$CH_4 + H_2O \leftrightarrow CO + 3H_2$	+ 206 MJ/kmol	Steam methane reforming reaction (R-8)

The gasification model is based on the following assumptions, *i.e.*:

(1) Pyrolysis oil feed rate is 1000 kg/h.
(2) Gasification is assumed to be steady state, isothermal, and simulated using a kinetic-free model [31].
(3) Pyrolysis oil devolatilization occurs instantaneously and the volatile products include H_2, CO, CO_2, CH_4, H_2S, NH_3, and H_2O.
(4) All gases are ideal gases and uniformly distributed in the gas phase.
(5) All reactions take place at a chemical equilibrium state and the pressure loss was not considered.

A kinetic-free equilibrium model was designed for the gasification process by using Aspen plus. Gasification process is usually divided into four stages, as presented in Figure 1: drying (R1), decomposition (R2), combustion (R3) and gasification (R4). **Table 6.2** lists a brief explanation of the blocks used in the gasification process. Firstly, the wet pyrolysis oil (stream 1) was fed into R1 block to model the drying process. Dry pyrolysis oil and moisture were separated by the SEP-1 block. Secondly, dry pyrolysis oil (stream 3) was fed into reactor R2 where pyrolysis oil is decomposed into its elemental components (C, H, O, N, S, etc.). The elemental distribution of pyrolysis oil was specified according to its ultimate analysis (see Table 1). R2 block was used to convert non-conventional pyrolysis oil into conventional components. The non-conventional definition of pyrolysis oil is shown in Appendix A. Thirdly, combustion of pyrolysis oil is modeled by a Gibbs reactor. The RGibbs reactor handles the complete chemical equilibrium by minimizing Gibbs-free energy. The decomposed pyrolysis oil enters the R3 block where partial oxidation and combustion reactions occur. After combustion, the produced syngas with steam originating from pyrolysis oil moisture was fed to gasification units. Lastly, gasification is also modeled by using a Gibbs reactor, the R4 block handling the calculation of the syngas component by minimizing Gibbs free energy [31].

Table 6.2 Description of Aspen plus blocks used in the gasification model

Flow sheet block ID	Aspen plus block ID	Description
R1	RStoic	Reactor with known conversion rate - used to extract moisture form pyrolysis oil. Operation at 150 °C.
SEP-1	Sep	Used to separate the moisture from the pyrolysis oil.
R2	RYield	Yield reactor - used to decompose non-conventional pyrolysis oil into its elemental components by FORTRAN statement. Operation at 500 °C.
R3	RGibbs	Gibbs free energy reactor - used to complete chemical equilibrium by minimizing Gibbs-free energy. Operation at 800 °C.
R4	RGibbs	Gibbs free energy reactor - used to calculate syngas composition by minimizing Gibbs-free energy. Operation temperature ranges from 400 °C to 1200 °C.

6.4.4 Rectisol® unit

The main purpose of Rectisol® is to clean up the outlet syngas of gasification to obtain a high-quality syngas that can be used for the methanol synthesis [12]. The Rectisol® process uses chilled methanol as the solvent to remove the major impurities, such as CO_2, H_2S, COS, CS_2, and HCN, producing a cleaner syngas. Thus, the Rectisol® system is able to obtain a pure syngas stream and simultaneously adjust its stoichiometric ratio to satisfy the requirements of methanol synthesis. In addition, the methanol used in the purification step can be reused over several cycles, making the process economically feasible.

It is worth noting that the stoichiometric number (SN) (**Equation 6.1**) for the syngas composition plays a dominating role in methanol synthesis reaction. The ideal value of SN is slightly higher than 2, indicating an excess of H_2 or less CO_2.

$$\mathrm{SN} = \frac{\mathrm{n(H_2) - n(CO_2)}}{\mathrm{n(CO) + n(CO_2)}}$$ **Equation 6.1**

Table 6.3 lists a brief explanation of the Aspen Plus blocks used in Rectisol® system. Firstly, after the gasification process, ash content in syngas (stream 6) was eliminated by the SEP-2 (Cyclone separator). Secondly, the syngas leaving the separator is cooled to a temperature of 80 °C by the C-1. Lastly, the RECTISOL® block in Aspen Plus is used to simulate Rectisol® process where the syngas (stream 10) was fed into Rectisol® columns at the bottom. Meanwhile, a 20 kmol/h flow rate of cooled solvent methanol (RE-MEOH), entering from the top of columns, interacts with the syngas. Post-treatment syngas (stream 11) is withdrawn from the top of Rectisol® column. Water, impurities and part of the CO_2 are absorbed by the cooled methanol (stream 12), flowing out from the bottom of the Rectisol® column. Meanwhile, SEP-4 is used to separate gas (impurities and CO_2) and liquid phase (methanol and H_2O) from the liquid phase. Another separator (SEP-5) is used to separate H_2O and methanol. After purification, the methanol (RE-MEOH) is re-introduced in to Rectisol® unit.

Table 6.3 Description of Aspen plus blocks used in Rectisol®

Flow sheet block ID	Aspen plus block ID	Description
SEP-2	SSplit	Used to separate ash from the syngas. Operation at 800 °C.
C-1	Heater	Used to decrease syngas temperature to 80 °C.
RECTISOL®	Radfrac	Used to remove acid syngas and partial carbon dioxide

6.4.5 Methanol synthesis and water gas shift reaction process

After syngas post-treatment, the syngas (stream 14) was introduced into the methanol synthesis reactor. At this step, CO_2 hydrogenation to methanol and water gas shift reaction over a commercial $Cu/ZnO/Al_2O_3$ catalyst occur simultaneously [33]. As the methanol synthesis is exothermic and volumetric reduction reaction, the productivity can be increased by rising pressure and reducing the reaction temperature. Therefore, the methanol synthesis reactor was assumed to operate at 250~350 °C and 50~150 bar [34]. The main reactions in the methanol synthesis unit can be expressed as described in the following reactions:

$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$ - 49.5 kJ/mol Methanol synthesis (R-10)

$CO + H_2O \leftrightarrow CO_2 + H_2$ - 41.2 kJ/mol Water gas shift (R-11)

The methanol synthesis model is based on several assumptions, *i.e.*:

(1) Pressure loss in the methanol synthesis reactor is not considered.
(2) Syngas is preheated sufficiently and the temperature distribution in the methanol synthesis reactor is assumed to be uniform.

Table 6.4 lists the blocks were applied in methanol synthesis system. The post-treatment syngas (stream 11) obtained from Rectisol® was heated up to 250 °C by H-1 and compressed to 50 bar by COMPR block. The methanol synthesis reactor is simulated by the R5 block where CO_2 hydrogenation and water gas shift reaction occur. The Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic model is applied in the format of the reactant fugacity of the hydrogenation of CO_2 and water gas shift. The kinetic parameters applied in the LHHW block are obtained from the William experimental results [35]. Finally, a SEP-3 block was used to separate residual syngas from the mixture of methanol and water.

The LHHW expression is presented in **Equation 6.2**:

$$R = (\text{kinetic term})\frac{(\text{driving} - \text{force term})}{(\text{adsorption term})}$$ **Equation 6.2**

The reaction rate for the production of methanol from carbon dioxide hydrogenation is given in **Equation 6.3**:

$$R_{CH_3OH}(\text{kmol/kgcat} \cdot \text{s}) = (k_{MeOH}p_{CO_2}p_{H_2})\frac{[1 - \frac{1}{K_{E1}}(\frac{p_{H_2O}p_{CH_3OH}}{p_{CO_2}p_{H_2}^3})]}{[1 + k_3\left(\frac{p_{H_2O}}{p_{H_2}}\right) + k_1\sqrt{p_{H_2}} + k_2p_{H_2O}]^3}$$ **Equation 6.3**

The reaction rate for the water gas shift reaction is given in **Equation 6.4**:

$$R_{WGS}(\text{kmol / kgcat} \cdot \text{s}) = (k_{WGS}p_{CO_2})\frac{[1 - \frac{1}{K_{E2}}(\frac{p_{H_2O}p_{CO}}{p_{CO_2}p_{H_2}})]}{[1 + k_3\left(\frac{p_{H_2O}}{p_{H_2}}\right) + k_1\sqrt{p_{H_2}} + k_2p_{H_2O}]}$$ **Equation 6.4**

Where R_i = reaction rate [mol/kg_{cat}*s]
k_i = kinetic factor [kmol/kg_{cat}*s*bar] or [kmol/kg_{cat}*s*bar^2]
p_i = partial pressure [bar]
K_{Ei} = equilibrium constant [-] or [bar^{-2}]
$k_{1/2/3}$ = adsorption constants [bar^n]

Table 6.4 Description of Aspen plus block used in methanol synthesis and operating condition

Flow sheet Block ID	Aspen plus block ID	Description
H-1	Heater	Used to heat up syngas to 250 °C
COMPR	MCompr	Used to compress syngas to 50 bar
R5	RPlug	Used to simulate methanol synthesis reactor
C-2	Heater	Used to cool down the outlet syngas of methanol synthesis reactors
SEP-3	Flash 2	Used to separate produced methanol and residual syngas

6.5 Results and discussion

6.5.1 Model validation

6.5.1.1 Gasification

The flowsheet result of gasification in Aspen Plus is presented in Appendix B. The simulation model is validated by using experimental data from gasification of pyrolysis oil published by Van Rossum *et al.* [21]. The experimental data and simulation results are shown in **Table 6.5**. In this research, pyrolysis oil is used to produce syngas through gasification in a fluidized bed with nickel-based catalysts at 800 °C. It may be observed that the model syngas concentration is in good agreement with the experimental results except the concentration of CO and CH_4. In the experiments, the steam methane reforming reaction is restricted by the reaction time so it cannot reach a state of the complete equilibrium [29]. Therefore, the concentration of CH_4 simulated by RGibbs reactor without the time limitation is very low and this part of CH_4 reacts with steam into CO and H_2 (R-8). Because the nitrogen and sulfur content in pyrolysis oil is relatively low, the content of H_2S and NH_3 in the produced syngas is low.

Table 6.5 Comparison between experimental and simulated results of gasification process

Syngas composition (mole %)	Experiment	Model	Difference
H_2	55.5	55.9	0.4
CO	19.3	24.0	4.7
CO_2	19.0	19.8	0.8
CH_4	5.4	0.3	5.1
C_2H_6	1.0	trace	-
H_2S	-	trace	-
NH_3	-	trace	-

6.5.1.2 Rectisol®

To validate the Rectisol® process model, the simulated results were compared with the experimental data. The flowsheet result of Rectisol® is presented in Appendix C. In Bell *et al.* research, Rectisol® is designed to process syngas from acid gas shift reactor prior to the synthesis of ammonia 1000 tons/day [36]. The Rectisol® columns are designed to remove most of the dissolved CO_2, H_2S and COS. The syngas, composed of H_2, N_2, Ar, CO, CH_4, CO_2, H_2S and COS, is fed to the bottom of the column, the chilled methanol is fed to the top of the Rectisol® column. As the gas flows upward in the Rectisol® column, downward flowing methanol absorbs H_2S, COS and CO_2, so the syngas leaving the top of Rectisol® column is nearly sulfur and CO_2 free. Liquid methanol is withdrawn from the bottom of the column, the results are presented in **Table 6.6**. The simulation results are compared with the experimental results. There is a small discrepancy between the experimental data and simulation results, but not significant. Therefore, the Rectisol® model could be considered as a valid model to simulate Rectisol® process.

Table 6.6 Comparison between simulated and experimental results of Rectisol®

Component dry basis	Feed syngas	Purified syngas experimental results	Simulated results
Pressure (MPa)	7.8	7.6	7.8
H_2	62.5%	95.3%	95.9%
N_2 + Ar	0.5%	0.8%	0.7%
CO + CH_4	2.7%	4.0%	3.4%
CO_2	34.1%	20 ppm	trace
H_2S + COS	0.3%	0.1 ppm	trace
Flow rate (kmol/h)	6021.1	3936.1	3890.3

6.5.1.3 Methanol synthesis

The flowsheet result of methanol synthesis in Aspen Plus is presented in Appendix D. The methanol synthesis simulation results are compared with the data obtained from the industrial methanol synthesis results [37]. Results obtained from the simulation and the corresponding industrial data are presented in Table 7. As the comparison between experimental and simulated results shows, the model produces results close to the reference data. The error between simulated results and experimental results is 0.7%. It is worth noting that the discrepancy between the content of CO and CO_2, this is due to the synthetic pathway of methanol in the practical experiment where both of CO and CO_2 participate into the methanol synthesis reaction. However, in the simulation, CO participates into the water-gas shift reaction instead of methanol synthesis. There is a difference between the reference and simulated pressure. This is because the syngas volume is reduced during methanol synthesis process, resulting in the decrease of the partial pressure of H_2, CO and CO_2. As a consequence, the side of the equilibrium with fewer moles is becoming more unfavorable [38]. Therefore, a higher reaction pressure is needed in the actual reaction to facilitate methanol synthesis. However, in the simulation, the methanol synthesis reactor pressure is fixed at 40 bar (**Table 6.7**). The simulated and experimental results of the methanol yield are approximately similar. Therefore, the model could be considered as a valid model to simulate the methanol synthesis process.

Table 6.7 Comparison between simulated and industrial results of methanol yield

	Feed	Outlet stream (industry)	Outlet stream (simulation)	Difference
Temperature (°C)	225	255	225	-
Pressure (bar)	69.7	66.7	40	-
Mass flow rate (kg/h)	57282.8	57282.8	57282.8	-
Components flow rate (kg/h)				
CO	10727.9	4921.0	4068.7	-17.3%
CO_2	23684.2	18316.4	19577.3	6.9%
H_2	9586.5	8013.7	8063.6	0.6%
H_2O	108.8	2309.3	1789.9	-22.5%
Methanol	756.7	11283.1	11364.6	0.7%
CH_4	4333.1	4333.1	4333.1	-
N_2	8072.0	8071.9	8072.0	-
Ethanol	0.6	8.7	0.6	-
Propanol	-	0.1	-	-
Methyl formate	13.0	25.6	13.0	-

6.5.2 Effect of operating conditions

In this section, the effect of the operating conditions, such as gasification temperature, pyrolysis-oil moisture content, Rectisol® temperature and pressure on syngas composition, SN and methanol yield as well as methanol synthesis operation conditions are discussed.

6.5.2.1 Effect of gasifier temperature

The gasification temperature is a key parameter for syngas production. **Figures 6.2** and **6.3** show the effect of gasifier temperature on syngas composition and SN. The gasifier temperature varies from 400 °C to 1200 °C. Low temperature conditions (from 400 °C to 600

°C) favor the production of CO_2 and CH_4. Increasing the temperature from 400 °C to 800 °C leads to a constant and significant increase in CO and H_2 concentrations. This phenomenon is caused by endothermic reactions like Boudouard (R-4), water gas shift (R-7), and methane steam reforming (R-8). According to Le Chatelier's principle, high temperatures favor the formation of endothermic reaction products [38]. Therefore, the CO and H_2 concentrations increase at high temperatures, while the CH_4 and CO_2 concentrations decrease. At high temperatures (above 800 °C), the concentrations of H_2 and CO_2 slightly decrease, while the concentration of carbon monoxide slightly increases. This is attributed to the water gas shift reaction (R-7). Due to its exothermic nature, this reaction is thermodynamically favored at low temperatures.

Figure 6.3 shows the effect of the gasification temperature on SN that closely determines the methanol yield. The SN value increased from a minimum of -0.49 (CO_2 content is greater than H_2) to a maximum of 0.85 when the temperature increased from 400 °C to 1000 °C. This is because steam methane reforming (R-8) and Boudouard (R-4) reactions are dominant reactions over the water gas shift (R-7) reaction [39]. However, when the temperature increased to 1000 °C, the SN value dropped to 0.67. This is because of the water gas shift reaction; the carbon dioxide production being favored at high temperatures. The effects of gasifier temperature on syngas composition and SN value is closed to previous experimental results. In van Rossum research [26], the effect on the trend of H_2, CO and CO_2 content is the same as our simulation, Due to the pyrolysis oil characteristics has a significant effect on the syngas composition, however, the trend of syngas SN value is the same, increasing and then decreasing.

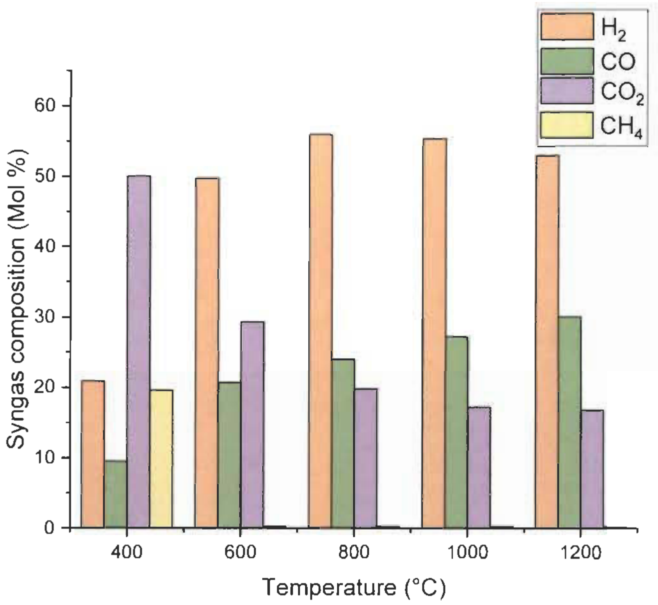

Figure 6.2 Effect of gasifier temperature on syngas composition.

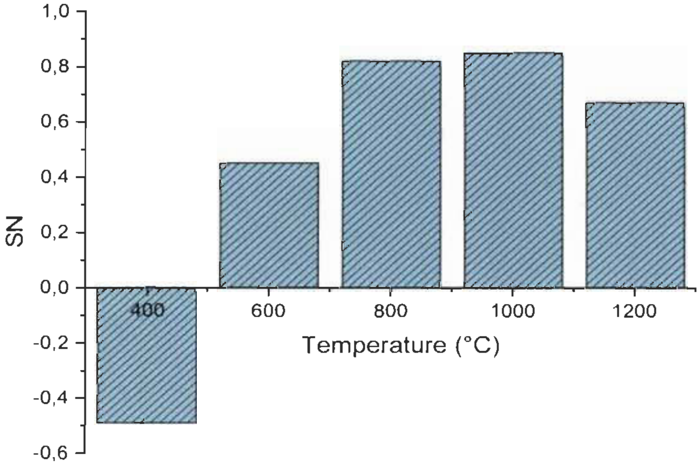

Figure 6.3 Effect of gasifier temperature on SN.

6.5.2.2 Effect of pyrolysis oil moisture content

Figure 6.4 and **6.5** present the effects of pyrolysis oil moisture content on syngas composition and SN between 10 wt.% and 50 wt.%. According to water gas shift reaction (R-7) and water gas reaction (R-6), moisture content in pyrolysis oil increases the mole fraction of H_2 and CO_2, while the amount of CO decreased. As a result, the SN value constantly increased from 0.805 to 0.865 with the pyrolysis oil moisture content from 10 wt.% to 30 wt.%. When the moisture content is more than 30 wt.%, the H_2 and CO_2 concentrations continually increase while the CO decreases and the SN value is maintained at 0.865. Therefore, the moisture content in pyrolysis oil seems to be the most beneficial around 30% because excess moisture content has no positive effect on syngas composition and SN value. In contrast, it will consume more heat during gasification process. The effect of pyrolysis oil moisture content on syngas SN value is also similar to Van Rossum experimental research [21]. In this study, beech oil is used to produce syngas through gasification, and the steam/ carbon ratio is increased from 2.1 to 3.2, resulting in an increase in the syngas SN value from 0.566 to 0.692.

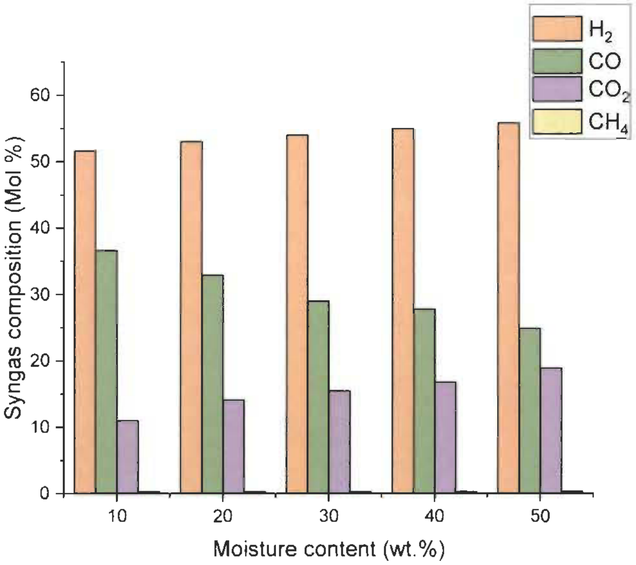

Figure 6.4 Effect of pyrolysis oil moisture content on syngas composition.

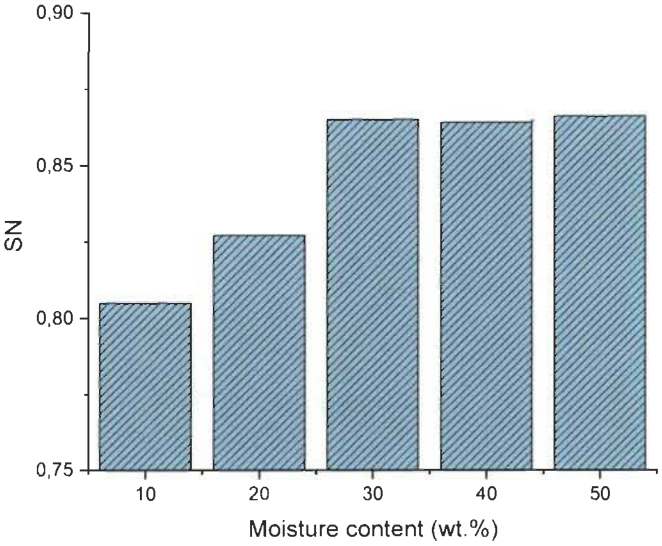

Figure 6.5 Effect of pyrolysis oil moisture content on SN.

6.5.2.3 Effect of Rectisol® operating temperature

As indicated in **Figures 6.3** and **6.5**, the SN of syngas produced from gasification is so low that it cannot satisfy the requirement of methanol synthesis. Therefore, a syngas post-treatment process like Rectisol® is needed to adjust its composition. **Figure 6.6** shows the effect of Rectisol® temperature on syngas composition, SN and methanol yield. As well known, the solubility of methanol to absorb CO_2 gradually decreases while the Rectisol® temperature increases [40]. When the Rectisol® temperature decreases from 40 °C to 40 °C, the content of CO_2 remaining in the syngas decreases from 6.175 kmol to 0.013 kmol. As a result, the SN continues to increase from 1.34 to 2.36 with the decrease of the Rectisol® temperature. As **Figure 6.7** indicated, when the temperature of Rectisol® was -20 °C, the SN value was close to 2. At this point, the methanol yield reached the maximum of 7.99 kmol. When the Rectisol® temperature was below -20 °C, the methanol yield decreased dramatically along with the decrease of Rectisol® temperature. This is caused by the low content of CO_2 in syngas to react with H_2 to synthesize methanol. When the Rectisol® temperature is higher than -20 °C, the methanol yield is also reduced due to excessive CO_2 in syngas that cannot satisfy SN requirement.

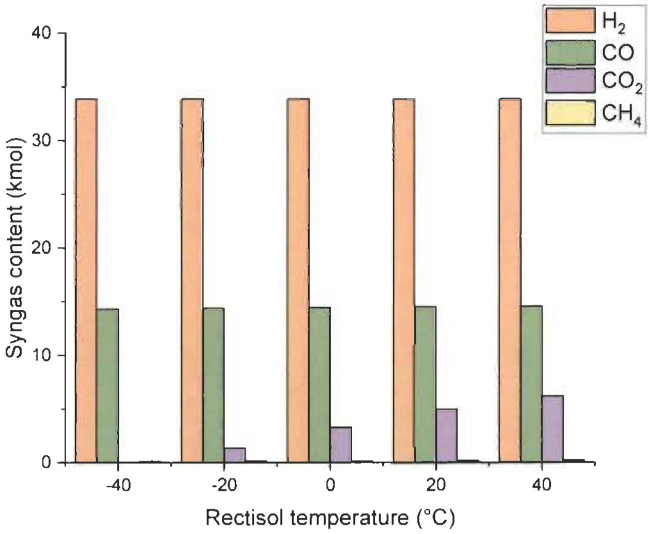

Figure 6.6 Effect of Rectisol® temperature on syngas composition (40 bar).

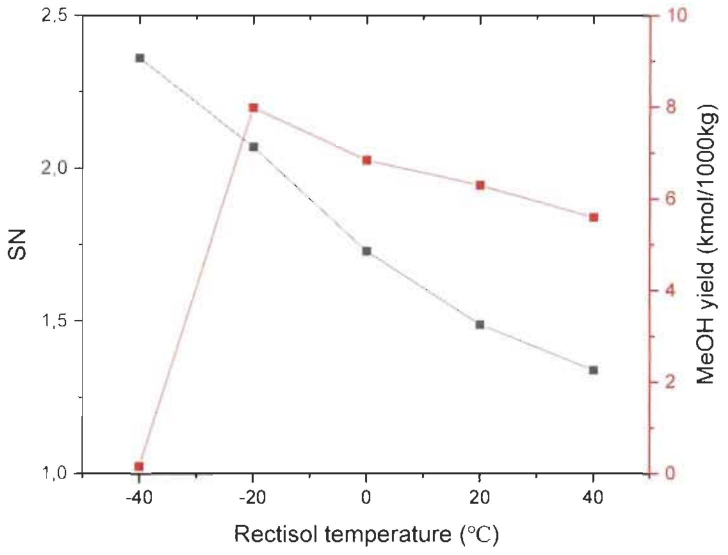

Figure 6.7 Effect of Rectisol® temperature on SN and methanol yield (40 bar).

6.5.2.4 Effect of Rectisol® operating pressure

The effects of Rectisol® pressure on the syngas composition, SN and methanol synthesis yield are presented in **Figures 6.8** and **6.9**. CO_2 content continuously decreases from 11.13 kmol to 0 kmol when the Rectisol® pressure raises from 1 bar to 80 bar. As a result, the SN increases from 0.87 to 2.5 while the Rectisol® pressure increases. When the pressure is around 40 bar, the SN value is close to 2 where the methanol yield reaches the maximum of 8.02 kmol. When the Rectisol® pressure increases from 40 bar to 60 bar, the solubility of methanol to absorb CO_2 continues to increase, producing a significant drop in the CO_2 content in the syngas. As a result, the methanol yield reaches the minimum of 0.01 kmol. This is because there is not enough CO_2 in the syngas to react with H_2 to produce methanol.

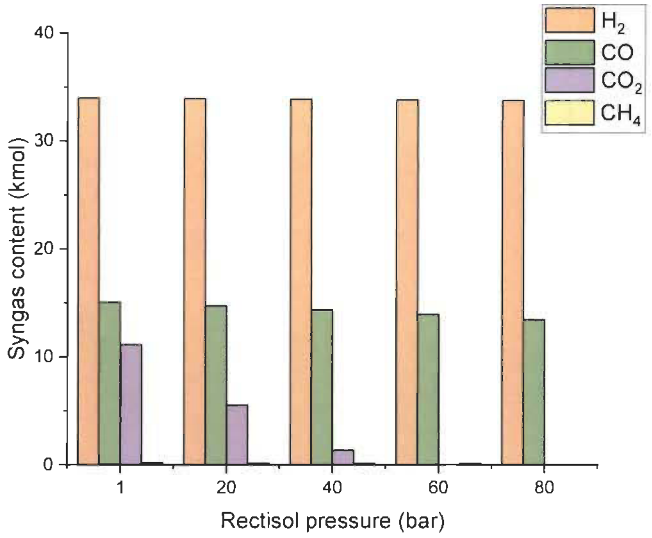

Figure 6.8 Effect of Rectisol® pressure on syngas composition (-20 °C).

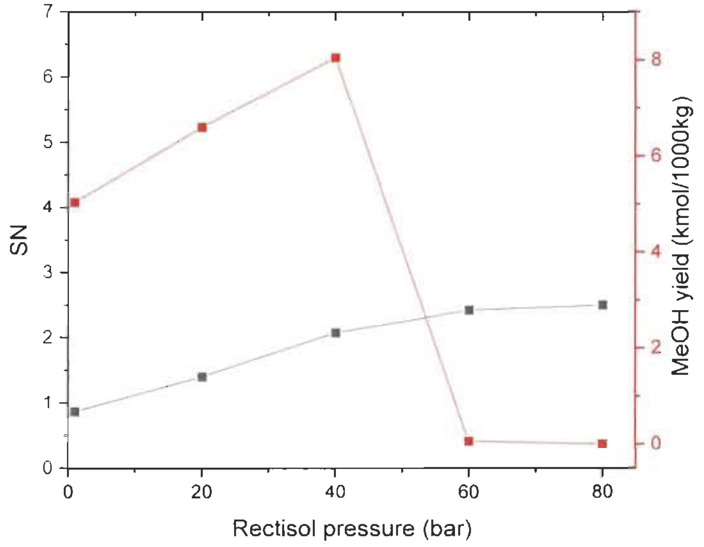

Figure 6.9 Effect of Rectisol® pressure on SN and methanol yield (-20 °C).

6.5.2.5 Effect of methanol synthesis operating temperature

The methanol synthesis reactor temperature is an influential parameter on the methanol yield. **Figure 6.10** shows the effect of temperature on methanol production between 150 and 350 °C. The methanol yield is improved with increasing reaction temperature from 150 °C to 250 °C, reaching a maximum of 7.99 kmol/1000 kg at 250 °C. This trend is consistent with the kinetics of methanol synthesis that high temperatures favor its production. However, when the temperature increases from 250 °C to 350 °C, yields decrease significantly. This phenomenon is due to CO_2 liquefaction, which is an exothermic reaction. With respect to methanol synthesis thermodynamics, the methanol synthesis reaction is favored at low temperatures. Figure 10 indicates that the optimal temperature for methanol synthesis is around 250 °C, which is in agreement with various studies reported [8, 41]. In those works, the typical operation temperature for methanol synthesis is in the range of 220 °C to 280°C.

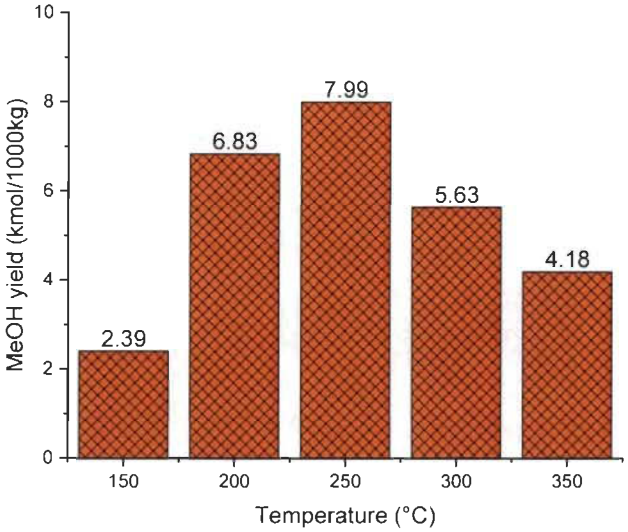

Figure 6.10 Effect of temperature on methanol yield (50 bar).

6.5.2.6 Effect of methanol synthesis operating pressure

Figure 6.11 shows the effect of methanol synthesis operating pressure on yield. It is observed that the methanol yield improves with increasing operating pressures, which is due to the reversible nature of the reaction (reducing the gas volume). Therefore, increasing reaction pressure favors the methanol production. For example, when the pressure increases from 1 bar to 50 bar, the methanol yield increases significantly from 0 kmol/1000 kg to 7.99 kmol/1000 kg. However, when the pressure increases from 50 bar to 150 bar, the yield increases barely from 7.99 kmol/1000 kg to 11.35 kmol/1000 kg. The methanol yield increase rate from 0 bar to 50 bar is more significant than the yields at a pressure between 50 bar and 150 bar. Besides, using strong operating pressures involve higher equipment requirements, price, and operational risks. Therefore, although the methanol production is favored at higher pressures, a pressure of 50 bar appears as a good compromise.

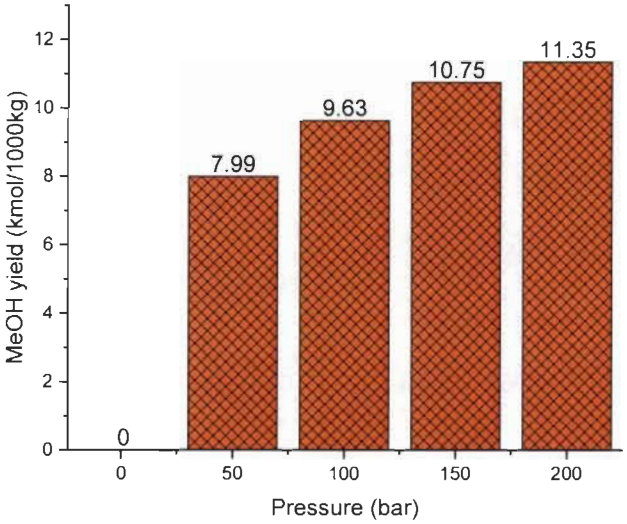

Figure 6.11 Effect of pressure on methanol yield (250 °C).

6.6 Conclusion

The objective of this study was to develop and validate a simulation model of methanol synthesis from a syngas obtained through pyrolysis oil gasification. For this purpose, Aspen Plus simulation software was used. The model was validated using experimental data from literature and the results show a good agreement between simulations and experimental data for gasification, Rectisol® and methanol synthesis processes. The validated model was then used to analyse the influence of operating conditions on key parameters.

More specifically, the influence of the gasification temperature and moisture content in pyrolysis oil on syngas composition and syngas SN value. Afterwards, Rectisol® operation condition and methanol synthesis operation condition on methanol yield were studied. When gasification temperature increased at 1000 °C, the concentration of CO and H_2 increased which results in the highest syngas SN value (0.85). The moisture content in pyrolysis oil should be kept at 30 wt.%, the SN reaches a maximum of 0.865. As the moisture content continues to increase, the syngas SN value is maintained at 0.865. The Rectisol® process was applied to absorb acid syngas and simultaneously adjust syngas SN value, Rectisol® unit was set at -20 °C and 40 bar. Then, syngas SN value reached a maximum of 2.07, the methanol yields also reached a maximum of 8.04 kmol. The methanol production is favored at high pressure and relatively low temperature. In this context, 50 bar and 250 °C were selected as the optimal operating conditions for the methanol synthesis.

Finally, Although the methanol yield of pyrolysis oil is relatively low compared to other feedstocks (e.g. biomass and natural gas), the high volumetric density of pyrolysis oil makes it less expensive to transport and store, this advantage gives biomass the opportunity to be used on a large-scale plant. Besides that, pyrolysis oil is a cleaner bioresource than its original biomass, syngas produced from pyrolysis oil contains less impurities, making the pyrolysis oil more suitable to methanol production process. This article briefly provides guidance for the future pyrolysis oil industrial application to produce methanol.

6.7 References

1. Taba, L.E., *et al.*, *The effect of temperature on various parameters in coal, biomass and CO-gasification: a review.* Renewable and Sustainable Energy Reviews, 2012. **16**(8): p. 5584-5596.

2. Zickfeld, K., S. Solomon, and D.M. Gilford, *Centuries of thermal sea-level rise due to anthropogenic emissions of short-lived greenhouse gases.* Proceedings of the National Academy of Sciences, 2017. **114**(4): p. 657-662.

3. McKendry, P., *Energy production from biomass (part 1): overview of biomass.* Bioresource technology, 2002. **83**(1): p. 37-46.

4. Ruiz, J.A., *et al.*, *Biomass gasification for electricity generation: Review of current technology barriers.* Renewable and Sustainable Energy Reviews, 2013. **18**: p. 174-183.

5. Rauch, R., J. Hrbek, and H. Hofbauer, *Biomass gasification for synthesis gas production and applications of the syngas.* Wiley Interdisciplinary Reviews: Energy and Environment, 2014. **3**(4): p. 343-362.

6. Abdoulmoumine, N., *et al.*, *A review on biomass gasification syngas cleanup.* Applied Energy, 2015. **155**: p. 294-307.

7. Moioli, S., L.A. Pellegrini, and S. Gamba, *Simulation of CO2 capture by MEA scrubbing with a rate-based model.* Procedia Engineering, 2012. **42**: p. 1651-1661.

8. Ortiz, F.G., *et al.*, *Methanol synthesis from syngas obtained by supercritical water reforming of glycerol.* Fuel, 2013. **105**: p. 739-751.

9. Gupta, M., I. Coyle, and K. Thambimuthu. *CO2 capture technologies and opportunities in Canada.* in *1st Canadian CC&S Technology Roadmap Workshop*. 2003.

10. Chihara, H., *Kagaku binran–kiso handbook of basic chemistry, 3rd edn, vol II.* Maruzen, Tokyo, 1984: p. 158.

11. Hochgesand, G., *Rectisol® and purisol.* Industrial & Engineering Chemistry, 1970. **62**(7): p. 37-43.

12. Gatti, M., *et al.*, *Review, modeling, Heat Integration, and improved schemes of Rectisol®®-based processes for CO2 capture.* Applied thermal engineering, 2014. **70**(2): p. 1123-1140.

13. Vancoillie, J., *et al.*, *The potential of methanol as a fuel for flex-fuel and dedicated spark-ignition engines.* Applied Energy, 2013. **102**: p. 140-149.

14. Breeze, P., *Chapter 8 - Direct Methanol Fuel Cell*, in *Fuel Cells*, P. Breeze, Editor. 2017, Academic Press. p. 75-82.

15. Larson, E.D. and R.E. Katofsky, *Production of hydrogen and methanol via biomass gasification*, in *Advances in thermochemical biomass conversion.* 1993, Springer. p. 495-510.

16. Chmielniak, T. and M. Sciazko, *Co-gasification of biomass and coal for methanol synthesis.* Applied energy, 2003. **74**(3-4): p. 393-403.

17. Alvarez, J., *et al.*, *Bio-oil production from rice husk fast pyrolysis in a conical spouted bed reactor.* Fuel, 2014. **128**: p. 162-169.

18. Staš, M., *et al.*, *Overview of analytical methods used for chemical characterization of pyrolysis bio-oil.* Energy & Fuels, 2014. **28**(1): p. 385-402.

19. Bridgwater, A. and M. Cottam, *Opportunities for biomass pyrolysis liquids production and upgrading.* Energy & Fuels, 1992. **6**(2): p. 113-120.

20. Radlein, D., *The production of chemicals from fast pyrolysis bio-oils.* Fast pyrolysis of biomass: a handbook, 1999. **164**.

21. Van Rossum, G., S.R. Kersten, and W.P. van Swaaij, *Catalytic and noncatalytic gasification of pyrolysis oil.* Industrial & engineering chemistry research, 2007. **46**(12): p. 3959-3967.

22. Huber, G.W., S. Iborra, and A. Corma, *Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering.* Chemical reviews, 2006. **106**(9): p. 4044-4098.

23. Demirbas, A., *The influence of temperature on the yields of compounds existing in bio-oils obtained from biomass samples via pyrolysis.* Fuel Processing Technology, 2007. **88**(6): p. 591-597.

24. Brown, R.C., D. Radlein, and J. Piskorz. *Pretreatment processes to increase pyrolytic yield of levoglucosan from herbaceous feedstocks.* in *ACS Symposium Series*. 2001. Washington, DC; American Chemical Society; 1999.

25. ÖZBAY, G., A. ÖZÇİFÇİ, and S. AYSAL, *PYROLYSIS OF BEECH WOOD CATALYSED BY FeCl3: PRODUCTION AND CHARACTERISATION OF BIO-OIL.* 9th Wood Science and Engineering in the Third Millennium–ICWSE, 2013. **1**: p. 75-81.

26. Rossum, G., Steam reforming and *gasification of pyrolysis oil.* 2009: University of Twente.

27. Oasmaa, A. and D. Meier, *Norms and standards for fast pyrolysis liquids: 1. Round robin test.* Journal of Analytical and Applied Pyrolysis, 2005. **73**(2): p. 323-334.

28. Krutof, A. and K. Hawboldt, *Blends of pyrolysis oil, petroleum, and other bio-based fuels: A review.* Renewable and Sustainable energy reviews, 2016. **59**: p. 406-419.

29. Zhang, Y., J. Xiao, and L. Shen, *Simulation of methanol production from biomass gasification in interconnected fluidized beds.* Industrial & engineering chemistry research, 2009. **48**(11): p. 5351-5359.

30. Yin, X., *et al.*, *Characteristics of the synthesis of methanol using biomass-derived syngas.* Energy & fuels, 2005. **19**(1): p. 305-310.

31. Begum, S., M. Rasul, and D. Akbar, *A numerical investigation of municipal solid waste gasification using aspen plus.* Procedia engineering, 2014. **90**: p. 710-717.

32. Ramzan, N., *et al.*, *Simulation of hybrid biomass gasification using Aspen plus: A comparative performance analysis for food, municipal solid and poultry waste.* Biomass and Bioenergy, 2011. **35**(9): p. 3962-3969.

33. Bussche, K.V. and G. Froment, *A Steady-State Kinetic Model for Methanol Synthesis and the Water Gas Shift Reaction on a Commercial Cu/ZnO/Al2O3Catalyst.* Journal of Catalysis, 1996. **161**(1): p. 1-10.

34. Zhang, C., *et al.*, *Efficient utilization of carbon dioxide in a gas-to-methanol process composed of CO2/steam–mixed reforming and methanol synthesis.* Journal of CO2 Utilization, 2016. **16**: p. 1-7.

35. Luyben, W.L., *Design and control of a methanol reactor/column process.* Industrial & Engineering Chemistry Research, 2010. **49**(13): p. 6150-6163.

36. Bell, D.A., B.F. Towler, and M. Fan, *Coal gasification and its applications.* 2010: William Andrew.

37. Chen, L., *et al.*, *Optimization of methanol yield from a Lurgi reactor.* Chemical engineering & technology, 2011. **34**(5): p. 817-822.

38. Atkin, P., *The elements of physical chemistry: with applications in biology.* 2000, WH Freeman and Company, New York.

39. Fernandez-Lopez, M., *et al.*, *Simulation of the gasification of animal wastes in a dual gasifier using Aspen Plus®.* Energy Conversion and Management, 2017. **140**: p. 211-217.

40. Pala, L.P.R., *et al.*, *Steam gasification of biomass with subsequent syngas adjustment using shift reaction for syngas production: An Aspen Plus model.* Renewable energy, 2017. **101**: p. 484-492.

41. Burr, B. and L. Lyddon. *A comparison of physical solvents for acid gas removal.* in *Gas Processors' Association Convention, Grapevine, TX.* 2008.

42. Trop, P., B. Anicic, and D. Goricanec, *Production of methanol from a mixture of torrefied biomass and coal.* Energy, 2014. **77**: p. 125-132.

6.8 Supplement information

Appendix A

Table 6.8 Pyrolysis oil non-conventional definition

Attribute ID:			
PROXANAL		SULFANAL	
MOISTURE	32.5	PYRITIC	0.001
FC		SULFATE	
VM		ORGANIC	
ASH			

Appendix B

Table 6.9 Gasification flowsheet in Aspen Plus

Component Mass flow (kg/hr)	1	2	3	MOISTURE	4	5	6
Temp (°C)	50	100	100	100	500	800	800
Pressure (bar)	1	1	1	1	1	1	1
Pyrolysis oil	1000						
Oil		675	675				
H_2O		325		325			
*H_2					4.15		
*O_2					32.82		
*C					30.40		
*N_2					0.27		
*S					0.001		
H_2O						trace	42.7
H_2						40.9	64.2
CO						570.1	386.0
CO_2						trace	500.4
CH_4						2.8	2.8
C						59.7	
H_2S						0.01	trace
H_3N						3.8	3.3
C_2H_6						trace	trace

*Elemental distribution

Appendix C

Table 6.10 Syngas post-treatment flowsheet in Aspen Plus

Mass Flow (kg/hr)	6	7	8	9	10	RE-MEOH	11	12	DIRTY GAS	MEOH-H_2O	DIRTY H_2O	13	14
Temp (°C)	800	800	800	80	80		-20	-20	-20	-20	-20	250	250
Pressure (bar)	1	1	1	1	40		40	40	1	1	1	40	50
H_2O	42.7		42.7	42.7	42.7			42.7		42.7	42.7		
H_2	64.2		64.2	64.2	64.2		64.2					64.2	64.2
CO	386.0		386.0	386.0	386.0		386.0					386.0	386.0
CO_2	500.4		500.4	500.4	500.4		50.2	450.2	450.2			50.2	50.2
CH_4	2.8		2.8	2.8	2.8		2.8					2.8	2.8
H_2S	trace		trace	trace	trace			trace	trace				
H_3N	3.3		3.3	3.3	3.3			3.3	3.3				
ASH	0	0											
MeOH						640		640		640			

Appendix D

Table 6.11 Methanol synthesis flowsheet in Aspen Plus

Component Mass flow (kg/hr)	**14**	**15**	**16**	**17**	**18**
Temp (°C)	250	250	50	50	50
Pressure (bar)	50	50	1	1	1
H_2	64.2	31.0	31.0	31.0	
CO	386.0	175.6	175.6	175.6	
CO_2	50.2	26.8	26.8	26.8	
CH_4	2.8	2.8	2.8	2.8	
H_2O		9.5	9.5		9.5
MeOH		257.3	257.3		257.3

6.9 Unit specification

6.9.1 Gasification

Table 6.12 Drying (RStoic) reactor specification

Temperature (°C)	100
Pressure (bar)	1
Fractional conversion	0.325 component of pyrolysis-oil

Table 6.13 Decomposition (Ryield) reactor specification

Temperature (°C)	500
Pressure (bar)	1
Yield options	Component yields
H_2	4.15
C	32.8
O_2	30.4
N_2	0.27
S	0.001

Table 6.14 Combustion and gasification (RGibbs) reactor specification

Calculation option	**Calculate phase equilibrium and chemical equilibrium**
Temperature (°C)	800
Pressure (bar)	1
Products	Identity possible products
Component	Valid phases
CO	Mixed
H_2	Mixed
CO_2	Mixed
CH_4	Mixed
NH_3	Mixed
H_2S	Mixed

6.9.2 Rectisol®

Table 6.15 Rectisol® (RadFrac) block specification (Configuration)

Calculation type	**Equilibrium**
Number of stages	15
Condenser	None
Reboiler	None

Valid phases	Vapor- Liquid
Convergence	Standard

Table 6.16 Steam: Feed

Name	Stage	Convention
9	1	Above-stage
10	15	On-stage

Table 6.17 Steam: Product

Name	Stage	Phase	Basis	Units
11	15	Liquid	Mole	kmol/hr
12	1	Vapor	Mole	kmol/hr

Table 6.18 Pressure specification

View	Top/Bottom
Top stage/ Condenser pressure (bar)	1~80

6.9.3 Methanol synthesis

Table 6.19 Methanol synthesis (RPLUG) reactor specifications

Reaction type:	**Reactor with specified temperature**
Configuration:	
Multitube reactor:	Number of tubes: 11458
Tube dimensions:	Length: 12.0 meters Diameter: 0.03675 meter
Catalyst specifications:	
Bed voidage	0.5
Particle density	2000 kg/m^3

Table 6.20 Water gas shift kinetic LHHW parameters

R1 ($CO_2 + H_2 \rightarrow CO + H_2O$)	
Kinetic factor	k = 1 n = 0 E = 0 kJ/kmol
Driving-force expressions (partial pressure):	
Term 1	
Concentration exponents for reactants	$CO_2 = 1$, $H_2 = 0$
Concentration exponents for products	CO = 0, $H_2O = 0$
Coefficients:	A = 4.80, B = -11398.2, C = 0, D = 0
Term 2	
Concentration exponents for reactants	$CO_2 = 0$, $H_2 = -1$

Concentration exponents for products	CO = 1, H_2O = 1
Coefficients:	A = 0.13, B = -6624.98, C = 0, D = 0
Adsorption expression:	
Adsorption term exponent:	1
Concentration exponents:	
Term 1:	H_2 = 0, H_2O = 0
Term 2:	H_2 = -1, H_2O = 1
Term 3:	H_2 = 0.5, H_2O = 0
Term 4:	H_2 = 0, H_2O = 1
Adsorptions constantes:	
Term 1:	A = 0, B = 0, C = 0, D = 0
Term 2:	A = 8.15, B =0, C = 0, D = 0
Term 3:	A = -6.45, B =2068.44, C = 0, D = 0
Term 4:	A = -34.95, B =14928.90, C = 0, D = 0

Table 6.21 Methanol synthesis kinetic LHHW parameters

R2 ($CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$)	
Kinetic factor	k = 1 n = 0 E = 0 kJ/kmol
Driving-force expressions (partial pressure)	
Term1	
Concentration exponents for reactants	CO_2 = 1, H_2 = 1
Concentration exponents for products	CH_3OH = 0, H_2O = 0
Coefficients:	A = -29.87, B = 4413.76, C = 0, D = 0
Term 2:	
Concentration exponents for reactants	CO_2 = 0, H_2 = -2
Concentration exponents for products	CH_3OH = 1, H_2O = 1
Coefficients:	A=17.55, B = -2645.97, C = 0, D = 0
Adsorption expression	
Adsorption term exponent:	3
Concentration exponents:	
Term 1:	H_2 = 0, H_2O = 0
Term 2:	H_2 = -1, H_2O = 1
Term 3:	H_2 = 0.5, H_2O = 0
Term 4:	H_2 = 0, H_2O = 1
Adsorptions constantes:	
Term 1:	A = 0, B = 0, C = 0, D = 0
Term 2:	A = 8.15, B =0, C = 0, D = 0
Term 3:	A = -6.45, B =2068.44, C = 0, D = 0
Term 4:	A = -34.95, B =14928.9, C = 0, D = 0

Chapter 7 - Article 3: Simulation and Techno-Economic Assessment of Bio-methanol from Biomass, Biochar and Pyrolysis Oil

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7.1 Foreword

This paper published a fuel synthesis application of pyrolysis oil. Based on the simulation of methanol synthesis in the previous paper, an economic analysis of the feasibility of producing methanol from pyrolysis oil was carried out. At the same time, the same model design and analysis were conducted between biomass and biochar. This comparison is used to test whether pyrolysis oil is potentially competitive. The economic evaluation is performed using three indicators such as NPV, IRR and DPBP. The sensitivity analysis is performed by varying parameters such as bio-methanol price, feedstock price, TCI and plant life to study the economic feasibility at different plant scales.

7.2 Abstract

In this paper, a model simulating bio-methanol production through gasification of different woody bioresources (pine biomass, biochar, and pyrolysis oil) is investigated using process simulation software Aspen Plus. The process consists of gasification, syngas post-treatment, methanol synthesis with recycling and purification. The model results are used as inputs in a techno-economic analysis of the process to assess the economic feasibility, as well as a sensitivity analysis to evaluate the impact of key variables. The economic evaluation is conducted by using three indicators, i.e., the net present value (NPV), internal rate of return (IRR), and discounted payback period (DPBP). The sensitivity analysis is achieved to investigate the economic feasibility of different plant scales, changing parameters such as bio-methanol price, feedstock price, total capital investment (TCI), and plant lifespan. The preliminary economic evaluation results revealed that bio-methanol production from biochar can be an attractive option. The IRR obtained in the biochar scenario is greater, compared to using pine biomass. The IRR obtained in the pyrolysis oil scenario hardly reaches 5% unless the price considered for bio-methanol is as high as 2300 $/ton. Moreover, our results show that the bio-methanol price, feedstock price and TCI are the most significant factors. Finally, for plant lifespan, the first 20 years seem to be the most crucial.

Keywords: pine biomass; biochar; pyrolysis oil; bio-methanol; Aspen Plus; Techno-economic analysis, sensitivity analysis, profitability analysis.

7.3 Introduction

Nowadays, the global energy consumption increases drastically, which has led to an alarming rise in emissions of greenhouse gases (GHG). Emissions produced from fossil fuels have a dominant influence on the atmospheric CO_2 concentration, which results in rising global temperatures. According to the International Energy Outlook [1], world energy-related CO_2 emissions will increase from 30.2 billion metric tons in 2008 to 43.2 billion metric tons in 2035. The depletion of fossil fuels and the environmental challenges are the main motivations for the development of renewable and sustainable energy technologies. In this context, bio-based energy sources are a renewable and environment-friendly alternative. Among those, biofuels are considered as one of the most promising alternatives to conventional fuels. In fact, biofuels can be produced from biomass and thus considered as a renewable energy. Biofuels produced from biomass are renewable and regenerative (unlike fossil fuels). In addition, the biomass captures the carbon dioxide produced during the combustion of these biofuels, making it possible to be carbon neutral and even to have negative impact [2].

Pyrolysis can be described as the thermal decomposition of biomass with little or no oxygen to produce solid (biochar), liquid (pyrolysis oil) and gas (syngas) products. Adapting the temperature and residence time in the reactor enables to modify the share of each of these products. For example, fast pyrolysis involves faster heating rates and shorter residence times than slow pyrolysis in order to favor the liquid fraction production [3]. Pyrolysis oil (or bio-oil) is a mixture of more than hundred compounds, and its chemical composition includes carboxylic acids, sugars, alcohols, aldehydes, ketones, esters, furan, and a wide range of aromatics [4]. Moreover, pyrolysis oil is known to present a high-water content, which fluctuates generally between 15 and 25 wt.% (depending on pyrolysis process and biomass used) [5-7]. On the other hand, carbon-rich solid material is also produced during pyrolysis. This material is often named "biochar" and often presents large microscopic surface and high ash content [8]. The biochar is produced from biomass by slow pyrolysis process, which utilizes intermediate temperatures (300~600℃) with an oxygen limited or oxygen free atmosphere to convert the solid biomass into biochar [9, 10]. The quality and yield of pyrolysis-oil and biochar production from biomass depend mainly on the operating conditions: temperature, heating rates and residence time [11].

In comparison with biomass, biochar and pyrolysis oil have several advantages. First of all, biochar produced from biomass through slow pyrolysis has a higher bulk density, which can be economically transported over long distances. This characteristic can be increased at higher temperature [12]. The major application of biochar is found in four main areas: (1) soil improvement, (2) waste management, (3) climate change mitigation, and (4) energy generation [13]. On the other hand, pyrolysis oil has the advantage of a low content in sulfur, nitrogen and ash, leading to a better environmental performance. Therefore, its combustion produces less harmful gas emissions such as nitrogen oxides (NOx) and sulfur dioxide (SO_2), compared to conventional fossil fuels. Besides, volumetric energy density of pyrolysis oil is about 5 times higher than the "bulk" biomass [14, 15], making transportation economically more attractive, especially over long distances [14]. Pyrolysis oil also presents a promising alternative for high-efficiency energy production. Current research is being carried out to use pyrolysis oil to generate heat and power [16] [17]. Alternatively, both pyrolysis oil and biochar can be used in biorefineries to produce biofuels (gasoline and diesel) through gasification process [17].

Gasification is regarded as a key technology to convert feedstock into syngas, which can be transformed into synthesized fuels (through Fischer-Tropsch process) and/or chemicals (e.g. methanol) [18]. Several publications and studies on gasification of biochar and pyrolysis oil in recent years have shown that this technique has become popular and promising. For example, Yan et al. [19] carried out gasification of pine sawdust biochar to produce syngas in a fixed bed. The hydrogen volume fraction reached up to 52.4% at 850 °C, with a steam flow of 165 g.min-1.kg-1 biochar. Chaudhari et al. [19] carried out steam gasification of bagasse biochar, and the maximum hydrogen volume fraction reached up to 76.2% at 700 °C and a steam flow rate of 20.8 g. min-1.kg-1 of biochar. Van Rossum et al. [20] studied the gasification of beech oil in fluidized bed and achieved a hydrogen volume fraction of 55.5% at around 800 °C.

Methanol is an energy-dense and reasonably stable liquid under normal conditions, which is considered as a potential renewable alternative fuel. Several advantages of methanol, such as higher boiling points, lower production cost, and enhanced energy security, make it widely used in the engines and fuel cells (e.g., as a fuel by itself, or to be blended with gasoline [21]). Methanol is also an important primary raw material for the chemical industry (e.g., as solvent, or as key molecule to produce formaldehyde, olefins, acetic acid, esters, etc.) [22]. Currently, about 90% of methanol produced comes from natural gas [23].

In this research, all processes such as gasification, syngas post-treatment, methanol synthesis, and methanol distillation have reached maturity. However, high feedstock costs compared to natural gas will limit the technology for years to come. Project evaluation is the key to evaluating economic feasibility, which can be accomplished by techno-economic analysis (TEA). TEA allows to assess economic feasibility of a project by varying different parameters to assess market availability [24].

In this paper, a model simulating bio-methanol production through the gasification of various feedstocks (biomass, biochar, and pyrolysis oil) was developed, validated and used to predict the bio-methanol yield. Firstly, the assumptions, the description, and the validation of the model are discussed. Thereafter, the TEA was conducted to evaluate key indicators, i.e., the net present value (NPV), discounted payback period (DPBP) and internal rate of return (IRR). Lastly, a sensitivity analysis is achieved to investigate the impact of several key parameters, such as the bio-methanol price, feedstock price, total capital investment (TCI), and plant lifespan at various plant scales.

7.4 Process modeling and analysis

7.4.1 Materials

The feedstock materials used in this study are pyrolysis oil, biochar and biomass. The biochar was produced from rapeseed cultivated in Germany and processed by pyrolysis using a Pyroformer apparatus at Aston University [25]. Pyrolysis oil was produced from beech chips in the pilot plant facility (200 kg/h) of the company BTG, Netherlands [20]. The pine biomass sample was chosen from the region of Castilla La Mancha (Spain) [26]. Proximate, ultimate and elemental analysis of each sample are presented in **Table 7.1**.

Table 7.1 Elemental and calorific analysis of pyrolysis oil, biochar and biomass

Composition	Pyrolysis oil [20]	Biochar [25]	Biomass [26]
Carbon (wt.%)	30.4 ~ 37.7	60.3	52.7
Hydrogen (wt.%)	7.6 ~ 7.9	4.0	5.5
Oxygen (wt.%)	54.4 ~ 61.7	27.2	41.7
Nitrogen (wt.%)	< 0.01	4.20	0.01
Sulfur (wt.%)	< 0.01	0.01	0.08
Ash (wt.%)	-	4.2	2.7
Gross calorific value (MJ/kg)	17	24	20

7.4.2 Modeling methodology

The whole process model was simulated by the Aspen Plus software. A schematic of the generalized process model presented in **Figure 7.1** shows that the following units are considered: gasification, syngas post-treatment, methanol synthesis and distillation. Firstly, feedstocks are fed to the gasifier unit to produce syngas via gasification. Syngas is then introduced into the post-treatment unit to remove impurities, such as H_2S, COS, NH_3, tar, and char. Post-treated syngas is fed into methanol synthesis unit to produce methanol via hydrogenation of CO_2 and CO. Lastly, distillation is achieved to separate synthetic methanol and unreacted syngas. Aspen plus blocks used in the simulation are described in **Table 7.2**.

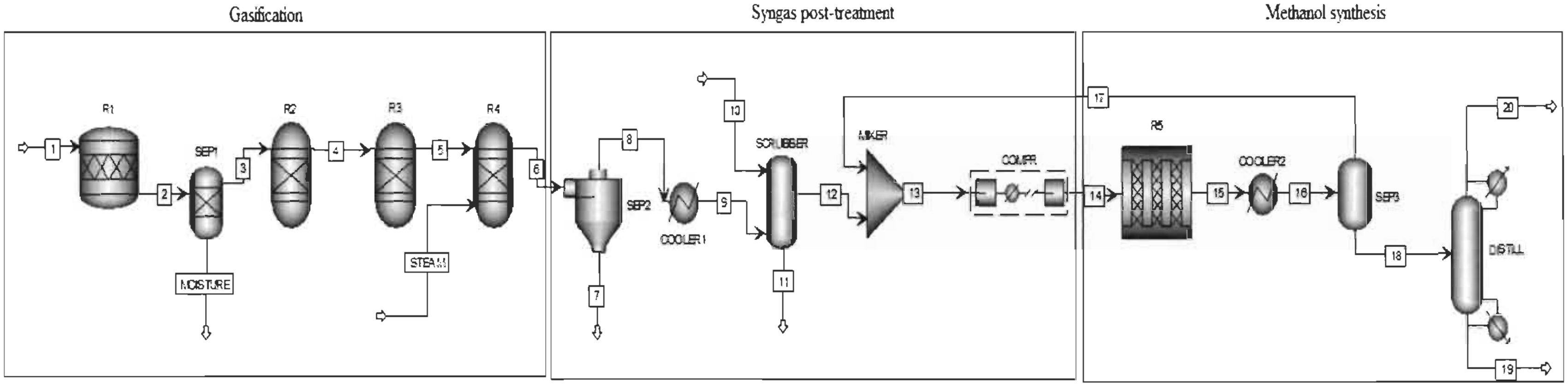

Figure 7.1 Process flow diagram of the Aspen Plus simulation of bio-methanol synthesis

Table 7.2 Reactor blocks description used in the simulation

Unit	Aspen plus Reactor block	Temperature (°C)	Pressure (bar)	Description
R-1	RStoic	100	1	Simulate drying process to extract moisture from feedstock
SEP-1	Sep	100	1	Separate moisture and feedstock
R-2	RYield	500	1	Decompose non-conventional feedstock into its components by FORTRAN statement
R-3	RGibbs	800	1	Complete chemical equilibrium by minimizing Gibbs free energy
R-4	RGibbs	800	1	Calculate syngas composition by minimizing Gibbs free energy
SEP-2	SSplit	800	1	Separate ash from syngas
COOLER1	Heater	60	1	Cool down syngas temperature
SCRUBBER	RadFrac	40	1	Remove H_2S, NH_3, and tar
M-1	MCompr	40	50	Compress syngas to high pressure
R-5	REquil	250	50	Methanol synthesis reactor
COOLER	Heater	60	1	Cool down produced methanol temperature
Flash	Flash 2	60	1	Separate gas stream with liquid stream
DISTILL	RadFrac	25	1	Distillate methanol

7.4.2.1 Gasification

When modeling gasification in Aspen Plus software, biomass, biochar and pyrolysis oil are specified as non-conventional (NC) components. The NC definitions of biomass, biochar, and pyrolysis oil are shown in Appendix A. Peng-Robinson equation of state with Boston-Mathias alpha function (PR-BM) was chosen to estimate all physical properties of the conventional components in the gasification process, which guarantees accurate calculation results in modeling light gases, alcohols, and hydrocarbons [27].

The gasification unit is composed of four parts, namely, drying (R1), decomposition (R2), combustion (R3), and gasification (R4) [28]. First of all, feedstock (stream 1) is fed into the drying chamber to extract moisture which is removed by a separator (SEP1). Then, the decomposition process is used to convert dry feedstock (stream 3) into its elemental composition (C, H, O, N, S, etc.) (stream 4). The combustion process is used to complete chemical equilibrium by minimizing the Gibbs-free energy. After combustion, the model of gasification process with steam is used to calculate syngas composition by minimizing Gibbs-free energy. Eventually, the whole gasification process generates a syngas (stream 6) composed mainly of CO, CO_2, H_2, and CH_4. The production of those gases and steam in the whole process can be explained by the reactions given in (R-1 – R-8), which occur at various stages [29]. Considering the heat loss, the gasifier efficiency is 72.9% [30].

$C + 1/2O_2 \rightarrow CO$	- 111 MJ/kmol	Combustion reaction (R-1)
$C + O_2 \rightarrow CO_2$	- 283 MJ/kmol	Combustion reaction (R-2)
$H_2 + 1/2O_2 \rightarrow H_2O$	- 286 MJ/kmol	Combustion reaction (R-3)
$C + CO_2 \leftrightarrow 2CO$	+172 MJ/kmol	Boudouard reaction (R-4)
$C + 2H_2 \leftrightarrow CH_4$	- 75 MJ/kmol	Methanation reaction (R-5)
$C + H_2O \leftrightarrow CO + H_2$	+131 MJ/kmol	Water gas reaction (R-6)
$CO + H_2O \leftrightarrow CO_2 + H_2$	- 41 MJ/kmol	Water gas shift reaction (R-7)
$CH_4 + H_2O \leftrightarrow CO + 3H_2$	+206 MJ/kmol	Steam methane reforming reaction (R-8)

7.4.2.2 Syngas post-treatment

The syngas post-treatment is composed of four units, namely, a cyclone (SEP2), a cooler (COOLER1), a water scrubber (SCRUBBER), and a multistage compressor (COMPR). The generated syngas is introduced into a cyclone to remove condensable materials and solids (stream 7) from syngas. Then, high temperature syngas from the cyclone is cooled to 60 °C by a cooler. Afterward, cold syngas (stream 9) is fed into a water scrubber used to remove impurities such as particulates, ammonia, halides, and tars. After quenching and removing impurities, the scrubbed syngas (stream 13) is compressed to high pressure by using a multistage compressor.

7.4.2.3 Methanol synthesis

After syngas post-treatment, the purified gases (stream 14) are sent into the methanol synthesis reactor where hydrogenation of CO_2 and CO occurs over a Cu-based catalyst.

Due to the principle of Le Chatelier, working at low-temperature and high-pressure favors the methanol synthesis. Therefore, the operating pressure and temperature of methanol synthesis are defined within 50-150 bar and 200-300 °C respectively, in the presence of Cu-based catalyst [31]. The methanol synthesis process is modelled by a stoichiometric reactor (R5) in Aspen plus software. Considering the side reactions in the methanol synthesis process, we assume that the efficiency of the methanol synthesis is 80%, as explained in Appendix B [32]. The reactions leading to methanol synthesis are expressed as follows:

$$\mathrm{CO} + 2\mathrm{H}_2 = \mathrm{CH}_3\mathrm{OH} \quad (\Delta \mathrm{H}_{300\mathrm{K}} = -90.77\ \mathrm{kJ/mol}) \qquad \textbf{Equation 7.1}$$

$$\mathrm{CO}_2 + 3\mathrm{H}_2 = \mathrm{CH}_3\mathrm{OH} + \mathrm{H}_2\mathrm{O}\ (\Delta \mathrm{H}_{300\mathrm{K}} = -49.16\ \mathrm{kJ/mol}) \qquad \textbf{Equation 7.2}$$

7.4.2.4 Methanol distillation

After methanol synthesis, the crude products (stream 15) which contains methanol and unreacted syngas are cooled to 80 °C by a cooler. Then, a flash (SEP3) unit allows to separate unreacted syngas from mixture of water and bio-methanol. The unreacted gas (stream 17) is discharged from the top outlet of flash and recycled into the methanol synthesis reactor. At the same time, the liquid stream (bio-methanol and steam: stream 18) is discharged from the bottom outlet of flash, which contains methanol and water. At last, the liquid stream is injected to the distillation (DISTILL) unit to purify methanol where product methanol is extracted at the upper stream (stream 20), the water and trace methanol (stream 19) are discharged from the bottom of distillation column.

7.4.3 Model validation and results

Both syngas composition produced during gasification and overall methanol yield by different feedstocks are listed in **Table 7.3**. The flow sheets of each scenario (biomass, biochar, and pyrolysis oil) in Aspen Plus are presented in Appendix B. The simulation model is validated by using experimental data about the gasification of pine biomass [26], biochar [25] and pyrolysis oil [20], respectively. As we can see, the syngas concentration is in good agreement with experimental results, except for the concentration of CH_4. Experimentally, the steam methane reforming reaction is limited by the reaction time, therefore it cannot reach the complete equilibrium state [33]. Thus, the concentration of methane simulated by RGibbs reactor is very low and this part of CH_4 reacts with steam into CO and H_2 (according to R-8). It may be observed that the bio-methanol yield produced from biochar reached up a maximum of 578.2 kg/ 1000 kg. This is due to its composition which contains the highest carbon content, compared to biomass and pyrolysis oil. Therefore, it required large quantity of water to complete water gas reaction (**R-6**). The content of CO and CO_2 increases with increasing carbon content in each feedstock (H_2 content can be supplied by steam to react with carbon and CO_2, according to R-6 and R-7). As expected, the bio-methanol yield produced from pyrolysis oil is the lowest. This result could be easily explained by the carbon content in pyrolysis oil, which is the lowest of the three chosen feedstocks (see **Table 7.1**). In previous studies [34], the overall efficiency of conversion of biomass, coal to bio-methanol is 50~60%, in our model, the overall bio-methanol yield is 58.3%, as presented in Appendix B. The simulated and experimental results of bio-methanol yield are approximately similar.

Table 7.3 Comparison between experimental and simulated syngas composition and bio-methanol yields

Syngas composition (vol %)	**Biomass (1000kg)+ H_2O (700 kg)**		**Biochar (1000kg)+ H_2O (1000 kg)**		**Pyrolysis oil (1000 kg^a)**	
	Experiment [26]	Model	Experiment [25]	Model	Experiment [20]	Model
H_2	45-55	57.1	56-58	56.2	55.5	55.9
CO	21-25	24.8	19-21	24.6	19.3	24.0
CO_2	18-22	17.8	20-21	18.9	19.0	19.8
CH_4	2-4	0.3	0.5-1	0.3	5.4	0.3
Bio-methanol yield (kg/1000 kg)	507.3		578.2		283.1	

a) water content comes from pyrolysis oil

7.5 Techno-economic analysis

The following techno-economic analysis uses the previous Aspen Plus simulations to evaluate the economic feasibility of a bio-methanol production plant using various bioresources, providing a basis for investment decisions.

7.5.1 Methodology

When calculating the techno-economic analysis, the costs can be divided into two main categories: capital and operating costs.

7.5.1.1 Total capital investment

To determine the costs of a bio-methanol production plant with different sizes and feedstocks, the total capital investment (TCI) should be estimated first. This first calculation is then used to establish the other costs. The capital investments of equipment such as the gasifier, syngas post-treatment units, and methanol synthesis reactor were determined by the six-tenth factor rule [35]. Equipment costs were updated by using the 2018 Chemical Engineering Plant Cost Index (CEPCI) [36]. The costs of each equipment are scaled from base equipment costs by following **Equation 7.3**, where: $Cost_1$ is the scaled new equipment cost and $Cost_0$ is the base equipment cost; $size_1$ is the size of new equipment and $size_0$ is the size of base equipment; *n* is the scaling exponent for a different system. Both scaling factor and base equipment cost come from literature [37].

$$Cost_1 = Cost_0 \left[\frac{size_1}{size_0}\right]^n \qquad \textbf{Equation 7.3}$$

The TCI of a chemical plant includes purchased equipment, installation, instruments, electrical systems, buildings, service facilities, supervision, contractor's fee, etc. TCI can be divided into 2 categories: fixed capital cost (FC) and working capital (WC) (**Equation 7.4**). FC is the capital needed to supply the manufacturing and plant facilities (**Equation 7.5**). WC is the capital needed to operate the plant until company gets income.

$$\text{TCI} = \text{Fixed Capital Cost (FC)} + \text{Working Capital (WC)} \qquad \textbf{Equation 7.4}$$

Where

$$\text{FC} = \text{Direct cost} + \text{Indirect cost} \qquad \textbf{Equation 7.5}$$

In general, plant scale strongly affects its economy, the equipment cost decreasing with the upscaling of plant capacity [37]. Therefore, before achieving the techno-economic analysis, it is necessary to hypothesize about the plant's capacity. In our study, we assume that the plant's capacities are 500 tons/day (TPD), 1000 TPD, 1500 TPD, 2000 TPD, and 2500 TPD respectively.

7.5.1.2 Total product cost

The total product cost (TPC) consists of all costs required for efficiently operating the plant over the plant's life. The total product cost (TPC) calculation was based on several economic assumptions that are listed in **Table 7.4**. TPC was calculated by following **Equation 7.6**.

Table 7.4 Economic assumptions for total product cost estimation

Item	Economic assumptions
1. Raw materials	Pyrolysis oil 117 US$/ton [38] Biochar 71 US$/ton [39] Biomass 40 US$/ton [40]
2. Utilizes (electricity, fuel, stream, water, air, refrigeration and cool agent)	10% of total product cost [41]
3. Operating & maintenance	
3.1 Operating labor	30,40,50,60, and 70 labors/shift for Cases 1,2,3,4, and 5 respectively, 3 shifts/day, 60,000 $/labor/year
3.2 Supervisory	20% of operating labor
3.3 Maintenance & Repairs	6% of fixed capital investment
3.4 Maintenance supplies	15% of maintenance and repairs
3.5 Laboratory charges	15% of operating labor
4. Patents & Royalties (Indirect cost)	1% of total product cost
5. Depreciation	Recovery period 20 years, salvage value 5%
6. Local taxes & insurance	3% of fixed capital investment
7. Plant overhead costs	60% of (3.1 + 3.2 + 3.3)
8. General expenses	
8.1 Administration	5% of production cost
8.2 Marketing	5% of total production cost
8.3 Research & Development	4% total production cost
9. Total Operating cost (TPC)	1 + 2 + 3 + 4 + 5 + 6 + 7 + 8

Where

$$TPC = C_R + C_U + C_{OM} + C_{PR} + C_D + C_{LI} + C_P + C_G$$ **Equation 7.6**

Where C_R, C_U, C_{OM}, C_{PR}, C_D, C_{LI}, C_P, and C_G represent the cost of raw material, utilities, operating and maintenance, patents and royalties, depreciation, tax and insurance, plant overhead, and general expenses, respectively. The depreciable value of an asset is the initial cost of the fixed capital investment minus the salvage value at the end of the considered depreciable life. For this chemical project, the salvage value is taken as 0. In this research, a straight-line calculation method was selected as **Equation 7.7**, due to it is a simple method and distributes depreciation evenly over the life of the property.

$$\text{Annual depreciation} = \frac{(\text{fixed capital investment } - \text{salvage value})}{\text{service life}}$$ **Equation 7.7**

Before calculating the TPC, a number of assumptions were adopted firstly, as listed in **Table 7.5**.

Table 7.5 Economic analysis assumptions.

Item	Economic assumptions
1. Steam	Self-produced
2. Project life	20 years + 3 years for construction
3. Plant uptime	350 days/year
4. Construction period	3 years
5. Construction inflation rate	2%/year
6. Income tax rate	35%
7. Interest rate	5%
8. Hurdle rate	10%
9. Bio-methanol price	1100 \$/ton [42]

7.5.1.3 Profitability indicators

Three indicators were chosen to assess the project profitability: Net Present Value (NPV), Internal Rate of Return (IRR), and discounted payback period (DPBP). The NPV, IRR and DPBP calculations are shown in the following **Equations (7.7, 7.8** and **7.9**). The IRR is defined as the discount rate i at where the NPV equals to zero. The minimum acceptable IRR and DPBP values are set as 5% and 10 years [30, 43, 44].

$$\mathrm{NPV} = \sum_{\mathrm{t}=1}^{\mathrm{n}} \frac{\mathrm{C_t}}{(1+\mathrm{i})^{\mathrm{t}}} - \mathrm{C_0}$$ **Equation 7.8**

$$NPV = \sum_{t=1}^{n} \frac{C_t}{(1+IRR)^t} - C_0 = 0$$ **Equation 7.9**

$$DPBP = A + \frac{B}{C}$$ **Equation 7.10**

Where i = discount rate;

t = number of time periods;
n = total number of years;
C_0 = total initial investment cost;
C_t = net cash inflow during the period;
A = last period with a negative discounted cumulative cash flow;
B = absolute value of discounted cumulative cash flow at the end of the period A;
C = discounted cash flow during the period after A.

7.5.2 Economic evaluation results

The main equipment costs estimation of methanol plant at different scales is shown in **Table 7.6**. The TCI of methanol synthesis process by different scales are listed in **Table 7.7**. The TCI listed in Table 7 for all cases are between 329 and 1050.5 M$. These estimations are close to previous research results, e.g., in [43] where the authors computed a TCI of 1036.21 M$ for a 2500 TPD-case of methanol production plant from carbon dioxide.

Even though the TCI increases with increasing plant capacity, the capital investment per TPD decreases simultaneously (economies of scale). The capital investment per TPD by various scales is illustrated in **Figure 7.2**. The results show that the capital investment per TPD gradually decreases with the increase in plant scale. This trend is consistent with economies of scale i.e., the cost per unit of production decreases as the scale increases. As the plant scale increases from 500 to 2500 TPD, we can observe a gradual decrease in TCI per TPD by different feedstocks: biomass (185.3 to 118.3 $/TPD), biochar (162.6 to 103.8 $/TPD), and pyrolysis oil (332.0 to 212.0 $/TPD).

Table 7.6 Methanol plant scale factors and main equipment costs estimation

No.	Description	Scaling factor	Case 1 (500 TPD) Cost [M$]	Case 2 (1000 TPD) Cost [M$]	Case 3 (1500 TPD) Cost [M$]	Case 4 (2000 TPD) Cost [M$]	Case 5 (2500TPD) Cost [M$]	Ref.
1	Gasification	0.75	11.0	18.6	25.2	31.2	36.9	[45]
2	Syngas cleaning up	0.70	26.8	43.6	57.9	70.8	82.8	[30]
3	Syngas compressor	0.85	4.9	8.9	12.6	16.1	19.4	[37]
4	Methanol synthesis	0.70	23.8	38.7	51.5	62.9	73.6	[45]
5	Methanol distillation	0.65	0.5	0.8	1.0	1.3	1.5	[30]
6	Coolers	0.80	1.4	2.5	3.5	4.4	5.3	[46]
7	Steam system & power generator (HRSG)	0.70	11.7	18.9	25.2	30.8	36.0	[30]
Total purchased equipment cost			80.1	132.0	176.9	217.5	255.5	n.a.
Total purchased equipment cost (delivered)			88.1	145.2	194.6	239.3	281.1	n.a.

Table 7.7 Total capital investment estimation

Items	**Ratio factor**	**Case 1 Cost [M$]**	**Case 2 Cost [M$]**	**Case 3 Cost [M$]**	**Case 4 Cost [M$]**	**Case 5 Cost [M$]**
1. Direct cost						
1.1 Purchased equipment (delivered)	1	88.1	145.2	194.6	239.3	281.1
1.2 Equipment installation	0.40 [47]	35.2	58.1	78.8	95.7	112.4
1.3 Instrumentation & controls	0.20 [47]	17.6	29.0	38.9	47.9	56.2
1.4 Piping	0.15 [47]	13.2	21.8	29.2	35.9	42.2
1.5 Electrical systems	0.15 [47]	13.2	21.8	29.2	35.9	42.2
1.6 Buildings	0.30 [48]	26.4	43.6	58.4	71.8	84.3
1.7 Yard improvements	0.10 [49]	8.8	14.5	19.5	23.9	28.1
1.8 Service facilities (waste treatment, receiving, shipping, packaging, storage, offices, etc.)	0.20 [50]	17.6	29.0	38.9	47.8	56.2
2. Indirect capital cost						
2.1 Engineering and supervision	0.25 [47]	22.0	36.3	48.8	59.8	70.3
2.2 Contingency	0.30 [50]	26.4	43.6	58.4	71.8	84.3
2.3 Contractors fees/overheads/profits	0.10 [50]	8.8	14.5	19.5	23.9	28.1
2.4 Start-up	0.10 [50]	8.8	14.5	19.5	23.9	28.1
3. Additional investment						
3.1 Working capital	0.15 FCI [48]	42.9	70.8	95.1	116.6	137.0
Fixed capital investment (FCI)	FCI=direct cost + indirect cost	286.1	471.9	633.7	777.6	913.5
Total capital investment (TCI)	TCI=FCI+ WC	329.0	542.7	728.8	894.2	1050.5

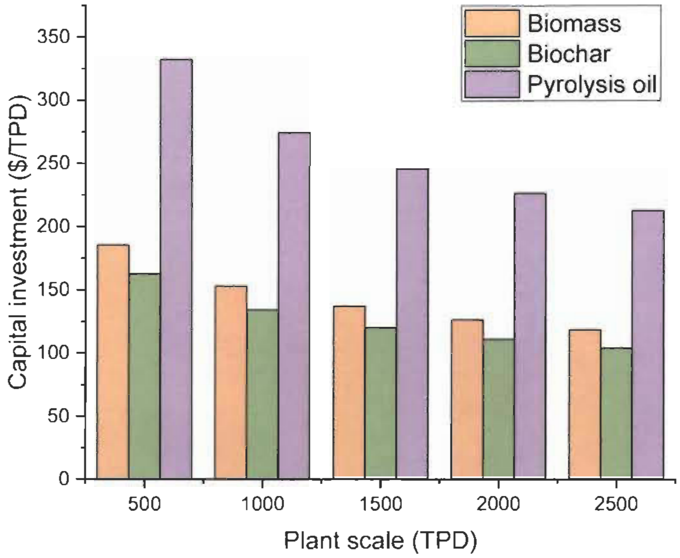

Figure 7.2 Effects of plant scale on the capital investment

Figure 7.3 shows the breakdown of total product costs (TPC) for different feedstocks at different scales. Higher plant scales lead to an increase of the TPC. In each case, the TPC of pyrolysis oil is higher than that of biochar and biomass. This result was expected given that pyrolysis oil price is the highest (**Table 7.4**). For example, the product cost of pyrolysis oil of Case 1 is 110.5M$, which is 4.7 M$ and 18.0 M$ higher than that of biochar and biomass. This is mainly due to the higher feedstock cost.

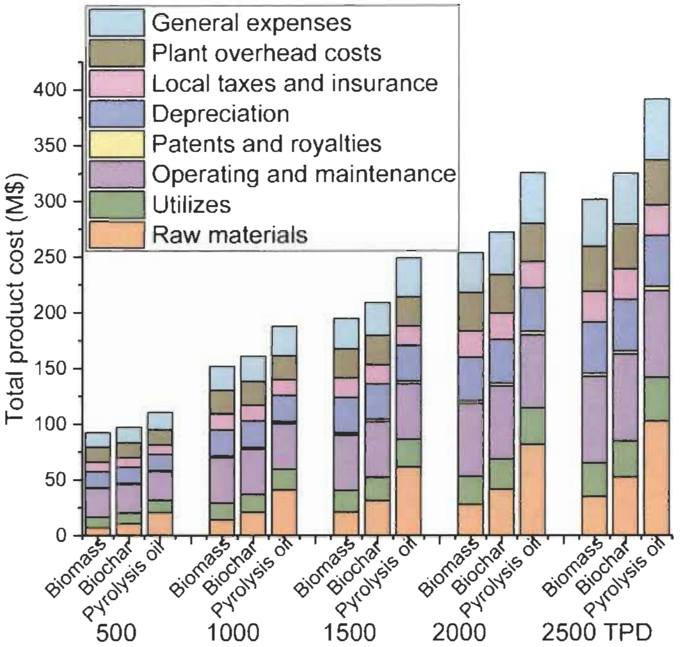

Figure 7.3 Total product cost of biomass, biochar, and pyrolysis oil at various plant scales

The economic evaluation is presented in **Table 7.8** for all feedstock and for the 2500-TPD case. For this analysis, the bio-methanol price was set at 1100 $/ton. As we can see, the NPV values of biomass and biochar are above 0, up to 1596.5 M$ in the biochar case, *i.e.*, 509.5M$ more than the biomass case. In terms of IRR and DPBP, the same trend as for the NPV is observed, the IRR and DPBP for the biochar case being respectively higher (7.8 % vs. 4.6 %) and lower (8.3 years vs. 11.1 years) than the biomass case.

On the other hand, it is not possible to accurately estimate NPV, IRR and DPBP for the pyrolysis oil case, a low methanol yield coupled with a high pyrolysis oil purchase price leading to revenues below production costs. This causes distortion in the calculation. Therefore, the results obtained are not included. Considering these results, biochar seems to be the most promising feedstock, compared to biomass and pyrolysis oil.

Table 7.8 Preliminary economic evaluation

	Biomass	**Biochar**	**Pyrolysis oil***
Plant scale (TPD)	2500	2500	2500
NPV (M$)	1087.0	1596.5	-
IRR (%)	4.6	7.8	-
DPBP (years)	11.1	8.3	-

*income is lower than cost

7.5.3 Sensitivity analysis

A sensitivity analysis was conducted to investigate the impact of different factors (*i.e.*, bio-methanol price, feedstock price, TCI, and project lifespan) on the project profitability at different plant scales, which enables to identify the most appropriate size of the plant. To perform the sensitivity analysis, a baseline must be defined for each case:

- Biomass case:
    - Bio-methanol price: 1100 $/ton.
    - Feedstock price (biomass): 40 $/ton.
    - TCI: ±0% (compared to TCI defined previously).
    - Project lifespan: 20 years.
- Biochar case:
    - Bio-methanol price: 1100 $/ton.
    - Feedstock price (biochar): 71 $/ton.
    - TCI: ±0% (compared to TCI defined previously).
    - Project lifespan: 20 years.
- Pyrolysis oil case:
    - Bio-methanol price: 2300 $/ton.
    - Feedstock price (biomass): 110 $/ton.
    - TCI: ±0% (compared to TCI defined previously).
    - Project lifespan: 20 years.

These baselines are used as benchmarks for the following sensitivity analysis. In the case of pyrolysis oil, it is difficult to reach the minimum IRR value when bio-methanol price is set at 1100$/ton, so we adjust the price of bio-methanol to 2300$/ton, the results of the sensitivity analysis are presented in **Table 7.9**.

Table 7.9 IRR (%) evolution as a function of key parameters

Parameters	Value	Case: Biomass (TPD)					Value	Case: Biochar (TPD)					Value	Case: Pyrolysis oil (TPD)				
		500	1000	1500	2000	2500		500	1000	1500	2000	2500		500	1000	1500	2000	2500
Bio-methanol price ($/ton)	900	-	-16.4	-7.2	-5.1	-2.9	900	-	-10.2	-3.4	-1.9	0.1	2100	-	-10.4	-6.0	-2.0	-0.1
	1000	-	-8.7	-2.4	-0.8	1.1	1000	-17.6	-4.8	0.6	2.2	4.2	2200	-	-7.4	-1.5	0.1	2.0
	1100	-16.7	-4.4	1.0	2.6	4.6	1100	-9.5	-0.9	4.1	5.8	7.8	2300	-	-5.0	0.4	2.0	4.0
	1200	-9.6	-1.1	4.0	5.7	7.7	1200	-5.2	2.4	7.2	9.1	11.1	2400	-13.1	-3.0	2.2	3.8	5.8
	1300	-5.7	1.9	6.8	8.6	10.7	1300	-1.8	5.3	10.2	12.2	14.4	2500	-9.9	-1.2	3.8	5.5	7.5
Feedstock price ($/ton)	20	-12.9	-2.1	2.3	3.9	5.9	50	-7.8	0.3	5.2	7.0	9.0	100	-	-3.6	1.7	3.3	5.2
	30	-14.3	-3.6	1.7	3.3	5.2	60	-8.7	-0.3	4.6	6.4	8.4	110	-	-4.3	1.0	2.6	4.6
	40	-16.7	-4.4	1.0	2.6	4.6	70	-9.5	-0.9	4.1	5.8	7.8	120	-	-5.0	0.4	2.0	4.0
	50	-18.4	-5.1	0.4	2.0	3.9	80	-10.5	-1.5	3.5	5.2	7.2	130	-	-5.9	-0.3	1.3	3.3
	60	-22.1	-5.9	-0.3	1.3	3.3	90	-11.6	-2.2	2.9	4.6	6.4	140	-	-6.7	-0.9	0.6	2.6
TCI (%)	-20	-12.0	-2.2	3.8	5.6	7.9	-20	-7.8	1.6	7.3	9.3	11.6	-20	-	-3.0	3.1	4.9	7.2
	-10	-12.7	-3.3	2.3	4.0	6.1	-10	-8.8	1.3	5.6	7.4	9.5	-10	-	-4.2	1.6	3.3	5.4
	0	-16.7	-4.4	1.0	2.6	4.6	0	-9.5	-0.9	4.1	5.8	7.8	0	-	-5.0	0.4	2.0	4.0
	+10	-17.2	-5.2	-0.1	1.4	3.3	+10	-10.2	-1.9	2.8	4.5	6.3	+10	-	-6.0	-0.7	0.9	2.7
	+20	-18.4	-5.9	-1.0	0.4	2.2	+20	-10.8	-2.8	1.7	3.3	5.0	+20	-	-6.7	-1.6	-0.1	1.6
Project lifespan (year)	10	-31.9	-14.6	-7.0	-4.8	-2.1	10	-22.2	-9.7	-2.8	-0.5	2.1	10	-	-15.6	-7.8	-5.6	-3.0
	15	-21.4	-7.5	-1.3	0.5	2.7	15	-13.7	-3.5	2.2	4.1	6.3	15	-	-8.3	-2.0	-0.2	2.0
	20	-16.7	-4.4	1.0	2.6	4.6	20	-9.5	-0.9	4.1	5.8	7.8	20	-	-5.0	0.4	2.0	4.0
	25	-16.1	-4.2	1.1	2.7	4.7	25	-9.3	-0.8	4.2	5.9	7.9	25	-	-4.9	0.5	2.1	4.1
	30	-15.8	-4.1	1.2	2.8	4.8	30	-9.1	-0.7	4.3	6.0	8.0	30	-	-4.8	0.6	2.20	4.2

- stands for income is lower than cost
Green stands for acceptable (IRR > 5%)
Red stands for unacceptable (IRR < 0%)

This sensitivity analysis enables to highlight the impacts of key-parameters on the project IRR. Table 9 presents the results of this analysis. In this table, a first general observation is the gradual increase of the IRR values when the plant scale increases from 500 to 2500 TPD, proving the interest of the economies of scale.

The selling price of bio-methanol is the most influential parameter that affects the IRR. In the case of biomass, it is worth noting that when the plant scale is expanded to 2500 TPD, even if the bio-methanol price is as low as 1000 $/ton, the IRR value is still above 0%. Moreover, as the bio-methanol price increases to 1300 $/ton, the IRR value increases above the minimum acceptable value (5%), reaching 6.8% at a minimum plant scale of 1500 TPD. For biochar, when the plant scale expands to 2500 TPD, the IRR value is still above 0% as the bio-methanol price is as low as 900 $/ton. When the bio-methanol price is set at 1300 $/ton, the IRR value increases above 5% at a minimum plant scale of 1000 TPD. With regard to the pyrolysis oil case, the bio-methanol yield simulated appears to be the lowest and the pyrolysis oil price is about 3 and 1.5 times that of biomass and biochar respectively (see Table 4). Therefore, it is difficult to yield economic benefits. Even if bio-methanol price is set at 2500 $/ton, IRR values remain negative at the plant scales of 500 and 1000 TPD. An IRR of 5.8% is reached for a plant with a scale of 2500 TPD coupled with a bio-methanol price of 2400 $/ton.

Feedstock price seems to be the least influential parameter, its variation being the least impactful on IRR value. When biomass price decreases to 30 $/ton, the IRR value is greater than 5% at a minimum plant scale of 2000 TPD. When the biochar price drops to 60 $/ton, the IRR value reaches 5% at a minimum plant scale of 1500 TPD. Even if the biochar price rises up to 90 $/ton, the IRR value is still above 5% at a plant scale of 2500 TPD. For pyrolysis oil, the best IRR value is obtained at a plant scale of 2500 TPD with pyrolysis oil price set up at 100$/ton, reaching to 5.2%.

TCI is the second most influential factor, its variation affecting the IRR value and the plant scale. When TCI decreases by 20%, the IRR value of biomass scenarios is greater than 5% at a minimum plant scale of 2000 TPD. It is worth noting that when TCI decreases by 20%, the IRR value of biochar scenarios is above 0% at a minimum plant scale of 1000

TPD. Even if TCI increases by 20%, the minimum acceptable IRR value is still reached. In the case of pyrolysis oil, when TCI is reduced by 20%, IRR value is close to the minimum acceptable value with 4.9% at a minimum plant scale of 2000 TPD.

Project lifespan seems to be more influential in the first 2 decades and less so thereafter. It could be explained by the inflation of the interest rate, which leads to a gradual depreciation of income as project lifespan extend. It is worth noting that when the biochar is used to produce bio-methanol, the IRR value is higher than 0%, even though the plant life is only 10 years.

In general, when the plant scale is less than 1000 TPD, even if the price of bio-methanol continues to rise, the minimum acceptable IRR value of 5 % is hard to reach for each case. The price of bio-methanol has a significant impact on the IRR value: the higher the price of methanol, the higher the internal rate of return. TCI appears to be the second significant parameter to achieve relevant objectives. Lower TCI means lower costs of operations and maintenance. From an industrial perspective, this concept can be applied in the future in regions with lower equipment costs, such as China, Africa, and India.

Biochar seems to be the most promising raw material to produce bio-methanol, as the IRRs obtained are more competitive than biomass at a reasonable price. In contrast, pyrolysis oil presents the worst trends. In each case, it is difficult to reach the 5% IRR value, even at the maximum scale suggested in the assumptions, *i.e.*, 2500 TPD. To improve the IRR value, it would be necessary to expand the plant scale or to increase the bio-methanol selling price.

7.6 Conclusions

The objective of this study was to develop a model to simulate the production of bio-methanol from different feedstocks (*i.e.*, biomass, biochar and pyrolysis oil), to assess the economic profitability of a project of bio-methanol production plant and to perform a sensitivity analysis highlighting the key parameters to be considered. The model developed in Aspen Plus includes gasification, syngas purification, methanol synthesis and distillation. The simulation results were validated with experimental data from the literature. The model was then used to assess the potential for producing bio-methanol from three feedstocks, namely pine biomass, biochar and pyrolysis oil. Simulation results show that biochar is the feedstock with the highest methanol production yield (578.2 kg/1000 kg) due to its higher carbon content. On the contrary, pyrolysis oil is the feedstock with the lowest yield (283.1 kg/1000 kg), due to its high water and low carbon content.

Based on the Aspen Plus model results, an economic evaluation was carried out to assess the economic feasibility using the IRR, NPV and DPBP profitability indicators. A sensitivity analysis was performed by varying several key parameters such as the selling price of bio-methanol, the price of feedstock, the total capital investment (TCI) and the project lifespan. In the case of biomass and biochar, it is possible to reach the 5% IRR threshold value when the price of bio-methanol is greater than or equal to 1100 US$/ton. On the other hand, pyrolysis oil appears to be the worst option, with a minimum methanol price of 2300 US$/ton required for minimum profitability. The results of the sensitivity analysis show that the price of bio-methanol, TCI, project lifespan, feedstock prices and project scale are key factors influencing the IRR value. (a few comments about the hierarchy of each parameter: the least and most influential parameters…)

Given the current price of conventional methanol, bio-methanol produced from bioresources is unfortunately not commercially competitive with conventional methanol. However, the emergence of new regulations (taxes on petroleum products, carbon credits, subsidies for the development of green fuels, etc.) should gradually reverse this trend. Moreover, such a process is directly in line with the sustainable development goals of the United Nations and the commitments of COP21.

7.7 References

1. Taba, L.E., et al., *The effect of temperature on various parameters in coal, biomass and CO-gasification: a review.* Renewable and Sustainable Energy Reviews, 2012. **16**(8): p. 5584-5596.

2. McKendry, P., *Energy production from biomass (part 1): overview of biomass.* Bioresource technology, 2002. **83**(1): p. 37-46.

3. Novotny, E.H., et al., *Biochar: pyrogenic carbon for agricultural use-a critical review.* Revista Brasileira de Ciência do Solo, 2015. **39**(2): p. 321-344.

4. Staš, M., et al., *Overview of analytical methods used for chemical characterization of pyrolysis bio-oil.* Energy & Fuels, 2014. **28**(1): p. 385-402.

5. Bridgwater, A. and M. Cottam, *Opportunities for biomass pyrolysis liquids production and upgrading.* Energy & Fuels, 1992. **6**(2): p. 113-120.

6. Radlein, D., *The production of chemicals from fast pyrolysis bio-oils.* Vol. 1. 1999: CPL Press: Newbury, UK.

7. Czernik, S., R. Evans, and R. French, *Hydrogen from biomass-production by steam reforming of biomass pyrolysis oil.* Catalysis Today, 2007. **129**(3): p. 265-268.

8. Kookana, R.S., et al., *3 biochar application to soil: agronomic and environmental benefits and unintended consequences.* Advances in agronomy, 2011. **112**(112): p. 103-143.

9. Bridgwater, A. and G. Peacocke, *Fast pyrolysis processes for biomass.* Renewable and sustainable energy reviews, 2000. **4**(1): p. 1-73.

10. Ronsse, F., et al., *Production and characterization of slow pyrolysis biochar: influence of feedstock type and pyrolysis conditions.* Gcb Bioenergy, 2013. **5**(2): p. 104-115.

11. Varma, A.K., R. Shankar, and P. Mondal, *A Review on Pyrolysis of Biomass and the Impacts of Operating Conditions on Product Yield, Quality, and Upgradation*, in *Recent Advancements in Biofuels and Bioenergy Utilization*. 2018, Springer. p. 227-259.

12. Sun, X., et al., *Characterization of 60 types of Chinese biomass waste and resultant biochars in terms of their candidacy for soil application.* Gcb Bioenergy, 2017. **9**(9): p. 1423-1435.

13. Shackley, S., et al., *Biochar, tool for climate change mitigation and soil management*, in *Geoengineering Responses to Climate Change*. 2013, Springer. p. 73-140.

14. Rossum, G., *Steam reforming and gasification of pyrolysis oil*. 2009: University of Twente.

15. van Rossum, G., S.R. Kersten, and W.P. van Swaaij, *Staged catalytic gasification/steam reforming of pyrolysis oil.* Industrial & Engineering Chemistry Research, 2009. **48**(12): p. 5857-5866.

16. Czernik, S. and A. Bridgwater, *Overview of applications of biomass fast pyrolysis oil.* Energy & fuels, 2004. **18**(2): p. 590-598.

17. Peters, J.F., D. Iribarren, and J. Dufour, *Life cycle assessment of pyrolysis oil applications.* Biomass Conversion and Biorefinery, 2015. **5**(1): p. 1-19.

18. Maity, S.K., *Opportunities, recent trends and challenges of integrated biorefinery: Part I.* Renewable and Sustainable Energy Reviews, 2015. **43**: p. 1427-1445.

19. Chaudhari, S., A. Dalai, and N. Bakhshi, *Production of hydrogen and/or syngas (H2+ CO) via steam gasification of biomass-derived chars.* Energy & fuels, 2003. **17**(4): p. 1062-1067.

20. Van Rossum, G., S.R. Kersten, and W.P. van Swaaij, *Catalytic and noncatalytic gasification of pyrolysis oil.* Industrial & engineering chemistry research, 2007. **46**(12): p. 3959-3967.

21. Elfasakhany, A., *Investigations on the effects of ethanol–methanol–gasoline blends in a spark-ignition engine: performance and emissions analysis.* Engineering Science and Technology, an International Journal, 2015. **18**(4): p. 713-719.

22. Bertau, M., et al., *Methanol: the basic chemical and energy feedstock of the future.* 2014: Springer.

23. Ogden, J.M., M.M. Steinbugler, and T.G. Kreutz, *A comparison of hydrogen, methanol and gasoline as fuels for fuel cell vehicles: implications for vehicle design and infrastructure development.* Journal of power sources, 1999. **79**(2): p. 143-168.

24. Towler, G. and R.K. Sinnott, *Chemical engineering design: principles, practice and economics of plant and process design.* 2012: Elsevier.

25. Sattar, A., et al., *Steam gasification of rapeseed, wood, sewage sludge and miscanthus biochars for the production of a hydrogen-rich syngas.* biomass and bioenergy, 2014. **69**: p. 276-286.

26. Puig-Gamero, M., et al., *Three integrated process simulation using aspen plus®: Pine gasification, syngas cleaning and methanol synthesis.* Energy conversion and management, 2018. **177**: p. 416-427.

27. Lee, C.-J., et al., *Optimal gas-to-liquid product selection from natural gas under uncertain price scenarios.* Industrial & Engineering Chemistry Research, 2008. **48**(2): p. 794-800.

28. Andrianopoulos, E., A. Korre, and S. Durucan, *Chemical process modelling of underground coal gasification and evaluation of produced gas quality for end use.* Energy Procedia, 2015. **76**: p. 444-453.

29. Moghadam, R.A., et al., *Investigation on syngas production via biomass conversion through the integration of pyrolysis and air–steam gasification processes.* Energy conversion and management, 2014. **87**: p. 670-675.

30. Tan, E.C., et al., *Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbons via Indirect Liquefaction. Thermochemical Research Pathway to High-Octane Gasoline Blendstock Through Methanol/Dimethyl Ether Intermediates*. 2015, National Renewable Energy Lab.(NREL), Golden, CO (United States).

31. Hamelinck, C.N. and A.P. Faaij, *Future prospects for production of methanol and hydrogen from biomass.* Journal of Power sources, 2002. **111**(1): p. 1-22.

32. Leonzio, G., *Methanol synthesis: optimal solution for a better efficiency of the process.* Processes, 2018. **6**(3): p. 20.

33. Zhang, Y., J. Xiao, and L. Shen, *Simulation of methanol production from biomass gasification in interconnected fluidized beds.* Industrial & Engineering Chemistry Research, 2009. **48**(11): p. 5351-5359.

34. Bromberg, L. and W.K. Cheng, *Methanol as an alternative transportation fuel in the US: Options for sustainable and/or energy-secure transportation.* Cambridge, MA: Sloan Automotive Laboratory, Massachusetts Institute of Technology, 2010.

35. Heo, J., B. Lee, and H. Lim, *Techno-economic analysis for CO2 reforming of a medium-grade landfill gas in a membrane reactor for H2 production.* Journal of Cleaner Production, 2018. **172**: p. 2585-2593.

36. Peters, M.S., et al., *Plant design and economics for chemical engineers*. Vol. 4. 1968: McGraw-Hill New York.

37. Sørensen, A., *Economies of scale in biomass gasification systems.* 2005.

38. Ringer, M., V. Putsche, and J. Scahill, *Large-Scale Pyrolysis Oil NREL/TP-510-37779 Production: A Technology November 2006 Assessment and Economic Analysis*. 2006, November.

39. Campbell, R.M., et al., *Financial viability of biofuel and biochar production from forest biomass in the face of market price volatility and uncertainty.* Applied energy, 2018. **230**: p. 330-343.

40. Gielen, D., *Renewable energy technologies: cost analysis series.* Sol Photovolt, 2012. **1**(1): p. 52.

41. Towler, G. and R. Sinnott, *Chemical engineering design: principles, practice and economics of plant and process design.* 2012: Elsevier.

42. Tock, L., M. Gassner, and F. Maréchal, *Thermochemical production of liquid fuels from biomass: Thermo-economic modeling, process design and process integration analysis.* Biomass and Bioenergy, 2010. **34**(12): p. 1838-1854.

43. Zhang, C., et al., *Efficient utilization of carbon dioxide in gas-to-liquids process: Process simulation and techno-economic analysis.* Fuel, 2015. **157**: p. 285-291.

44. Ward, C., *Improved agricultural water management for Africa's drylands.* 2016: The World Bank.

45. Andersson, J., J. Lundgren, and M. Marklund, *Methanol production via pressurized entrained flow biomass gasification–Techno-economic comparison of integrated vs. stand-alone production.* Biomass and Bioenergy, 2014. **64**: p. 256-268.

46. Ng, K.S. and J. Sadhukhan, *Process integration and economic analysis of bio-oil platform for the production of methanol and combined heat and power.* biomass and bioenergy, 2011. **35**(3): p. 1153-1169.

47. Lemmens, S., *Cost engineering techniques and their applicability for cost estimation of organic Rankine cycle systems.* Energies, 2016. **9**(7): p. 485.

48. Shah, A., N. Baral, and A. Manandhar, *Technoeconomic analysis and life cycle assessment of bioenergy systems*, in *Advances in Bioenergy*. 2016, Elsevier. p. 189-247.

49. García-Gutiérrez, P., et al., *Techno-economic feasibility of selective CO2 capture processes from biogas streams using ionic liquids as physical absorbents.* Energy & Fuels, 2016. **30**(6): p. 5052-5064.

50. Peters, M.S. and K.D. Timmerhaus, *Plant design and economics for chemical engineers*. 1980.

7.8 Supplementary information

Appendix A

Table 7.10 Biomass NC definition

Attribute ID:			
PROXANAL		SULFANAL	
MOISTURE	4.4	PYRITIC	0.08
FC	31.3	SULFATE	
VM	61.6	ORGANIC	
ASH	2.7		

Table 7.11 Biochar NC definition

Attribute ID:			
PROXANAL		SULFANAL	
MOISTURE		PYRITIC	0.01
FC		SULFATE	
VM		ORGANIC	
ASH	4.2		

Table 7.12 Pyrolysis-oil NC definition

Attribute ID:			
PROXANAL		SULFANAL	
MOISTURE	32.5	PYRITIC	0.001
FC		SULFATE	
VM		ORGANIC	
ASH			

Appendix B

Flowsheet in Aspen plus

Table 7.13 Flowsheet in Aspen plus (Biomass)

Stream No.	1	3	Moisture	steam	6	7	9	10	11	14	15	16	17	18	20
Temp (°C)	40	100	100	100	800	800	80	20	26.2	42.6	250	50	50	65	65
Pressure (bar)	1	1	1	1	1	1	1	1	1	55	55	1	1	1	1
Flowrates (kg/h)															
Biomass	1000														
Dry biomass		956													
H_2O			44.0	700	32.3		32.3	200	229.4	2.9	4.8	4.8		45.3	
H_2					114.2		114.2			114.2	31.1	31.1	31.1		
CO					694.4		694.4			694.4	121.2	121.2	121.2		
CO_2					783.2		783.2			783.2	778.7	778.7	778.7		
CH_4					4.8		4.8			4.8	4.8	4.8	4.8		
NH_3					trace		trace		trace						
H_2S					trace		trace		trace						
Ash					27.0	27.0									
MeOH											659.0	659.0		869.8	866.3

Methanol yield = theoretical methanol yield* gasifier efficiency (0.729) * methanol synthesis efficiency (0.8) = 507.3 kg

Table 7.14 Flowsheet in Aspen plus (Biochar)

Stream No.	1	3	Moisture	steam	6	7	9	10	11	13	14	15	16	17	18	20
Temp (°C)	40	100	100	100	800	800	80	20	29.1	44.3	44.3	250	50	50	65	65
Pressure (bar)	1	1	1	1	1	1	1	1	1	1	55	55	1	1	1	1
Flowrates (kg/h)																
Biochar	1000															
Dry biochar		1000														
H_2O			0	1000	15.9		15.9	200	213.8	2.1	2.1	5.5	5.5		48.1	
H_2					129.9		129.9			129.9	129.9	35.2	35.2	35.2		
CO					795.2		795.2			795.2	795.2	145.6	145.6	145.6		
CO_2					959.2		959.2			959.2	959.2	950.9	950.9	950.9		
CH_4					6.0		6.0			6.0	6.0	6.0	6.0	6.0		
NH_3					51.7		51.7		51.7							
H_2S					trace		trace		trace							
Ash					42.0	42.0										
MeOH											749.1	749.1			991.5	984.6

Methanol yield = theoretical methanol yield* gasifier efficiency* methanol synthesis efficiency = 578.2 kg

Table 7.15 Flowsheet in Aspen plus (Pyrolysis oil)

Stream No.	1	3	Moisture	steam	6	7	9	10	11	13	14	15	16	17	18	20
Temp (°C)	60	100	100	100	800	800	80	20	22.5	42.2	42.2	250	50	50	65	65
Pressure (bar)	1	1	1	1	1	1	1	1	1	1	55	55	1	1	1	1
Flowrates (kg/h)																
Pyrolysis oil	1000															
Dry oil		675														
H_2O			325	325	42.7		42.7	200	241.1	1.6	1.6	3.1	3.1		27.3	
H_2					64.2		64.2			64.2	64.2	18.1	18.1	18.1		
CO					386.0		386.0			386.0	386.0	68.9	68.9	68.9		
CO_2					500.4		500.4			500.4	500.4	496.7	496.7	496.7		
CH_4					2.8		2.8			2.8	2.8	2.8	2.8	2.8		
NH_3					33.0		33.0		33.0							
H_2S					trace		trace		trace							
Ash																
MeOH												365.4			487.3	485.4

Methanol yield = theoretical methanol yield* gasifier efficiency* methanol synthesis efficiency = 283.1 kg

Chapter 8 – Conclusions

8.1 Main conclusions

The main purpose of this work has been to identify potential applications of pyrolysis oil. Present thesis is bringing forth new avenues in a developing field of green energy or energy vector (biofuels) production. Indeed, we have developed new strategies and performed work in new, previously unexplored avenues. First, the use of pyrolysis oil for the production of syngas and biofuel has not been reported in the literature before present thesis. Second, the influence of many parameters such as moisture content, gasifier temperature, syngas post-treatment, methanol synthesis temperature and pressure, on the syngas and biofuel production has also not been explored. Last but not least, the marketability of using pyrolysis oil to produce bio-methanol has not been investigated before present work. To address these questions and solve the issues, we used Aspen Plus to simulate the gasification and methanol synthesis processes. Specifically, we propose that the syngas produced by pyrolysis oil gasification, with a sufficient degree of purity related to syngas cleaning, can be used directly in fuel cells or for biofuel production. The effect of many factors on syngas composition are examined. For synthetic biofuels, the effect of some parameters on bio-methanol synthesis is explored. One innovation point is the syngas is purified by a Rectisol® unit, which changes the syngas SN value and increases methanol yield. Finally, the feasibility of producing methanol from pyrolysis oil at different scales was analyzed through techno-economic analysis. In order to assess the potential of pyrolysis oil, the same evaluation was achieved for biochar and pine biomass to see whether pyrolysis oil was a suitable candidate for methanol production.

Several conclusions were highlighted in the course of this study:

- If syngas produced from pyrolysis oil gasification is used in fuel cells: O_2 and air, which will reduce the syngas lower heating value (LHV) value, should not be used as a gasifying agent; moisture content in pyrolysis oil should be minimized; syngas should be produced at higher temperatures so that the syngas has a higher enthalpy value.

- If syngas is used to synthesize methanol or Fischer-Tropsch fuel: a small amount of O_2 can be used to adjust the H_2:CO molar ratio; the syngas should be produced at 1000 °C, where the H_2:CO molar ratio is equal to 2; furthermore, moisture content in the pyrolysis oil should be around 40 wt.% in order to maximize production yields.
- For fuel synthesis, the syngas gasifying temperature should be at 1000 °C with a maximum SN value of 0.85. The moisture content in pyrolysis oil should be kept at 30 wt.% with a SN value of 0.865. The Rectisol® unit for purifying syngas and adjusting syngas composition should be set at -20 °C and 40 bars, where syngas SN value reached a maximum of 2.07. For methanol synthesis reactor, 50 bar and 250 °C were selected as the optimal operating conditions for the methanol synthesis. Thus, it was possible to reach a maximum methanol yield of 8.04 kmol.
- Producing methanol from pyrolysis oil is technically feasible, but industrially complex. The high purchase price coupled with its low carbon content in pyrolysis oil (compared to biomass and biochar) are factors that reduce the profitability of such a project. On the contrary, biochar seems to be a promising candidate for the production of methanol. Although expensive to purchase, it allows for high methanol yields due to its high carbon content, thus generating more easily profits. Biochar can also be a by-product of another project (e.g. IH2 from Shell technology) and such an avenue could be further explored for its economic feasibility.
- A sensitivity analysis was carried out by varying several realistic parameters such as bio-methanol price, feedstock price, total capital investment (TCI) and plant life. Bio-methanol price appeared as the most significant factor. For biochar, when the bio-methanol price is 1100 $/ton, the project can achieve its economic benefit at the minimum plant scale 1000 TPD.

8.2 Main contributions

Throughout this work, we have simulated pyrolysis oil gasification for different purposes. Through the simulations carried out, our results have highlighted that the gasification conditions and moisture content in pyrolysis oil have a significant impact on syngas properties. These results could be used as reference when gasifying other feedstocks. Subsequently, we simulated the methanol synthesis from pyrolysis oil, in which Rectisol® technology was used for syngas post-treatment. We have shown that the gasification conditions and the moisture content in the pyrolysis oil, as well as the operating conditions of the Rectisol® and methanol reactors have an impact on the methanol yield. The study of the various parameters enabled us to propose a production plan maximizing gas and then methanol yields, potentially applicable for future industrialization. Through techno-economic analysis, we have determined that the pathway of methanol production from pyrolysis oil is feasible but not financially viable. However, we found that the pathway for producing methanol from biochar was more attractive than that of biomass and pyrolysis oil.

8.3 Future work

First of all, gasification experiments at pilot or demonstration scales should be conducted to validate the simulation results with actual experimental data. It should however be noted that the obtention of such "demonstration experiments" would be quite expensive. For instance, the work to be performed by the BioÉnegie La Tuque project to just do that will costs around 12 million $Can. We have used here literature data as the thesis project could not afford such costs. We have also demonstrated that validations that the reaction conditions such as gasifier temperature and moisture content in pyrolysis oil are in agreement with the simulation results.

The above studies show that the pathway of producing methanol from pyrolysis oil is not currently economically viable. However, future work may explore the potential applications of pyrolysis oil in other areas. For example, it can be burned in a boiler along with other feedstock to generate heat and power. Furthermore, part of pyrolysis oil can also be extracted for value creation from high value-added products: for example, chemical compounds such as aldehydes, phenols and laevoglucose can be extracted from pyrolysis oil. Applications like liquid smoke, adhesives and fertilizer have also be identified and explored in the literature.

Based on previous research, biochar appears to be a promising feedstock to produce methanol. Some work will need to be done to further explore the possibility of producing methanol from biochar and biomass in regions such as South Africa, China, and India, where the cost of equipment, feedstock and labor is cheaper.

While simulating the methanol synthesis process, we found that not all the carbon in biomass, biochar and pyrolysis oil can be converted to methanol: this is due to insufficient hydrogen produced during the gasification process, essentially because biomass lacks the proper percentage of hydrogen in its elemental composition. Therefore, given Canadian abundant water resources and low electricity costs, we can obtain extra hydrogen through water electrolysis to ensure full utilization of carbon, which makes full use of the carbon and potentially reduces the cost of methanol production.

A sensitivity analysis will be continuing to be carried out by varying several realistic parameters especially some national policies, such as carbon tax, etc.

We will update the CanmetENERGY Center software I-BIOREF with our research results, which will help us to develop this project more systematically in the future.

References

1. Mirandola, A. and E. Lorenzini, *Energy, environment and climate: From the past to the future.* International Journal of Heat and Technology, 2016. **34**(2): p. 159-164.

2. Yüksel, I., *Global warming and renewable energy sources for sustainable development in Turkey.* Renewable energy, 2008. **33**(4): p. 802-812.

3. Kunwar, B., et al., *Plastics to fuel: a review.* Renewable and Sustainable Energy Reviews, 2016. **54**: p. 421-428.

4. Kato, N., *Analysis of structure of energy consumption and dynamics of emission of atmospheric species related to the global environmental change (SOx, NOx, and CO2) in Asia.* Atmospheric Environment, 1996. **30**(5): p. 757-785.

5. Taba, L.E., et al., *The effect of temperature on various parameters in coal, biomass and CO-gasification: a review.* Renewable and Sustainable Energy Reviews, 2012. **16**(8): p. 5584-5596.

6. Lane, J. *GRFA: Commit to biofuels policies to achieve COP21 targets*. 2016, june 18; Available from: https://www.biofuelsdigest.com/bdigest/2016/06/18/grfa-commit-to-biofuels-policies-to-achieve-cop21-targets/.

7. Razmjoo, A., et al., *Stand-alone hybrid energy systems for remote area power generation.* Energy Reports, 2019. **5**: p. 231-241.

8. Kanase-Patil, A., R. Saini, and M. Sharma, *Integrated renewable energy systems for off grid rural electrification of remote area.* Renewable Energy, 2010. **35**(6): p. 1342-1349.

9. Hoicka, C.E. and I.H. Rowlands, *Solar and wind resource complementarity: Advancing options for renewable electricity integration in Ontario, Canada.* Renewable Energy, 2011. **36**(1): p. 97-107.

10. Thomaidis, N.S., et al., *Optimal management of wind and solar energy resources.* Computers & Operations Research, 2016. **66**: p. 284-291.

11. Vourvoulias, A., *Pros and Cons of Solar Energy.* 2014/08/05.

12. Tanksale, A., J.N. Beltramini, and G.M. Lu, *A review of catalytic hydrogen production processes from biomass.* Renewable and Sustainable Energy Reviews, 2010. **14**(1): p. 166-182.

13. Levin, D.B. and R. Chahine, *Challenges for renewable hydrogen production from biomass.* International Journal of Hydrogen Energy, 2010. **35**(10): p. 4962-4969.

14. Brown Robert, C., *Biorenewable Resources: Engineering New Products from Agricultural*. 2003, USA: Iowa State Press.

15. OKUMURA, Y. and K. OKAZAKI, *Pyrolysis and gasification experiments of biomass under elevated pressure condition.* Journal of Environment and Engineering, 2009. **4**(1): p. 24-35.

16. TIBDEWAL, S., U. SAXENA, and A.V. GURUMOORTHY, *Hydrogen economy vs. Methanol economy.* International Journal of Chemical Sciences, 2014. **12**: p. 1478-1486.

17. Fiedler, E., et al., *Methanol.* Ullmann's encyclopedia of industrial chemistry, 2000.

18. Thomas, C., et al., *Fuel options for the fuel cell vehicle: hydrogen, methanol or gasoline?* International Journal of Hydrogen Energy, 2000. **25**(6): p. 551-567.

19. Chourou, W., *Développement et évaluation des modèles hauteur-diamètre des pins gris et des épinettes noires à l'échelle provinciale et écorégionale de l'Alberta et du Québec.* 2014.

20. *Area(1000 ha) of forest and non-forest land in Canada.* May 13, 2016; Available from: http://www.nrcan.gc.ca/forests/report/area/17601.

21. Ge, X., et al., *Conversion of Lignocellulosic Biomass Into Platform Chemicals for Biobased Polyurethane Application*, in *Advances in Bioenergy*. 2018, Elsevier. p. 161-213.

22. Sullivan, A.L. and R. Ball, *Thermal decomposition and combustion chemistry of cellulosic biomass.* Atmospheric Environment, 2012. **47**: p. 133-141.

23. Novotny, E.H., et al., *Biochar: pyrogenic carbon for agricultural use-a critical review.* Revista Brasileira de Ciência do Solo, 2015. **39**(2): p. 321-344.

24. Briens, C., J. Piskorz, and F. Berruti, *Biomass valorization for fuel and chemicals production--A review.* International Journal of Chemical Reactor Engineering, 2008. **6**(1).

25. Cherubini, F., et al. *IEA Bioenergy Task 42 on Biorefineries: Co-production of fuels, chemicals, power and materials from biomass*. 2007. IEA.

26. Biernat, K. and P.L. Grzelak, *Biorefinery systems as an element of sustainable development*, in *Biofuels-Status and Perspective*. 2015, InTech.

27. Takkellapati, S., T. Li, and M.A. Gonzalez, *An overview of biorefinery-derived platform chemicals from a cellulose and hemicellulose biorefinery.* Clean technologies and environmental policy, 2018. **20**(7): p. 1615-1630.

28. Naik, S.N., et al., *Production of first and second generation biofuels: a comprehensive review.* Renewable and Sustainable Energy Reviews, 2010. **14**(2): p. 578-597.

29. Sun, Y. and J. Cheng, *Hydrolysis of lignocellulosic materials for ethanol production: a review.* Bioresource technology, 2002. **83**(1): p. 1-11.

30. Karimi, K., S. Kheradmandinia, and M.J. Taherzadeh, *Conversion of rice straw to sugars by dilute-acid hydrolysis.* Biomass and Bioenergy, 2006. **30**(3): p. 247-253.

31. Yu, Y., X. Lou, and H. Wu, *Some recent advances in hydrolysis of biomass in hot-compressed water and its comparisons with other hydrolysis methods.* synthesis, 2008. **35**: p. 36.

32. Bobleter, O., *Hydrothermal degradation of polymers derived from plants.* Progress in polymer science, 1994. **19**(5): p. 797-841.

33. Pérez, J., et al., *Biodegradation and biological treatments of cellulose, hemicellulose and lignin: an overview.* International Microbiology, 2002. **5**(2): p. 53-63.

34. Jönsson, L.J. and C. Martín, *Pretreatment of lignocellulose: Formation of inhibitory by-products and strategies for minimizing their effects.* Bioresource Technology, 2016. **199**: p. 103-112.

35. Mosier, N., et al., *Features of promising technologies for pretreatment of lignocellulosic biomass.* Bioresource technology, 2005. **96**(6): p. 673-686.

36. Kim, Y., et al., *Enzyme hydrolysis and ethanol fermentation of liquid hot water and AFEX pretreated distillers' grains at high-solids loadings.* Bioresource Technology, 2008. **99**(12): p. 5206-5215.

37. Romano, R.T. and R. Zhang, *Co-digestion of onion juice and wastewater sludge using an anaerobic mixed biofilm reactor.* Bioresource Technology, 2008. **99**(3): p. 631-637.

38. Ferreira, A.F., *Biorefinery Concept.* 2017. **57**: p. 1-20.

39. Council, N.R., *Opportunities and Obstacles in Large-Scale Biomass Utilization: The Role of the Chemical Sciences and Engineering Communities: A Workshop Summary.* 2012: National Academies Press.

40. Zafar, S., *The Concept of Biorefinery.* 2019/11/16.

41. Bridgwater, A.V., *Review of fast pyrolysis of biomass and product upgrading.* Biomass and bioenergy, 2012. **38**: p. 68-94.

42. Cherubini, F., *The biorefinery concept: using biomass instead of oil for producing energy and chemicals.* Energy Conversion and Management, 2010. **51**(7): p. 1412-1421.

43. Bridgwater, A. and G. Peacocke, *Fast pyrolysis processes for biomass.* Renewable and sustainable energy reviews, 2000. **4**(1): p. 1-73.

44. Senneca, O., *Kinetics of pyrolysis, combustion and gasification of three biomass fuels.* Fuel Processing Technology, 2007. **88**(1): p. 87-97.

45. Huber, G.W., S. Iborra, and A. Corma, *Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering.* Chemical reviews, 2006. **106**(9): p. 4044-4098.

46. Mohan, D., C.U. Pittman, and P.H. Steele, *Pyrolysis of wood/biomass for bio-oil: a critical review.* Energy & fuels, 2006. **20**(3): p. 848-889.

47. Zaman, C.Z., et al., *Pyrolysis: A Sustainable Way to Generate Energy from Waste*, in *Pyrolysis*. 2017, BoD–Books on Demand. p. 1.

48. Fisher, T., et al., *Pyrolysis behavior and kinetics of biomass derived materials.* Journal of analytical and applied pyrolysis, 2002. **62**(2): p. 331-349.

49. Rossum, G., *Steam reforming and gasification of pyrolysis oil.* 2009: University of Twente.

50. Sikanen, L., D. Röser, and A. Asikainen, *Machinery and systems in different scales of forest fuel supply chains.* 2005, Elgin: METLA-Finnish Forest Research Institute.

51. Canabarro, N., et al., *Thermochemical processes for biofuels production from biomass.* Sustainable Chemical Processes, 2013. **1**(1): p. 22.

52. Pecha, B., *Understanding and controlling lignocellulosic pyrolysis for the production of renewable fuel and chemical precursors.* 2017.

53. Lee, Y., et al., *Characteristics of biochar produced from slow pyrolysis of Geodae-Uksae 1.* Bioresource Technology, 2013. **130**: p. 345-350.

54. Bridgwater, A. and M. Cottam, *Opportunities for biomass pyrolysis liquids production and upgrading.* Energy & Fuels, 1992. **6**(2): p. 113-120.

55. Radlein, D., *The production of chemicals from fast pyrolysis bio-oils.* Vol. 1. 1999: CPL Press: Newbury, UK.

56. Pollard, A.S., M.R. Rover, and R.C. Brown, *Characterization of bio-oil recovered as stage fractions with unique chemical and physical properties.* Journal of Analytical and Applied Pyrolysis, 2012. **93**: p. 129-138.

57. Demirbas, A., *The influence of temperature on the yields of compounds existing in bio-oils obtained from biomass samples via pyrolysis.* Fuel Processing Technology, 2007. **88**(6): p. 591-597.

58. Solar, J., et al., *Influence of temperature and residence time in the pyrolysis of woody biomass waste in a continuous screw reactor.* Biomass and Bioenergy, 2016. **95**: p. 416-423.

59. Garcia, L.a., et al., *Catalytic steam reforming of bio-oils for the production of hydrogen: effects of catalyst composition.* Applied Catalysis A: General, 2000. **201**(2): p. 225-239.

60. Galdámez, J.R., L. García, and R. Bilbao, *Hydrogen production by steam reforming of bio-oil using coprecipitated Ni-Al catalysts. Acetic acid as a model compound.* Energy & Fuels, 2005. **19**(3): p. 1133-1142.

61. Crocker, M., *Thermochemical conversion of biomass to liquid fuels and chemicals.* 2010: Royal Society of Chemistry.

62. Oasmaa, A. and D. Meier, *Norms and standards for fast pyrolysis liquids: 1. Round robin test.* Journal of Analytical and Applied Pyrolysis, 2005. **73**(2): p. 323-334.

63. LaClaire, C.E., C.J. Barrett, and K. Hall, *Technical, environmental and economic feasibility of bio-oil in new hampshire's north country.* Durham, NH: University of New Hampshire, 2004.

64. Oasmaa, A. and S. Czernik, *Fuel Oil Quality of Biomass Pyrolysis OilsState of the Art for the End Users.* Energy & Fuels, 1999. **13**(4): p. 914-921.

65. Czernik, S., R. Evans, and R. French, *Hydrogen from biomass-production by steam reforming of biomass pyrolysis oil.* Catalysis Today, 2007. **129**(3): p. 265-268.

66. Kechagiopoulos, P.N., et al., *Hydrogen production via steam reforming of the aqueous phase of bio-oil in a fixed bed reactor.* Energy & Fuels, 2006. **20**(5): p. 2155-2163.

67. Bridgwater, A.V., *Renewable fuels and chemicals by thermal processing of biomass.* Chemical Engineering Journal, 2003. **91**(2): p. 87-102.

68. *Biofuels: Pyrolysis Oils.* November 16,2013.

69. Oasmaa, A. and S. Czernik, *Fuel oil quality of biomass pyrolysis oils state of the art for the end users.* Energy & Fuels, 1999. **13**(4): p. 914-921.

70. Czernik, S. and A. Bridgwater, *Overview of applications of biomass fast pyrolysis oil.* Energy & fuels, 2004. **18**(2): p. 590-598.

71. Chaichan, M.T., *Combustion and emissions characteristics for DI diesel engine run by partially-premixed (PPCI) low temperature combustion (LTC) mode.* International Journal of Mechanical Engineering (IIJME), 2014. **2**(10): p. 7-16.

72. Kookana, R.S., et al., *3 biochar application to soil: agronomic and environmental benefits and unintended consequences.* Advances in agronomy, 2011. **112**(112): p. 103-143.

73. Brewer, C.E., et al., *New approaches to measuring biochar density and porosity.* Biomass and Bioenergy, 2014. **66**: p. 176-185.

74. Liu, Z., et al., *Production of solid biochar fuel from waste biomass by hydrothermal carbonization.* Fuel, 2013. **103**: p. 943-949.

75. Jeguirim, M. and L. Limousy, *Char and Carbon Materials Derived from Biomass: Production, Characterization and Applications*. 2019: Elsevier.

76. Luo, L., et al., *Sorption and desorption of pentachlorophenol to black carbon of three different origins.* Journal of hazardous materials, 2011. **185**(2): p. 639-646.

77. Chun, Y., et al., *Compositions and sorptive properties of crop residue-derived chars.* Environmental science & technology, 2004. **38**(17): p. 4649-4655.

78. Kan, T., V. Strezov, and T.J. Evans, *Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters.* Renewable and Sustainable Energy Reviews, 2016. **57**: p. 1126-1140.

79. Boateng, A.A., et al., *Bench-scale fluidized-bed pyrolysis of switchgrass for bio-oil production.* Industrial & Engineering Chemistry Research, 2007. **46**(7): p. 1891-1897.

80. Mullen, C.A., et al., *Analysis and comparison of bio-oil produced by fast pyrolysis from three barley biomass/byproduct streams.* Energy & Fuels, 2009. **24**(1): p. 699-706.

81. Mohan, D., et al., *Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production.* Journal of colloid and interface science, 2007. **310**(1): p. 57-73.

82. Salehi, E., J. Abedi, and T. Harding, *Bio-oil from sawdust: pyrolysis of sawdust in a fixed-bed system.* Energy & Fuels, 2009. **23**(7): p. 3767-3772.

83. Verma, M., et al., *Biofuels production from biomass by thermochemical conversion technologies.* International Journal of Chemical Engineering, 2012. **2012**.

84. López, M.B., et al., *Composition of gases released during olive stones pyrolysis.* Journal of analytical and applied pyrolysis, 2002. **65**(2): p. 313-322.

85. Rasul, M. and M.I. Jahirul, *Recent developments in biomass pyrolysis for bio-fuel production: Its potential for commercial applications.* Central Queensland University, Centre for Plant and Water Science, Faculty of Sciences, Engineering and Health, 2012.

86. Meier, D., *Pyrolysis Oil Biorefinery.* Adv Biochem Eng Biotechnol, 2017.

87. YANG, S.-w., et al., *Preparation and Adsorption Properties of Bamboo-based Activated Carbon by Chemical Activation under Vacuum.* Guangzhou Chemical Industry, 2012. **12**: p. 036.

88. Cao, X. and W. Harris, *Properties of dairy-manure-derived biochar pertinent to its potential use in remediation.* Bioresource technology, 2010. **101**(14): p. 5222-5228.

89. Dias, B.O., et al., *Use of biochar as bulking agent for the composting of poultry manure: effect on organic matter degradation and humification.* Bioresource technology, 2010. **101**(4): p. 1239-1246.

90. Gaunt, J.L. and J. Lehmann, *Energy balance and emissions associated with biochar sequestration and pyrolysis bioenergy production.* Environmental Science & Technology, 2008. **42**(11): p. 4152-4158.

91. Rondon, M., J. Ramirez, and J. Lehmann. *Charcoal additions reduce net emissions of greenhouse gases to the atmosphere.* in *Proceedings of the 3rd USDA Symposium on Greenhouse Gases and Carbon Sequestration in Agriculture and Forestry*. 2005.

92. *production process and applications.* Available from: http://superstoneclean.com/iwamoto-mineral-biochar-machine/.

93. Patrick, J.W., et al., *Process Development Unit for Integrated Studies of Syngas Cleaning.* 2011.

94. Morgalla, M., *Benzene-char conversion and particle-vapor characterization in biomass gasification*. 2018, Linnaeus University Press.

95. Basu, P., *Combustion and gasification in fluidized beds*. 2006: CRC press.

96. Zhang, L., C.C. Xu, and P. Champagne, *Overview of recent advances in thermo-chemical conversion of biomass.* Energy Conversion and Management, 2010. **51**(5): p. 969-982.

97. Zafar, S., *Summary of Biomass Combustion Technologies*. February 3,2020.

98. Abdoulmoumine, N., et al., *A review on biomass gasification syngas cleanup.* Applied Energy, 2015. **155**: p. 294-307.

99. Feedstock, E.W., *Equipment Design and Cost Estimation for Small Modular Biomass Systems, Synthesis Gas Cleanup, and Oxygen Separation Equipment.* 2006.

100. Din, Z.U. and Z. Zainal, *Biomass integrated gasification–SOFC systems: Technology overview.* Renewable and Sustainable Energy Reviews, 2016. **53**: p. 1356-1376.

101. Stuart, P.R. and M.M. El-Halwagi, *Integrated biorefineries: design, analysis, and optimization.* 2012: CRC press.

102. Li, C. and K. Suzuki, *Tar property, analysis, reforming mechanism and model for biomass gasification—an overview.* Renewable and Sustainable Energy Reviews, 2009. **13**(3): p. 594-604.

103. Van Paasen, S., J. Kiel, and H. Veringa, *Tar formation in a fluidised bed gasifier.* Impact of fuel properties and operating conditions, 2004.

104. Zeng, X., et al., *Recent progress in tar removal by char and the applications: A comprehensive analysis.* Carbon Resources Conversion, 2020. **3**: p. 1-18.

105. Zwart, R., et al., *Tar removal from low-temperature gasifiers.* 2010.

106. Hervy, M., et al., *H2S removal from syngas using wastes pyrolysis chars.* Chemical Engineering Journal, 2018. **334**: p. 2179-2189.

107. Borg, Ø., et al., *Effect of biomass-derived synthesis gas impurity elements on cobalt Fischer–Tropsch catalyst performance including in situ sulphur and nitrogen addition.* Journal of Catalysis, 2011. **279**(1): p. 163-173.

108. Yamada, M., et al., *Novel Catalytic Properties of Rh Sulfide for the Synthesis of Methanol from CO + H2 in the Presence of H2S.* Catalysis Letters, 2002. **78**(1/4): p. 195-199.

109. Andreasen, A. and S. Mayer, *Use of seawater scrubbing for SO2 removal from marine engine exhaust gas.* Energy & Fuels, 2007. **21**(6): p. 3274-3279.

110. Jafarinejad, S., *Petroleum waste treatment and pollution control.* 2016: Butterworth-Heinemann.

111. Lien, C.-C., J.-L. Lin, and C.-H. Ting, *Water scrubbing for removal of hydrogen sulfide (H2S) inbiogas from hog farms.* Journal of Agricultural Chemistry and Environment, 2014. **3**(02): p. 1-6.

112. Sasaoka, E., et al., *Role of H2O in oxidative regeneration of ZnS formed from high-temperature desulfurization ZnO sorbent.* Industrial & engineering chemistry research, 2000. **39**(10): p. 3844-3848.

113. Wheelock, T.D. and T.T. Akiti Jr, *Core-in-shell sorbent for hot coal gas desulfurization*. 2004, Google Patents.

114. Wang, J., B. Liang, and R. Parnas, *Manganese-based regenerable sorbents for high temperature H2S removal.* Fuel, 2013. **107**: p. 539-546.

115. Wang, Z. and M. Flytzani-Stephanopoulos, *Cerium oxide-based sorbents for regenerative hot reformate gas desulfurization.* Energy & fuels, 2005. **19**(5): p. 2089-2097.

116. Nord, L.O. and O. Bolland, *Carbon Dioxide Emission Management in Power Generation*. 2020: John Wiley & Sons.

117. Kazmerski, L., *Renewable and sustainable energy reviews.* Renew. Sustain. Energy Rev, 2016. **38**: p. 834-847.

118. Luis, P., *Use of monoethanolamine (MEA) for CO2 capture in a global scenario: Consequences and alternatives.* Desalination, 2016. **380**(Supplement C): p. 93-99.

119. Vega, F., et al., *Solvents for carbon dioxide capture*, in *Carbon Dioxide Chemistry, Capture and Oil Recovery*. 2018, IntechOpen Limited London, UK.

120. Gupta, M., I. Coyle, and K. Thambimuthu. *CO2 capture technologies and opportunities in Canada.* in *1st Canadian CC&S Technology Roadmap Workshop*. 2003.

121. Chihara, H., *Kagaku binran–kiso handbook of basic chemistry, 3rd edn, vol II.* Maruzen, Tokyo, 1984: p. 158.

122. Hochgesand, G., *Rectisol and purisol.* Industrial & Engineering Chemistry, 1970. **62**(7): p. 37-43.

123. Gatti, M., et al., *Review, modeling, Heat Integration, and improved schemes of Rectisol®-based processes for CO2 capture.* Applied Thermal Engineering, 2014. **70**(2): p. 1123-1140.

124. James, A.K., et al., *Investigation of air and air-steam gasification of high carbon wood ash in a fluidized bed reactor.* Energy and Environment Research, 2014. **4**(1): p. 15.

125. Basu, P., *Biomass gasification, pyrolysis and torrefaction: practical design and theory*. 2018: Academic press.

126. Carbo, M., et al., *Steam demand reduction of water–gas shift reaction in IGCC power plants with pre-combustion CO 2 capture.* International Journal of Greenhouse Gas Control, 2009. **3**(6): p. 712-719.

127. Tang, Z., et al., *Modified zeolite membrane reactor for high temperature water gas shift reaction.* Journal of Membrane Science, 2010. **354**(1): p. 114-122.

128. Ratnasamy, C. and J.P. Wagner, *Water gas shift catalysis.* Catalysis Reviews, 2009. **51**(3): p. 325-440.

129. Pasel, J., et al., *Test of a water–gas-shift reactor on a 3kW e-scale—design points for high-and low-temperature shift reaction.* Journal of power sources, 2005. **152**: p. 189-195.

130. Callaghan, C.A., *Kinetics and catalysis of the water-gas-shift reaction: A microkinetic and graph theoretic approach.* 2006, Naval Undersea Warfare Center.

131. Zhu, M. and I.E. Wachs, *Iron-Based Catalysts for the High-Temperature Water–Gas Shift (HT-WGS) Reaction: A Review.* ACS Catalysis, 2015. **6**(2): p. 722-732.

132. Jain, R. and R. Maric, *Synthesis of nano-Pt onto ceria support as catalyst for water–gas shift reaction by Reactive Spray Deposition Technology.* Applied Catalysis A: General, 2014. **475**: p. 461-468.

133. Reddy, G.K., et al., *Long-term WGS stability of Fe/Ce and Fe/Ce/Cr catalysts at high and low steam to CO ratios—XPS and Mössbauer spectroscopic study.* Applied Catalysis A: General, 2012. **415-416**: p. 101-110.

134. Kim, S.-J., et al., *Effect of pressure on high-temperature water gas shift reaction in microporous zeolite membrane reactor.* Industrial & Engineering Chemistry Research, 2012. **51**(3): p. 1364-1375.

135. Morpeth, L., et al., *Effect of H 2 S on the performance of La 0.7 Ce 0.2 FeO 3 perovskite catalyst for high temperature water–gas shift reaction.* international journal of hydrogen energy, 2012. **37**(2): p. 1475-1481.

136. Nikolova, D., et al., *The state of (K)(Ni) Mo/γ-Al 2 O 3 catalysts after water–gas shift reaction in the presence of sulfur in the feed: XPS and EPR study.* Applied Catalysis A: General, 2006. **297**(2): p. 135-144.

137. Sasaki, T., et al., *Reaction mechanism analysis for molybdenum-based water-gas shift catalysts.* Applied Catalysis A: General, 2017. **532**: p. 105-110.

138. Bonomi, A., et al., *Virtual biorefinery.* Cham: Springer International Publishing, 2016.

139. Milani, D., et al., *A model-based analysis of CO2 utilization in methanol synthesis plant.* Journal of CO2 Utilization, 2015. **10**: p. 12-22.

140. Olah, G.A., *After oil and gas: methanol economy.* Catalysis Letters, 2004. **93**(1): p. 1-2.

141. Bermúdez, J.M., et al., *CO2 reforming of coke oven gas over a Ni/γAl2O3 catalyst to produce syngas for methanol synthesis.* Fuel, 2012. **94**: p. 197-203.

142. Bailey, S., et al., *A DRIFTS study of the morphology and surface adsorbate composition of an operating methanol synthesis catalyst.* Catalysis letters, 1994. **30**(1-4): p. 99-111.

143. Chinchen, G., et al., *'The activity of Cu-ZnO-Al2O3 methanol synthesis catalysts.* Preprint, American Chem. Soc., Div. Fuel Chem, 1984. **29**(5): p. 178-188.

144. Ribeiro, A.M., et al., *Syngas stoichiometric adjustment for methanol production and co-capture of carbon dioxide by pressure swing adsorption.* Separation Science and Technology, 2012. **47**(6): p. 850-866.

145. Waugh, K., *Methanol synthesis.* Catalysis letters, 2012. **142**(10): p. 1153-1166.

146. Wang, L., et al., *SURFACE CRAZING OF Mn--Cu WEATHERING STEEL.* Acta Metallurgica Sinica, 2010. **46**(6): p. 723-728.

147. Liu, X.-M., et al., *Recent Advances in Catalysts for Methanol Synthesis via Hydrogenation of CO and CO2.* Industrial & Engineering Chemistry Research, 2003. **42**(25): p. 6518-6530.

148. Samei, E., M. Taghizadeh, and M. Bahmani, *Enhancement of stability and activity of Cu/ZnO/Al2O3 catalysts by colloidal silica and metal oxides additives for methanol synthesis from a CO2-rich feed.* Fuel Processing Technology, 2012. **96**: p. 128-133.

149. Fan, L. and K. Fujimoto, *Promotive SMSI Effect for Hydrogenation of Carbon Dioxide to Methanol on a Pd/CeO 2 Catalyst.* Journal of Catalysis, 1994. **150**(1): p. 217-220.

150. Ma, Y., et al., *Study on the sulfur tolerance of catalysts for syngas to methanol.* Catalysis Communications, 2008. **10**(1): p. 6-10.

151. Mekhilef, S., R. Saidur, and A. Safari, *Comparative study of different fuel cell technologies.* Renewable and Sustainable Energy Reviews, 2012. **16**(1): p. 981-989.

152. Romano, M.C., V. Spallina, and S. Campanari, *Integrating IT-SOFC and gasification combined cycle with methanation reactor and hydrogen firing for near zero-emission power generation from coal.* Energy Procedia, 2011. **4**: p. 1168-1175.

153. Plus, A., *11.1 User Guide.* Aspen Technology, September-2011, 2001.

154. Lauer, M. *Methodology guideline on techno economic assessment (TEA).* in *Workshop WP3B Economics, Methodology Guideline*. 2008.

155. Van Rossum, G., S.R. Kersten, and W.P. van Swaaij, *Catalytic and noncatalytic gasification of pyrolysis oil.* Industrial & engineering chemistry research, 2007. **46**(12): p. 3959-3967.

156. Sattar, A., et al., *Steam gasification of rapeseed, wood, sewage sludge and miscanthus biochars for the production of a hydrogen-rich syngas.* biomass and bioenergy, 2014. **69**: p. 276-286.

157. Puig-Gamero, M., et al., *Three integrated process simulation using aspen plus®: Pine gasification, syngas cleaning and methanol synthesis.* Energy conversion and management, 2018. **177**: p. 416-427.