Fractionation of Pyrolysis Liquids with Supercritical Carbon Dioxide

DISSERTATION

with the aim to achieve the doctoral degree at the Faculty of Mathematics, Informatics and Natural Science

Department of Biology

University of Hamburg

submitted by

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from Jiangsu (China)

Hamburg 2018

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Date of the oral defense: 27.03.2018

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I hereby confirm that I have written this thesis on my own and that I have not used any other media or materials than the ones referred to in this thesis.

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Acknowledgements

This thesis was prepared in the time between October 2012 and March 2018 at the Center for Wood Science of the University of Hamburg. The thesis was supported by funding from China Scholarship Council and DAAD Merit stipendium.

My sincere thanks go to Dr. Dietrich Meier for his interesting topic. He supervised the whole thesis and guided me since he picked me up from the airport through my whole time living in Hamburg. I enjoyed working in his group.

My warm thanks go to Prof. Dr. Bodo Saake from the University of Hamburg for his support of my work. Only with his support can I finish my research work. I appreciate his unlimited trust and invaluable discussions on my topic. I learned much from his profound wood chemistry knowledge.

My warm thanks go to Patrick Eidam, who helped me not only for the laboratory work but also a better living in Hamburg. His patient answer to my all kinds of questions is precious for me. Thanks to Jan Ole Strüven, who gave me valuable suggestions on my experimental work. His strict attitude to the science is what I admire. Thanks to Michael Windt for his interesting and humorous discussions on the work and life.

I am particularly grateful to other members of Dr. Meier’s group, Ingrid Fortmann, Silke Radtke, Christiane Riegert. Ingrid patiently taught me to analyze GC-MSD/FID data with Mass Finder. Silke helped me with sample preparation and instrument operation. Christiane helped me to analyze elemental results.

Dr. Jörn Appelt, our new group leader, thanks for your support of my work and discussions on my results. Thanks Dr. Eoin Butler who instructed me in the operation of the laboratory fluidized bed pyrolysis plant.

My sincere thanks go to those who have made my life in Hamburg colorful: Dr. Dongsheng, Wei, Dr. Kesheng Shu, Dr. Ping Ren, Dr. Xiaojun Wu, Tianyi Wang, etc.

Thanks to my parents, Fuliang Xu and Shuping Feng, my grandparents, Tianfu Feng and Aifang Xu, I would not finish anything without your support. Thanks to Ning Tian, who encouraged me all the time.

Special thanks to Tschin from TU Graz, who opened a world to me I have never seen before.

List of papers and author's contribution

Paper 1:

Yongshun Feng, Dietrich Meier

Extraction of value-added chemicals from pyrolysis liquids with supercritical carbon dioxide. Journal of Analytical and Applied Pyrolysis 113 (2015): 174-185.

Author Y. Feng planned and carried out the $scCO_2$ extraction experiments and the products analysis work and was the main contributor to the interpretation of the results and the writing of the manuscript. D. Meier instructed the work and took part in the planning of the experiments and helped to solve problems during experimental work. D. Meier reviewed and commented on the manuscript and supervised Y. Feng's doctoral studies.

Paper 2:

Yongshun Feng, Dietrich Meier

Comparison of supercritical CO_2, liquid CO_2, and solvent extraction of chemicals from a commercial slow pyrolysis liquid of beech wood. Biomass and bioenergy 85 (2016): 346-354.

Author Y. Feng planned and carried out the different extraction experiments and the products analysis work and was the main contributor to the interpretation of the results and the writing of the manuscript. D. Meier instructed the work and took part in the planning of the experiments and helped to solve problems during experimental work. D. Meier reviewed and commented on the manuscript and supervised Y. Feng's doctoral studies.

Paper 3:

Yongshun Feng, Dietrich Meier

Supercritical carbon dioxide extraction of fast pyrolysis oil from softwood. The Journal of Supercritical Fluids 128 (2017): 6-17.

Author Y. Feng planned and carried out the experiments of $scCO_2$ extraction of BTG oil and the products analysis work and was the main contributor to the interpretation of the results and the writing of the manuscript. D. Meier instructed the work and took part in the planning of the experiments and helped to solve problems during experimental work. D. Meier reviewed and commented on the manuscript and supervised Y. Feng's doctoral studies.

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Summary

In this thesis, the $scCO_2$ extraction of value-added chemicals from different pyrolysis liquids was investigated. Pyrolysis liquids studied included a commercial slow pyrolysis liquid (PF oil) from charcoal production (proFagus GmbH, Bodenfelde, Germany), two fast pyrolysis liquids (upper phase (TI-U) and lower phase (TI-L)) self-produced in a pilot plant at Thünen Institute, Hamburg, Germany, and two fast pyrolysis liquids (fresh and aged) commercially produced at BTG BV, Enschede, the Netherlands.

In the pressure range of 150-250 bar, the extraction yield of PF oil was 42.1-53.5 wt% while the TI oils gave 7.4-15.0 wt%. Water had a negative influence on the extraction yield. As a consequence, water should be removed from pyrolysis liquid if high extraction yields are required. The extraction yields were largely increased when the pressure was raised from 150 to 200 bar but only a further slight increase was observed in the pressure range between 200 and 250 bar. From an economical point of view, 200 bar is a reasonable pressure for the $scCO_2$ extraction of pyrolysis liquids. The extraction yields could also be increased by raising the flow rate, however, higher flow rates also accelerated the evaporation rate of the extracts in the collector system. Losses accounted for a significant portion of the mass balance, ranging from 9.8 wt% to 24.6 wt%. As the extracts consisted mainly of volatile compounds, they were quickly evaporated with a higher CO_2 gas flow. To find a remedy, the condensation system was expanded with cooled wash bottles filled with isopropanol and an activated carbon filter. With these measures, losses were reduced to a minimum of 4.2 wt%. The isopropanol wash bottle trapped 11.2-14.9 wt% of compounds while the AC filter trapped 6.5-9.3 wt% of the volatiles from the PF oil.

Before $scCO_2$ extraction, the pyrolysis liquids were adsorbed on different carrier materials. The tests of three different carrier materials (glass beads, activated carbon, and SiO_2) and the loading ratios were conducted with BTG oil at 200 bar. Glass beads gave the highest extraction yield with 15.5-21.6 wt% but showed a very low adsorption. The adsorption of 1 g pyrolysis liquid required at least 17 g glass beads. The loading ratio of SiO_2 and AC was 1:1 and the extraction yield was 6.4-13.1 wt%. A low extraction temperature of 60 °C yielded more extracts and fewer off-gases compared to a higher extraction temperature of 80 °C. The off-gases maximum was obtained with AC as carrier at high temperatures.

In six hours runs, the $scCO_2$ extraction process was evaluated using different pyrolysis liquids. The following parameters and settings were investigated: pressure (100, 200, 300 bar), temperature (60 °C, 80 °C), and carrier (SiO_2, AC). The results revealed that the extraction process was dissolution controlled at 100 bar with very low yields as the $scCO_2$ had a low solubility for the components in the pyrolysis liquids. The extraction process was similar to that of the broken and intact cell model at 200 and 300 bar. The initial extraction period was dominated by dissolution while at a later period diffusion was the dominant environment. The extraction yields were higher at higher pressure and lower temperatures. The influence of temperature became smaller with increasing pressure as temperature influences both solvent density, vapor pressure, and mass transfer. When the pressure is above 300 bar, an increase in temperature would still promote the extraction rate.

Around 50 wt% of PF and TI-U oil could be qualified and quantified by GC-MSD/FID while around 75 wt% of the detectable peaks in the chromatogram could be analyzed. Acids were extracted with $scCO_2$ but with limited enrichment effect. Low temperature, a high oil loading ratio, and a short extraction time could improve the extraction effect of acids. Aldehydes in pyrolysis liquids had a low concentration. The carrier material was the most important factor to influence the enrichment efficiency of aldehydes and it increased with longer extraction times. Ketones were the most abundant chemicals in pyrolysis liquids. Different ketones showed different extraction profiles. Most ketones were enriched in the extracts but the enrichment coefficient decreased with longer extraction time. The enrichment coefficient of furans from TI and BTG oils was higher than from PF oil. Phenols are valuable compounds but were present in low concentrations in pyrolysis liquids. They could be effectively extracted with $scCO_2$. Their concentrations changed little with longer extraction times.

Zusammenfassung

In dieser Arbeit wurde die Extraktion von Wertstoffen mit überkritischem CO_2 aus vier verschiedenen Pyrolyseflüssigkeiten untersucht. Ein Pyrolyseöl (PF-Öl) stammte aus der langsamen Pyrolyse von Buchenholz für die Holzkohleproduktion (proFagus GmbH, Bodenfelde, Deutschland) und stellt eine Nebenfraktion dar, die bei der Herstellung von Raucharomen anfällt. Weiterhin wurden zwei Fraktionen eines Bio-Öls aus Flash-Pyrolyse untersucht, das in der Pilotanlage des Thünen Instituts für Holzforschung, Hamburg erzeugt wurde. Das Öl wurde in eine Oberphase (TI-U) und eine Unterphase (TI-L) aufgeteilt. Zusätzlich wurden zwei weitere Flash-Pyrolyseöle aus kommerzieller Produktion von BTG BV, Enschede, Niederlande, in die Untersuchungen einbezogen. Die Öle unterschieden sich durch ihre Lagerzeiten von weinigen Tagen bzw. einigen Monaten.

Im Druckbereich von 150-250 bar lagen die Extraktionsausbeuten von PF-Öl zwischen 42,1 und 53,5 Gew.-%, während die TI-Öle 7,4 bis 15,0 Gew.-% ergaben. Wasser hatte einen negativen Einfluss auf die Extraktionsausbeute. Folglich sollte Wasser aus der Pyrolyseflüssigkeit entfernt werden, wenn hohe Extraktionsausbeuten gewünscht sind. Die Extraktionsausbeuten konnten gesteigert werden, wenn der Druck von 150 auf 200 bar erhöht wurde; im Druckbereich zwischen 200 und 250 bar wurde nur ein leichter Anstieg der Ausbeuten beobachtet. Aus ökonomischer Sicht sind daher 200 bar ein adäquater Druck für die $scCO_2$-Extraktion von Pyrolyseflüssigkeiten.

Die Extraktionsausbeuten können auch durch Erhöhung der Fließgeschwindigkeit des Gases erhöht werden, allerdings beschleunigt sich dadurch auch die Verdampfungsrate der Extrakte in dem Kollektorsystem. Da die Extrakte hauptsächlich aus flüchtigen Verbindungen bestanden, wurden sie schnell mit einem höheren CO_2-Gasstrom ausgetragen. Infolgedessen machten Verluste zunächst einen wesentlichen Teil der Massenbilanz aus, die von 9,8 Gew.-% bis 24,6 Gew.-% reichten. Um Abhilfe zu schaffen, wurde das Kondensationssystem mit gekühlten Waschflaschen - die mit Isopropanol gefüllt waren - und einem Aktivkohlefilter erweitert. Mit diesen Maßnahmen konnten die Verluste auf ein Minimum von 4,2 Gew.-% reduziert werden. Die Isopropanol-Waschflaschen enthielten 11,2-14,9 Gew.-% der Extrakte, während mit dem AC-Filter 6,5-9,3 Gew.-% der flüchtigen Bestandteile aus dem PF-Öl gesammelt werden konnten.

Vor der $scCO_2$-Extraktion wurden die Pyrolyseflüssigkeiten auf verschiedenen Trägermaterialien adsorbiert. Die Tests mit drei verschiedenen Trägermaterialien (Glasperlen, Aktivkohle und Silica) und unterschiedlichen Beladungsverhältnissen wurden mit BTG-Öl bei 200 bar durchgeführt. Glasperlen ergaben die höchste Extraktionsausbeute mit 15,5 bis 21,6 Gew.-%, zeigten jedoch eine sehr geringe Adsorption. Die Adsorption von 1 g Pyrolyseflüssigkeit erforderte mindestens 17 g Glasperlen. Das Beladungsverhältnis von SiO_2 und AC betrug 1: 1 und die Extraktionsausbeute betrug 6,4 bis 13,1 Gew.-%. Eine relativ niedrige Extraktionstemperatur von 60°C ergab mehr Extrakte und weniger Abgase im Vergleich zu einer höheren Extraktionstemperatur von 80°C. Das Abgasmaximum wurde mit AC als Träger bei hohen Temperaturen erhalten.

In einem sechs Stunden dauernden Versuch wurde der $scCO_2$-Extraktionsprozess unter Verwendung verschiedener Pyrolyseflüssigkeiten erprobt und bewertet. Die folgenden Parameter und Einstellungen wurden untersucht: Druck (100, 200, 300 bar), Temperatur (60 ° C, 80 ° C) und Träger (SiO_2, AC). Die Ergebnisse zeigten, dass die Extraktion bei 100 bar durch das Löseverhalten der Verbindungen kontrolliert wurde mit dem Ergebnis sehr geringer Ausbeuten, da $scCO_2$ eine geringe Löslichkeit für die Komponenten in den Pyrolyseflüssigkeiten zeigte. Der Extraktionsprozess ähnelt dem des gebrochenen und intakten Zellmodells bei 200 und 300 bar. In diesen Modell dominiert in der Anfangsphase der Extraktion das Lösungsvermögen, während im späteren Verlauf der Extraktion die Diffusion das vorherrschende Prinzip ist. Die Extraktionsausbeuten verbesserten sich bei höherem Druck und niedrigeren Temperaturen. Der Einfluss der Temperatur wurde mit zunehmendem Druck kleiner, da die Temperatur sowohl die Lösungsmitteldichte als auch den Dampfdruck und den Massentransfer beeinflusst. Wenn der Druck über 300 bar liegt, würde eine Temperaturerhöhung immer noch die Extraktionsrate fördern.

Etwa 50 Gew.-% PF- und TI-U-Öl konnten durch GC-MSD/FID qualifiziert und quantifiziert werden, während etwa 75 Gew .-% der detektierbaren Peaks im Chromatogramm analysiert werden konnten. Die Säuren wurden mit $scCO_2$, jedoch mit begrenztem Anreicherungseffekt, extrahiert. Niedrige Temperaturen, ein hohes Ölbeladungsverhältnis und eine kurze Extraktionszeit könnten die Extraktionswirkung von Säuren verbessern. Aldehyde hatten in den untersuchten Pyrolyseflüssigkeiten eine geringe Konzentration. Das Trägermaterial war der wichtigste Faktor, um die Anreicherungseffizienz von Aldehyden zu beeinflussen, zusätzlich wurden sie durch längere Extraktionszeiten angereichert. Ketone waren die häufigsten Chemikalien in den untersuchten Pyrolyseflüssigkeiten. Verschiedene Ketone zeigten unterschiedliche Extraktionsprofile. Die meisten Ketone wurden in den Extrakten angereichert, aber ihr Anreicherungskoeffizient nahm mit längerer Extraktionszeit ab. Der Anreicherungskoeffizient von Furanen aus TI- und BTG-Ölen war höher als von PF-Öl. Phenole sind wertvolle Verbindungen, aber in Pyrolyseflüssigkeiten in geringen Konzentrationen vorhanden. Sie konnten effektiv mit $scCO_2$ extrahiert werden. Ihre Konzentrationen änderten sich allerdings wenig bei längeren Extraktionszeiten.

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Abbreviation used in the thesis:

SiO_2: silica gel

AC: activated carbon

GB: glass beads

PF oil: slow pyrolysis liquid produced by proFagus (Bodenfelde, Germany) charcoal company

TI oil: fast pyrolysis liquids produced by Thünen Institute, including both TI-U and TI-L oils

TI-U oil: Upper oil phase of fast pyrolysis liquid produced by Thünen Institute

TI-L oil: Lower oil phase of fast pyrolysis liquid produced by Thünen Institute

BTG oil: fast pyrolysis liquid produced by Biomass Technology Group (Enschede, The Netherlands)

SFE: supercritical fluid extraction

$scCO_2$: supercritical carbon dioxide

GC-MSD/FID: gas chromatography coupled in parallel with mass selective detector and flame ionization detector

GPC: gel permeation chromatography

1 Introduction

1.1 Background

The thermo-chemical utilization of wood has a long history which is shown in Figure 1. Even in ancient Egypt, people were acquainted with methods of recovering distillation products resulting from the process of carbonization. The liquid wood tar and pyroligneous acid were produced from the destructive distillation of wood and used for embalming (KLAR, 1925). Chemicals such as methanol, acetic acid and acetone could be obtained from condensable distillates from wood which is shown in Figure 2. The application of wood condensates was common in the chemical industry. For example, a large amount of wood spirit was required for the dye industry in 1856. Wood also served as the main energy resources before 1880 when coal succeeded wood as the main energy resources. Since the 1900s, the production of chemicals from wood had declined sharply due to the development of the coal and petroleum industry. However, the three oil shocks between 1970 and 1990 combined with environmental and political concerns made it mandatory to develop new processes for the production of renewable energy and materials.

Wood and other forms of lignocellulosic biomass are one of the main renewable and sustainable feedstocks available in considerable amounts. Lignocellulosic biomass is of particular interest as it can be thermos-chemically converted into storable gaseous, liquid and solid products with potential use both as fuels and chemicals. Processes that convert wood and other forms of biomass into liquids mainly include catalytic-chemical, thermo-chemical and biological processes. As a promising thermo-chemical method, fast pyrolysis is of great interest as it gives the highest liquid yields of up to 75 wt%. Moreover, fast pyrolysis is two or three times cheaper than gasification or fermentation (ANEX *et al.*, 2010). Solid biomass is pyrolyzed at 400-500 °C at short residence time (1-2 seconds) without oxygen to produce hot vapors which are further condensed to produce a liquid product. The liquid product from fast pyrolysis is generally called fast pyrolysis liquid or bio-oil.

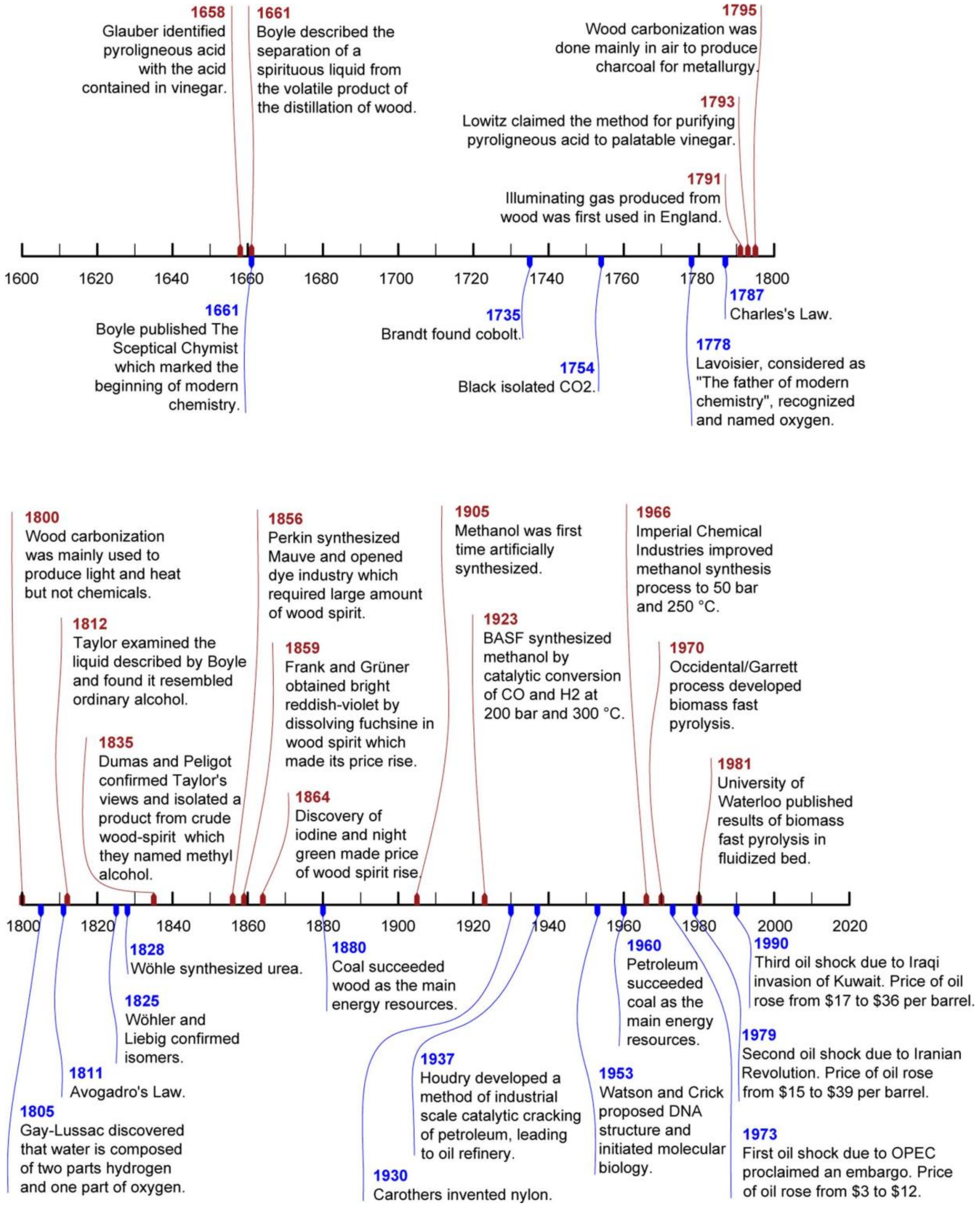


Figure 1: History of chemistry and thermo-chemical utilization of wood.

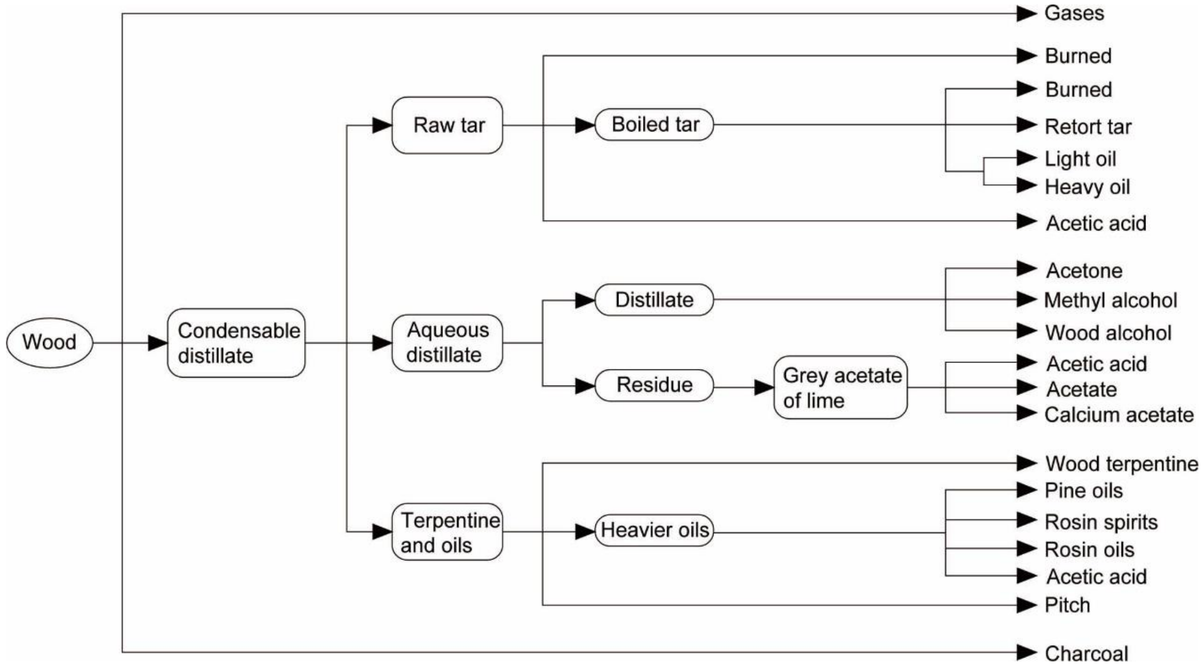


Figure 2: Chemical products from wood destructive distillation (VEITCH, 1907).

Another source of liquid products from woody biomass is derived from charcoal industry. The pyroligneous acid and wood tar are by-products of charcoal production. In the charring process of proFagus GmbH (Bodenfelde, Germany), 3 tons of untreated beech wood are carbonized to produce 1 ton of barbecue charcoal and 2 tons of by-products (acids, tars). Although they use distillation and extraction techniques to produce acetic acid and smoke flavorings, a large amount of residue cannot be further used chemically and are burned for process energy production.

Several fast pyrolysis technologies for the production of pyrolysis liquids have been developed and some are even developed to semi-commercial scale by several companies (MEIER *et al.*, 2013). Here, the bio-oils are burned to replace fossil fuel like heavy fuel oil or natural gas. The direct use as transportation fuels is impossible as the liquids have poor volatility, high viscosity, corrosiveness, cold flow and coking (CZERNIK *et al.*, 2004). They have to be upgraded if they are to be used as a replacement for diesel or gasoline fuels.

Pyrolysis liquid is a complex mixture of organic compounds along with 15-30 wt% water. These chemicals are derived from depolymerization and fragmentation reactions of cellulose, hemicellulose, and lignin. Several hundred organic compounds have been found in pyrolysis liquid and most of them are in low concentrations. The complexity of pyrolysis liquid provides the potential for obtaining chemicals (MEIER *et al.*, 1999). Various value-added compounds can be extracted from pyrolysis liquids, such as acetic acid, hydroxyacetaldehyde, levoglucosan, levoglucosenone, furfural, phenolic compounds, and other valuable chemicals. Different applications can be developed from the whole pyrolysis liquids and their fractionations, such as resins, fertilizers, road deicers, liquid smoke, etc.

The separation and fractionation of pyrolysis liquids are of vital importance if they are to be used for chemicals production. Even dated back to wood destructive distillation, the efficient separation of pyroligneous acids to obtain pure compounds was already the research focus. Almost all separation methods in organic chemistry have been tried to separate pyrolysis liquids. Distillation can separate pyrolysis liquid into different fractions but with limited effects. Pyrolysis liquid cannot be completely vaporized and produces a solid residue of around 50 wt% when heated above 100 °C. Liquid-liquid extraction is the best method to obtain pure compounds but a multi-step extraction with large amounts of solvents is required. The recovery of solvents makes solvent extraction not economically attractive for chemicals production. Other separation methods such as chromatography, centrifugal separation, fractional condensation, membrane separation also show limited effects due to the complex nature of pyrolysis liquid.

Supercritical fluids are a unique class of solvent and their study had begun since the 19th century. Tour first observed the occurrence of supercritical phase in 1822 and Gore published the earliest work on CO_2 as a solvent in 1861 (MCHUGH *et al.*, 1986). A number of works had been done on the solubility and phase behavior of various materials in liquid CO_2 in the 19th century. In the 1970s, Zosel reported the decaffeination of green coffee with CO_2 with great success and promoted supercritical fluid extraction technology (ZOSEL, 1974, ZOSEL, 1978). Since 1980, the supercritical fluid extraction (SFE) from natural products developed rapidly. It has been used to extract natural materials (REVERCHON *et al.*, 2006), essential oils (XU *et al.*, 2011), herbal drugs (LANG *et al.*, 2001), anti-oxidants (BRAGA *et al.*, 2008), etc. Brunner reported the supercritical fluids in industrial and near-to-industry applications, indicating that the variety of possible applications for supercritical fluids is endless (BRUNNER, 2010).

In terms of pyrolysis liquids separation, the supercritical carbon dioxide ($scCO_2$) proves to be an alternative other than organic solvents. It is non-toxic and the recycling is not necessary. Selectivity of valuable chemicals can be adjusted by process optimization. Therefore, the $scCO_2$ extraction of pyrolysis liquids was systematical studied in this research.

1.2 Objectives

The objective of this research is to study selective extraction of pyrolysis liquids with $scCO_2$. In biorefinery concepts, the production of platform chemicals is of great interest and importance both from the chemical and economical perspectives. The extraction with organic solvents has been tried but with little success and the need to recycle the solvents. As a non-toxic solvent, CO_2 has been used to selectively extract chemicals from the plant and other materials (CAPUZZO *et al.*, 2013). The selectivity of $scCO_2$ can be modified by adjusting the extraction conditions. The applications of $scCO_2$ in extracting pyrolysis liquids have rarely been reported. Hence, in my research, the $scCO_2$ extraction of pyrolysis liquids has been systematically studied.

In order to get an impression on the $scCO_2$ extraction effects on pyrolysis liquids, the initial experiments were carried out using both slow and fast pyrolysis liquids at different pressures. The properties of the crude pyrolysis liquids, the $scCO_2$ extracts, and the residue were analyzed in detail. Based on the experience and knowledge from this part of experiments which were mainly reported in Publication 1 (FENG *et al.*, 2015), the amount of chemicals present in different pyrolysis liquids and their distribution in $scCO_2$ extracts and residue became clear.

With various separation methods, the final purpose of pyrolysis liquids separation is the production of value-added chemicals or the removal of unwanted compounds. To compare the efficiency of $scCO_2$ extraction, other methods including liquid CO_2 and organic solvents were tested. CO_2 at liquid and supercritical state has different properties and this fact helps to influence the chemical composition of the extract. A given solute may have a different solubility in subcritical or supercritical CO_2, often an order of magnitude or so (HYATT, 1984). Therefore, the extraction effect of pyrolysis liquids was compared between liquid and supercritical CO_2. As a non-polar molecule, CO_2 in condensed state behaves like non-polar organic hydrocarbon solvents (DARR *et al.,* 1999). For the comparison, solvent extraction with hexane and acetone was performed using pyrolysis liquids. The feedstocks were commercial slow pyrolysis liquids adsorbed on SiO_2 as carrier material. The carrier may also influence the selectivity of the extraction process. Moreover, different loading ratios were studied in this part of the work and the main results were published in Publication 2 (FENG *et al.,* 2016).

As the focus of this thesis is on the $scCO_2$ extraction of fast pyrolysis liquids, a more detailed extraction on commercial fast pyrolysis BTG oil was carried out. The extraction process was investigated by applying different extraction pressures, temperatures, and carrier types. The $scCO_2$ extracts were collected and analyzed every hour in a six hours run. As a result, the extraction process with the progression of main chemicals could be monitored. Based on the results, a profound knowledge of the $scCO_2$ extraction on fast pyrolysis liquid was obtained and the main results were reported in Publication 3 (FENG *et al.*, 2017).

The main part of the experiments deals with the $scCO_2$ extraction of different pyrolysis liquids, the application of different extraction methods for slow pyrolysis liquid, the continuous extraction over six hours with hourly collection of extracts, and the analysis of the composition of the extracts. The 21 important and major chemical compounds were determined to calculate extraction efficiency, enrichment coefficients and in some cases the distribution coefficients.

2 Current state of knowledge

2.1 Fast pyrolysis technologies

Lignocellulosic biomass undergoes thermal degradation and depolymerization through pyrolysis and the hot vapors are condensed into pyrolysis liquid. With very high heating rates, fast pyrolysis is the most efficient method to produce pyrolysis liquids with a conversion rate of around 75 wt% based on dry biomass. After drying and grinding to small particles, all kinds of lignocellulosic biomass can be directly transferred into pyrolysis liquids.

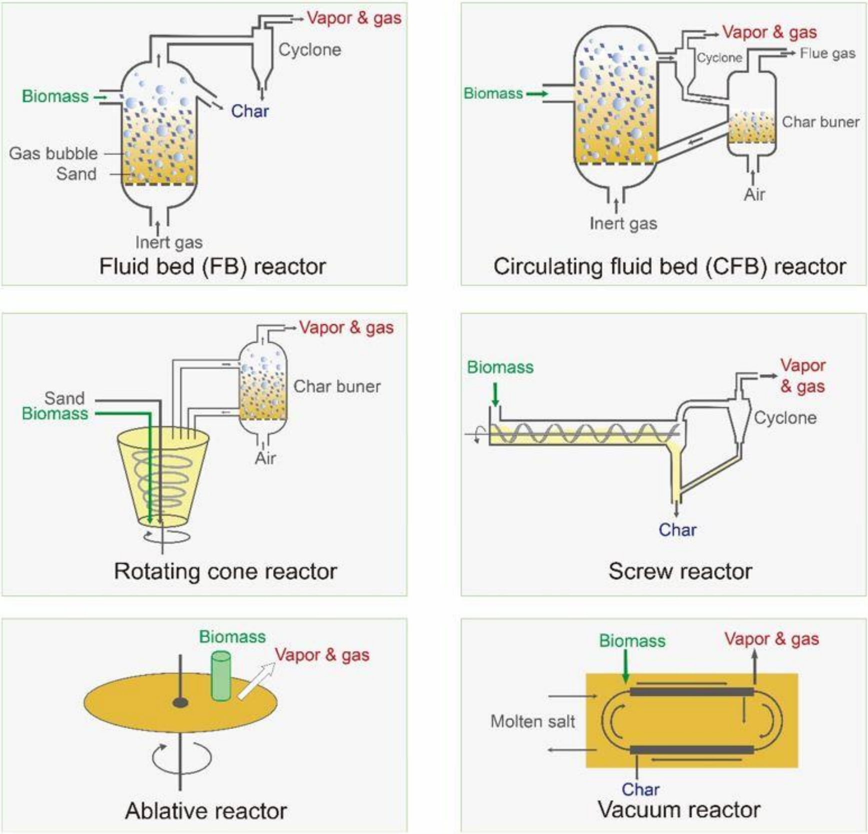


Figure 3: Schematic illustration of main fast pyrolysis reactors.

The essential features of a fast pyrolysis process include rapid heating of biomass in absence of oxygen and rapid cooling of vapors, a carefully controlled reaction temperature of around 500 °C with vapor residence time typically less than 2 seconds (BRIDGWATER *et al.*, 1999). Different types of reactors have been designed and built to fulfill such features, mainly including fluidized bed reactors, circulating fluidized bed reactors, rotating cone reactors, ablative pyrolysis reactors, and vacuum pyrolysis reactors. A schematic illustration of these technologies is shown in **Figure 3**.

Fluid bed reactors were first developed for the catalytic cracking of petroleum. For biomass fast pyrolysis, they were applied by the University of Waterloo in 1981. It is the most popular configuration due to the high heat transfer efficiency, the ease of operation and scale-up (BRIDGWATER *et al.*, 2000). The fluidized hot sand particles provide rapid heating of biomass. The efficiency of heat which transfers from hot sand to biomass is high but from the heating coil to fluid bed is low. The fluidizing gas needs to be pre-heated. Biomass is pyrolyzed in the fluid bed reactor. Char is separated by overflow tubes and cyclones. Hot vapors are condensed by quench coolers to give the pyrolysis liquid. It consists of condensable vapors and a non-miscible quenching liquid, e.g. hydrocarbon. Part of the non-condensable gases are further used as the bubbling gas, the rest is burnt to provide heat for the system or to dry the biomass. The separated char is burnt to provide further process heat.

Circulating fluid bed (CFB) reactors were first developed for clean combustion of coal. Based on fluid bed technology, CFB solves the problem of low efficiency of heat transfer from heating coil to the sand. The sand together with char are subjected by high gas velocities into the combustor where char is burnt and the hot sand is recycled into the fluid bed reactor. The residence time of char is almost the same as for vapors and gases. Extensive char removal is needed otherwise the char content in pyrolysis liquid is high. Similar to fluid bed technology, careful treatment of non-condensable gases is required for the cleaning, compressing and pre-heating when recycled.

Ablative reactors heat biomass directly and they do not require fluidizing gas or small biomass particles. Ablation is a process that removes material from the surface of an object by heat. The ablative reactor consists of a hot rotating surface (ca. 600 °C) such as rotating disc or rotating drum where biomass is pressed and heated. The pressing forces can be generated mechanically. The surface of wood particles “melts” and evaporates once they contact the hot disc. It is like melting butter in a frying pan (BRIDGWATER, 2012). The reaction rate is determined by the pressure instead of heat transfer through biomass particles, hence, large biomass particles and even wood chips can be used. The heat transfer rate is not as effective as with fluid beds. Ablative reactors are mechanically driven, thus they are more complex than fluid bed reactors and more difficult to scale up.

The rotating cone reactor was invented by Twente University and developed by Biomass Technology Group (BTG) BV, Enschede, NL. The original idea came out in 1989 based on an ablative principle which used neither gas nor sand (VENDERBOSCH *et al.*, 2010). Considering that the mixing of biomass particles and hot inert particles is the most effective way to transfer heat to biomass, sand was selected as heat carrier in the rotating cone reactor. Biomass particles and sand are fed in separate lines to the bottom of the rotating cone. The centrifugation forces (up to 600 rpm) drive hot sand and biomass up to the rim of the rotating heated cone. Biomass particles degrade due to contact with the hot surface and hot sand. Vapors are collected conventionally. Char and sand drop into a fluid bed combustor where char is burned to heat the sand and hot sand is recycled into the rotating cone. The initial reactor accepted biomass particles with the size less than 1 mm while the improved reactor can be operated with particles up to 10 mm.

Screw reactors move biomass through a hot reactor by mechanical forces. The mechanical forces can move different types or sizes of biomass, therefore screw reactors are particularly suitable for heterogeneous feed materials. Sand is used as heat carrier in the reactor for a rapid heating of biomass. Pyrolysis of biomass occurs at about 500 °C. The residence time of hot vapors can be in the range of 5 to 30 s depending on the design and size of the reactor. Due to the long residence time, the liquid product yield is lower than fluid bed along with a higher yield of char (BRIDGWATER, 2012). The laboratory and demonstration scale of a twin screw reactor was used and developed at Karlsruhe Institute of Technology (KIT).

Vacuum reactor is a special pyrolysis reactor operated under a reduced pressure of about 0.15 bar. It was first developed by the University of Laval in Canada. Biomass is introduced into to form moving bed in the vacuum chamber. The moving bed is heated by heating plates filled with hot molten salt. The vacuum enables a rapid removal of hot vapors. Large biomass particles are acceptable in this process but the heat transfer rate to the biomass is low. Therefore, the liquid yield is only 35-50 wt% based on dry biomass along with a higher char yield. The vacuum pyrolysis reactor was tested in 1997 and a pilot plant with 3.5 ton/h was operated until 2004. The system requires high vacuum which is complicated and costly, thus it is difficult to operate at commercial or large scale.

The advantages and disadvantages of the main pyrolysis reactors are listed in Table 1.

Table 1: The advantages and disadvantages of main biomass pyrolysis reactors.

Pyrolysis reactors	Advantages	Disadvantages
Bubbling fluid bed	• Efficient heat transfer • Good temperature control • Easy to operate and scale up • Consistent performance • High liquid yields of 70-75% • Well-understood technology	• Biomass needs to be grinded • Limited heat transfer at large scale • Unavoidable fine chars • Inert gas is required
Circulating fluid bed	• Circulation of hot sand	• Complex hydrodynamics • Careful char combustion
Ablative reactor	• No grinding is needed • No inert gas is needed	• Mechanical energy is needed • Limited heat transfer • Costly scale up
Rotating cone reactor	• Easy separation of sand char • Less inert gas is needed	• Complex operation • Liquid yields of 60-70%
Screw reactor	• Suitable for heterogeneous feed • No inert gas is needed	• Long vapor residence time
Vacuum pyrolysis	• No grinding is needed • No inert gas is needed • Less char in pyrolysis liquid	• Low liquid yields of 35-50% • Mechanically complicated

2.2 Pyrolysis liquid in general

Pyrolysis (Greek: pyros, a fire, + lysis) is the heating of a substance in the absence of air until it decomposes (SOLOMONS *et al.*, 2016). Pyrolysis liquid commonly refers to liquid condensed from thermal degradation vapors of cellulose, hemicellulose, and lignin with rapid temperature increase. It is dark brown, free-flowing liquid that comprises complex oxygenated compounds (MOHAN *et al.*, 2006). Pyrolysis liquid has several synonyms, such as pyrolysis oil, pyroligneous acid, pyrolytic tar, wood liquid, liquid wood, wood distillate, wood oil, liquid smoke, bio-oil, etc. Pyrolysis liquid and bio-oil are most often used. Pyrolysis liquid is formed by freezing intermediates and therefore self-reactive and has phase separation with the storage time. It is thermally unstable. The yield and composition are influenced by feedstock and process conditions (BRIDGWATER, 2012). It can be considered as micro-emulsions and has multi-phase structures (GARCIA-PEREZ *et al.*, 2006). Instead of pure chemicals, the nature of pyrolysis liquid is a mixture and the composition can vary in a wide range depending on feedstock and process conditions. Since fast pyrolysis is nowadays the main technology to maximize liquid yield, the term “fast pyrolysis bio-oil” is defined as follows with a CAS number of 1207435-39-9 (ELLIOTT, 2013):

Liquid condensate recovered by thermal treatment of lignocellulosic biomass at short vapor residence time (typically less than 5 seconds) typically at between 450 and 600 °C, at near atmospheric pressure or below, in the absence of oxygen, and using small (typically less than 5 mm) dry (typically less than 10% water) biomass particles. A number of engineered systems have been used to effect high heat transfer into the biomass particle and quick quenching of the vapor product, usually after removal of solid byproduct "char", to recover a single phase liquid product. Bio-oil is a complex mixture of, for the most part, oxygenated hydrocarbon fragments derived from the biopolymer structures. It typically contains 15-30% water. Common organic components include acetic acid, methanol, aldehydes and ketones, cyclopentenones, furans, alkyl-phenols, alkyl-methoxy-phenols, anhydrosugars, and oligomeric sugars and water-insoluble lignin-derived compounds. Nitrogen-containing and sulfur-containing compounds are also sometimes found depending on the biomass source.

2.3 Chemical properties of pyrolysis liquid

As the main feedstock for pyrolysis, wood is composed mainly of cellulose, hemicellulose, lignin, and extractives, as shown in Figure 4. Through pyrolysis processes, the large molecules of the three main components degrade into small molecules.

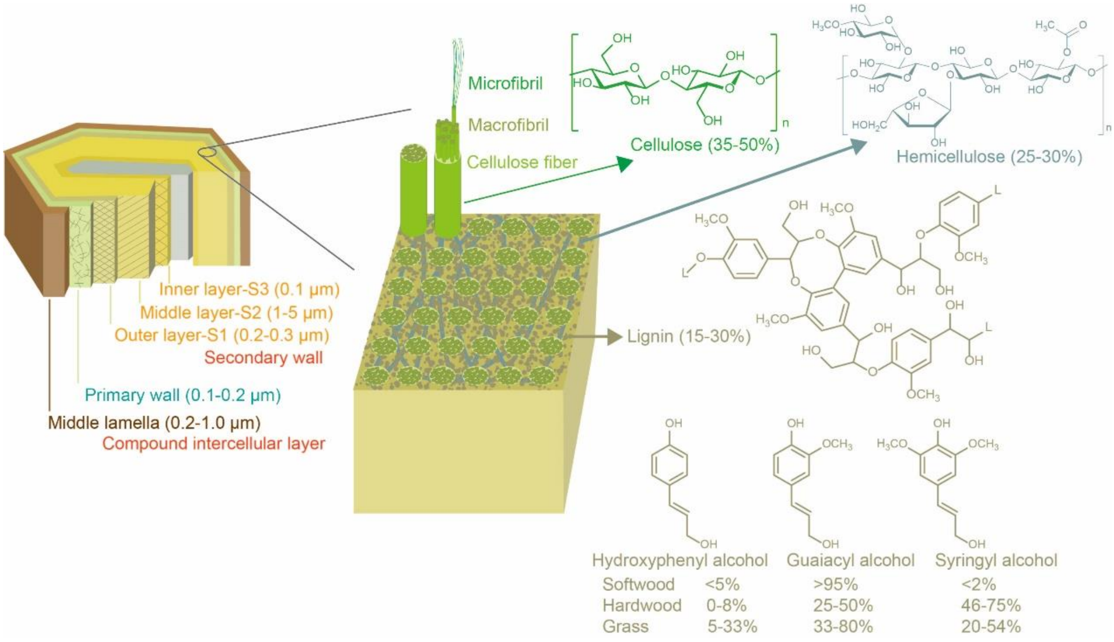


Figure 4: Arrangement of cellulose, hemicellulose, and lignin in lignocellulosic biomasses.

2.3.1 Pyrolysis of cellulose

Cellulose is the main component in the cell wall of lignocellulosic biomass. Unlike starch which contains α(1→4) glucosidic linkage, the D-glucopyranoside units in cellulose are β-glycosidic linkages. Celluloses from different origins have different molecular weights. Cellulose from cotton contains around 3000 glucose unit. Around 100-200 parallel cellulose molecules combine together through hydrogen bonding to form micro-fibers

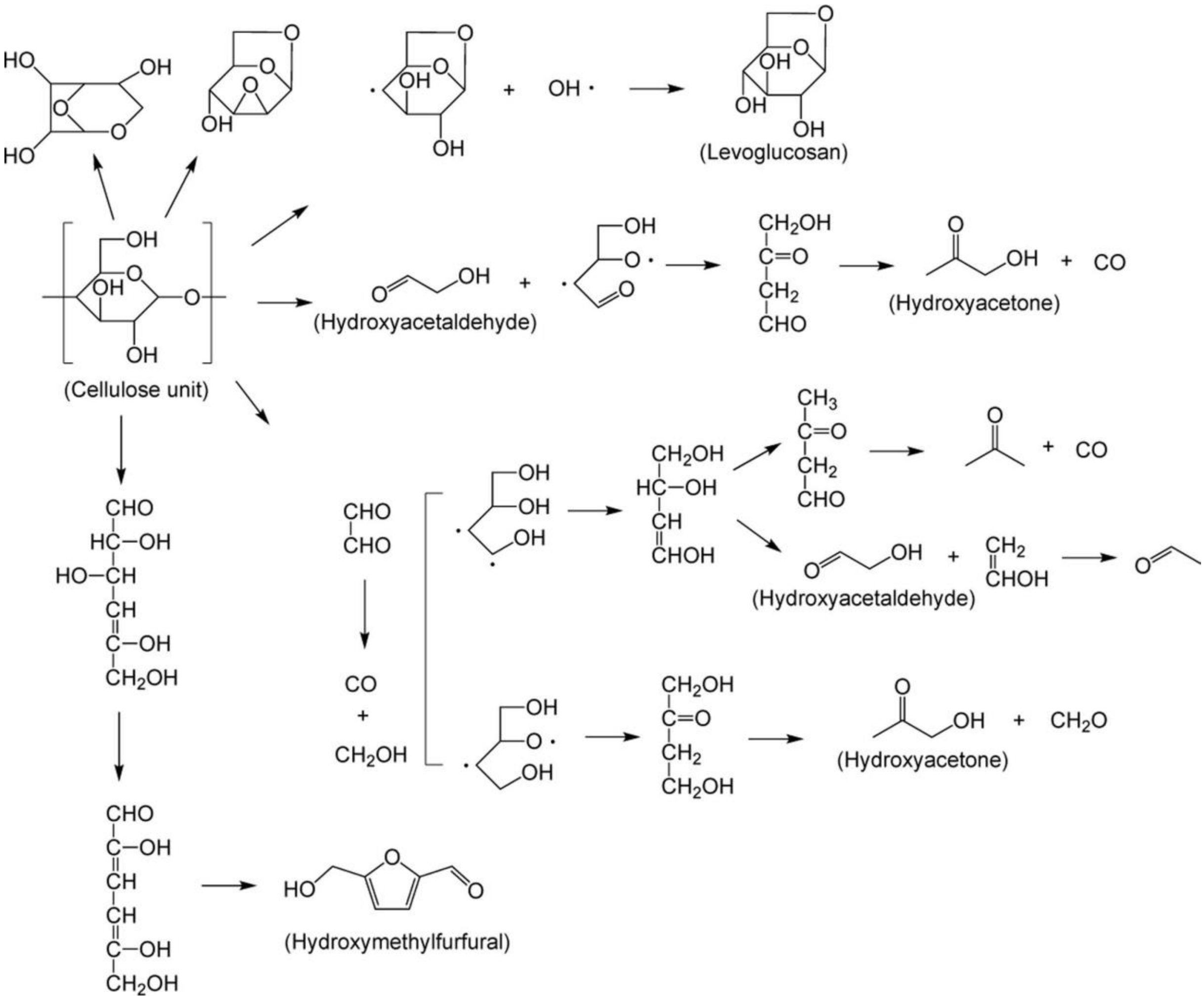


Figure 5: The major pyrolytic pathways of cellulose fast pyrolysis (SHEN *et al.*, 2009).

Pyrolysis of cellulose starts at 150 °C. When below 300 °C, cellulose pyrolysis involves elimination of water, formation of radicals, carbonyl, carboxyl and hydroperoxide groups, CO and CO_2. When above 300 °C, cellulose is transformed to activated cellulose and pyrolyzed further in two parallel pathways: depolymerization and fragmentation. Depolymerization forms anhydrosugars, levoglucosan, furans, pyrans, cyclopentanones, and their derivatives (SHAFIZADEH *et al.*, 1973). Fragmentation mainly forms hydroxyacetaldehyde, acetol, and other alcohols, esters and other products (SHEN *et al.*, 2009). The detailed possible pathways for the pyrolysis of cellulose are shown in Figure 5.

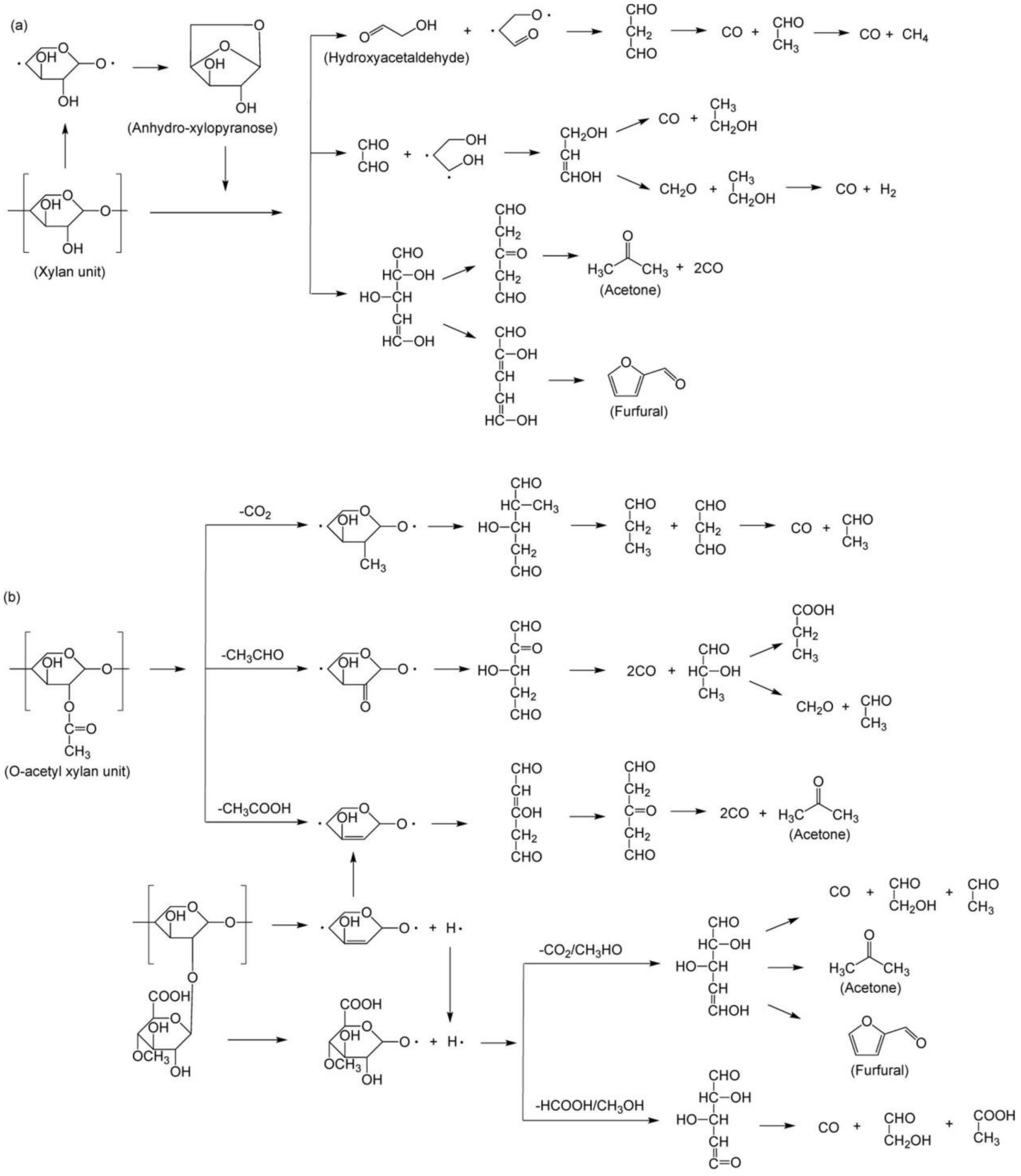


Figure 6: (a) Major pyrolytic pathways of the main chain of O-acetyl-4-O-methylglucurono-xylan. (b) The major pyrolytic pathways of O-acetylxylan and 4-O-methylglucuronic acid unit (SHEN *et al.*, 2010).

2.3.2 Pyrolysis of hemicellulose

Hemicelluloses are closely associated with cellulose and lignin in the cell wall. They are heterogeneous amorphous polysaccharides with building blocks of pentoses (mainly D-xylose and L-arabinose) and hexoses (mainly D-glucose, D-mannose, and D-galactose). Most hemicelluloses have a degree of polymerization of about 200. The primary components of hemicellulose are glucomannan and xylan. Hemicelluloses are less thermally stable than cellulose. Pyrolysis of xylan involves thermal cleavage of the glycosidic groups, resulting in glycosyl units which are partly degraded into volatile products and char (SHAFIZADEH *et al.*, 1972). The possible pathways for the pyrolysis of hemicelluloses are shown in Figure 6.

2.3.3 Pyrolysis of lignin

Lignin surrounds holocellulose like cement and fills the spaces between the other cell wall components. It is an amorphous material formed by polymerization of three aromatic monomeric alcohols: *p*-hydroxyphenyl-, coniferyl-, and sinapylalcohol-. It is the most thermally stable component of biomass. Pyrolysis of lignin covers a whole temperature range of 150-900 °C (YANG *et al.*, 2007). The liquid products from pyrolysis of lignin can be classified into three groups:

(1) light compounds, such as methanol and acetic acid;
(2) monomeric phenolic compounds, such as phenols, catechols, cresols;
(3) large molecular oligomers, known as pyrolytic lignin.

Besides the three main components of wood, there are some other components in wood including starch, extractives, proteins, some water-soluble organic compounds and inorganic compounds (ash). The pyrolysis of biomass is the combination of the three main components as well other components contained in biomass.

2.3.4 Chemical reactions in pyrolysis liquid during storage

As bio-oil is derived from the random thermal decomposition of the components of biomass, it has a wide range of chemical compounds. Pyrolysis liquid comprises more than 300 compounds and cannot be fully analyzed. According to organic functional groups, compounds in pyrolysis liquid can be divided into following groups: (1) acids and esters; (2) aldehydes and ketones; (3) alcohols and ethers; (4) aromatics and phenols; (5) carbohydrates; (6) others. Except for nucleic acids and proteins, compounds in pyrolysis liquid contain almost all the organic functional groups, although many of them are in very low concentrations. Part of these chemicals can polymerize with the time and form new components. It is impossible to make clear all the chemical reactions in bio-oil. Diebold proposed most important reactions that probably occur within bio-oil as follows (DIEBOLD, 2000):

(1) Organic acids with alcohols to form esters and water
(2) Organic acids with olefins to form esters
(3) Aldehydes and water to form hydrates
(4) Aldehydes and alcohols to form hemiacetals or acetals and water
(5) Aldehydes to form oligomers and resins
(6) Aldehydes and phenols to form resins and water
(7) Aldehydes and proteins to form oligomers
(8) Organic sulfur to form oligomers
(9) Unsaturated compounds to form polyolefins
(10) Air oxidation that forms acids and reactive peroxides

2.4 Value-added chemicals from biomass and pyrolysis liquid

2.4.1 Value-added chemicals from biomass

Biomass as feedstock for production of materials and chemicals has a long history. Wood products industry and pulp and paper industry are the two main industries based on wood. The earliest chemical exploitation of biomass was to produce ethanol through oxidative fermentation of sugars. Other chemicals produced through fermentation include acetic acid, lactic acid which are still widely used today. Methane produced from biomass through anaerobic digestion had reached industrial scale since the 1970s. Biodiesel produced from vegetable oil such as soybean oil has already emerged in the market. Polyhydroxyalkanoates produced from fermentation is a biodegradable polymer used in the biomedical sector.

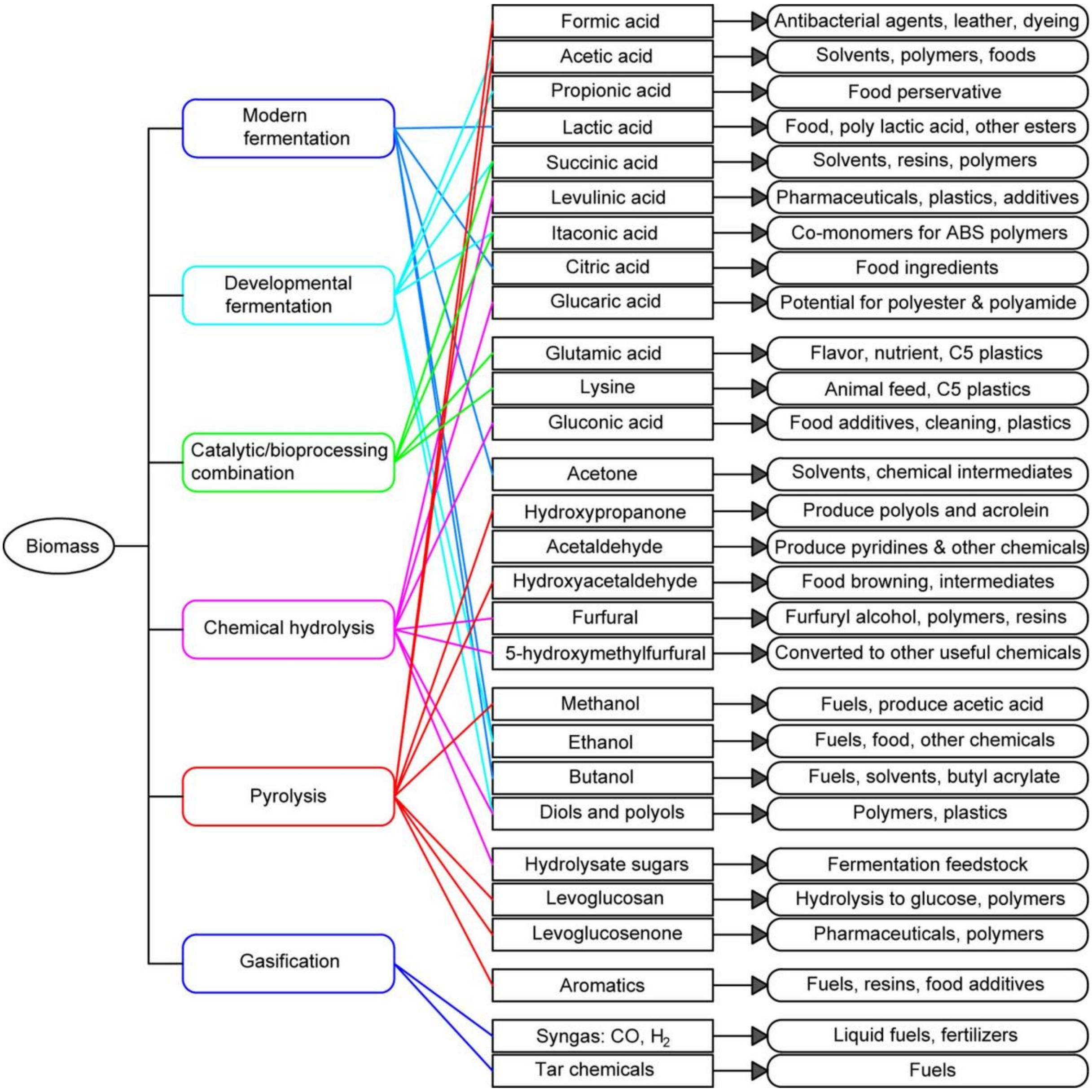


Figure 7: Chemicals from biomass through different technologies and their possible applications.

The current manufactures of chemicals and the industries are largely dependent on fossil fuel which is facing the problem of depletion. Furthermore, the petroleum-based economy faces economic, environmental and political concerns (VISPUTE *et al.*, 2010). Renewable biomass has the potential to become the basis of chemicals for the chemical industry. Biomass contains mainly cellulose, hemicellulose, and lignin which is the most abundant and inexpensive sustainable source of carbon that can be used for the production of chemicals and fuels. Various value-added chemicals can be produced from biomass through extraction or conversion methods. By gentle heating or by steam distilling of certain plants, essential oils composed mainly of terpenoids can be isolated. These bio-active chemicals can be used in pharmaceuticals and cosmetics. The conversion methods include biological, chemical, and thermochemical strategies. The biological conversion strategy comprises known modern fermentation techniques and their further developmental by use of genetically engineered organisms. The chemical conversion is through hydration, dehydration, and hydrogenation of biomass in solvents in presence of catalysts. The thermochemical conversion includes combustion, pyrolysis or gasification. The specification of the different methods to produce different chemicals is shown in Figure 7.

Several hundred chemicals can be produced from biomass through different methods but not all of them are useful according to the current market requirement and technology development. To exploit chemicals from biomass, the value-added intermediates from biomass need to be defined firstly. These intermediates are of vital importance as they link different biorefinery concepts and target markets. In order to evaluate top value-added chemicals, the US Department of Energy (DOE) screened over 300 chemicals based on raw material, estimated processing costs, estimated selling price, and the technical complexity associated with the best available processing pathway and the market potential. The strategic fit criteria were further used including direct product replacement, novel products, and building block intermediates. The result is shown in Figure 8. Figure 8 shows that value-added chemicals derived from biomass can be mainly divided into alcohols, acids, sugars, aromatics, and others.

Alcohols from biomass of high value comprise mono-alcohols such as methanol, ethanol, butanol; diols such as 1,2-propanediol, 1,3-propanediol, 1,4-propanediol, 2,3-butanediol; triols such as glycerol, 1,2,4-butanetriol; polyols such as xylitol, arabitol, and sorbitol.

Before the petroleum era, methanol was produced by the destructive distillation of wood. It was called “wood alcohol” and was the primary component of “wood spirit”. Today, it is produced from catalytic hydrogenation of carbon monoxide. Methanol is primarily used as feedstock for the production of other chemicals, such as formaldehyde, acetic acid, dimethyl ether, and methyl-tert-butyl ether (MTBE). It is also used as a transesterification agent in the production of biodiesel. Ethanol is mostly produced by the fermentation of sugars by yeasts. The industrial production of ethanol is realized by the acid-catalyzed hydration of ethene. It is widely used as beverage, solvent, fuel, and as the feedstock for other chemicals. Butanol is a minor product of the fermentation of sugars and can be used as food flavorings. It is industrially produced from the petroleum feedstock propylene and used as an intermediate in the production of butyl esters. The diols and polyols are precursors of polymers.

Acids mainly include monocarboxylic acids and their derivatives such as formic acid, acetic acid, propionic acid, butyric acid, hydroxyacetic acid, hydroxypropionic acid, lactic acid, levulinic acid; dicarboxylic acids and their derivatives such as oxalic acid, succinic acid, itaconic acid, malic acid, fumaric acid, glucaric acid, glutamic acid, aspartic acid, etc. Carboxylic acids are currently produced based on petroleum-based chemicals and are used for the production of other chemicals and polymers.

Carboxylic acids are mainly produced by the oxidation of alkenes, aldehydes, alcohols, benzenes, etc. Besides chemical synthesis, acetic acid and propionic acid can also be produced by fermentation. Acetic acid is widely used in medical, food, and polymer industries while propionic acid is best known as a food preservative. Butyric acid is industrially prepared by the fermentation of sugar from starch and used for various butyrate esters.

Succinic acid is now commercially produced through chemical synthesis and fermentation of glucose. It is nontoxic and used as food additive and precursor for polymers and solvents. Currently, itaconic acid is industrially produced by fermentation of carbohydrates such as glucose and molasses. Its production is on relatively small scale and high cost and applied as a co-monomer in the production of polymers. Levulinic acid is a useful platform chemical with multi-functionality which is used for pharmaceutical, plasticizers and other additives. It is basically obtained from cellulose after hydrolysis to hydroxymethylfurfural. It can be synthesized into valuable products such as levulinate esters used as a solvent; γ-valerolactone or 1,4-pentanediol used as a polyester monomer; methyltetrahydrofuran used as a gasoline blending component.

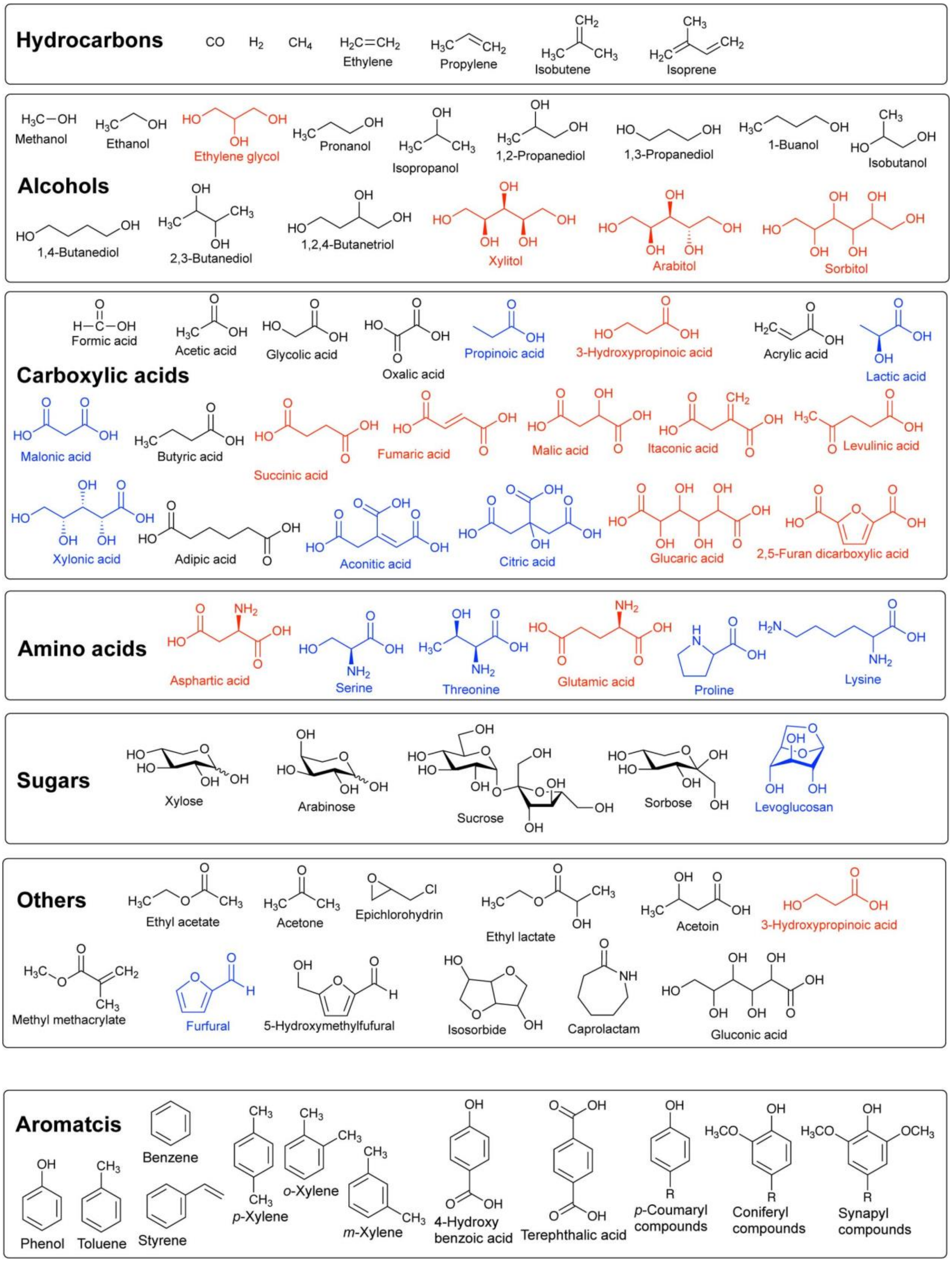


Figure 8: Value-added chemicals from biomass: chemicals in blue color are selected as Top 30 chemicals from biomass, chemicals in red color are selected as Top 12 chemicals from biomass by Department of Energy in the USA.

Sugars such as cellulose and hemicellulose are the main components of wood. They can be converted by acid-catalyzed hydrolysis into monosaccharides such as glucose, xylose, arabinose, and sorbose. Xylose is the main building block for the hemicellulose xylan. It is produced by hydrolysis of hemicellulose and used for the production of furfural and xylitol. Levoglucosan is formed from pyrolysis of cellulose. It can be hydrolyzed into fermentable glucose or utilized in the synthesis of chiral polymers. Another sugar such as sorbose is used for the production of vitamin C. Sucrose is used as table sugar. Most of the monosaccharides are not considered as valuable chemicals from lignocellulosic biomass as the market for such monosaccharides is small.

Aromatic compounds that can be obtained from biomass are mainly derived from lignin. The commercial use of lignin at present includes the production of synthetic vanillin and dimethylsulfoxide (DMSO). The primary applications of lignin are the production of dispersants, emulsifiers, binders, and sequestrants. Smaller applications include adhesives and polymer modifiers. Monomeric and oligomeric aromatic compounds can be derived from lignin through pyrolysis, gasification, or hydroliquefaction. Aromatic compounds that can be obtained from lignin include phenol; benzene/toluene/xylene (BTX); lignin monomers such as propylphenol, eugenol, syringol; aromatic acids and aromatic polyols such as cresols, catechols, and resorcinols. These aromatic compounds and their derivatives are potentially valuable if they can be properly separated. The complex and inconsistent nature of lignin makes the application of lignin still a challenge.

Other compounds that can be derived from biomass include CO, H_2, CH_4, ethylene, acetone, hydroxypropanone, hydroxybutanone, butyrolactone, furfural, hydroxymethylfurfural, etc. Furfural is formed by acid catalyzed dehydration of 5-carbon sugars particularly xylose present in hemicellulose. It is readily hydrogenated into useful intermediates such as furfuryl alcohol used for thermoset polymers and resins, and tetrahydrofurfuryl alcohol used as a non-hazardous solvent in agricultures. Furfural can be oxidized into furoic acid used as a food preservative and flavoring agent. Hydroxyfurfural is formed by acid catalyzed dehydration of 6-carbon sugars such as fructose. It is unstable and reacts to form levulinic acid. Hydroxyfurfural itself has few applications but can be converted into other useful compounds such as 2,5-furandicaboxylic acid used as a replacement of terephthalic acid for the production of polyesters; 2,5-dimethylfuran used as biofuel; γ-valerolactone used for the production of polymers.

2.4.2 Value-added chemicals from pyrolysis liquid

Pyrolysis liquid is the condensable portion of the thermal depolymerization of biomass in the absence of oxygen. The components of pyrolysis liquid are dependent on the feedstock and pyrolysis conditions, such as temperature, heating rate, residence time, etc. The typically known compounds in fast pyrolysis liquids are shown in Figure 9 and Figure 10. From the figure we can see that bio-oil contains carboxylic acids, esters, aldehydes, ketones, alcohols, furans, pyrans, phenols, guaiacols, syringols and other compounds. There are still many high molecular weight compounds in pyrolysis liquid that cannot be readily identified. Most of the Top 10 or even Top 30 value-added compounds from biomass do not appear in pyrolysis liquids. The major high-value compounds from the bio-oil foreseen are organic acids, furfurals, and levoglucosan (JONG *et al.*). Therefore, the definition of value-added chemicals from pyrolysis liquid should be carefully considered regarding to its composition and its applications. Some applications of fast pyrolysis liquids were proposed which is shown in Figure 11 (RADLEIN, 1999).

Pyrolysis liquids can be used as a source of renewable chemical products and materials. According to IEA Bioenergy Task 34 Direct Thermochemical Liquefaction, materials and products that can be produced from pyrolysis liquid include liquid smoke, adhesives and resins, bio-bitumen, preservatives, hydroxyacetaldehyde, and levoglucosan. These components are considered as an important potential use although most of them have not reached the commercial application.

Hydroxyacetaldehyde is the second most abundant organic compound in pyrolysis liquids after acetic acid. It is the simplest molecule that contains both an aldehyde and hydroxyl function. The functional groups at its two carbon adjacent carbons impart hydroxyaldehyde high chemical reactivity and make it useful for heterocyclic chemistry or polymerization into macromolecules.

Levoglucosan is degraded from pyrolysis of cellulose with the yield close to 60% when the feedstock is washed with acids. It can be hydrolyzed and converted to other valuable chemicals including alcohols and lipids. It can also be used as a fermentation sugar or for the production of polymers.

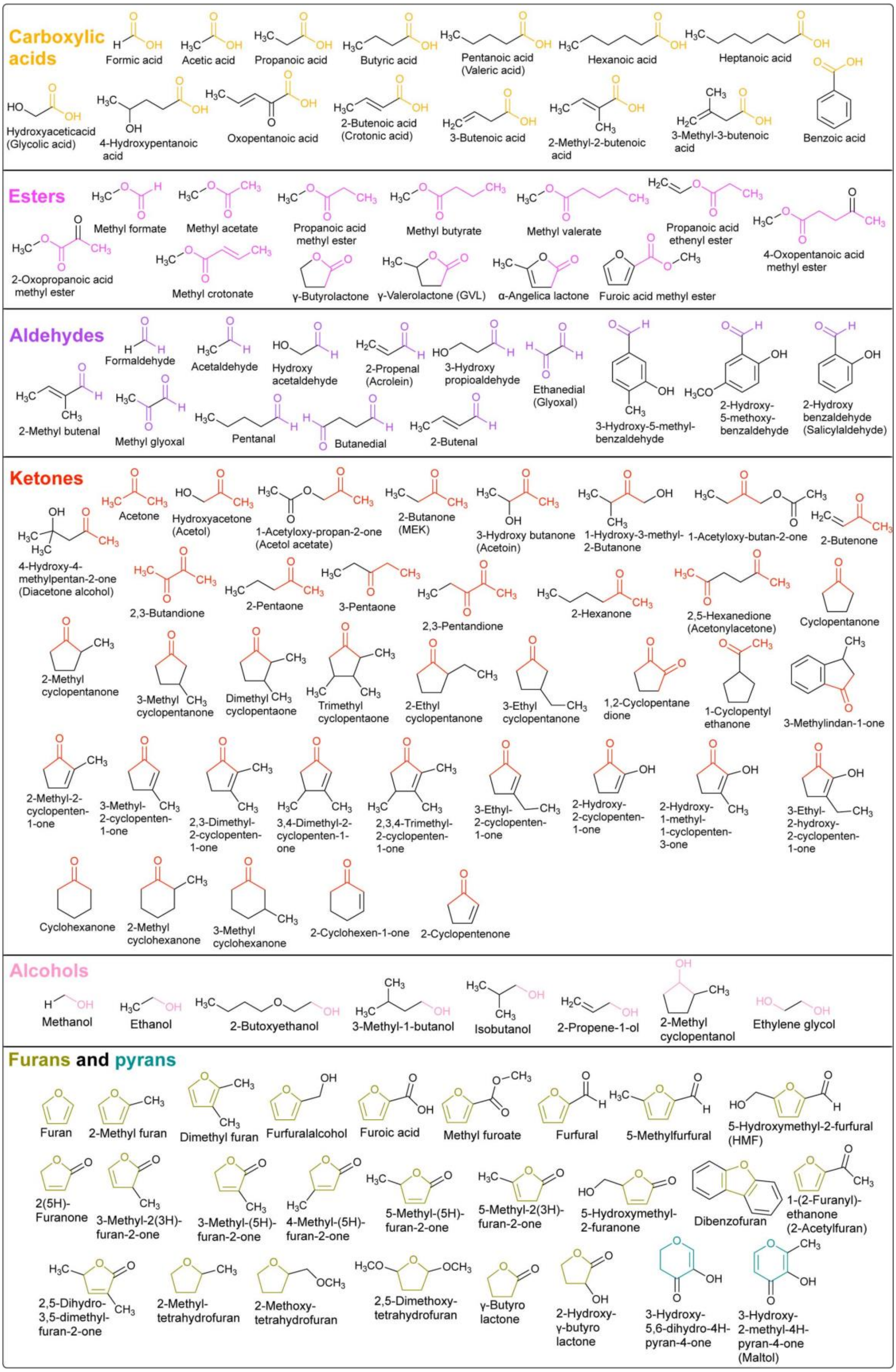


Figure 9: Typical non-aromatic chemicals from pyrolysis liquid.

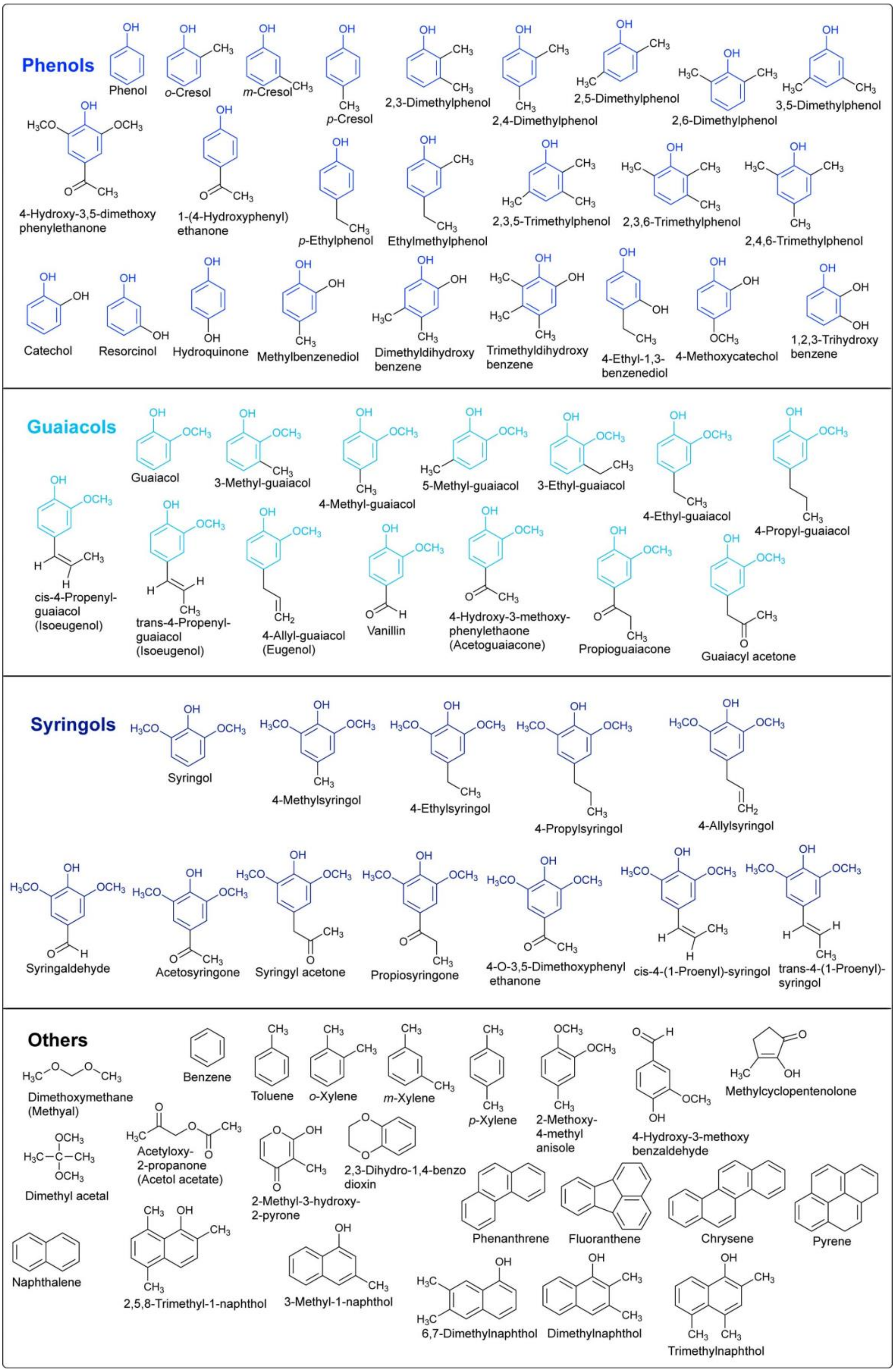


Figure 10: Typical aromatic chemicals from pyrolysis liquid.

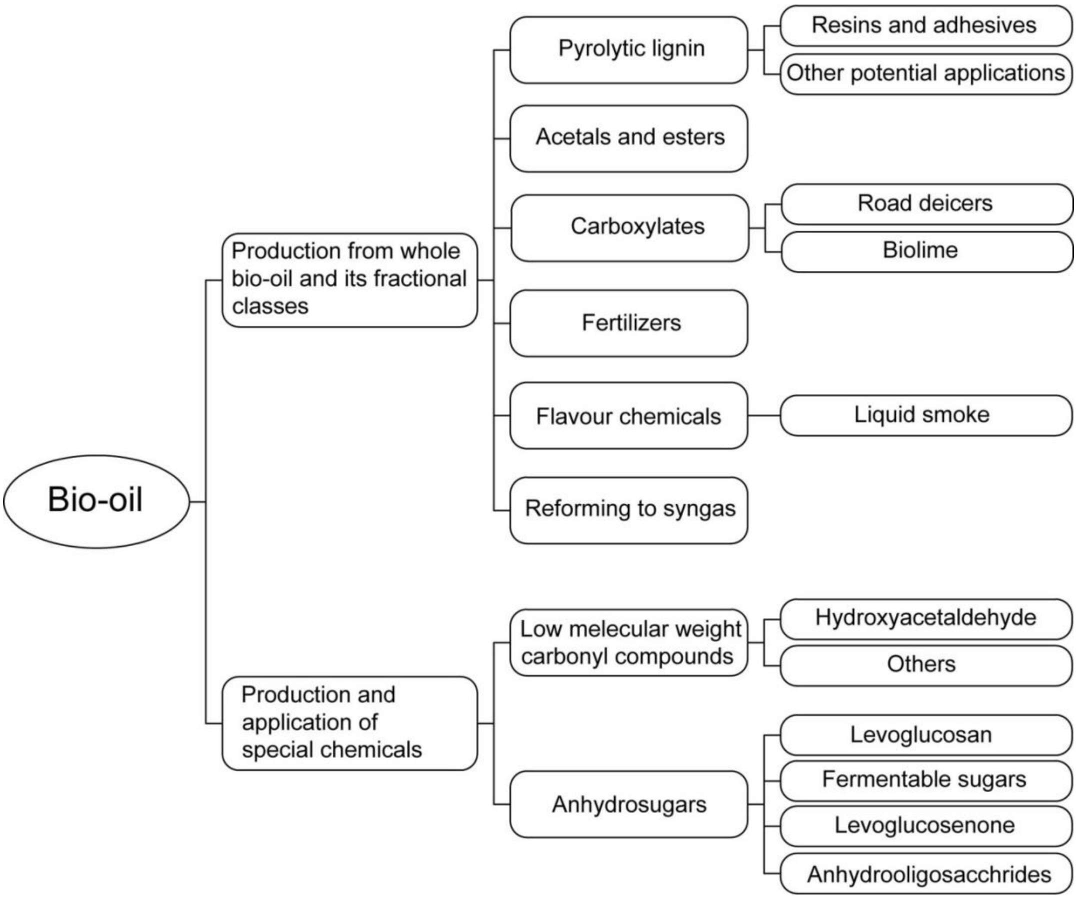


Figure 11: The production of chemicals from fast pyrolysis bio-oil (RADLEIN, 1999).

Furfural is another valuable compound that is present in pyrolysis liquid. The production and application of furfural have been discussed previously. Levoglucosan and furfural are the two compounds in pyrolysis liquid which are regarded as Top 30 value-added chemicals from biomass.

Liquid smoke is the only commercial product from pyrolysis liquids. It was first distributed by E.H. Wright in 1895 and produced by Red Arrow Products Company using fast pyrolysis technology since the 1990s. It is also a by-product of proFagus charcoal company. Liquid smoke is used to treat certain foods such as meat and fish with special color and flavor which are positively perceived by consumers.

Phenol formaldehyde resins are synthesized from phenol and formaldehyde currently derived from petroleum. Renewable biomass has the potential to provide phenols through pyrolysis. Phenols can be obtained by fractionation of pyrolysis liquids. The amount of phenol in pyrolysis liquids is low. The less active fraction of phenolic compounds contains mainly alkylated phenols and aromatic ethers that may replace 10-40% of phenol in PF resin production. However, the useful monomeric aromatics in pyrolysis liquids are in low content of 5-15%.

Table 2: Value-added chemicals from bio-oil proposed by Zhu et al. (ZHU *et al.*, 2010).

Target chemicals	**Selective pyrolysis**
Acetic acid	• Low pyrolysis temperature below 300 °C • Catalytic pyrolysis using NaY catalyst
Hydroxyacetaldehyde	• Adding small amount of ash or alkaline cations
Furfural	• Impregnation of biomass with acids such as $ZnCl_2$ or $MgCl_2$ • Use microwave-assisted fast pyrolysis
1-Hydroxy-3,6-dioxabicyclo[3.2.1]octan-2-one	• Use cellulose mixed with nanopowder aluminum titanate • Increase pyrolysis temperature to 500 °C
Levoglucosan	• Use pure cellulose or demineralized biomass • Adding of small amount of acids or acidic salts
Levoglucosenone	• Impregnation of biomass with phosphoric acid or $Fe_2(SO_4)_3$ • Cracking of vapors with solid super acids catalyst
Anhydro-oligosaccharides	• Higher pyrolysis temperature (850-1200 °C) and shorter residence time (35-75 ms)
Light aromatic hydrocarbons	• Catalytic cracking of vapors with $CoMo\text{-}S/Al_2O_3$ catalyst • Catalytic upgrading of bio-oil with HZSM-5 catalyst
Phenolic compounds	• Impregnation of biomass with alkaline compounds • Cracking of vapors with Pd/SBA-15 catalyst
Other valuable chemicals	• Impregnation of biomass • Catalytic cracking of vapors

Bitumen is used as roofing material due to its water resistance property. It is made up of highly sticky and viscous organic liquids from fossil. A heavy fraction of pyrolysis liquid containing manly aromatics is regarded as suitable alternative material of bitumen after further thermal treatment (HEERES, 2012). Various organic compounds in pyrolysis liquid such as acids and aromatics make it exhibit properties of a preservative. It can be potentially used as a wood preservative (FREEL *et al.*, 2002).

Zhu et al. reviewed 10 types of value-added chemicals that can be obtained from selective fast pyrolysis of biomass by catalyst utilization (ZHU *et al.*, 2010). The production of target chemicals can be enhanced by using different catalyst or proper pyrolysis conditions which is shown in Table 2

2.5 Separation and fractionation methods of pyrolysis liquid

Separation of pyrolysis liquid is important both for upgrading to fuels and for the production of chemicals. The upgrading of pyrolysis liquid can be designed similar to a traditional refinery including technologies such as hydrogenation, cracking, esterification, emulsification and steam reforming. According to Wang's view (WANG, 2013), hydrogenation can achieve an 80% deoxygenation of bio-oil while heterocyclic compounds such as furan are difficult to convert. Catalytic cracking can efficiently convert alcohols, acids, and ketones, while aldehydes, phenols, and pyrolytic lignin tend to form deposits or coking. Esterification is generally used to convert acids to esters that have a high heating value. Emulsification can make bio-oil and diesel homogeneous and stable. However, acids make the emulsions corrosive, high water content lowers the heating value and high molecular weight compounds reduce volatility. Steam reforming is efficient for alcohols and acids but other oxygenated compounds such as phenols and sugars show inferior behavior and easily to coke. If the bio-oil is separated into different phases and upgraded with different technologies accordingly, it could be more efficient and high-grade fuels could be obtained.

The chemical application of pyrolysis liquid cannot be directly achieved as it is a mixture of several hundred organic components. It must be separated for specialty chemicals or chemical groups. Most of the compounds contained in pyrolysis liquid are reactive and in very low concentrations, typically less than 1%. Therefore, the nature of pyrolysis liquid makes its separation very difficult. Existing commonly used fractionation methods of pyrolysis liquid are shown in Figure 12 which are discussed in the following.

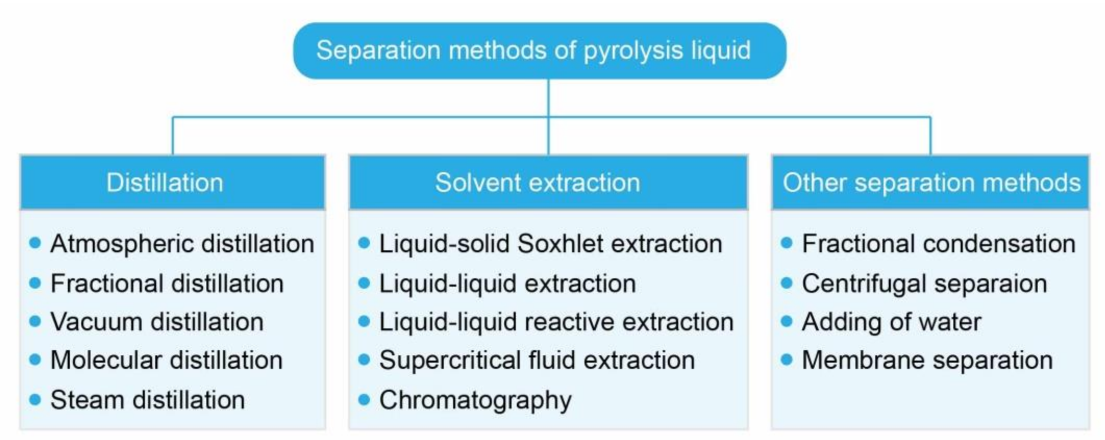


Figure 12: Separation methods of pyrolysis liquid.

2.5.1 Atmospheric distillation

Distillation and rectification are extensively used in a petroleum refinery and also considered to be the only economically feasible pathway to separate bio-oil in biorefinery (ZHANG *et al.*, 2013). For liquids that boil below 150 °C and have at least 25 °C difference in boiling points, simple distillation can be used to separate them. Otherwise, the compounds are possible to degrade at too high temperatures and cannot be clearly separated. It is the least complex distillation method carried out at atmospheric pressure. It separates liquids with different boiling points based on equilibrium.

Bio-oil produced from rice husk was distilled in the temperature range of 150-240 °C and six fractions were obtained (ZHANG *et al.*, 2013). It was estimated that 51.9 wt% distillate was recovered but with 71.6 wt% water content while only 30.3 wt% in raw bio-oil. The extraction efficiency of acetic acid, propionic acid and furfural reached 88.3 wt%, 91.8 wt%, and 85.1 wt%. But the separation of phenolic compounds was low. Chemical reactions were proposed during distillation due to the newly formed ketones. Further separations were still needed for the pure compound production.

The atmospheric distillation shows little accomplishment due to the complex composition and instability of pyrolysis liquids. Pyrolysis liquids cannot be completely vaporized and produce a solid residue of around 50 wt% of the original liquid when heated above 100 °C. The distillate is a mixture of volatile organic compounds and water which needs further separation.

One possible route is to separate pyrolysis liquids into different fractions with other separation methods. Then appropriate fractions are distilled further.

2.5.2 Fractional distillation

For liquids that have close boiling points less than 25 °C apart, fractional distillation needs to be used. Also at atmospheric pressure, an additional fractionation column is added between the distillation flask and condenser in fractionation distillation compared with simple distillation. The fractionation column is filled with inert objects like glass beads or steel wool to increase the surface area. The vapor rises up the column, condensates on the surfaces, refluxes back down, and evaporates again with rising heat. Each time the vapor consists of a higher proportion of the compound with a lower boiling point. Finally, liquids with fairly close boiling points can be separated with this technique.

The tail-gas bio-oils collected from the electrostatic precipitator (ESP) were distilled by fractional distillation in the temperature range of 60-350 °C (ELKASABI *et al*., 2014). The tail-gas oil produced six fractions with concentrated aromatics while the regular bio-oil produced only three fractions. Naphthalene of 95% purity was finally isolated when horse manure was used as feedstock. However, the tail-gas bio-oil accounted only a small amount of the whole bio-oil and the concentrated distilled fractions were still a mixture which needed further isolation.

Capunitan et al. tried fractional distillation of bio-oil derived from pyrolysis of corn stover (CAPUNITAN *et al*., 2013). Approximate 10 g of bio-oil was put in the flask and three fractions were obtained: fraction 1 with 33.7% below 100 °C, fraction 2 with 4.7% between 100 and 180 °C, fraction 3 with 45.3% between 180 and 250 °C. The first fraction contained mainly water and a light distillate. The middle fraction consisted of aromatics, oxygenates and some phenolic compounds. The heavy fraction mainly consisted of phenolic compounds with low water content, which was regarded as the best material for the further upgrading.

As pyrolysis liquid contains various components, fractional distillation proves to be an appropriate distillation method. The recovery of pure compounds from pyrolysis liquid still remains a problem even with fractional distillation. It is better to combine it with other separation methods.

2.5.3 Vacuum distillation

For liquids that have boiling points over 150 °C, vacuum distillation should be used. The decrease of ambient pressure leads to lower boiling points of a liquid. Therefore, it is particularly useful for the thermally sensitive compounds which degrade at high temperatures.

Zheng et al. performed reduced pressure distillation on bio-oil with the pressure of 20 mbar and temperature of 80 °C (ZHENG *et al.*, 2011). The yield of distillates was 61 wt% with water phase of 29 wt% and residue of 10 wt%. It was proven that the distillates contained a higher heating value, lower corrosivity, and better stability compared with original bio-oil.

Vacuum distillation is more expensive and the operation is more complicated than simple distillation. It avoids the polymerization of pyrolysis liquid at high temperatures. It distills pyrolysis liquid into different fractions at low temperatures. It can be used as one step in a multi-step separation of pyrolysis liquid.

2.5.4 Steam distillation

Steam distillation is mainly used to distill heat-sensitive organic compounds that are immiscible with water. By introducing steam into the sample flask, the thermal sensitive compounds are volatilized at a temperature close to 100 °C at atmospheric pressure. Most of the temperature sensitive essential oils from the plant are extracted by steam distillation.

Murwanashyaka et al. carried out steam distillation of pyrolysis liquid from vacuum pyrolysis of birch wood at a temperature of 105 °C (MURWANASHYAKA *et al.*, 2001). The light compounds were separated from heavy compounds at a low temperature. A yield of 14.9 wt% of a volatile fraction based on feed oil was recovered at a steam:oil ratio of 27:1. The light steam distilled fraction was concentrated with phenolic compounds but no significant modification of the chemical composition of the pyrolysis oil was observed. It was found to be chemically and thermally stable when subjected to further purification processes. It was re-distilled with reduced pressure distillation under a pressure of 7 mbar. The syringol-rich fraction was further extracted with solvents and syringol with a purity of 92.3% was finally obtained.

Similar to vacuum distillation, steam distillation can be used as an alternative separation method of pyrolysis liquid. It should be combined with other separation methods to achieve the separation of target chemicals from pyrolysis liquid.

2.5.5 Molecular distillation

Molecular distillation is commonly used to distill heat-sensitive materials, particularly useful for the large molecular compound in the range of 500 to 1000 Dalton. It is a variation of vacuum distillation. Under pressures of 10^{-6} times atmospheric pressure or less, the mean free path of molecules is comparable to the size of the equipment (LUTISAN *et al.*, 1995). Unlike vacuum distillation, in which liquid mixtures are constantly heated, molecular distillation minimizes the time the liquid mixture spends in contact with the heat source.

Wang et al. studied molecular distillation of bio-oil with the feedstock of Mongolian Scotch pine (WANG *et al.*, 2009). Bio-oil with an amount of 150-200 g was introduced into distillation unit with a feeding rate of 1 mL/min. Three fractions, as light, middle and heavy fraction, were obtained with a total recovery over 97 wt%. Acids and unsaturated alcohols were completely isolated while ketones, phenols, and catechols were enriched in different fractions. The pyrolysis characteristics of the three fractions were further studied (GUO *et al.*, 2010). Results showed that the light fraction contained mainly water and acids. The middle and heavy fraction gave 25-30 wt% char residue. Around 20 wt% pyrolytic lignin could be extracted from the heavy fraction with water and methanol (WANG *et al.*, 2015). Wang et al. further adopted molecular distillation of two successive distillation processes with pressures of 1600 and 340 Pa, respectively (GUO *et al.*, 2010). Bio-oil was pretreated by traditional vacuum distillation to remove water. The yields of two distilled fractions were 26.4 wt% and 22.6 wt%. The distilled fractions were rich in low molecular weight compounds such as acids and ketones. The evaluation method indicated that acetic acid and1-hydroxy-2-propanone were very easily distilled from the residual fraction while 5-hydroxymethylfuraldehyde and 1,2-benzenediol were very difficult to distill.

Bio-oil can be separated into different fractions with various enriched fractions by molecular distillation. Molecular separation enables high efficiency of bio-oil at low temperatures. As a single separation method, pure compounds are not possible to be obtained by molecular distillation and the fractions are needed to be further upgraded. Integrated with other separation methods, molecular distillation is a good separation method for the thermal sensitive compounds contained in bio-oil.

Overall, the limited application of distillation to pyrolysis liquid is attributed to the nature of pyrolysis liquid. It cannot be completely vaporized. The challenges for pyrolysis liquid distillation are as follows:

(1) low concentration of most component;
(2) close boiling points;
(3) thermal sensitive;
(4) high boiling points of high molecular compounds.

2.5.6 Liquid-liquid extraction

According to different polarities, organic solvents have a different solubility for specific chemical compounds. Performed under room temperature and ambient pressure, organic solvents can extract a specific compound with a well-designed procedure. As with distillation, solvent extraction is also based on equilibrium.

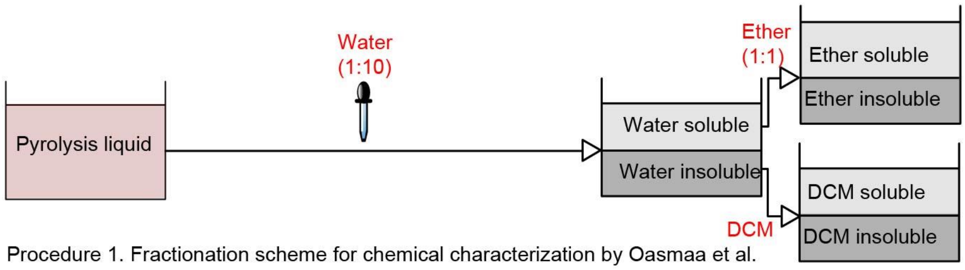
Solvents used for extraction of pyrolysis liquids are summarized in Table 3. A good solvent should have the following characteristics: (1) high selectivity; (2) good solubility of desired chemicals; (3) low boiling point to be removed afterward; (4) non-toxic.

Bio-oil can be separated into different chemical groups by their polarities with liquid-liquid extraction. Wei et al. tried organic solvents (hexane, petroleum ether, and chloroform) to extract the aqueous phase of bio-oil (WEI *et al.*, 2014). The phase soluble in organic solvents had high concentrations of phenols and guaiacols while the water-soluble phase contained mainly acids, alcohols, and sugars. However, the one-step solvent separation is not able to ensure a clear separation of bio-oil.

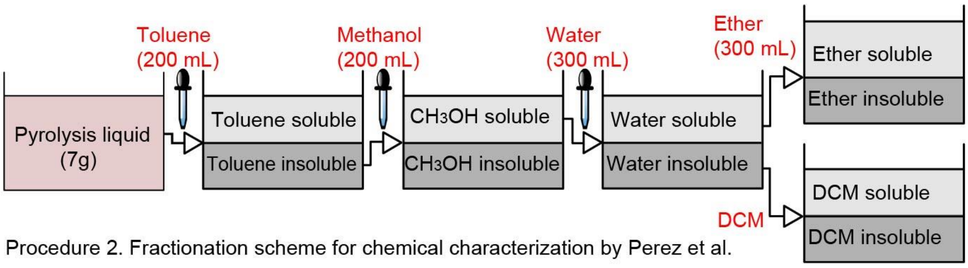
Table 3: Properties of typical solvents used for extraction of pyrolysis liquids

Solvents	**Density (g/mL)**	**Polarity**	**Boiling point (°C)**	**Vapor pressure (kPa at 20 °C)**	**Solubility in water (g/100 mL)**
Pentane	0.63	0.0	36	57.9	0.40
Hexane	0.66	0.0	69	17.6	0.095
Toluene	0.87	2.3	111	2.8	0.052
Ether	0.71	2.9	35	58.7	6.05
DCM	1.33	3.0	40	46.5	1.72
Ethyl acetate	0.90	4.3	77	9.7	8.30
Ethanol	0.79	5.2	78	6.0	miscible
Acetone	0.78	5.4	56	24.3	miscible
Methanol	0.79	6.6	65	13.0	miscible
Water	1.00	9.0	100	2.3	miscible

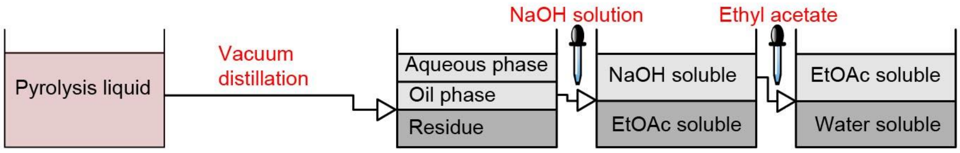
Oasmaa et al. used sequential solvent fractionation in order to find a simple and fast method to characterize pyrolysis liquids (SIPILA *et al.*, 1998, OASMAA *et al.*, 2003). In Oasmaa's procedure, water, diethyl ether, and DCM were used as solvents as shown in Figure 13. Water was first used to separate pyrolysis liquid. The water-soluble fraction mainly contained most of small organic compounds and sugars and these two fractions were further separated by diethyl ether as sugar is insoluble in ether. The water-insoluble fraction was pyrolytic lignin. It was further washed with DCM to obtain low-molecular-mass (LMM) lignin and extractives. The DCM insoluble fraction contained mainly high-molecular-mass (HMM) lignin and solids. Hence, four fractions with totally different composition were obtained with this method but most of the small organic chemicals were still mixed in the ether-soluble fraction. Therefore this method is helpful for pyrolysis liquid characterization but not sufficient for the separation of value-added chemicals.



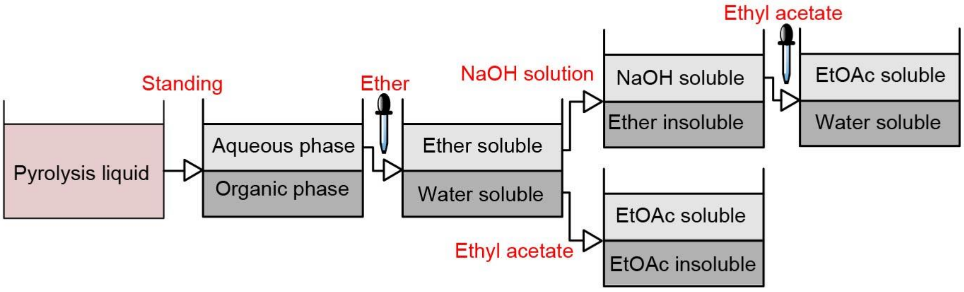
Procedure 1. Fractionation scheme for chemical characterization by Oasmaa et al.



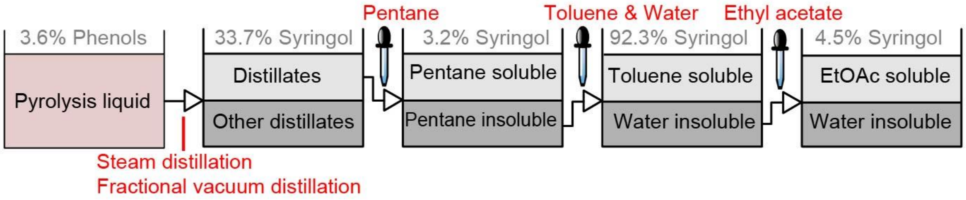
Procedure 2. Fractionation scheme for chemical characterization by Perez et al.



Procedure 3. Separation of valuable phenols from wood tar by Amen-Chen et al.



Procedure 4. Separation of phenolic fraction from pyrolysis liquid for anti-fungal application by Mourant et al.



Procedure 5. Separation of syringol from pyrolysis liquid by Murwanashyaka et al.

Figure 13: Various procedures of liquid-liquid extraction of pyrolysis liquid.

Based on Oasmaa's procedure, Perez et al. additionally used toluene and methanol so that six fractions were finally obtained as shown in Figure 13 (GARCIA-PEREZ *et al.*, 2007). Toluene was first used to extract compounds derived from wood extractives. The toluene-insoluble fraction was solubilized in methanol and filtrated to remove the char, non-polar waxy materials, and other very heavy oligomeric compounds. The methanol soluble fraction was further separated according to Oasmaa's procedure. Most of aldehydes, ketones, monomeric phenols were found in ether soluble and water soluble fractions, whereas hydrocarbons were concentrated in the toluene fraction. Although bio-oil was separated into six fractions, various compounds were still distributed into different fractions. Furthermore, the small sample size and a large quantity of solvents made this separation method only suitable for the characterization of bio-oil.

One purpose of solvent extraction of pyrolysis liquid is for better characterization, as described above. The other purpose is to extract the valuable chemicals from pyrolysis liquid. Phenols, acids, and sugars are of interest due to their high value and high content in pyrolysis liquid.

Phenols are useful chemicals as they have both germicidal and antiseptic properties. They can also be used for the production of adhesives and polymers. The acidic nature of phenols makes them soluble in alkali solutions. When the pH of alkaline solutions is higher than 11, distribution coefficient of phenolics towards aqueous phases are favored (GREMINGER *et al.*, 1982). When pH is below 7, they are better extracted from the aqueous phase with ketone and ester solvents. Chen et al. separated phenols from the oil phase of pyrolysis liquid by using alkaline extraction (AMEN-CHEN *et al.*, 1997). In Chen's procedure shown in Figure 13, wood tar was first vacuum distilled. An amount of 2-6 g oil phase was extracted with NaOH solution to generate water-soluble phenolate ions. The solution was acidified to a pH close to 6 with sulfuric acid. Ethyl ether was then used to extract phenols from the acidified solution. More than 60 wt% selected phenols could be extracted. The extraction effect was better when higher concentrated NaOH solutions were used. However, most of the phenols contents in wood tar had a low content (<1 wt%) and no pure fractions could be obtained. Mourant et al. used a similar alkaline extraction procedure of phenols from aqueous fraction of bio-oil as shown in Figure 13. The diethyl ether fraction was particularly rich in phenolics and very efficient against decay by fungi. Murwanashyaka et al. used water and organic solvents to extract syringol from pyrolysis liquid shown in Figure 13 (MURWANASHYAKA *et al.*, 2001). The pyrolysis liquids were first steam distilled and further fractionated by vacuum distillation. The fraction rich in syringol (33.7 wt%) was used for further solvent extraction. This fraction was extracted with pentane and the pentane insoluble fraction was extracted with toluene. The toluene soluble fraction had a syringol content as high as 92.3 wt%.

Acetic acid is an important industrial commodity as a solvent and raw material to produce vinyl acetate and polymers. It can be effectively extracted with aliphatic tertiary amines which are commonly used for the recovery of carboxylic acids from fermentation broths and waste water (KERTES *et al.*, 1986). Heeres et al. for the first time used tri-n-octylamine (TOA) diluted in octane to extract acetic acid from bio-oil (MAHFUD *et al.*, 2008). Bio-oil was diluted in an organic co-solvent such as THF or ethanol. TOA was diluted in hydrocarbon solvents such as hexane or octane. Two bio-oils with acetic acid content of 1.4 wt% and 6.2 wt% were used as feedstock. Bio-oil diluted in THF (23 vol.%-77 vol.%) was extracted with TOA diluted in octane (50 vol.%-50 vol.%) with the best extraction results. An extraction efficiency of 93 wt% could be obtained while 10 wt% of TOA was transferred into the bio-oil phase which is a disadvantage due to that the relative expensive TOA (4-15 wt%) were transferred into bio-oil. This makes the recycling of TOA complicated and renders bio-oil less attractive due to the nitrogen content in TOA. To avoid this problem, the aqueous fraction of bio-oil was used as feedstock and extracted with TOA diluted in 2-ethyl-hexanol (RASRENDRA *et al.*, 2011). A recovery of 86% acetic acid together with other acids was obtained. Besides organic acids, certain phenolics and ketones were also extracted into the organic phase and further separation was required when pure compounds were desired. Vitasari et al. used TOA diluted in 2-ethyl-hexanol to extract both acetic acid and glycolaldehyde from the aqueous fraction of bio-oil (VITASARI *et al.*, 2012). Acetic acid was further recovered by distillation and glycolaldehyde was subjected to back-extraction with water.

Sugars are among main the chemicals in bio-oil and can be extracted with water as they have good hydrophilicity. But water is also able to extract many other polar chemicals. Wang et al. developed a multi-step approach to purify sugars from the water-soluble fraction of bio-oil (WANG *et al.*, 2016). The crude bio-oil was filtered and distilled by molecular distillation. The heavy fraction was dissolved in methanol and extracted with water. The water-soluble fraction was extracted with DCM to obtain a phenolic fraction. The DCM insoluble fraction was enriched with sugar and was further extracted with water and ethanol-water. The ethanol-soluble fraction contained monosaccharides such as levoglucosan, glucose, and xylose, whereas the ethanol-insoluble fraction contained a small amount of cellobiose besides other monosaccharides.

In general, solvent extraction is the best method to obtain pure compounds from pyrolysis liquids. However, a multi-step extraction with various kinds of solvents is necessary. The recovery of solvents makes this separation method not economically attractive for the production of chemicals from pyrolysis liquid.

2.5.7 Chromatography

Chromatography is a technique to separate a mixture, either preparative to separate the components for later use, or analytical to separate a small amount of material for analysis. It is based on partition coefficient of a compound and differential partitioning between the mobile and stationary phase. There are many types of chromatography, such as paper chromatography, thin layer chromatography (TLC), liquid column chromatography, size exclusion chromatography, ion-exchange chromatography, affinity chromatography, gas chromatography, etc. Liquid column chromatography is usually used to separate pyrolysis liquids into different groups according to the polarity of molecules contained in pyrolysis liquids.

Table 4: Column fractionation of bio-oil from vacuum pyrolysis of softwood bark (BA *et al.*, 2004).

Solvent	Chemicals identified
Pentane	alkanes, alkenes, and some ketones and ergosterols
Benzene	polycyclic aromatic hydrocarbons (PAHs) and some aldehydes, fatty acid esters and fatty alcohols
DCM	phenol derivatives and several fatty and resin acid esters
Ethyl acetate	Benzenediols and some phenol compounds, fatty, and resin acids
Methanol	Sugars

Ba et al. characterized different fractions of bio-oil produced from vacuum pyrolysis of softwood bark using open column chromatography (BA *et al.*, 2004). A mass of 1 g of bio-oil different phases were fractionated in a glass column pack with 15 g SiO_2 with the following solvents: 100 mL pentane, 100 mL benzene, 100 mL dichloromethane (DCM), 100 mL ethyl acetate, 100 mL methanol. The fractionation results are shown in Table 4. Similar compounds were found both in upper and bottom layers, which was an indication of incomplete separation.

The liquid chromatograph is an efficient technique for the separation of pure compounds. However, high consumption of solvents and regeneration of silica gel solid phase make this technique tedious and uneconomic. It is suggested to be used as a final purification step of a specific component rather than as a preparative separation of the whole pyrolysis oil (AMEN-CHEN *et al.*, 1997).

2.5.8 Addition of water

The early research of pyrolysis liquid had already demonstrated the preparation of pyrolytic lignin by addition of water. The addition of water was even developed as a standard method to separate pyrolytic lignin. According to the precipitation method proposed by Meier et al., 60 mL of pyrolysis liquid was added dropwise to 1 L of ice-cooled water with stirring of 6000 rpm and the precipitation of pyrolytic lignin started. The pyrolytic lignin was filtered over a Büchner funnel and suspended again in water to wash out water-soluble products. The water-insoluble was filtered and dried under vacuum at room temperature. The solid pyrolytic lignin was obtained with color between light and dark brown (SCHOLZE *et al.*, 2001). It is speculated that the pyrolytic lignin is dissolved in water-soluble organics of pyrolysis liquids with around 25 wt% water. When more water is added to pyrolysis liquid, most of the water-soluble organics are extracted into the water, leading to the precipitation of pyrolytic lignin. Meier et al. further characterized pyrolytic lignin with Py-GC/MS, FTIR, GPC, NMR, SEC, MALDI-TOF-MS, LDI-TOF-MS, and Py-FIMS. They confirmed that pyrolytic lignin was similar to milled wood lignin and the formation of pyrolytic lignin was a combination of thermal ejection and recombination reactions (SCHOLZE *et al.*, 2001, BAYERBACH *et al.*, 2006, BAYERBACH *et al.*, 2009).

Vitasari et al. investigated the influence of stirring rate and water-to-oil ratio on the extraction capability of pyrolytic lignin (VITASARI *et al.*, 2011). With stirring rate of 400 rpm, 20 °C, 24 h, water-to-oil ratio of 0.65:1 for pyrolysis liquid from forestry residue and 0.5:1 (the minimum water amount to ensure complete phase separation) for pyrolysis liquid from pine, 80-90 wt% of acetic acid, acetol, glycoaldehyde and levoglucosan could be extracted, while 40-80 wt% of furfural, furanone, guaiacols and syringol could be extracted.

The addition of water is useful to extract polar compounds in pyrolysis liquid. Pyrolysis liquid is separated into less complex fractions after water extraction. Water is also the cheapest solvent and non-toxic. However, water is not a selective method and water dilution reduces the aqueous concentration.

2.5.9 Fractional condensation

Hot vapors and aerosols are formed immediately after pyrolysis of biomass. Vapors are mainly the decomposition of carbohydrates while aerosols are non-volatile lignin-derived oligomers (MOHAN *et al.*, 2006). Fractional condensation is designed to recover different components from the mixture of vapors and aerosols. Different condensers with decreased temperatures enable a multi-stage condensation according to boiling points. It avoids reheating of the heat-sensitive pyrolysis liquid. As a consequence, several fractions with different compositions and properties can be obtained.

Westerhof et al. used a condenser train of two counter-current spray columns with feedstock of pine (WESTERHOF *et al.*, 2011). The scheme was (a) spray column at 20-115 °C, (b) spray column at 20 °C. The first condenser operated at around 70-90 °C gave a heavy oil with 20 wt% sugars and 40 wt% lignin-derived oligomers. Aqueous liquid was collected from the second condenser with 40 wt% light organics. It was a cheap downstream approach to concentrate compounds in chemical classes. Pollard et al. integrated three condensers and two electrostatic precipitators (ESP) to recover five fractions from red oak fast pyrolysis (POLLARD *et al.*, 2012). The scheme was (a) cooler at 345 °C, (b) ESP, (c) cooler at 129 °C (d) ESP, (e) cooler at 77 °C. Five stages were designed with the aim to capture levoglucosan, aerosols, phenols, water and light oxygenated compounds separately. The first two fractions contained most of the energy content, water-insoluble, and solids while the last fraction consisted mainly water and organic acids. Eight chemical categories were identified in all five factions thus the selectivity was not very high. Yin et al. used four condensers from 24-37 °C and an ESP to characterize bio-oil obtained from fast pyrolysis of sweet sorghum bagasse (YIN *et al.*, 2013). The scheme was (a) cooler at 37 °C, (b) cooler at 25 °C, (c) cooler at 23.5 °C, (d) cooler at 24 °C, (e) ESP. The first fraction accounted for 65.7 wt% and the ESP fraction accounted for 17.1 wt% of the bio-oil. The small temperature difference mainly influenced the yield and water content of different fractions. Other properties and main composition did not change too much. Gooty et al. used a condenser train (a) cyclonic cooler at 80 °C, (b) ESP at 30, 50, and 70 °C, (d) cyclonic cooler at 0 °C to trap pyrolysis vapors from birch bark and Kraft lignin (GOOTY *et al.*, 2014, GOOTY *et al.*, 2014). Oil collected from the first two condensers had a water content of less than 1 wt% and showed over 90% energy recovery. Oil produced from Kraft lignin contained 94% of the phenolic compounds present in the raw bio-oil. Sui et al. enlarged the temperature difference of the condenser as (a) cooler at 300 °C, (b) cooler at 100 °C, (c) cooler at 0 °C, (d) cooler at -20 °C to condense vapors from cotton stalk pyrolysis (SUI *et al.*, 2014). The first two fractions had a low water content (below 3 wt%) but also a low yield (5-8 wt% of bio-oil). The third fraction accounted for the highest yield of 77 wt% of bio-oil and contained 90 wt% of the water and acetic acid. The process was not predictable as certain components were found unexpected in various fractions.

Fractional condensation is a promising, relatively cheap and simple method to separate pyrolysis vapors into different fractions. The problem is that some chemicals are distributed in all fractions, which makes the fractions not very distinctive. The separation steps are difficult to control so that selectivity is lower than expected. To improve selectivity, the ESP and temperature of condensers need to be carefully designed and controlled. In addition, the composition of fractions is also largely dependent on the feedstock and pyrolysis conditions, which should also be taken into account. Furthermore, the condensation mechanisms are still not clearly understood and need more research efforts.

2.5.10 Centrifugal separation

Centrifugation is a separation process which uses centrifugal force to promote the sedimentation of heterogeneous mixtures or the settling of particles in a solid-liquid mixture. Lighter particles and high-density particles are formed as two major phases in the vessel during centrifugation. It is commonly used in the water treatment. Centrifugation was tried to separate tar from pyroligneous acid in the 19th century but all the attempts had failed (KLAR, 1925). Its application in separation of pyrolysis liquid is also limited. It can be used as a pre-treatment or post-treatment method.

2.5.11 Membrane separation

Membrane separation can selectively separate materials via different pore sizes in membrane structures. It can operate without heating which is an advantage for thermally-sensitive materials. According to driving force of the operation, it can be divided into four categories: (1) pressure driven operations; (2) concentration driven operations; (3) electric potential gradient operations; (4) temperature gradient operations. The pressure-driven operations are feasible to be applied to separate pyrolysis liquids. They include microfiltration (MF), ultrafiltration (UF), nano-filtration (NF) and reverse osmosis (RO) which is shown in Figure 14.

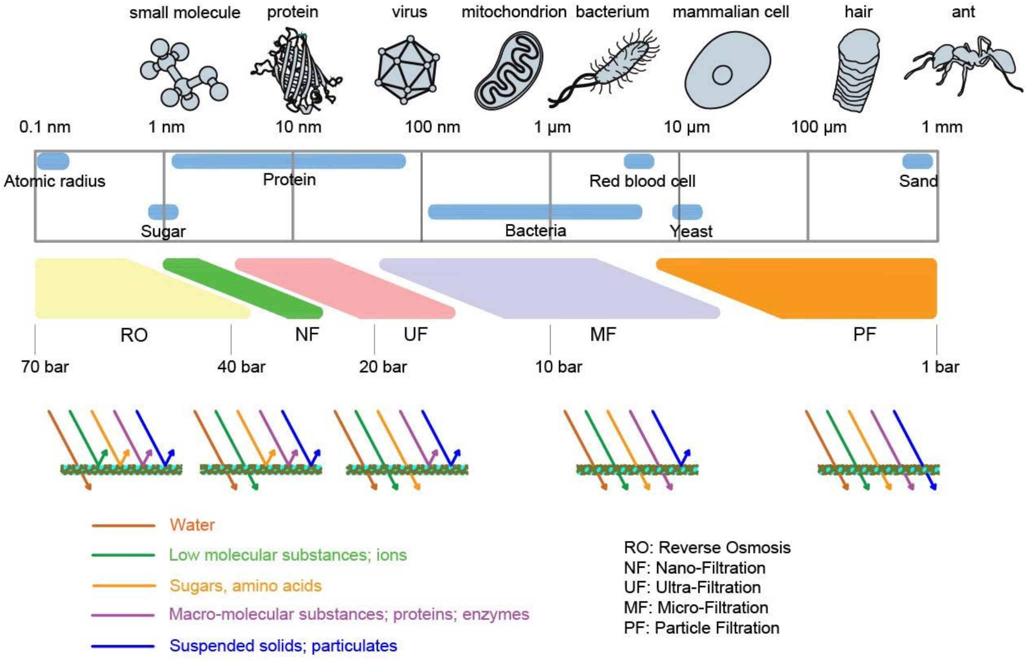


Figure 14: Characterization of Membrane separation.

The char particles present in bio-oil are responsible for its inferior quality. Huber’s research team proposed a membrane approach for fast pyrolysis oil stabilization. They used microfiltration with ceramic membranes of nominal pore sizes 0.5 and 0.8 μm to remove char particles larger than 1 μm from the bio-oil with the feedstock of white oak (JAVAID *et al.*, 2010). The microscopic image showed that char particles were removed from bio-oil with lower ash content in permeates. Due to the fouling of the membrane, a successive treatment was needed for the membrane cleaning. Subsequently, they used nano-filtration and reverse osmosis with even smaller membrane pore sizes to remove acetic acid from model aqueous phase of pyrolysis oils (TEELLA *et al.*, 2011). The separation of acids and low molecular weight sugars appeared to be feasible when phenolic compounds were removed and high transmembrane pressure was applied.

Membrane separation provides an alternative to separate pyrolysis liquid. The solid char particles in pyrolysis liquid can be effectively removed with particle and micro-filtration. For nano-filtration or smaller pore size membranes, bio-oil cannot be directly used as feed but has to be separated in advance. On the other hand, bio-oil can cause irreversible damage to the membranes. Fouling remains the biggest challenge for the membrane separation due to pore constriction, pore blockage, and formation of a cake layer on the membrane surface. The selective separation of certain low molecular compounds from bio-oil is still unclear. Furthermore, the cost of operation process needs to be considered when more efficient membrane separation processes are designed in the future.

2.5.12 scCO_2 extraction of bio-oil

When a gas or liquid is transformed into a supercritical state, it has many special characteristics and solvent properties. The properties of liquefied CO_2 make it suitable for use as a solvent in the series of conventional organic solvents. It is widely used in the extraction of natural matter, such as essential oils, herbal drugs, antioxidants and other materials. CO_2 behaves like non-polar hydrocarbon solvents, such as hexane. It does not react strongly with typical organic bases but forms solids with aliphatic amines. It has a strong homogenizing action for pairs of immiscible or partially miscible liquids. Therefore, CO_2 can be applied as a good solvent due to its unique advantages:

(1) readily available and inexpensive;
(2) liquefiable at low temperatures and pressures;
(3) non-flammable;
(4) nontoxic and environmentally friendly;
(5) chemically inert;
(6) no solvent residue.

When CO_2 is used as a solvent, the solubility of organic compounds needs to be considered. Chemicals that have good solubility in CO_2 include:

(1) aliphatic hydrocarbons up to at least C_{20};
(2) most small aromatic hydrocarbons;

(3) halocarbons, aldehydes, esters, ketones, and low alcohols.

Chemicals that have poor solubility in CO_2 include:
(1) polycyclic hydrocarbons;
(2) higher alcohols, glycols, and glycerol;
(3) phenols, anilines, hydroquinone, and other polyhydroxy aromatics;
(4) polar compounds, such as amides, ureas, urethanes, and azo dyes;
(5) large molecules with molecular weights above around 500.

At a pressure of 1 atmosphere, the gaseous CO_2 undergoes phase transition directly to a solid below -78.5 °C. CO_2 has no liquid state at pressure below 5.1 bar. The critical point of CO_2 is 31.1 °C and 73.8 bar, which is shown in Figure 15. Above the critical point, CO_2 is transformed into the supercritical fluid state. The subcritical CO_2 behaves like a liquid but the supercritical CO_2 behaves like a gas, although it has a higher density than liquid CO_2 when highly compressed. The $scCO_2$ has higher diffusivity, lower viscosity and lower surface tension than does the subcritical liquid phase of CO_2. These special properties give $scCO_2$ superior solvent properties over liquid CO_2. As a solvent, supercritical CO_2 offers more advantages over liquid CO_2: (1) higher solubility with increasing pressure; (2) density variable over a wide range; (3) a wider range of operating pressures and temperatures available (HYATT, 1984).

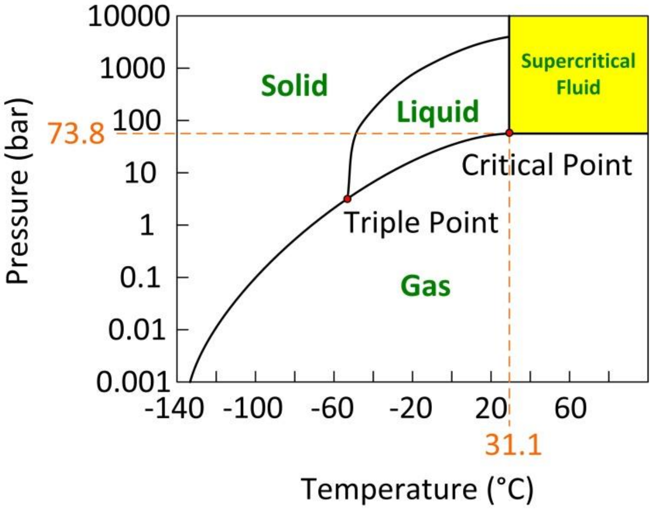


Figure 15: The critical point of CO_2.

Meier first used $scCO_2$ extraction to separate different pyrolysis liquids and a report was available (MEIER, 2003). Naik et al. first published results of using $scCO_2$ to fractionate bio-oil produced from mixed biomass of wheat and wood sawdust (ROUT *et al.*, 2009). An amount of 50 g bio-oil was adsorbed in 2 mm glass beads with fractionation temperature of 45 °C and CO_2 flow rate of 30 g/min. Three fractions of $scCO_2$ extracts were collected every two hours at 250 bar, then the pressure was increased to 300 bar and a fourth fraction was obtained. All fractions were found to contain less than 3 wt% water as original bio-oil contained around 45 wt% water. The first fraction contained furanoids, pyranoids, and oxygenated benzenoids while the fourth fraction contained fatty acids and high molecular mass alcohols. They further used $scCO_2$ to extract bio-oil from wheat-hemlock pyrolysis at 100, 250 and 300 bar successively to obtain three fractions. The composition of fractions from low pressures (100 and 250 bar) was similar to that of the first fraction while higher pressure was similar to that of the fourth fraction.

Wang et al. employed $scCO_2$ to separate simulated and real bio-oil (WANG *et al.*, 2010). The content of aldehydes, ketones, and phenols increased in the $scCO_2$ extracts while the content of acids and water decreased. The maximum extraction efficiency of bio-oil reached 88.6 wt% on a dry basis and the extracts had almost 100% volatility. Maqbool et al. used $scCO_2$ to separate bio-oil and the extracts were enriched with carboxylic acids and phenolic compounds (MAQBOOL *et al.*, 2017). Cheng et al. used $scCO_2$ to extract oxygenated compounds from bio-oil with pressures of 100, 200, and 300 bar. Three fractions were obtained with different compositions which accounted for 71.1 wt% of the bio-oil (CHENG *et al.*, 2016). Mudraboyina used an additional column in the $scCO_2$ extraction of lignin microwave-pyrolysis oil to extract single ring phenolic components. The column was packed with Dixon rings and a temperature gradient of 55-95 °C was applied. They found that lower pressure, higher temperature and higher flow rate favored the extraction of single ring phenols. The supercritical fluid rectification yielded up to 73 wt% single ring phenolic components (MUDRABOYINA *et al.*, 2015).

Current research efforts of $scCO_2$ extraction of pyrolysis liquids have demonstrated its potential for the fuel and fine chemicals production. The distribution coefficient of single compounds should be evaluated in order to improve the selectivity of extraction. Moreover, extraction parameters need to be optimized. In my thesis, I tried to identify important influencing factors and study the potential of $scCO_2$ extraction using slow and fast pyrolysis liquids.

3 Experimental

3.1 Pyrolysis liquids

Pyrolysis liquids used in my work included proFagus (PF) oil, Thünen Institute (TI) oil, and Biomass Technology Group (BTG) oil. proFagus oil was produced from slow pyrolysis while TI oil and BTG oil were produced from fast pyrolysis. TI oil was further divided into TI-U oil and TI-L oil which represented the upper phase and lower phase of TI oil.

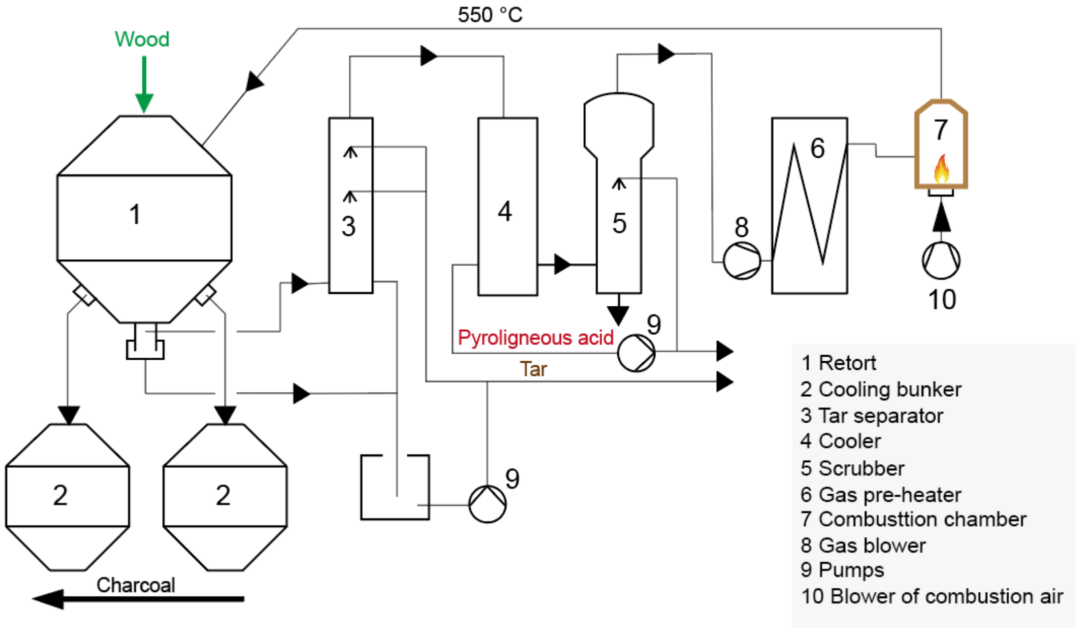


Figure 16: Scheme of the carbonizing plant using the Degussa process to produce proFagus oil.

proFagus oil. The proFagus oil is provided by the German charcoal company proFagus (Bodenfelde). In the process, 3 tonnes of untreated beech wood yield 1 tonne of barbecue charcoal and 2 tonnes of by-products. The company produces approximately 35000 tonnes of barbeque charcoal and around 25000 tonnes of crude wood tar annually. The carbonization process is known as Degussa process and shown in Figure 16. The Degussa process is different from other processes as 90% of the heat energy is produced from burning of by-products.

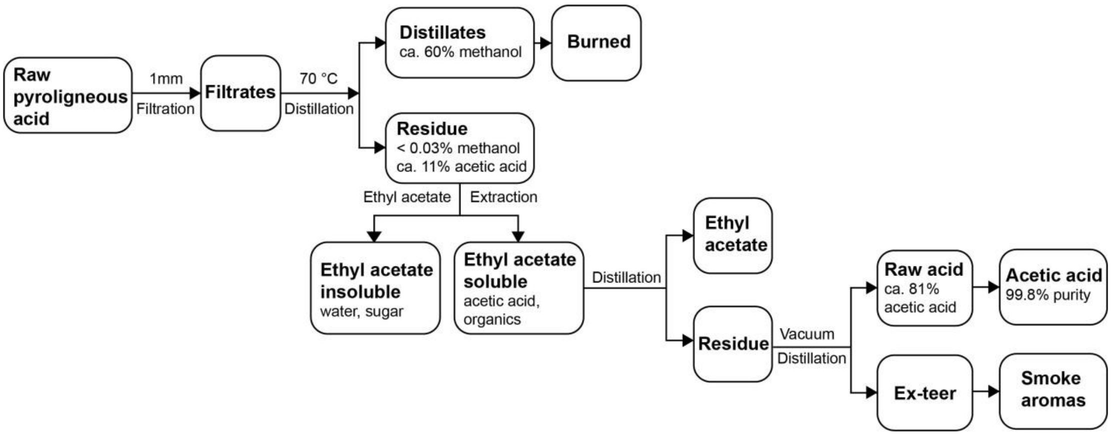


Figure 17: The treatment of proFagus raw pyroligneous acid and production of Ex-teer.

The beech wood is first dried to 15-18 wt% water content. Then it is heated to 550 °C under exclusion of air in six retorts operated in series (25 tonnes capacity for each retort) for 13-20 hours. The raw pyroligneous acid is filtered through the pore size of 1 mm. Then it is distilled at 70 °C to produce methanol. The distillate contains around 60 wt% methanol and is burned in the boiling system. The remaining pyroligneous acid has a methanol content of 0.03 wt% and acetic acid content of around 11 wt%. It is further extracted with ethyl acetate in order to extract acetic acid and ethyl acetate is recovered by distillation. The remaining residue is vacuum distilled to obtain the raw acid (containing ca. 81 wt% acetic acid) and “Ex-teer”, shown in Figure 17. The “proFagus oil” used in the thesis corresponds to the Ex-teer, which is further processed for the manufacture of liquid smoke. Therefore, the PF oil (Ex-teer) has a low content of acetic acid (ca. 1.3 wt%) but a high content of propanoic acid (ca. 4.0 wt%). PF oil has a low water content (<1 wt%) as the ethyl acetate has a poor solubility in water.

Thünen Institut oil. TI oil was self-made in the pilot pyrolysis plant at Thünen Institute in cooperation with the University of Hamburg. The scheme of the pyrolysis plant is shown in Figure 18. The pilot pyrolysis plant has a feed rate of 5 kg/h. The feedstock was beech wood and pyrolysis temperature was set at 475 °C. Isopar® was used as the quench liquid as it is immiscible with pyrolysis liquid.

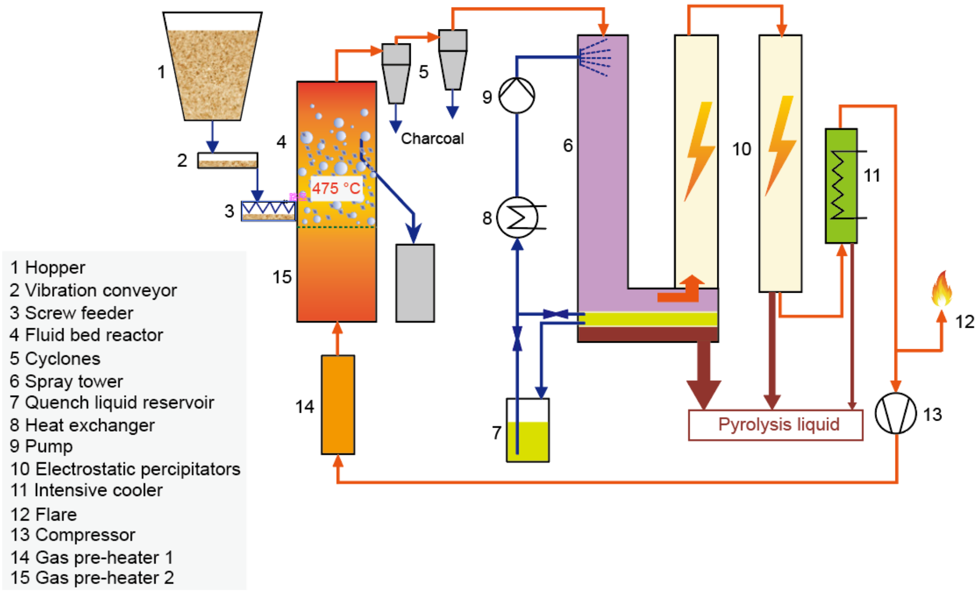


Figure 18: Schematic diagram of TI oil production.

Table 5: BTG bio-oil properties.

State	Liquid
Appearance	Dark brown
Odor	Strong characteristic, smoky
Boiling point	< 100 °C (start of char formation, polymerization)
Pour point	-20 °C
Flash point	> 62 °C
Evaporation rate	not available
Vapor pressure	not available
Density	1150-1200 kg/m^3
Viscosity 20°C	60-225 cSt
Viscosity 50°C	10-30 cSt
Water-insoluble	Soluble in water at concentration < 30% water
Corrosion rate	Negligible for: SS316L, SS304L, Copper (99.9% electrolytic), polyethylene HDPE, polypropylene PP, 1.39 mm/yr for SAE carbon steel and 1.32 mm/yr for aluminum
pH	2.5-3.5
Explosive properties	No heat and shock explosive
Auto ignition temperature	> 500 °C
Decomposition temperature	> 150 °C

BTG oil. BTG oil was provided by BTG-BTL (BTG BioLiquids B.V., the Netherlands), which was established by BTG (Biomass Technology Group BV, the Netherlands). The raw material was pine wood and the process was fast pyrolysis with a rotating cone reactor. The common name of this commercial product is “wood oil” with the trade name “wood, hydropyrolyzed”. The definition is defined as “A complex combination of organic compounds obtained from the thermal decomposition of wood”. The information on basic physical and chemical properties provided by BTG is listed in Table 5.

Two different BTG bio-oils were used in the work, namely BTG aged bio-oil and BTG fresh bio-oil. The aged BTG oil was produced in summer 2014 and fresh BTG oil was produced in January 2015. Both oils were received in February 2015. The BTG oils were stored at 5 °C after the reception. Due to the possible phase separation of bio-oils with storage time, the bio-oils were vigorously shaken before extraction or analysis to achieve one phase.

3.2 $scCO_2$ extraction

All $scCO_2$ extractions were carried out in the $scCO_2$ extraction plant but with several modifications. The original $scCO_2$ extraction plant with two pressure separators is shown in Figure 19. Some modifications to the extracts collection system were made which is shown in Figure 20. The pressure was replaced with glass collector so that the extracts could be collected and weighted hourly. The off-gases were further trapped with cotton wool, activated carbon filters, and wash bottles. A photo of $scCO_2$ extraction plant is shown in Figure 21.

The $scCO_2$ extraction of PF oil, TI-U and TI-L oil was first carried out with pressures of 150, 200, and 250 bar. The extracts were collected hourly over six hours run and mixed together afterward. The residue was washed with acetone. The composition of both extracts and residue was analyzed for the extracts collected at 150 bar. The procedure of the experimental work was described in a publication work (FENG *et al.*, 2015). As PF oil was adsorbed on SiO_2, different loading ratios of 100:40 and 100:80 were tested and the results are described in a publication work (FENG *et al.*, 2016). Finally, the $scCO_2$ extraction of BTG oil was carried out with the pressures of 100, 200 and 300 bar, temperatures of 60 and 80 °C, and the carriers activated carbon and SiO_2. All extracts were collected and analyzed every hour. The extraction efficiency and enrichment coefficient of the main components were calculated individually. The experimental procedure with the corresponding results were described and discussed in a publication work (FENG *et al.*, 2017).

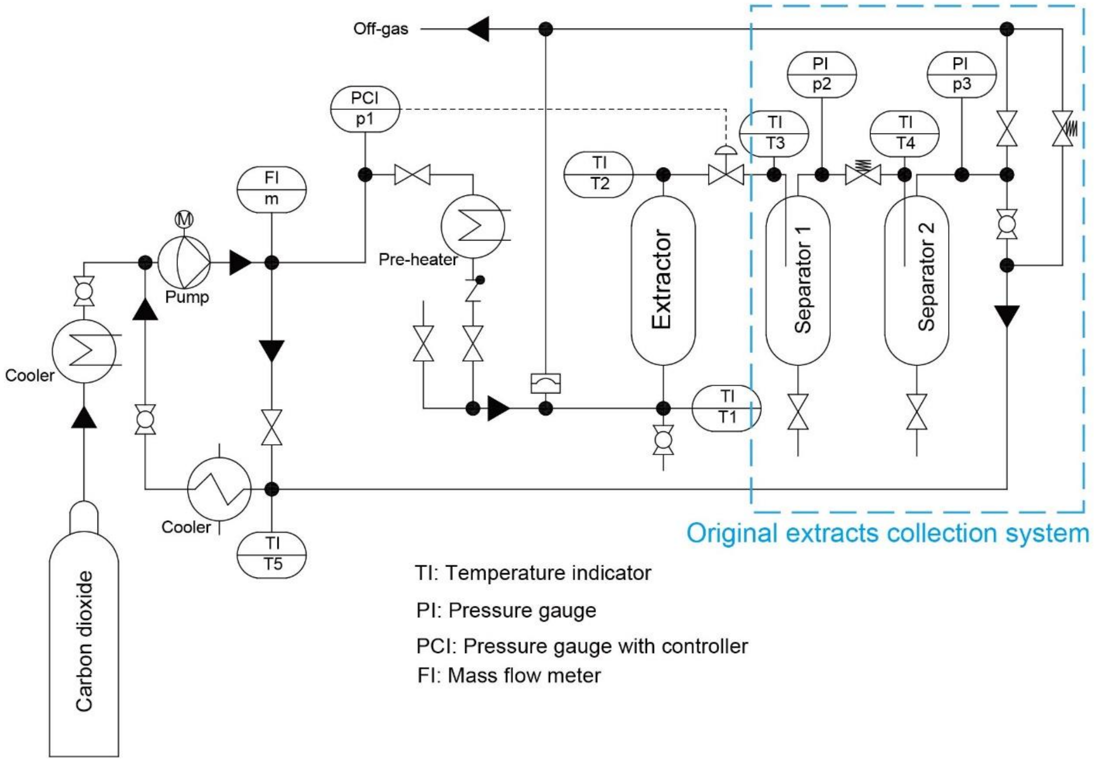


Figure 19: Original schematic diagram of $scCO_2$ extraction.

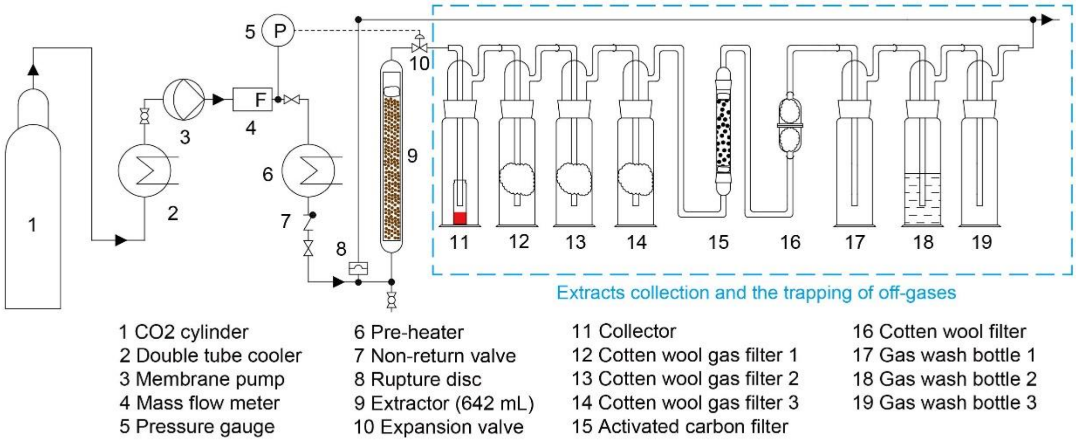


Figure 20: Schematic diagram of $scCO_2$ extraction with modifications.

Figure 21: Photo of the $scCO_2$ extraction plant.

3.3 Liquid CO_2 extraction

Liquid CO_2 extraction was carried out in a pressurized Soxhlet extractor. Around 7 g PF oil was adsorbed on SiO_2 with loading ratios of 100:40 and 100:80. The Soxhlet extractor was placed in the pressure vessel filled with dry ice and immersed in a water bath. The detailed procedure was described in a publication work (FENG *et al.*, 2016).

3.4 Solvent extraction

CO_2 is non-polar compound and the solvent properties of $scCO_2$ were reported to be similar to *n*-hexane (DARR *et al.*, 1999). Therefore, hexane was used to extract PF oil for the comparison with CO_2 extraction. The residue was further extracted with acetone as pyrolysis liquid is completely soluble in acetone. PF oil was adsorbed on SiO_2 and the extraction was done with a Soxhlet extractor. The detailed procedure was described in a publication work (FENG *et al.*, 2016).

3.5 Products analysis

3.5.1 Water content

The water content of pyrolysis liquid cannot be measured based on mass losses by drying methods as it contains many volatile substances. Karl Fischer titration is a well-established method to determine the water content of pyrolysis liquid. The Karl Fischer reagents selectively react with water even in trace amounts according to the following redox equation:

$2H_2O+SO_2+I_2=H_2SO_4+2HI$

Methanol was used as the solvent to dissolve pyrolysis liquid and Hydranal Composit 2 was used as the KF reagent. KF reagent can adsorb water from the air. Therefore, the titer was determined with pure water and subtracted if the KF reagent was not used for more than 12 hours.

A syringe was used to transfer liquid samples into the reaction cup when the liquid samples were homogeneous. For samples which were not homogenous, a self-made carrier boat was used as the medium.

All the determination was repeated three times and the average value was used.

3.5.2 Elemental analysis

The elemental composition of liquid samples was performed using a Vario EL from Elementar, Hanau, Germany. Carbon, hydrogen, and nitrogen were measured directly. Nitrogen was neglected as its content was too low and below the calibration range. Oxygen was calculated by difference shown in the formula below. All the determinations were made in duplicate and the average value was used.

$$O\% = 100 - (\%C + H\%)$$

3.5.3 Higher heating value

Heating value is an important parameter in terms of fuel application but not for the separation of chemical products. Nevertheless, the heating value of pyrolysis liquid and the extracts were estimated according to the Dulong's formula as follows:

$$\mathrm{HHV}[\mathrm{MJ\ kg^{-1}}] = [338.2 \times \%\mathrm{C} + 1442.8 \times \left(\%\mathrm{H} - \frac{\%\mathrm{O}}{8}\right)] \times 0.001$$

3.5.4 GC-MSD/FID analysis

The individual component in crude pyrolysis liquids, extracts and residue were qualified an quantified by GC-MS/FID. The MS signal was used for the qualification and FID signal was used for quantification. The conditions of GC-MS/FID were set as in Table 6 (MEIER *et al.*, 2014).

Table 6: The operation conditions of GC-MSD/FID.

Gas chromatograph	Hewlett Packard HP 6890, with micro-flow splitter
Mass selective detector	Hewlett Packard HP 5972
Autosampler	CTC Analytics (Combi Pal)
Carrier gas	Helium, constant flow
Column (medium polar)	Varian DB 1701, 60 m × 0.25 mm, film thickness 0.25 µm, coating material is 14% Cyanopropylphenyl-86% dimethylsiloxane copolymer
Injection volume	1 µL
Split ratio	1:15
Injector	250 °C
Flame ionization detector	280 °C
Ion source	140 °C
Ionization energy	70 eV
Over program	45 °C, hold for 4 min, 3°C/min to 280 °C, hold for 20 min
Data evaluation	MassFinder4®

3.5.5 GPC analysis

The residue of the $scCO_2$ extraction was tarry-like and contained mainly high molecular compounds. GPC was used to explore the molecular size distribution of the residues. The conditions of GPC analysis is shown in Table 7. Samples were dissolved in dimethylsulfoxide (DMSO) in the concentration of 1-2 mg/ml. Around 0.1% lithium bromide was added to the solvent to avoid associations between molecules and column gel. The sample solutions were put on the rotary mixer for at least 12 hours to ensure complete dissolution. Afterwards, the solutions were filtered with filters of 0.2 µm pore size. Ten polyethylene glycol standard samples were used for calibration. Data were analyzed with Agilent HPLC Chemstation and the GPC add-on software (PSS). The number-average molecular weight (Mn) and the weight-average molecular weight (Mw) were calculated.

Table 7: The operation conditions of GPC.

System	Agilent HPLC 1100 Series
Detector	Variable wavelength detector (UV detector, λ=254 nm); Refractive Index Detector (RID) at 40 °C
Pre-column	Varian type Polar Gel L, length 50 mm, i.d. 7.5 mm
Main column 1	type Polar Gel L, length 300 mm, i.d. 7.5mm from Polymer Laboratories
Main column 2	type Polar Gel L, length 300 mm, i.d. 7.5mm from Polymer Laboratories
Eluent	DMSO + 1 % lithiumbromide (LiBr)
Mobile phase flow rate	0.8 mL/min
Injection volume	100 µl
Oven temperature	60°C
Calibration range	106-21030 g/mol

3.5.6 Sample and numerical calculation of experimental data

In $scCO_2$ extraction, pyrolysis liquid was adsorbed on the solid carriers before putting into the extractor. During sample preparation, some volatile components escaped from the pyrolysis liquid, leading to the loss of actual transferred oil weight. For $scCO_2$ extraction of BTG oil, experiments were designed so that 100 g pyrolysis liquid was adsorbed on 100 g carrier. In order to improve results, the losses of pyrolysis liquid during sample preparation were subtracted according to the following equations. The weight of scCO$_2$ extracts was directly obtained by weighing while the residue was obtained by calculation.

$$M_{transf.} = M_{to.b.} - M_{se} - M_{wool} - (100 - M_{ca.n.})$$

$$M_{resid.} = M_{to.a.} - M_{se} - M_{wool} - (100 - M_{ca.n.})$$

$$Y_{extr.} = \frac{M_{extr.}}{M_{transf.}} \times 100\%$$

$$Y_{resid.} = \frac{M_{resid.}}{M_{transf.}} \times 100\%$$

where $M_{transf.}$ is the weight of actual oil that is transferred into the steel basket, $M_{to.b.}$ is the total weight of loaded steel basket before put into the extractor, $M_{to.a.}$ is the total weight of loaded steel basket after extraction, M_{se} is the weight of clean empty steel basket, M_{wool} is the weight of cotton wool, $M_{ca.n.}$ is the weight of carrier that is not transferred into the basket, $Y_{extr.}$ is the yield of the extracts, $Y_{resid.}$ is the yield of the residue.

Pyrolysis liquids contain many organic compounds and most of them are in low concentration. For the main and most abundant compounds, extraction efficiency and enrichment coefficient are calculated based on GC-MS/FID results according to the following equation. Furthermore, distribution coefficients are calculated for the scCO$_2$ extraction of different pyrolysis liquids at 150 bar as the residue was also analyzed under this condition.

$$Ex = \frac{m^i_{extr.}}{m^i_{crude\ oil}} \times 100\%$$

$$En = \frac{C^i_{extr.}}{C^i_{crude\ oil}}$$

$$Di = \frac{C^i_{extr.}}{C^i_{residue}}$$

where Ex is extraction efficiency of component i, $m^i_{extr.}$ is amount of i in the extracts, $m^i_{crude\ oil}$ is amount of i in the crude pyrolysis liquid; En is enrichment coefficient of component i, $C^i_{extr.}$ is concentration of i in the extracts, $C^i_{crude\ oil}$ is concentration of i in the crude pyrolysis liquid; Di is distribution coefficient of component i, $C_{residue}^{i}$ is concentration of i in the residue.

4 Results and discussion

4.1 Mass balance of different extraction processes

The feasibility of $scCO_2$ extraction of pyrolysis liquid is determined by the yield and quality of extracts. The extraction yield and mass balance were calculated for different pyrolysis liquids extracted under different conditions. Preliminary studies were done taking into account the $scCO_2$ extraction of PF oil and TI oils. Afterwards, the mass balances were improved by adding wash bottles and an activated carbon filter in the condensation train. The effects were tested with PF oil as feedstock. The optimal loading ratios on different carriers were tested using BTG oil. Finally, systematic $scCO_2$ extractions of BTG oil were carried out at 100, 200 and 300 bar, 60 and 80 °C, and with the carriers SiO_2 and AC.

4.1.1 Mass balance of $scCO_2$ extraction of PF oil, TI-U oil, and TI-L oil

The $scCO_2$ extractions under different fixed pressures were done for different pyrolysis liquids so the influence of pressures can be compared. The results are shown in Table 8. When the pressure was set to 80 bar, which is slightly above the critical pressure of 73 bar, the extraction yield was as low as 2.1 wt% for PF oil. The extraction ability of $scCO_2$ at low pressures (slightly above the critical pressure) is too poor to extract chemicals from pyrolysis liquid.

In the pressure range of 150-250 bar with 60 °C and a CO_2 flow rate of 10 g/min, the extraction yield for TI-U oil was 7.4-11.1 wt%, for TI-L oil it was 9.9-15.0 wt%, for PF oil it was 37.4-54.1 wt%. The extraction yield of slow pyrolysis PF oil was much higher compared to fast pyrolysis oils. With the same process conditions, the extraction yield is highly dependent on the properties of pyrolysis liquids. The most important difference between slow and fast pyrolysis liquids used in the experiments is the water content. Water has a negative influence on the extraction yield especially when the water content exceed 18% (NAGY, 2010). For all pyrolysis liquids, the extraction yield increases with the increase of pressure. However, the extraction yield was largely improved when pressure increased from 150 bar to 200 bar whereas there is only a slight increase in yield between 200 bar and 250 bar. With regards to economy, 200 bar is the appropriate pressure for the extraction.

Table 8: Mass balance of $scCO_2$ extraction of PF oil and TI oils at fixed pressures.

Feed-stock	Conditions	Extracts (wt%)	Residue (wt%)	Total mass (wt%)	CO_2 amount (g)
PF oil	(100_SiO_2+80)_80_60_5_8*	2.1	88.1	90.2	2218
PF oil	(50_SiO_2+50)_150_50_3_6	37.4	49.6	87.0	1692
PF oil	(100_SiO_2+80)_150_60_5_8	43.7	43.3	87.0	2204
PF oil	(100_SiO_2+80)_150_60_10_8	42.1	37.0	79.1	4716
PF oil	(100_SiO_2+80)_200_60_10_8	53.5	33.9	87.4	4465
PF oil	(100_SiO_2+80)_250_60_10_8	54.1	32.1	86.2	4686
TI-U oil	(125_SiO_2+100)_150_60_10_6	7.4	76.5	83.9	3198
TI-U oil	(125_SiO_2+100)_200_60_10_6	10.2	76.9	87.1	3456
TI-U oil	(125_SiO_2+100)_250_60_10_6	11.1	73.4	84.5	3418
TI-L oil	(100_SiO_2+80)_150_60_10_6	9.9	65.5	75.4	3280
TI-L oil	(100_SiO_2+80)_200_60_10_6	13.4	63.9	77.3	3335
TI-L oil	(100_SiO_2+80)_250_60_10_6	15.0	64.6	79.6	3451

*: The naming of conditions is defined as follows: (weight of carrier in g_carrier type + weight of pyrolysis liquid in g)_pressure in bar_temperature in °C_CO_2 flow rate in g/min_extraction time in hour.

During the extraction process, the CO_2 flow rate was set to a constant value. However, the high-pressure pump was unable to deliver a constant flow under the selected extraction conditions. Considering the performance of needle valve, the maximum CO_2 flow rate was suggested as 15 g/min. The CO_2 consumption is listed in the Table 8. Different CO_2 flow rates of 3, 5, and 10 g/min were tried with PF oil at 150 bar. When the CO_2 flow rate increased from 3 g/min to 5 g/min and the time increased from 6 h to 8 h, the extraction yield increased from 37.4 wt% to 43.7 wt%. When the CO_2 flow rate increased to 10 g/min, the extraction yield decreased to 42.1 wt%. The $scCO_2$ extracts from pyrolysis liquid are volatile. As a consequence, higher CO_2 flow rates promote the evaporation rate of the extracts resulting in fewer extracts. The extracts obtained per 100 g CO_2 reached the highest yield with low CO_2 flow rate and short extraction time. The extraction efficiency during later period was much lower than that of the beginning period, therefore the whole extraction efficiency was lower with longer extraction time.

The residue of PF oil was 32.1-49.6 wt%, TI-U oil was 73.4-76.9 wt%, and TI-L oil was 63.9-65.5 wt%. More extracts lead to fewer residue but not in the linear ratio. For example, at 200 bar, the extraction yield of TI-L oil was 2.3 wt% higher than TI-U oil but with 13.0 wt% less residue. The residue is related to water content and organic components of the pyrolysis liquids. More organic components and less water content in pyrolysis liquids lead to more losses and fewer residues.

The total recovered mass of TI-L oil was 75.4-79.6 wt%, TI-U oil was 83.9-87.1 wt%, and PF oil was 86.2-90.2 wt% under different conditions. For all the pyrolysis liquids, the losses account for an important part of the mass balance, from 9.8 wt% to 24.6 wt%. Both the volatile components that cannot be trapped in the collector system and those that evaporate from the extracts contribute to the losses.

4.1.2 Improvement of mass balance for the scCO$_2$ extraction of PF oil

Several methods were applied to minimize the losses by using cotton wool in the collector series, a wash bottle with organic solvents and a filter with activated carbon. The results of mass balance improvement of PF oil extraction are shown in Table 9. The mass balance was improved to up to 95.8 wt%. Wash bottles with isopropanol could trap 11.2-14.9 wt% compounds with no obvious influence of cold trapping. Acetone in wash bottle could trap 0.6-3.0 wt% at room temperature but 13.9 wt% with dry ice cold trapping. Acetone is much more volatile compared to isopropanol. Therefore, if a wash bottle is needed, isopropanol at room temperature is recommended. Cotton wool in the collector (number 12-14 in Figure 20) could trap 5.1-6.5 wt%. The cotton wool after extraction had a strong smell and the color changed to light yellow as shown in Figure 22. Distilled acetone was used to wash the cotton wool and it was removed by rotary evaporation. Components trapped by cotton wool were analyzed by GC-MSD/FID, their composition was found to be similar to the extracts. The filter (number 15 in Figure 20) followed by cotton wool could trap 6.5-9.3 wt%. Filter and wash bottle were not used at the same time because the vapors from wash bottle could be adsorbed in the filter.

Table 9: Improvement of mass balance with wash bottle and filters.

Feedstock	Conditions	Extracts (wt%)	Residue (wt%)	Wash bottle (wt%)	Cotton wool (wt%)	Filter (wt%)	Total mass (wt%)
PF oil	(100_SiO_2+40)_200_60_7_6*	23.8	47.3	14.0 (ic)	/	/	85.0
PF oil	(100_SiO_2+40)_200_60_7_6	26.5	47.3	13.6 (ir)	/	/	87.3
PF oil	(100_SiO_2+40)_200_60_7_6	24.0	51.3	/	6.5	9.3	91.0
PF oil	(100_SiO_2+50)_200_60_7_6	28.5	45.6	13.4 (ir)	/	/	87.5
PF oil	(100_SiO_2+60)_200_60_7_6	28.8	47.3	14.9 (ir)	/	/	91.0
PF oil	(100_SiO_2+60)_200_60_7_6	33.3	44.0	3.0 (ar)	5.8	/	86.2
PF oil	(100_SiO_2+80)_200_60_7_6	41.3	38.1	13.9 (ac)	/	/	93.3
PF oil	(100_SiO_2+80)_200_60_7_6	41.3	42.3	11.8 (ir)	/	/	95.4
PF oil	(100_SiO_2+80)_200_60_7_6	36.6	42.8	2.5 (ar)	/	/	81.9
PF oil	(100_SiO_2+80)_200_60_7_6	38.6	41.0	0.6 (ar)	7.1	/	87.4
PF oil	(100_SiO_2+80)_200_60_7_6	42.8	41.4	/	5.1	6.5	95.8
PF oil	(150_AC+50)_200_60_7_6	9.6	64.0	11.2 (ir)	/	/	84.8

*: The naming of conditions is defined as follows: (weight of carrier in g_carrier type + weight of pyrolysis liquid in g)_pressure in bar_temperature in °C_CO_2 flow rate in g/min_extraction time in hour. (ic): isopropanol in cold trapping by dry ice. (ir): isopropanol at room temperature. (ac): acetone in cold trapping by dry ice. (ar): acetone at room temperature.

From Table 9 it can be observed that there is a significant influence of loading ratios on the extraction yield. The SiO_2:oil ratio of 100:40 gave 23.8-26.5 wt% extracts, the ratio of 100:60 gave 28.8-33.3 wt% extracts, and the ratio of 100:80 gave 36.6-42.8 wt% extracts. Higher loading ratio leads to higher extraction yield which can largely improve the extraction efficiency. When activated carbon was used as the oil carrier, only 9.6 wt% extracts were obtained even with loading ratio of 150:50. The type of oil carrier is also an important factor that influences the extraction yields.

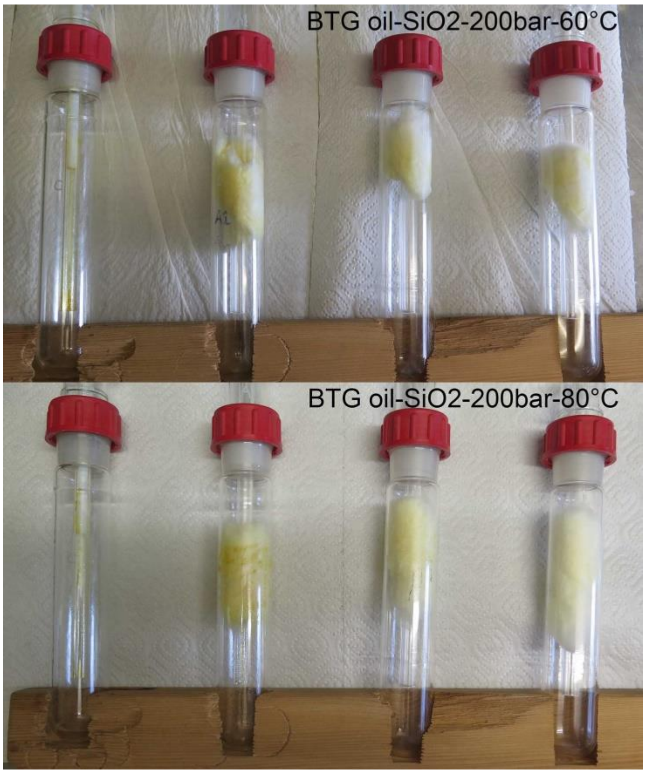


Figure 22: The color of cotton wool after $scCO_2$ extraction of BTG oil.

4.1.3 Influence of carriers and loading ratios for the $scCO_2$ extraction of BTG oil

Pyrolysis liquid is loaded on the carrier either by "absorption" through surface tension or by "adsorption" through nano-pores and Van der Waals forces. Three different carriers were tested, including glass beads, SiO_2 and activated carbon for BTG oil. Glass beads "carry" by absorption, the other two carriers are mainly by adsorption. The types of carrier and loading ratio not only influence the extraction yield but also influence the extraction selectivity. Results of different carriers and loading ratio are shown in Table 10. Glass bead as the carrier showed the highest extraction yield with 15.5-21.6 wt%, comparing to SiO_2 and AC with the yield of 6.3-8.1 wt%. However, the absorption ability of glass bead is the lowest one. At least 17 g glass beads are needed to absorb 1 g bio-oil. Therefore, glass beads are not used for further extractions. When SiO_2 was overloaded with bio-oil (around 2 g bio-oil was adsorbed in 1 g SiO_2), high extraction yield with 16.9 wt% was obtained. However, the mixing of bio-oil and carrier could not be accurately controlled due to overloading. The carrier of SiO_2 and AC with mixing ratio of 1:1 was used for the further $scCO_2$ extraction of BTG oil.

Table 10: Test of different carriers and optimal loading ratio

Feedstock	**Conditions**	**Loading ratio (carrier: oil)**	**Residue (wt %)**	**Extracts (wt %)**	**In wool (wt %)**	**Total mass (wt %)**	**CO_2 amount (g)**
BTG aged oil	(84.7_SiO_2+42.4)_200_60_7_6*	2.0:1	71.7	7.5	2.8	82.1	2375
BTG aged oil	(86.1_SiO_2+43.1)_200_60_7_5	2.0:1	77.7	6.3	1.4	85.4	1723
BTG fresh oil	(244.7_GB+14.8)_200_60_7_6	16.5:1	37.8	15.5	4.7	58.1	2726
BTG fresh oil	(251.6_GB+8.8)_200_60_7_6	28.6:1	37.5	21.6	6.8	65.9	2717
BTG fresh oil	(30.7_SiO_2+10.2)_200_60_7_6	3.0:1	62.7	6.9	2.9	72.5	2641
BTG fresh oil	(40.0_AC+28.4)_200_60_7_6	1.4:1	64.1	8.1	1.1	73.2	2380
BTG fresh oil	(70.0_AC+10.3)_200_60_7_6	6.8:1	45.6	2.9	1.9	50.5	2386
BTG fresh oil	(30.0_SiO_2+62.9)_200_60_7_6	0.5:1	57.4	16.9	1.9	76.2	2674

*: The naming of conditions is defined as follows: (weight of carrier in g_carrier type + weight of pyrolysis liquid in g)_pressure in bar_temperature in °C_CO_2 flow rate in g/min_extraction time in hour.

4.1.4 Mass balance of $scCO_2$ extraction of BTG oil

The $scCO_2$ extraction of BTG oil was carried out with SiO_2 and AC under different pressures and temperatures. The mass balance results are shown in Table 11. Pressure and temperature are the two most important factors that influence the extraction yield. The extraction yield at 100 bar was below 1.1 wt%, at 200 bar it was in the range of 6.4-13.1 wt%, at 300 bar it was 13.1-14.3 wt%. Obviously, high pressure leads to high extraction yield and less residue. When the pressure was slightly above the CO_2 critical pressure (73 bar), the extraction yield of BTG oil was very low and almost no extracts could be collected for the further analysis. Therefore, for $scCO_2$ extraction of fast pyrolysis liquid like BTG oil, the starting pressure is suggested to be higher than 200 bar. Low temperature of 60 °C led to more extracts than high temperature of 80 °C. Low temperature led to also more residues but much fewer off-gases. The amount of off-gases is mainly influenced by temperature rather than pressure. At 200 bar, the extraction yield was highly dependent on the temperature. But the influence of temperature at 300 bar was not pronounced. AC as carrier led to both fewer extracts and residues but more off-gases. The off-gases reached the highest amount with high temperature and AC as the carrier.

Table 11: BTG oil mass balance results

Feedstock	**Conditions**	**Residue (wt%)**	**Extracts (wt %)**	**cotten wool (wt%)**	**Filter (wt%)**	**Total mass (wt %)**	**CO_2 amount (g)**
BTG fresh oil	(100_SiO_2+100)_100_60_7_6*	86.1	1.1	1.2	5.7	94.1	2808
BTG fresh oil	(100_SiO_2+100)_100_80_7_6	86.4	0.2	0.6	3.9	91.1	2920
BTG fresh oil	(100_AC+100)_100_60_7_6	87.0	0.6	0.7	3.5	91.9	2712
BTG fresh oil	(100_AC+100)_100_80_7_6	84.6	0.1	0.2	4.0	88.9	2879
BTG fresh oil	(100_SiO_2+100)_200_60_7_6	75.7	13.1	1.2	4.5	94.5	2970
BTG fresh oil	(100_SiO_2+100)_200_80_7_6	73.2	9.9	2.4	4.7	90.2	2744
BTG fresh oil	(100_AC+100)_200_60_7_6	72.7	12.4	1.1	3.8	90.1	2805
BTG fresh oil	(100_AC+100)_200_80_7_6	70.4	7.7	2.5	5.4	86.0	2845
BTG aged oil	(100_SiO_2+100)_200_60_7_6	78.4	10.3	1.2	2.9	92.8	2763
BTG aged oil	(100_SiO_2+100)_200_80_7_6	77.3	6.4	2.1	3.7	89.6	2549
BTG fresh oil	(100_SiO_2+100)_300_60_7_6	76.0	14.3	1.4	2.6	94.3	2325
BTG fresh oil	(100_SiO_2+100)_300_80_7_6	70.9	13.1	1.8	4.4	90.3	2416
BTG fresh oil	(100_AC+100)_300_60_7_6	72.1	13.6	1.4	3.4	90.5	2504
BTG fresh oil	(100_AC+100)_300_80_7_6	66.2	14.3	2.9	5.5	88.9	2863

*: The naming of conditions is defined as follows: (weight of carrier in g_carrier type + weight of pyrolysis liquid in g)_pressure in bar_temperature in °C_CO_2 flow rate in g/min_extraction time in hour.

4.2 Characterization of the $scCO_2$ extraction processes

4.2.1 Process model of $scCO_2$ extraction of pyrolysis liquid

The extracts from the $scCO_2$ extraction of different pyrolysis liquids were collected and weighed every hour in a six hours run. Therefore, the extraction curves against recovery time are obtained. There are several models to describe $scCO_2$ extraction process. The models can be used to optimize the extraction process by changing suitable parameters and finally to achieve maximum economic value.

In this work, pyrolysis liquid is adsorbed on a solid carrier and then continuously extracted with $scCO_2$ in the batch reactor. That is comparable to the extraction of substances from solid substrates. In this case, the extraction process can be divided into two types: (1) the diffusion controlled process; (2) the dissolution controlled process as demonstrated in Figure 23. In the diffusion controlled process, the extractant has a good solubility in $scCO_2$. The extraction is rapid in the initial phase until the easily accessible extractant in the surface is depleted. Then the extraction rate becomes much slower due to the slow diffusion of extractant inside the particle and finally reaches 100% extraction. The extraction process can be optimized by maximizing diffusion. Higher temperature or a proper oil carrier is able to promote diffusion whereas the influence of pressure, flow rate or a modifier is less important.

In the dissolution controlled process, the extraction rate is almost constant with time. Extractant diffuses easily from the inside of the particle and accumulates on the surface. The $scCO_2$ is always saturated with the extractant while the extractant has a poor solubility in $scCO_2$. Therefore, methods to improve the solubility of the extractant can improve the extraction efficiency. Increasing the pressure or using a modifier are typical measures to improve the $scCO_2$ solubility. Moreover, in a dissolution controlled process, more extracts can be obtained by increasing the flow rate of $scCO_2$.

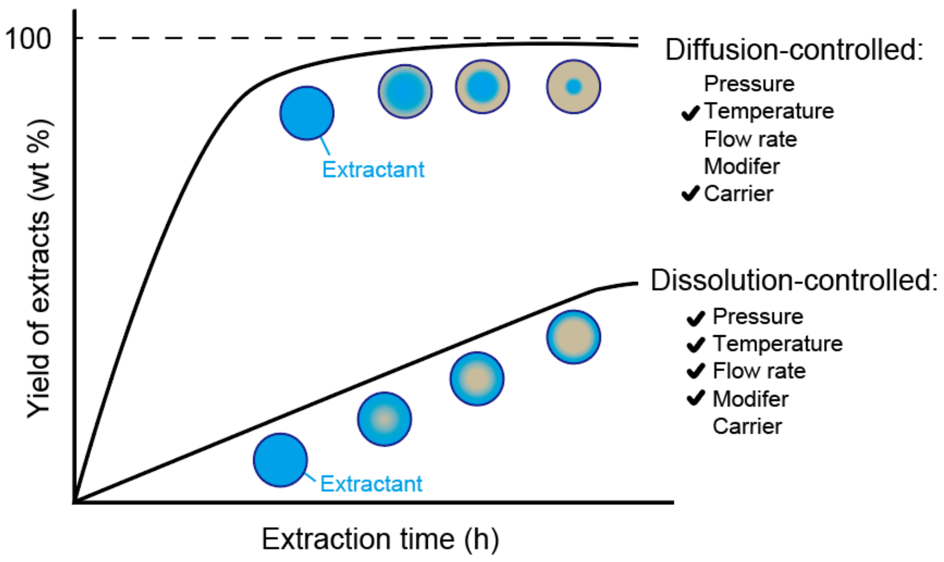


Figure 23: Different extraction principles of $scCO_2$ processes (CLIFFORD *et al.*, 1998).

In practice, the $scCO_2$ extraction process is usually a combined process with both dissolution and diffusion. Sovova proposed a broken and intact cell (BIC) model for the extraction of oils from natural materials shown in Figure 24 (SOVOVA, 1994). The idea of the BIC model is based on the fact that natural materials are usually pre-treated by grinding or crushing before loading to the $scCO_2$ extractor. The BIC model is applicable in situations where the extractant at the outer surfaces of the particles is readily accessible to the SFE solvent while the rest in intact cells is less accessible. It was presumed that pyrolysis liquid adsorbed on SiO_2 or AC with different loading ratios conform to this model. In this model, the overall extraction process is divided into three periods controlled by different mass transfer mechanisms: (1) constant extraction rate period; (2) falling extraction rate; (3) diffusion controlled period, as shown in Figure 25.

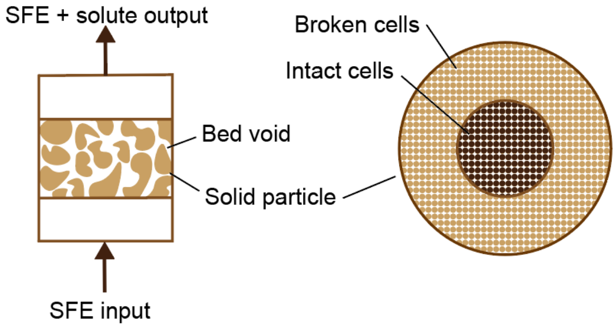


Figure 24: Particle scheme for the broken and intact cell (BIC) model (HUANG *et al.*, 2012).

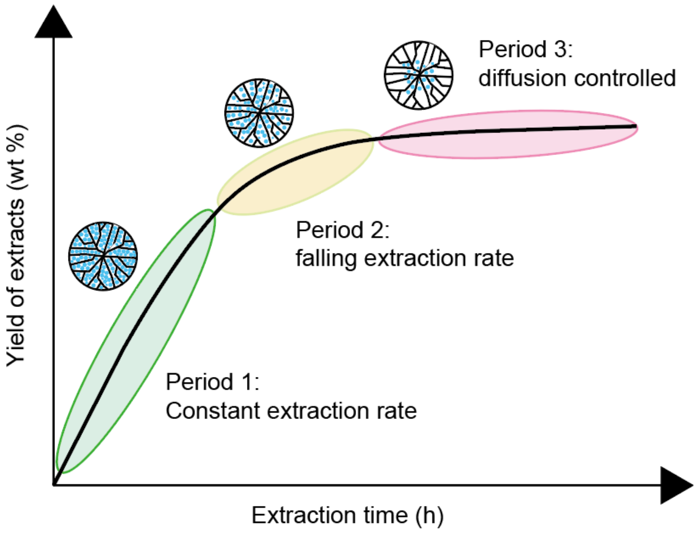


Figure 25: The overall extraction process of BIC model.

In the first extraction period, $scCO_2$ is saturated with the easily accessible extractant and the extraction rate depends on the solubility of the extractant. Therefore, this period is controlled by dissolution. The falling extraction rate period is a transition period when diffusion starts combined with convection. The easily accessible extractant at the entrance of the reactor has depleted but still exist at the outlet of the reactor. Diffusion commences for particles without easily accessible extractant. At the end of this period, all the easily accessible extractants have been removed. In the last period, the less accessible extractants in intact cells are slowly extracted by diffusion (HUANG *et al.*, 2012).

4.2.2 Influence of pressure on the $scCO_2$ extraction processes

Figure 27 shows that extraction efficiency of pyrolysis liquids at 100 bar was constant with very low yields. The extraction process is a dissolution controlled process. Most of the components in pyrolysis liquid are polar and not sufficiently dissolved in non-polar CO_2 especially at low pressures where the $scCO_2$ solvolysis capacity is low. However, at higher pressures above 200 bar, the extraction rate was largely improved but decreased with the time, indicating there was a combined effect of both dissolution and diffusion. The extraction yield of PF oil reached more than 50 wt% and the extraction rate was much slower at the later extraction period (see Figure 26). The extraction of PF oil had reached the diffusion controlled period according to the BIC model. The extraction curves of TI oils and BTG oil did not flatten off during the six hours run, indicating that the extraction was incomplete.

During the extraction process, the flow rate was set to 7 g/min but it fluctuated during the extraction. Therefore, the extraction yields per hour were calculated based on the amount of 500 g CO_2.

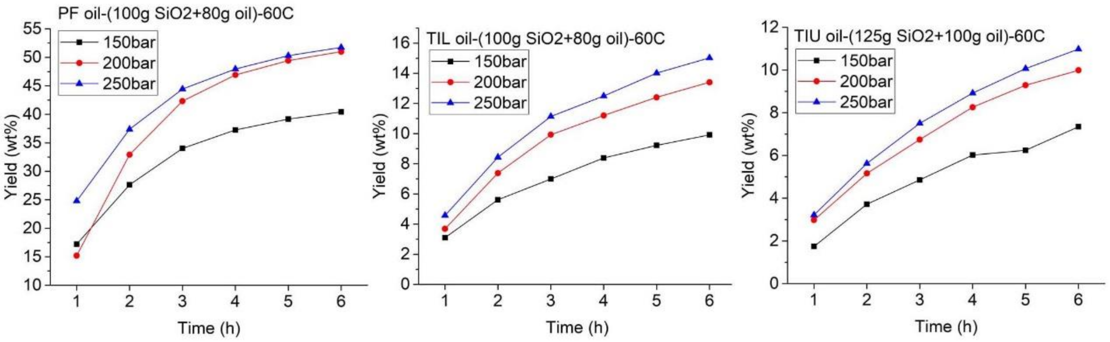


Figure 26: Influence of pressure on the $scCO_2$ extraction of PF, TI-U, and TI-L oils.

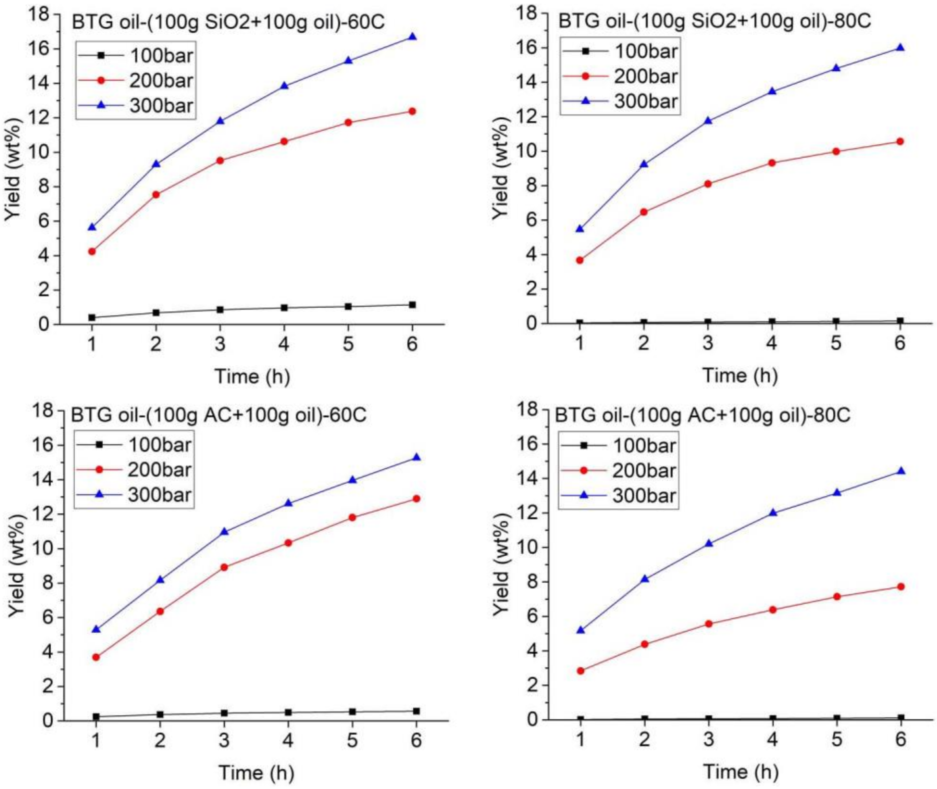


Figure 27: Influence of pressures on the $scCO_2$ extraction of BTG oil at different temperatures (60, 80 °C) and carriers (SiO_2 and AC).

In the gas extraction of a solid substrate, the main parameters that influence the extraction process are pressure, temperature, solvent ratio, and solid particle size. When the temperature is constant, the solvent power in general increases with pressure resulting in the increase of the amount of extracts. Figure 26 shows that the amount of extracts increased with the increase of pressure for different pyrolysis liquids. In the pressure range of 150 to 250 bar, the extraction yield at 150 bar was much lower compared to 200 and 250 bar while the difference between 200 and 250 bar was not obvious. In the pressure range of 100 to 300 bar to extract BTG oil, less than 1.5 wt% of extracts were obtained at 100 bar while the amount of extracts was 7.7-12.9 wt% at 200 bar and 14.4-16.7 wt% at 300 bar. It is concluded that the $scCO_2$ extraction of fast pyrolysis liquid is very low at low pressures below 200 bar. If high extraction yield is required, the pressure should be set above 200 bar which agrees with the previous result.

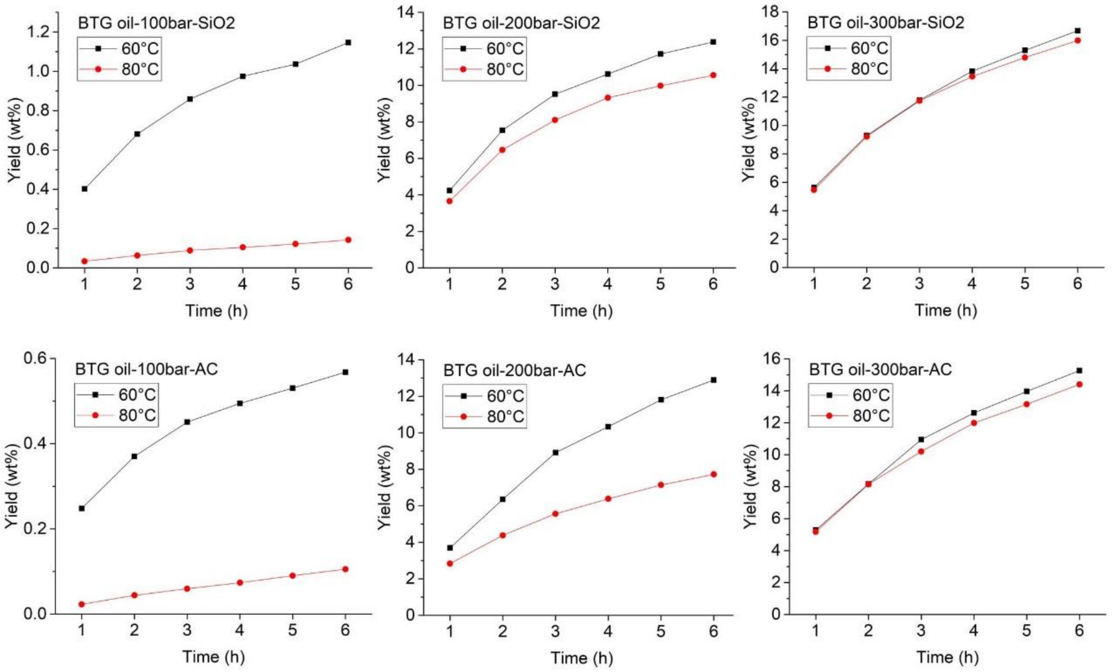


Figure 28: Influence of temperature on the $scCO_2$ extraction of BTG oil at different pressures (100, 200, 300 bar) and carriers (SiO_2 and AC).

4.2.3 Influence of temperature on the $scCO_2$ extraction processes

The influence of temperature on the $scCO_2$ extraction process is more difficult to explain than the pressure. The solubility of a compound and its extraction rate increases with increasing density while the density of $scCO_2$ is dependent on the pressure and temperature as depicted in Figure 29. High pressure and low temperature results in a high density. On the other hand, high temperature leads to lower density, however, it improves mass transfer and vapor pressure. At low pressures, the extraction rate decreases with the increase of temperature due to the decrease of fluid density. At high pressures, the extraction rate increases with the increase of temperature due to higher vapor pressure and mass transfer (BRUNNER, 2013). Figure 28 shows that at 100 bar, the extraction yield and extraction rate were much higher at 60 °C than at 80 °C. The influence of temperature was less pronounced when the pressure increased to 200 bar and could even be neglected when the pressure was further increased to 300 bar. In my experiments, the highest operation pressure was 300 bar so all the experiments were done below 300 bar. According to the theory and experimental data, extraction rate and extraction yield are higher at pressures higher than 300 bar at higher temperatures.

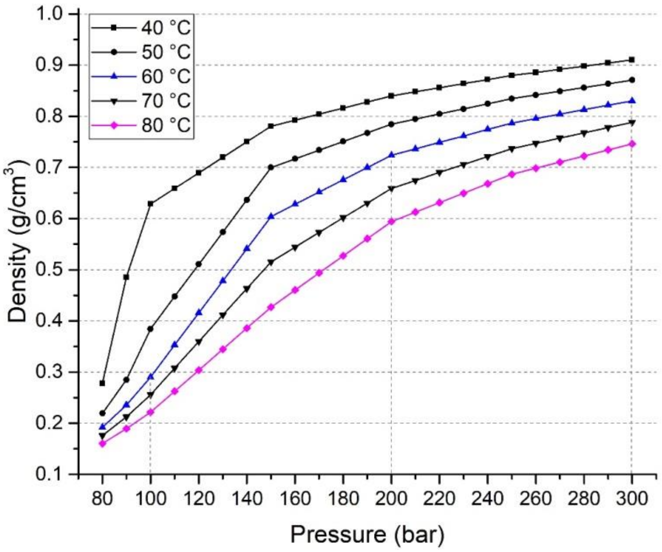


Figure 29: Density of $scCO_2$ at different temperatures and pressures.

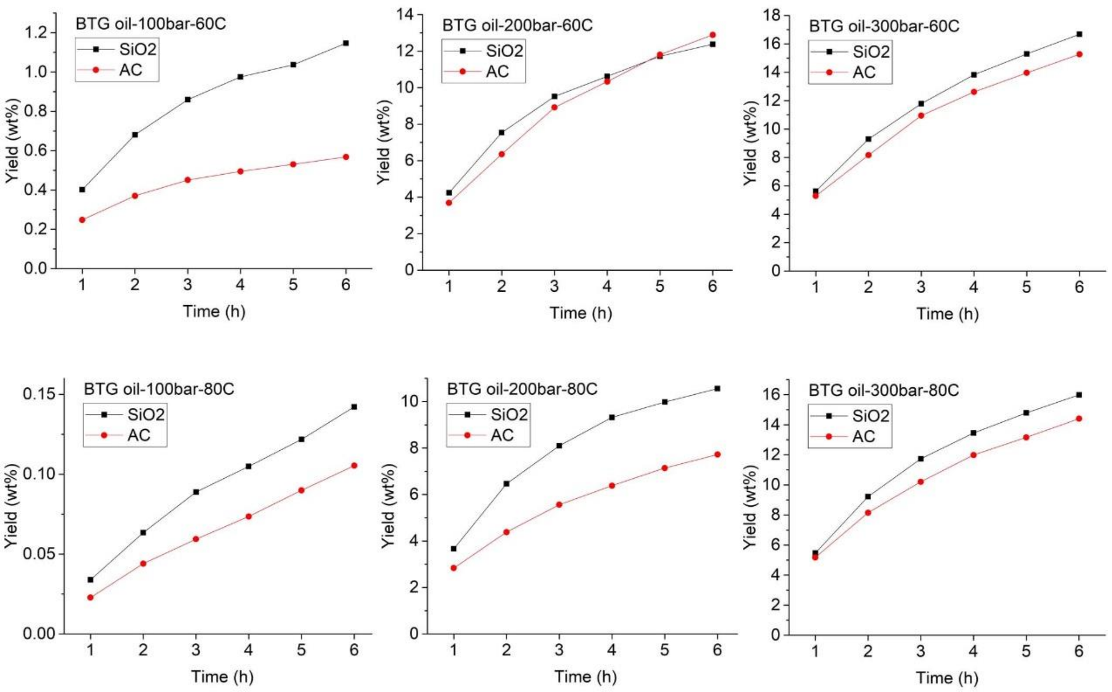


Figure 30: Influence of carrier on the scCO$_2$ extraction of BTG oil at different pressures (100, 200, 300 bar) and temperatures (60, 80 °C).

4.2.4 Influence of other parameters on the scCO$_2$ extraction processes

Carrier influences the extraction process through different mass transfer limitations. Porous carriers used to adsorb pyrolysis liquid in my experiments are SiO$_2$ and AC. There are many small channels in the carrier particles and the length of these channels determines mass transport. The transport rate of pyrolysis liquid in the solid carrier is the main factor to influence the mass transfer. The particle size can also influence mass transfer as small particles can hinder fluid flow in the fixed bed. Because pyrolysis liquid is a mixture of several hundreds of chemicals, they have different adsorption ability on the carrier. Selective extraction can be achieved by using different carriers. Figure 30 shows that SiO$_2$ as carrier always gave higher yields than AC. The influence of the carrier on the extraction rate and extraction yield at low pressures was more obvious than at high pressure. For SiO$_2$, two different SiO$_2$:oil ratios (100:40 and 100:80) were compared in the extraction of PF oil at 200 bar, as presented in Figure 31. The extraction rate with a loading ratio of 100:80 was much higher than that of 100:40. The total extraction yield for the 100:80 loading was 40.9 wt% while for the loading 100:40 it was only 23.4 wt%. Thus, higher loading ratio gave higher extraction yield but the loading ratio should be carefully controlled to make sure the pyrolysis liquid is completely adsorbed.

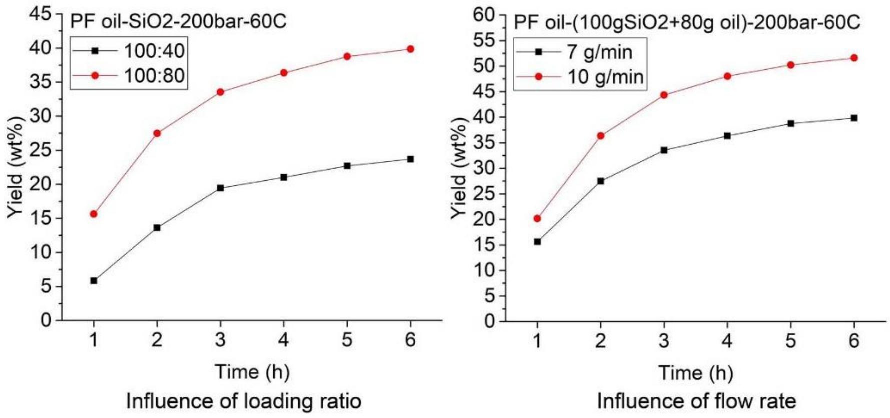


Figure 31: Influence of loading ratio and CO_2 flow rate on the $scCO_2$ extraction of PF oil, and BTG oil.

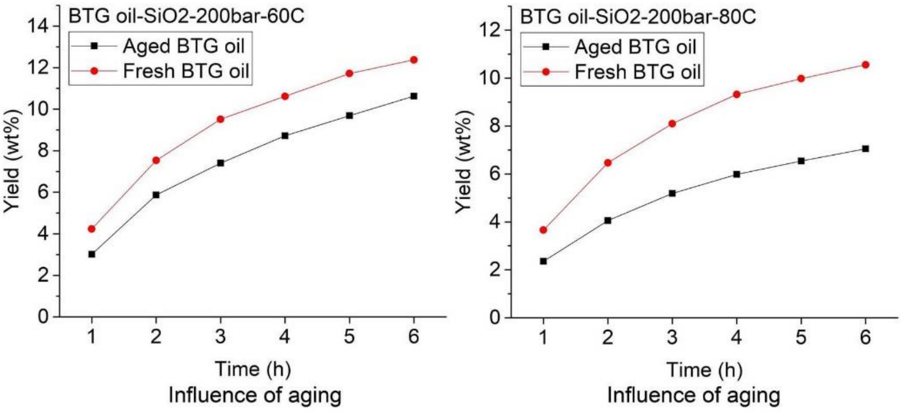


Figure 32: Influence of aging on the $scCO_2$ extraction of BTG oil at different temperatures (60, 80 °C).

Once pressure and temperature are selected, adjustment of the solvent ratio through controlling the flow rate is the most important factor to influence the extraction rate. Higher solvent ratios led to a higher extraction rate and extraction yield as demonstrated in Figure 31. A flow rate of 10 g/min gave a much higher extraction rate and a total yield of 51.6 wt% compared to a flow rate of 7 g/min with a yield of 39.8 wt%. However, higher solvent ratios cause higher capital and solvent cycling cost. In these experiments, the needle valve worked well at 7 g/min. When the flow rate was set to 10 g/min, dry ice was formed due to phase transformation in the needle valve which could cause a blockage. Thus, the flow rate of 7 g/min was set for most of the experiments.

The $scCO_2$ extraction of aged BTG oil was carried out at 200 bar with SiO_2 as carrier shown in Figure 32. The extraction yield of fresh BTG oil was around 2 wt% higher that of aged BTG oil. During aging, higher molecular compounds are formed due to polymerization along with the formation of some water, which are unfavorable to the $scCO_2$ extraction.

4.3 Composition of pyrolysis liquids and their $scCO_2$ extracts

4.3.1 Comparison of water content between pyrolysis liquid and $scCO_2$ extract

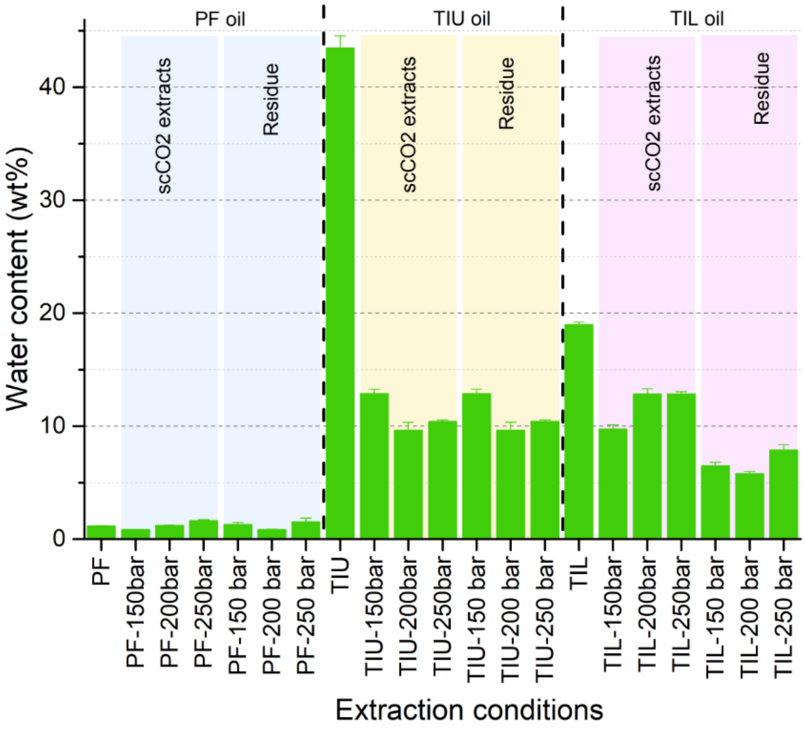


Figure 33: Water content of fixed pressure extraction at 150, 200, and 250 bar of PF, TI-U, and TI-L oil.

Fast pyrolysis liquid contains a certain amount of water which forms a single phase with other organic chemicals. In this study, the slow pyrolysis liquid PF oil contained a very small amount of water, around 1 wt% or less. For other fast pyrolysis liquids, the water content was: TI-U oil 43.4 wt%, TI-L oil 19.0 wt%, fresh BTG oil 25.4 wt%, aged BTG oil 28.0 wt%.

After a certain storage time, the upper phase of pyrolysis liquid contains a higher amount of water than the lower phase. The water content in aged pyrolysis liquid is higher than in fresh pyrolysis liquid.

Since PF oil contained 1.1 wt% of water, the water content in $scCO_2$ extracts and residue did not change much, as shown in Figure 33. The extraction process itself does not produce any water. The $scCO_2$ extraction efficiency of water is very low. Furthermore, the presence of water can decrease the solubility of organic chemical compounds in pyrolysis liquid. Due to the low content of water in PF oil, the extraction yield is much higher compared to other pyrolysis liquids containing more water. It has been proven that for the $scCO_2$ extraction of plant material such as paprika, the water content in the range of 7 to 17 wt% had no significant effect while above 18 wt% the extraction efficiency was largely decreased (NAGY, 2010). Therefore, if higher extraction yields are favored, the water content of pyrolysis liquid should be lowered.

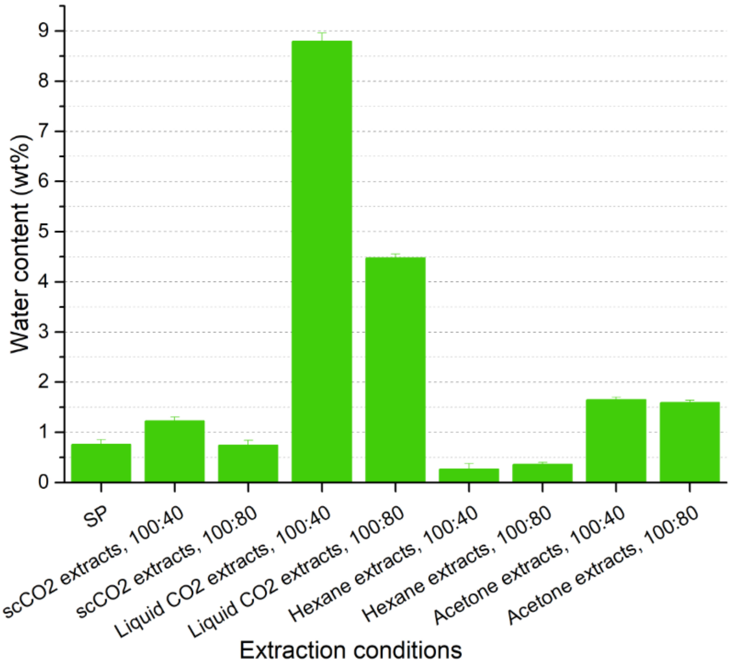


Figure 34: Water content of extracts obtained from $scCO_2$, liquid CO_2 and solvent extraction of PF oil.

The upper phase of fast pyrolysis liquid (TI-U oil) had a water content of 43.4 wt%. The water content of the $scCO_2$ extracts and the residue decreased to 14.4-19.4 wt% and 9.6-12.9 wt%, respectively. The lower phase of fast pyrolysis liquid (TI-L oil) had a lower water content of 19.0 wt% and it also decreased to 9.7-12.8 wt% in the $scCO_2$ extracts and to 5.8-7.9 wt% in the residue. It could be found that the water content in $scCO_2$ extracts decreased to one third or half of the original pyrolysis liquid. The residue also contained a certain amount of water but it was about 5 wt% lower than the $scCO_2$ extracts. During the $scCO_2$ extraction, water contained in bio-oil can be removed by several methods: it can be extracted with $scCO_2$, left in the residue, adsorbed on the carrier, evaporate with the off-gases, or react with other chemical compounds in pyrolysis liquid in the $scCO_2$ environment. The carrier used for $scCO_2$ extraction of PF and TI oils was SiO_2 which has a strong affinity for water. The residue was first washed with purified acetone and then the acetone was removed by rotary evaporation which could lead to some losses of water. In the literature, it was reported that water in pyrolysis liquids was removed to a large extent by $scCO_2$ extraction, from 46.8 wt% of the crude bio-oil to 2.5 wt% of the extracts (ROUT *et al.*, 2009). This is probably due to the extraction conditions and the carrier used to adsorb the bio-oil. A comparison of the water content of extracts from different extraction conditions is shown in Figure 34.

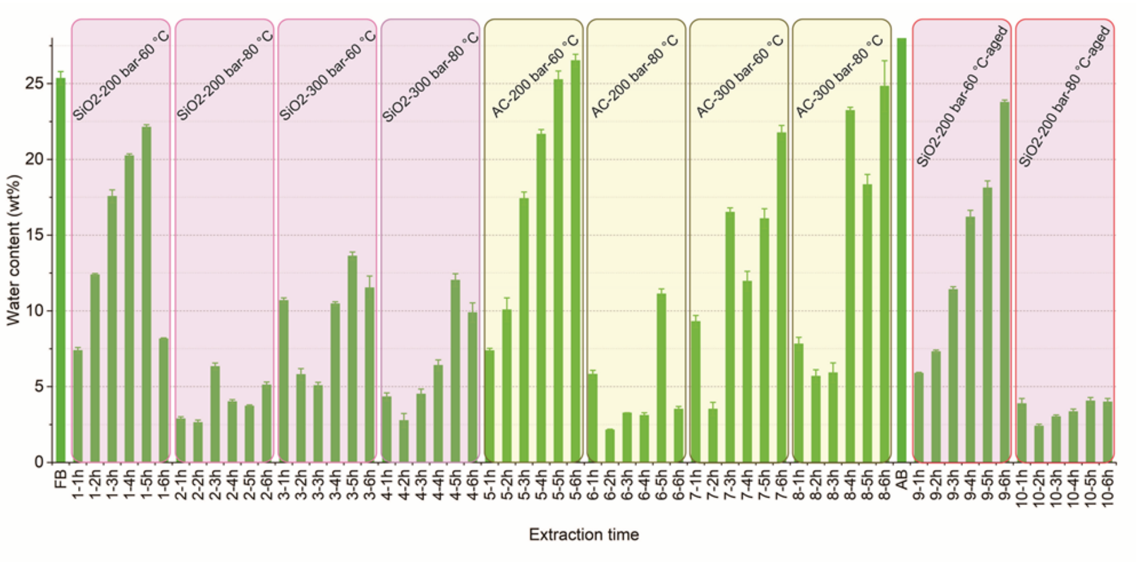


Figure 35: Water content sCO_2 extracts from BTG oil.

The extracts from the $scCO_2$ extraction of BTG oil were collected every hour so that the changes of the water content in the course of extraction could be monitored, results are presented in Figure 35. The water content of fresh and aged BTG oil was 25.4 wt% and 28.0 wt% respectively. Water still existed in the extracts although at a lower level. At 200 bar and 60 °C, the water content increased with the extraction time from ca. 7.4 wt% to ca. 26.5 wt% for all the monitored conditions. At 200 bar and 80 °C, the water content of the extracts did not change very much with time, namely only from 2.6 wt% to 6.3 wt%. At 300 bar, the water content of the extracts varied between 3.5 wt% and 24.8 wt% with extraction time without showing a clear trend. It is interesting to see that the water content of the extracts increased with the extraction time when a low pressure (200 bar) and a low temperature (60 °C) were applied. Still more work is needed to explore the mechanism of water removal from the extracts with the extraction time.

4.3.2 Comparison of organic chemicals in PF and TI oils and their scCO$_2$ extracts

The PF oil and TI oils are produced from beech wood and therefore they have many components in common. After the phase separation with the storage time, the property of upper phase and lower phase of TI oil is quite different. Besides the obvious difference in water content, the amount of compounds quantified by GC-MSD/FID for TI-U oil and TI-L oil was 53.7 wt% and 26.7 wt% on a dry basis, respectively. The amount of quantified compounds for PF oil was 51.0 wt%. Although the compounds present in PF oil and in the two phases of TI oil were similar but their amount differed significantly which is discussed in the following.

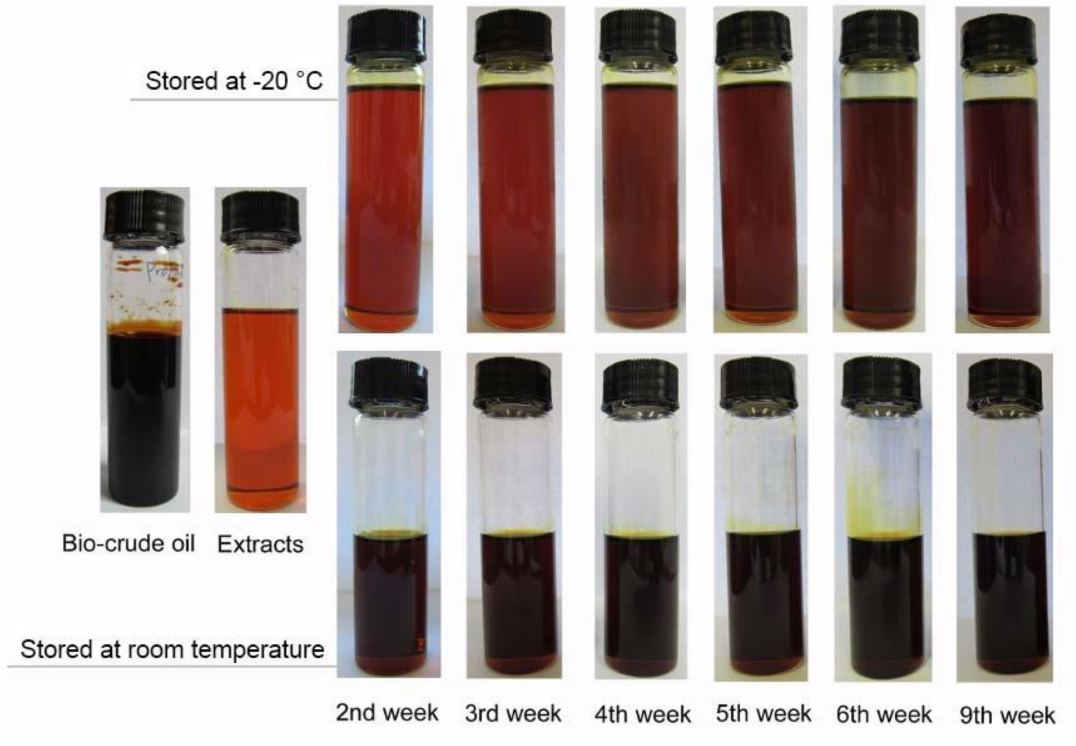


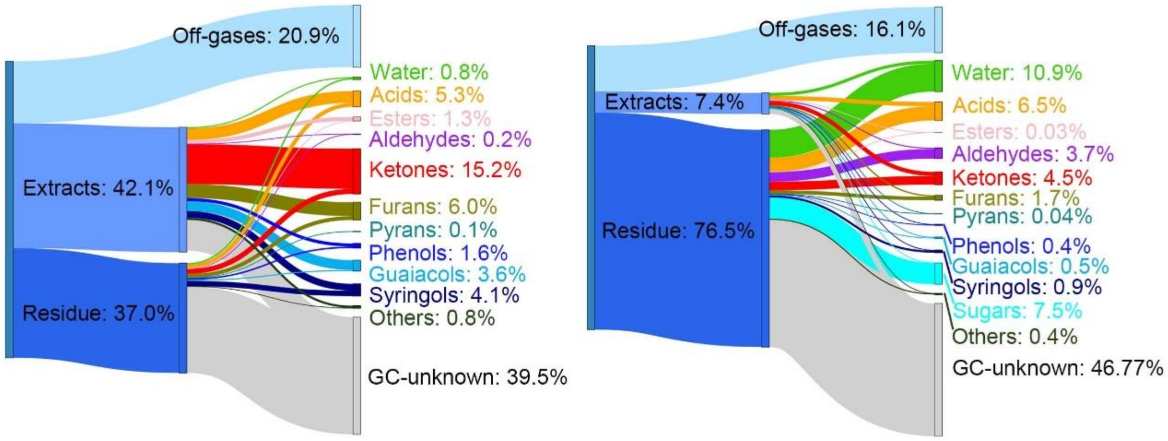
Figure 36: Photo of scCO$_2$ extracts from PF oil.

A photo of PF oil and scCO$_2$ extracts is shown in Figure 36. The full analysis of pyrolysis liquid composition is not possible at present. GC-MSD/FID is a useful tool to separate and identify chemical components in pyrolysis liquid providing both qualification and quantification information, although it cannot detect compounds with high boiling points or thermally unstable. In this study, the comparison of organic chemicals between crude pyrolysis liquid and the extracts is based on the GC-MSD/FID analysis. The composition of $scCO_2$ extracts and residue obtained at 150 bar from PF, TI-U and TI-L oils were analyzed in detail.

The organic chemicals detected in pyrolysis liquids in my study are divided into 12 groups: (1) Acids; (2) Esters; (3) Alcohols; (4) Aldehydes; (5) Ketones; (6) Furans; (7) Pyrans; (8) Phenols; (9) Guaiacols; (10) Syringols; (11) Sugars; (12) Others.

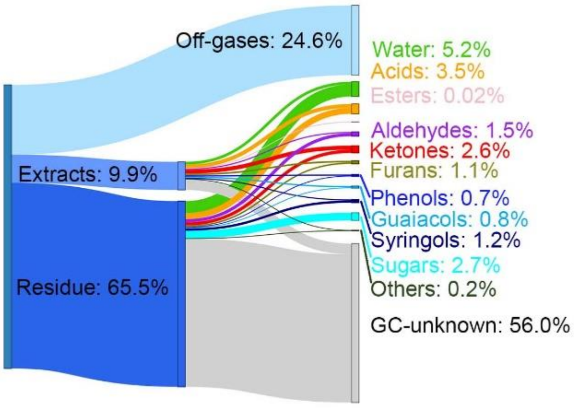
The composition of PF and TI oils and their $scCO_2$ extracts and residue at 150 bar were analyzed in detail with the results shown in Table 2 in a publication (FENG *et al.*, 2015). In order to get a better understanding of carbon balance, the content of chemicals was calculated on the water-free basis. The residue of PF oil, TI-U oil, and TI-L oil were analyzed by GPC for the molecular weight distribution and the results are shown in Figure 12 in a publication (FENG *et al.*, 2015). Due to the removal of water and light molecular weights compounds, the molecular distribution curves of TI oil residues moved to higher molecular weight. There is a strong peak at around 1500 g/mole for all the residues.

The distribution of chemical groups is shown in Figure 37, Figure 38, Figure 39, and Figure 40. The comparison of chemical groups between crude pyrolysis liquids and their $scCO_2$ extracts are discussed in the following paragraphs.



PF oil-150bar-(100g SiO2+80g oil)-60°C

TIU oil-150bar-(100g SiO2+80g oil)-60°C



TIL oil-150bar-(100g SiO2+80g oil)-60°C

Figure 37: Distribution of chemical groups for scCO$_2$ extraction of PF, TI-U, and TI-L oils.

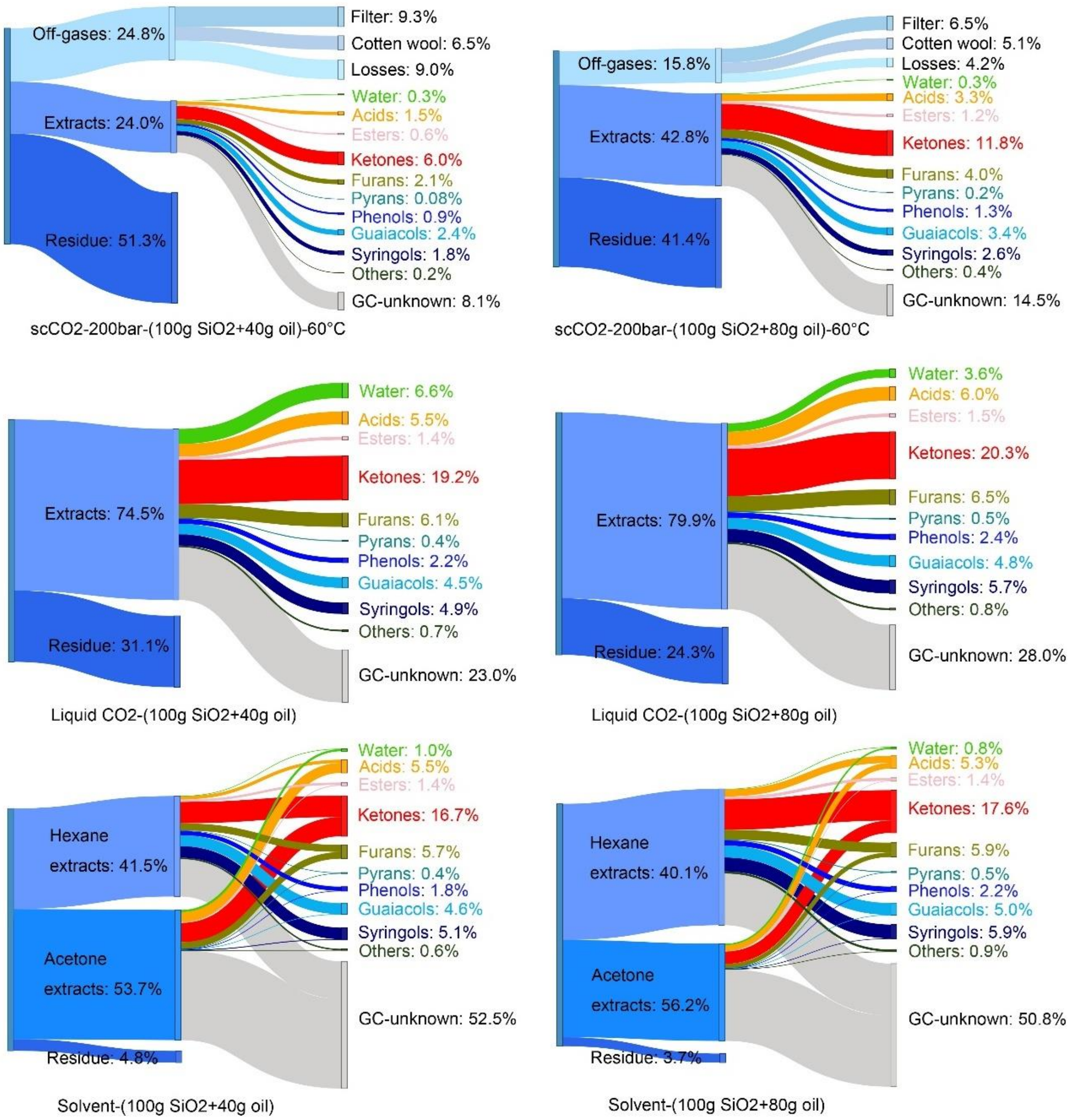
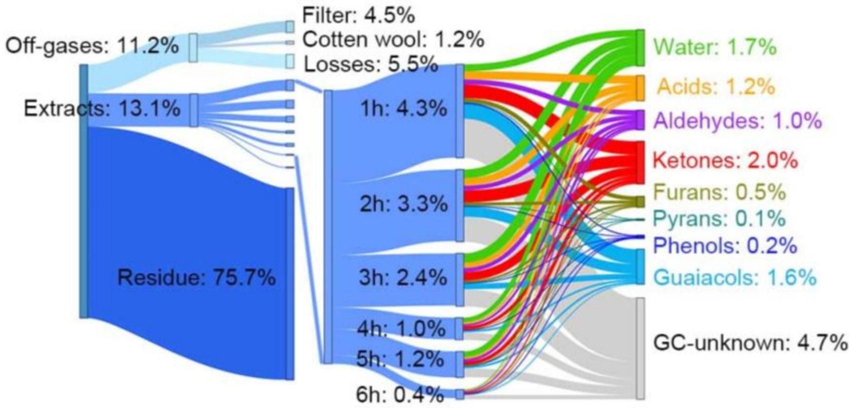
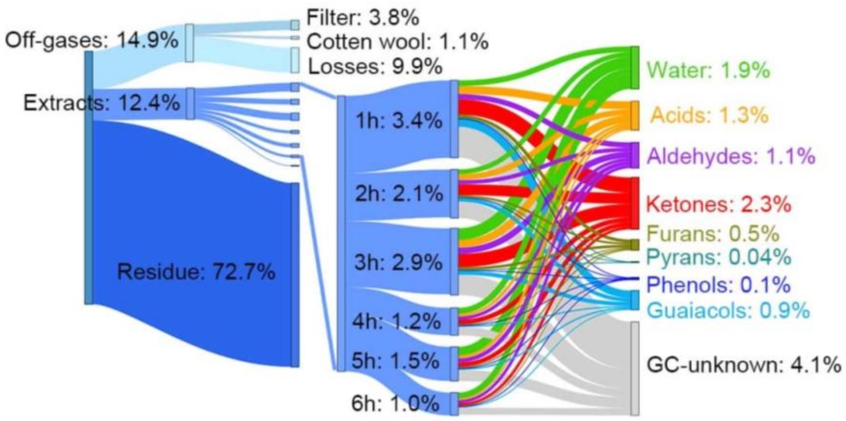


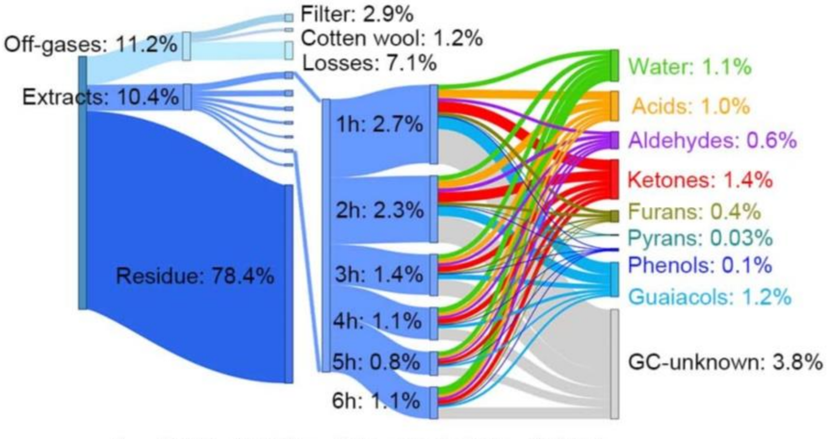
Figure 38: Distribution of chemical groups for different extraction methods of PF oil.



Fresh BTG oil-200bar-(100g SiO2+100g oil)-60°C

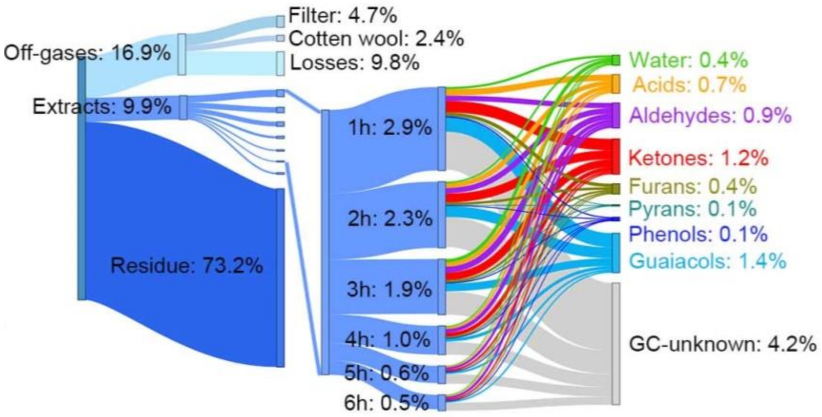


Fresh BTG oil-200bar-(100g AC+100g oil)-60°C

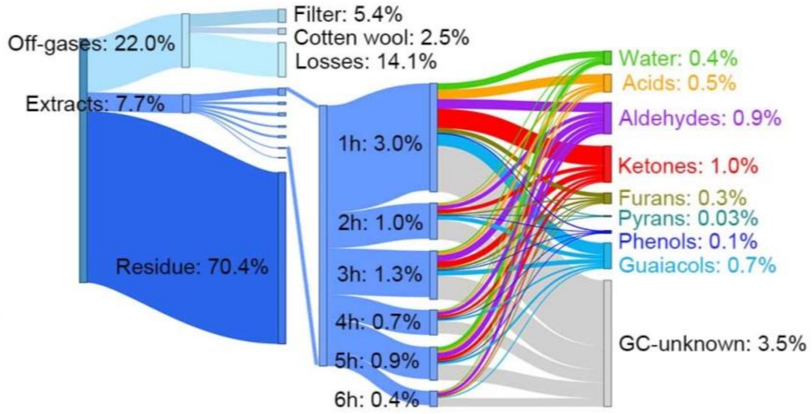


Aged BTG oil-200bar-(100g SiO2+100g oil)-60°C

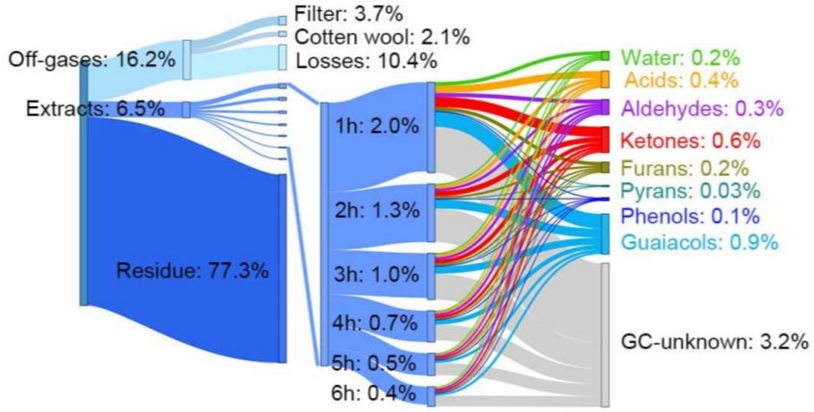
Figure 39: Distribution of chemical groups for $scCO_2$ extraction of BTG oil and progression with time at 60 °C.



Fresh BTG oil-200bar-(100g SiO2+100g oil)-80°C



Fresh BTG oil-200bar-(100g AC+100g oil)-80°C



Aged BTG oil-200bar-(100g SiO2+100g oil)-80°C

Figure 40: Distribution of chemicals groups for $scCO_2$ extraction of BTG oil and progression with time at 80 °C.

Acids are the most abundant chemicals in pyrolysis liquid. They are useful platform chemicals but lead to handling difficulties when present in pyrolysis liquid. Therefore, they are preferred to be extracted with organic solvents (MAHFUD *et al.*, 2008, RASRENDRA *et al.*, 2011, TEELLA *et al.*, 2011). PF oil had already been extracted for the commercial production of acetic acid. The acids content in PF oil was as low as 6.5 wt% while TI-U oil contained 17.2 wt%, TI-L oil contained 8.9 wt%. The acids are mainly in the form of aliphatic and fatty acids with different carbon numbers, such as formic acid, acetic acid, propionic acid, butyric acid. Butenoic acid was also detected in pyrolysis liquids. Among all the acids, acetic acid is the major acid in fast pyrolysis liquid with 15.1 wt% in TI-U oil and 7.3 wt% in TI-L oil, following by propionic acid with 2.0 wt% in TI-U oil and 1.4 wt% in TI-L oil. The acids in PF oil were mainly contributed by propionic acid with the amount of 3.9 wt%. Acids can be effectively enriched in the $scCO_2$ extracts.

Esters are present in low quantities in pyrolysis liquids. In crude pyrolysis liquids, they were not quantified due to their trace amount. In the $scCO_2$ extracts, 0.2 wt% of propanoic acid ethenyl ester was identified in the extracts from both TI-U and TI-L oil. In the $scCO_2$ extracts of PF oil, four esters were identified: 2-oxopropanoic acid methyl ester, furoic acid methyl ester, propionic acid ethenyl ester, and 4-oxopentanoic acid methyl ester. Their total amount was 3.2 wt% showing a good extraction effect of esters.

Alcohols were detected in very small amounts in pyrolysis liquids used in this study. The only alcohol found in pyrolysis liquids was ethylene glycol from TI-U oil and its residue with the amount of 0.6 wt% and 0.5 wt% respectively. According to the amount of ethylene glycol, the extraction effect of alcohol with $scCO_2$ is not obvious.

Aldehydes in pyrolysis liquids exist mainly in the form of 2-hydroxylacetaldehyde and 3-hydroxypropionadehyde. 2-Hydroxylacetaldehyde was not found in PF oil but with a high amount in fast pyrolysis liquids, 6.8 wt% in TI-U oil and 1.9 wt% in TI-L oil. The enrichment effect of 2-hydroxylacetaldehyde was not obvious and its content in $scCO_2$ extracts even decreased to 3.7 wt% for TI-U oil. The content of 3-hydroxypropionadehyde was 0.2 wt% in PF oil and the $scCO_2$ extraction showed no enrichment effect. Its content in TI oils was higher, 0.8 wt% in TI-U oil and 0.4 wt% in TI-L oil, which could be enriched to 1.9 wt% and 1.3 wt% in the $scCO_2$ extracts. Some benzaldehydes were found in the $scCO_2$ extracts of TI-L oil such as 2-hydroxybenzaldehyde, 2-hydroxy-5-methoxybenzaldehyde, 3-hydroxy-4-methylbenzaldehyde. Aldehydes were considered as the most sensitive substances present in the liquid products produced from wood distillation. They could not be readily separated by any process of fractional distillation (KLAR, 1925). They easily react with other chemicals to form aldehyde-resin during storage. The low content of aldehydes in PF oil is one of the factors that make it much more stable than TI oil.

Ketones are other abundant chemicals besides acids in pyrolysis liquid and many of them can be identified by GC-MSD/FID. Ketones in pyrolysis liquid exist mainly in two types: (1) aliphatic ketones, such as propanone, butanone and their derivatives; (2) cyclopentenone and its derivatives. Their total content in PF oil was 22.2 wt%. Acetol and 1-acetyloxy-propan-2-one are the main ketones which account for 5.6 wt% and 6.0 wt%, respectively. In TI oils, the content of ketones was 11.3 wt% for TI-U oil and 5.7 wt% for TI-L oil. The highest single ketone was acetol which was 8.2 wt% for TI-U oil and 3.4 wt% for TI-L oil. Most of the ketones were enriched in the $scCO_2$ extracts. The enrichment coefficient of some typical ketones is discussed in the following chapter.

Furans in the form of various derivatives were identified in the pyrolysis liquids. They are mainly products from depolymerization of cellulose. The structure of furan is similar to ether but its properties are more like those of benzene. Furans in pyrolysis liquids are mainly furaldehydes and furanones. The total amount of furans was found 8.1 wt% in PF oil, 2.9 wt% in TI-U oil, and 1.9 wt% in TI-L oil. Higher amount of furans were found in PF oil, indicating that more furans were formed during the slow pyrolysis process. 2-Furanldehyde has the highest content amongst the other furans, 3.8 wt% in PF oil and 5.4 wt% in its $scCO_2$ extracts, 0.8 wt% in TI-U oil and 2.6 wt% in its $scCO_2$ extracts, 0.9 wt% in TI-L oil and 2.6 wt% in its $scCO_2$ extracts. The contents of other furans are less than 1 wt% but most of them can be enriched in $scCO_2$ extracts.

Pyrans are other heterocyclic groups present in pyrolysis liquids. Unlike furans, pyrans were present in very low concentrations mainly in the form of maltol. Maltol was found in a concentration of 0.3 wt% in the residue of PF oil. Another pyran, 3-hydroxy-5,6-dihydro-pyran-4*H*-4-one was found in a concentration of 0.1 wt% in TI-U oil and its extracts and residue. Maltol is used as a flavor enhancer in cakes and bread. It can be extracted from pyrolysis liquid or wood tar. In terms of maltol production from pyrolysis liquid, biomass that contains a high amount of maltol has to be used as feedstock, such as the bark of larch tree or pine needles.

Phenols are present in all kinds of pyrolysis liquids. The aromatic compounds in pyrolysis liquids are derived from lignin and comprise phenols, guaiacols, syringols, and polycyclic aromatics. Phenols, especially monomeric phenols are considered to be valuable chemicals from lignin. They are used for the synthesis of phenol formaldehyde resin. One research topic is to convert lignin into phenols by hydrocracking (STRÜVEN *et al.*, 2016). Phenols in pyrolysis liquid are mainly present in the form of phenol, methyl phenol, and dimethyl phenol. Phenol was present in a low concentration in pyrolysis liquids (<1 wt%). The total amount of phenolic compounds was 2.0 wt% in PF oil, 0.6 wt% in TI-U oil and 0.9 wt% in TI-L oil. All these identified phenols were enriched in the $scCO_2$ extracts.

Guaiacols are other aromatic chemicals present in pyrolysis liquid either from hardwood or softwood. Guaiacol has more derivatives than phenol, i.e. when the hydrogen in the aromatic ring at the third or fourth position is substituted by methyl, ethyl, propyl or propenyl groups. The total amount of guaiacols was 5.1 wt% in PF oil, 0.7 wt% in TI-U oil, and 1.2 wt% in TI-L oil. 2-Methoxyphenol has the highest content among different derivatives of guaiacols. Vanillin, as a guaiacyl aldehyde, is commonly used as a flavoring agent. Vanillin was found in TI-U oil and TI-L oil with a content of 0.2 wt% and almost the same content in the $scCO_2$ extracts.

Syringols are only present in pyrolysis liquids produced from hardwood. Similar to guaiacols, the hydrogen in syringol aromatic ring at the fourth position is substituted by methyl, ethyl, propyl or propenyl groups, resulting in various derivatives. The total amount of syringols was 6.0 wt% in PF oil, 1.3 wt% in TI-U oil, and 1.6 wt% in TI-L oil. Like other aromatics, syringols could be found in $scCO_2$ extract but the enrichment effect was not obvious. Both guaiacol and syringol are important components in liquid smoke while guaiacol contributes mainly to the taste and syringol is mainly responsible for the smoky aroma. Therefore, the extraction of aromatic compounds from pyrolysis liquid is important for different reasons. The evaluation of $scCO_2$ extraction of aromatic compounds is needed due to the importance of this group compounds. The lower phase of fast pyrolysis liquid contains a higher content of aromatic compounds than the upper phase. It indicates that during the storage, more aromatic compounds are present in the lower phase of pyrolysis liquid. The tarry, lower phase is mainly composed of high molecular weight aromatics.

Sugars in pyrolysis liquid are mainly present in the form of andydrofuranoses and anhydropyranoses. PF oil contains no sugar due to the pre-treatment process. In crude fast pyrolysis liquids, the content of levoglucosan reached to 9.9 wt% in TI-U oil and 2.7 wt% in TI-L oil. Levoglucosan and acetic acid are the most abundant single compounds present in fast pyrolysis liquids. Levoglucosan is water soluble. Its content in the upper oil phase which contains more water is much higher than in the lower tarry phase. All the sugars could not be extracted with $scCO_2$ and they were left in the residue. In terms of sugar separation, $scCO_2$ is an effective method to get rid of sugars in the pyrolysis liquid.

4.4 Extraction efficiency and enrichment coefficient of main chemicals

Pyrolysis liquid contains large amount of different chemicals. Most of them are in low concentrations but can be extracted or enriched with different extraction methods. For pyrolysis liquids used in the thesis, i.e. PF oil, TI oils, and BTG oil, 21 primary chemicals including water were analyzed for the extraction efficiency and enrichment coefficient. The experiments used for data analysis included three parts: (1) preliminary study of $scCO_2$ extraction of PF oil, TI-U oil, and TI-L oil, shown in Figure 41; (2) different extraction methods of PF oil, shown in Figure 42; (3) extracts collected every hour from $scCO_2$ extraction of BTG oil. For the first part, the residue was also recovered and analyzed by GC-MSD/FID, therefore the distribution coefficient was additionally calculated. For the other two parts, only the crude pyrolysis liquids and extracts were analyzed by GC-MSD/FID, therefore the analysis was focused on the calculation of extraction efficiency and enrichment coefficient.

Extraction efficiency is an important factor to evaluate different extraction processes. In ideal cases, it varies from 0% to 100%, where 0% means that a chemical cannot be extracted, and 100% means that a chemical can be completely extracted. It is calculated based on the concentration of one chemical and the extraction yield. It needs to be demonstrated that there could be deviations for the extraction yield of different extraction methods. The extraction yield is relatively stable for $scCO_2$ extraction. But for the liquid CO_2 extraction, the yield could be much higher than the actual yield. The dry ice used in the liquid CO_2 extraction condenses the water from the environment during sample preparation and the extraction process. Since the sample size was small, the water condensed from the air and significantly raised the extraction yield, resulting in an extraction efficiency value over 100%. For solvent extraction, the solvent was rotary evaporated in order to recover the extracts. But the solvent mixed with the extracts could not be completely evaporated. In the meantime, some chemicals in the extracts were lost together with the solvents. The enrichment coefficient is dependent on the concentration of a chemical in crude pyrolysis liquid and extracts. When enrichment coefficient of one chemical equals 1, this chemical cannot be enriched in the extracts but remains in the same concentration as in the crude pyrolysis liquid. The higher the enrichment coefficient, the higher is the concentration of a component in the $scCO_2$ extract.

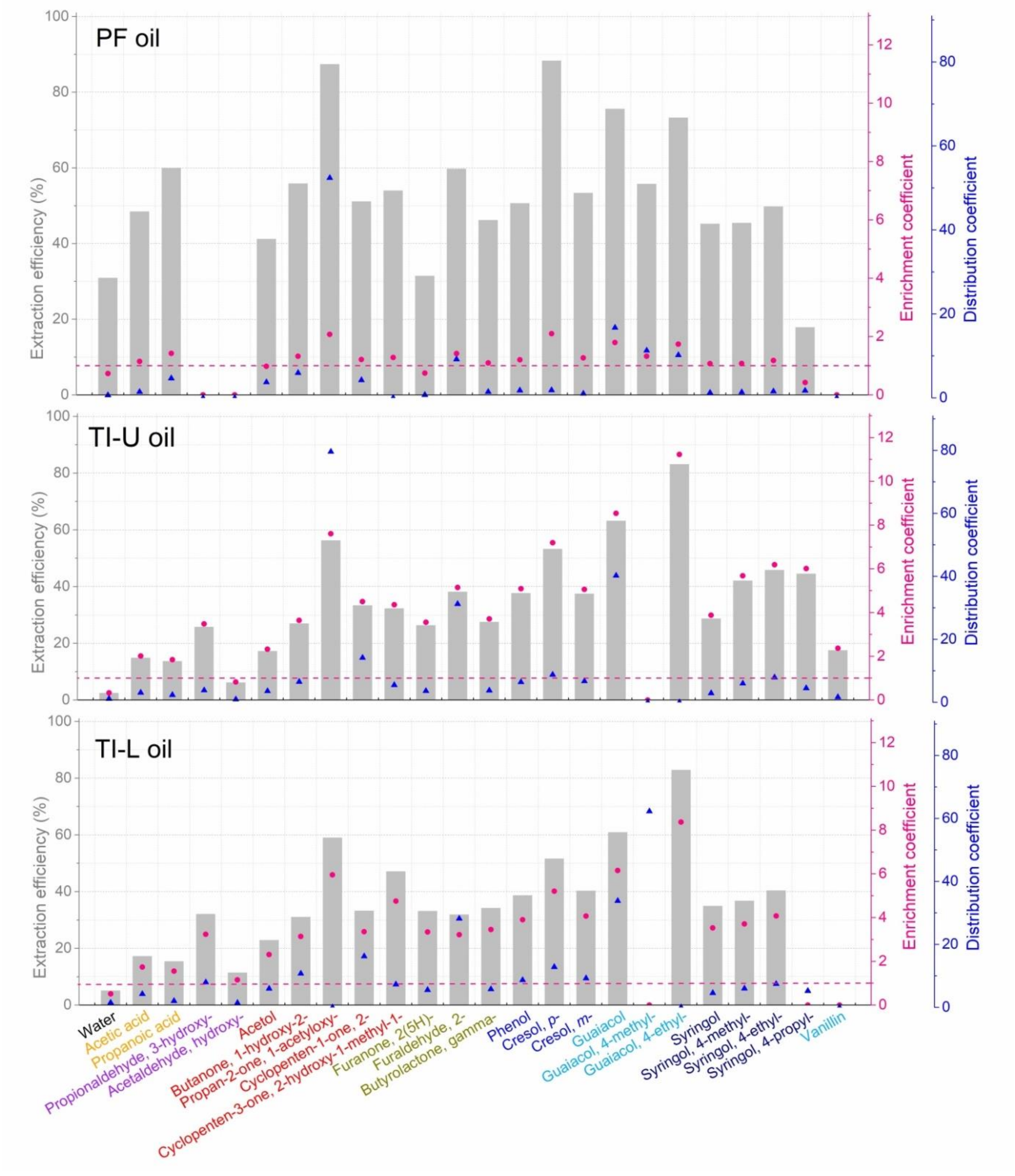


Figure 41: Extraction efficiency and enrichment coefficient of $scCO_2$ extraction of PF, TI-U and TI-L oil.

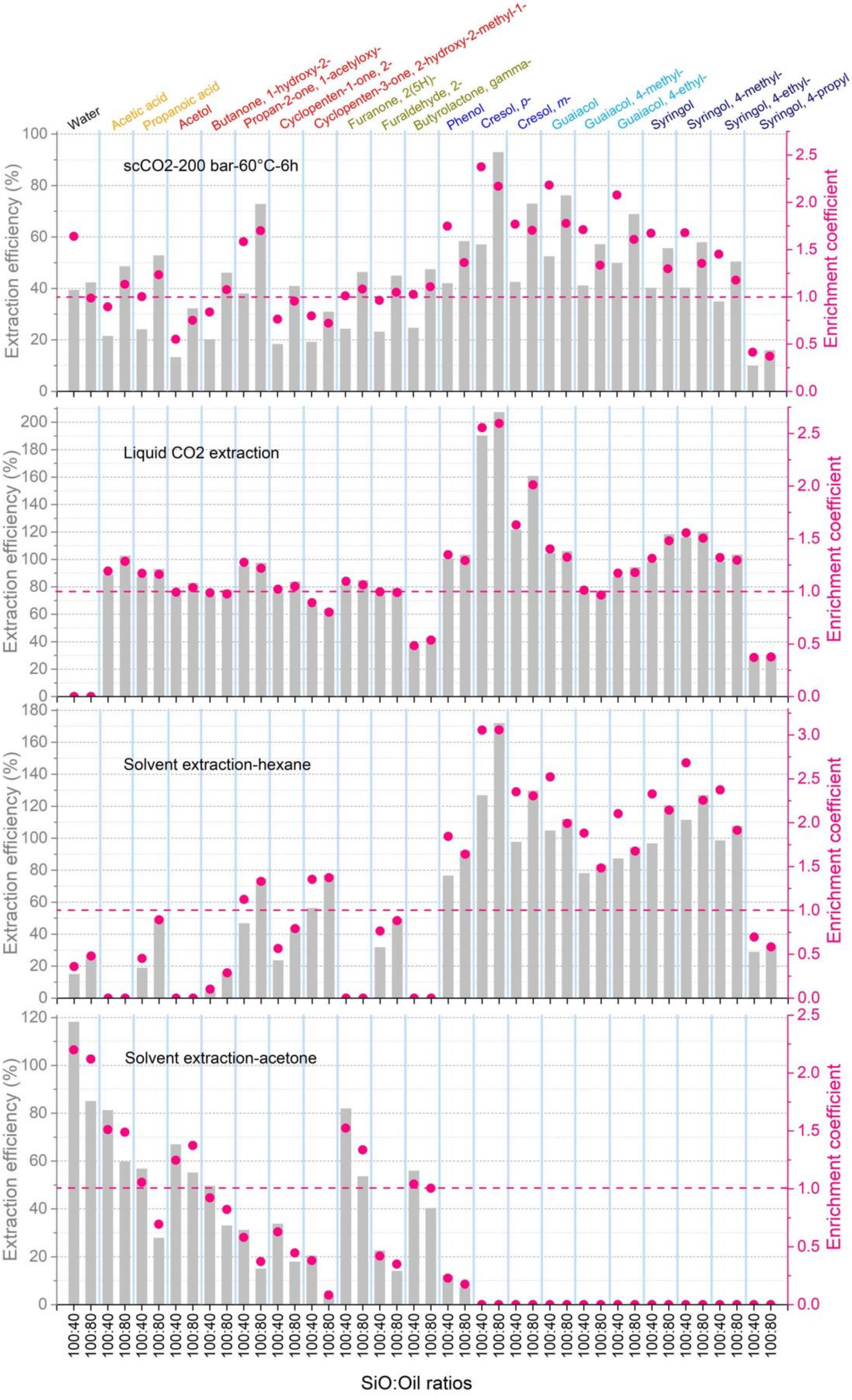


Figure 42: Extraction efficiency and enrichment coefficient of different methods with PF oil.

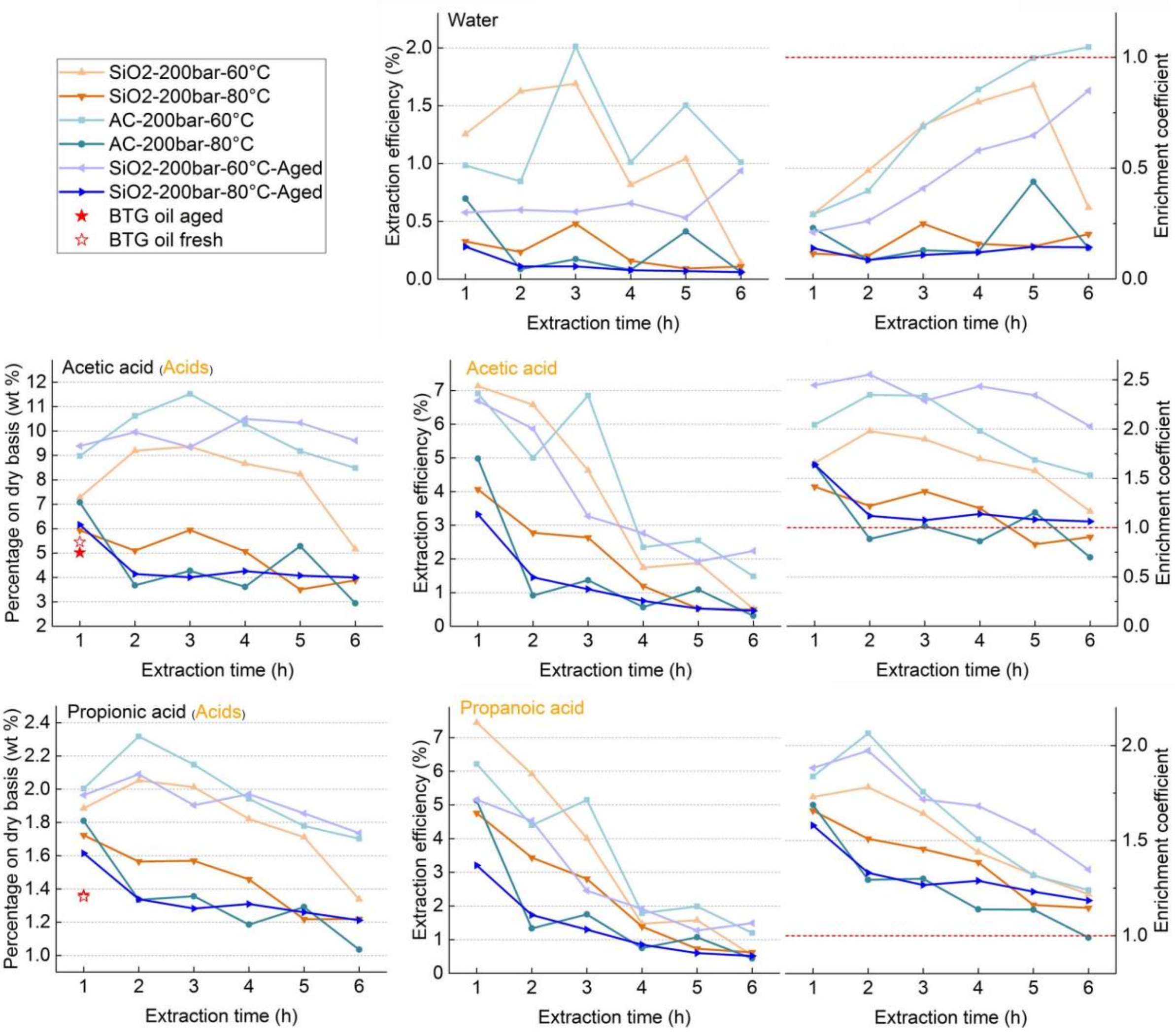


Figure 43: Extraction efficiency and enrichment coefficient of water and acids from BTG oil.

4.4.1 Water

Water is the only inorganic liquid present in pyrolysis liquids which has a negative influence on the extraction of organic chemicals during $scCO_2$ extraction. The concentration of water in crude pyrolysis liquid and extracts was discussed in the previous chapter with the result that water could not be effectively extracted with CO_2. Extraction coefficient shows that only 2.5% and 5.1% could be extracted from TI-U and TI-L oil.

Liquid CO_2 extraction of water from PF oil was not evaluated as it condensed much water from the air. The hexane extraction of water showed an efficiency of 27.0% but acetone extraction efficiency was high of 85.0% due to the polarity properties of the solvents.

For BTG oil, the total water extraction efficiency ranged from 0.7% to 7.4% under different extraction conditions as shown in Figure 43. Extraction efficiency was higher at lower temperature. The enrichment coefficient of water at low temperature increased with the extraction time but was below 1, especially for the first three hours at high temperature it was lower than 0.3. This provides an alternative to reduce the water content in pyrolysis liquids. As a polar solvent, scCO_2 has a poor extraction efficiency of water. Furthermore, SiO_2 as the carrier can adsorb certain amount of water that could not be extracted with scCO_2.

4.4.2 Acids

Acetic acid is one of the main components in pyrolysis liquids with concentrations over 10 wt% depending on the feedstock and process conditions. Its content in PF oil was around 1.3 wt% which was much lower than in normal pyrolysis liquid. Even with such a low content, the scCO_2 extraction efficiency of acetic acid from PF oil could reach 48.4% at 150 bar. This was much higher compared to TI oils which gave 14.9% for the upper phase and 17.3% for the lower phase. Propionic acid is also present in almost all pyrolysis liquids although not in such a high content as acetic acid. Their contents in PF, TI-U and TI-L oils were 3.9 wt%, 2.0 wt%, and 1.4 wt%, respectively. The scCO_2 extraction efficiency of propionic acid from PF oil was 60.0% while from TI-U and TI-L oil they were 13.7% and 15.4%. The extraction efficiency of acids from PF oil was much higher than from TI oil which is due to high extraction yield of PF oil. However, the enrichment coefficient of TI oil was slightly higher than from PF oil. The enrichment coefficient of acids from PF oils was in the range of 1.1-1.4 while from TI oil it was 1.6-2.0. The low enrichment coefficients show that acids can only be slightly enriched in scCO_2 extracts. The effect is even better when fast pyrolysis liquids are used. The distribution coefficient of acids in PF oil and TI oils was in the range of 1.5-4.7 and 2.0-4.3.

Liquid CO_2 and solvent extraction of acids from PF oil also showed on the one hand a high extraction efficiency but on the other hand a low enrichment coefficient. For both scCO_2 and liquid CO_2 extractions, a higher oil loading ratio led to a higher extraction efficiency. The extraction efficiency of acetic acid with liquid CO_2 was 102.6% due to the condensed water in the extract, making the extraction yield higher than the true value. Acetic acid cannot be extracted with hexane as it is insoluble in hexane but it can be extracted with acetone with a maximum extraction efficiency of 81.2%. Different from acetic acid which could not be extracted with hexane, 17.8% and 56.7% of propionic acid was extracted with hexane with a SiO_2:oil ratio of 100:40 and 100:80. The rest could be further extracted with acetone. The enrichment coefficient of acids from PF oil with different extraction methods was between 0.5 and 1.5. It indicates that large amount of acids were extracted from PF oil but the concentration in the extracts did not increase much.

The extraction efficiency of acetic acid from BTG oil by continuous $scCO_2$ extraction was in the range of 0.3-7.1% with a maximum after the first hour of the six hours run as shown in Figure 43. Then it decreased quickly with extraction time to 0.3%. The decrease of extraction efficiency is mainly due to the decrease of extraction yield while the enrichment coefficient was stable during the whole extraction process. Fewer extracts were obtained with longer extraction times but the concentration of acetic acid in the $scCO_2$ extracts collected each hour did not change significantly. Temperature was the most important factor to influence the extraction effect of acetic acid. Both extraction efficiency and enrichment coefficient at low temperature were higher than at high temperature. At 80 °C, the enrichment coefficient was around 1.0 or even less, showing that acetic acid had similar or lower concentration in the $scCO_2$ extracts than the original BTG oil. Acetic acid was always enriched in the extracts at 60 °C with an enrichment coefficient of 1.2 to 2.6. The influence of other parameters such as carrier and aging was not significant. The extraction profile of propionic acid from BTG oil in the six hours run was similar to acetic acid. Unlike acetic acid, the concentration of propionic acid in the extracts decreased slightly with time and the enrichment coefficient decreased accordingly from 2.1 to 1.0. The main extraction was finished after four hours.

The $scCO_2$ extraction efficiency of acids from PF oil reached more than 50 wt% but for fast pyrolysis liquid containing certain amount of water, the value was below 26 wt%. The enrichment coefficient of acetic acid and propionic acid from different pyrolysis liquids with different methods was in the range of 0.7 to 2.6. Hence, acids can be enriched in the extracts but with a limited enrichment effect. Low temperature, high oil loading ratio, and short extraction time lead to a high enrichment coefficient of acids in the $scCO_2$ extracts.

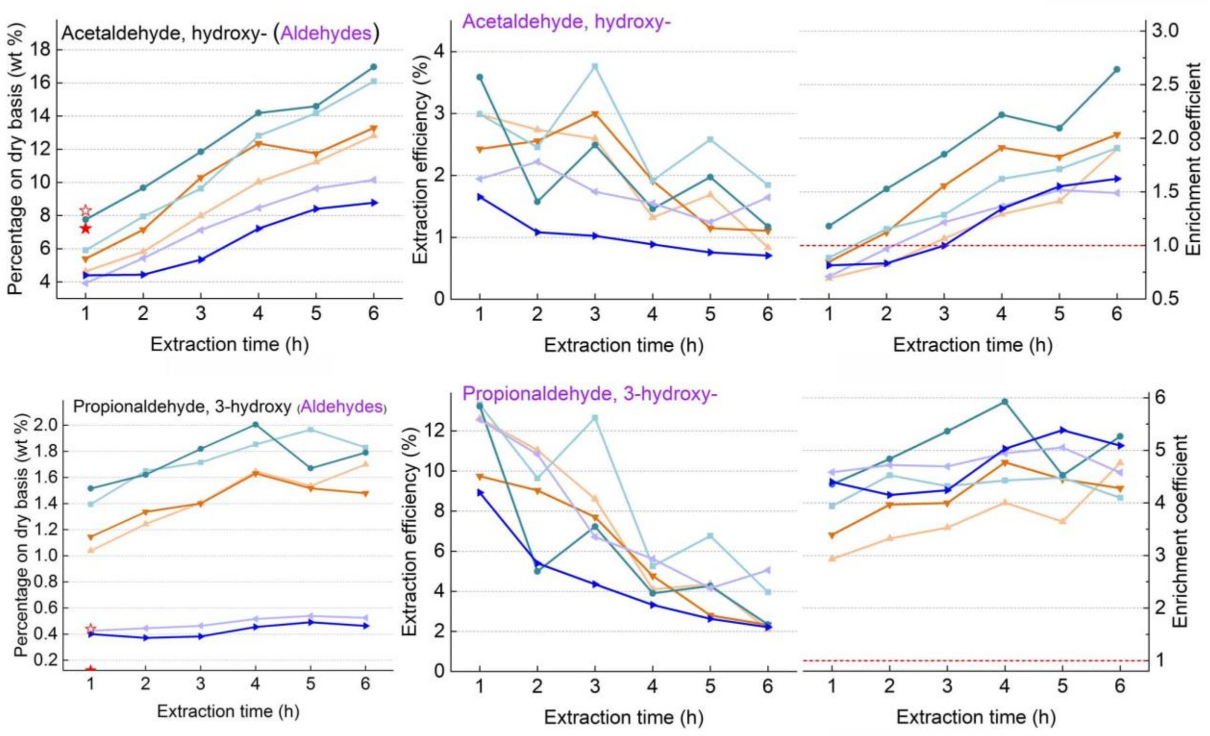


Figure 44: Extraction efficiency and enrichment coefficient of aldehydes from BTG oil.

4.4.3 Aldehydes

Aldehydes selected for the analysis were hydroxyacetaldehyde and 3-hydroxypropionaldehyde. Due to their low contents in PF oil (< 0.2 wt%), aldehydes were only analyzed for TI oil and BTG oils. Hydroxyacetaldehyde had a high content in TI-U oil (6.8 wt%), while TI-L oil had 1.9 wt%. The enrichment coefficient of hydroxyacetaldehyde was 0.8 and 1.2 for TI-U and TI-L oil, respectively. Despite of the high content in the upper phase of TI oil, hydroxyacetaldehyde could not be enriched in the scCO$_2$ extracts with the distribution coefficient of 0.9. It was slightly enriched in the extraction of the lower phase with the distribution coefficient of 1.4. The low enrichment coefficient resulted in a low extraction efficiency of 6.1% for the upper phase and 11.4% for the lower phase. Another aldehyde, 3-hydroxypropionaldehyde had a low content of 0.9 wt% in TI-U oil and 0.4 wt% in TI-L oil but showed a much higher enrichment coefficient of 3.5 and 3.2, respectively. The extraction efficiency of 3-hydroxypropionaldehyde reached 25.8% for TI-U oil and 32.1% for TI-L oil. The distribution coefficient reached 3.8 for TI-U oil and 8.0 for TI-U oil. The enrichment coefficient of 3-hydroxypropionaldehyde from the two phases of TI oil was similar to each other although the water content of the two phases was totally different. It can be concluded that the water influence on the $scCO_2$ extraction of 3-hydroxypropionaldehyde is not significant.

The content of hydroxyacetaldehyde and 3-hydroxypropinaldehyde in fresh BTG oil was 6.2 wt% and 0.3 wt% respectively with an enrichment coefficients in the range of 0.7-2.6 and 2.9-5.9 under different conditions as shown in Figure 44. The extraction efficiency of hydroxyacetaldehyde was in the range of 6.1-15.6% and for 3-hydroxypropinaldehyde it was in the range of 26.8-51.6%. Since small aldehydes molecules with few carbons atoms are better soluble in $scCO_2$, the lower enrichment coefficient of hydroxyacetaldehyde could be due to the carrier. The carrier might have more adsorption ability for small aldehydes. The enrichment coefficient of hydroxyacetaldehyde was below 1 in the first hour meaning that its concentration in the $scCO_2$ extracts was even lower than in the original BTG oil. The enrichment coefficient of both aldehydes in the $scCO_2$ extracts increased with the extraction time. It reached to 2.6 for hydroxyacetaldehyde and 5.3 for 3-hydroxypropinaldehyde after sixth hours. The increase of hydroxyacetaldehyde concentration with the time is probably due to the bio-oil carrier which determines diffusion. Although aldehydes are very soluble in $scCO_2$, their initial concentrations in the extracts are low because they are restrained in the carrier. With the extraction time, more hydroxyacetaldehyde diffuses from the carrier, leading to a concentration increase in the extracts. That AC as carrier had an obviously higher enrichment coefficient than SiO_2 and confirmed this deduction. The influence of other parameters such as temperature and aging was not significant.

For aldehydes, less 3-Hydroxypropinaldehyde than hydroxyacetaldehyde was present in the pyrolysis liquids, but better enriched in the $scCO_2$ extracts. The enrichment coefficient of aldehydes increased with extraction time. The carrier types were the most important factor to influence the enrichment effect. By using fresh pyrolysis liquids, longer extraction times, high temperatures or AC as carrier, more aldehydes can be extracted from the crude pyrolysis liquids.

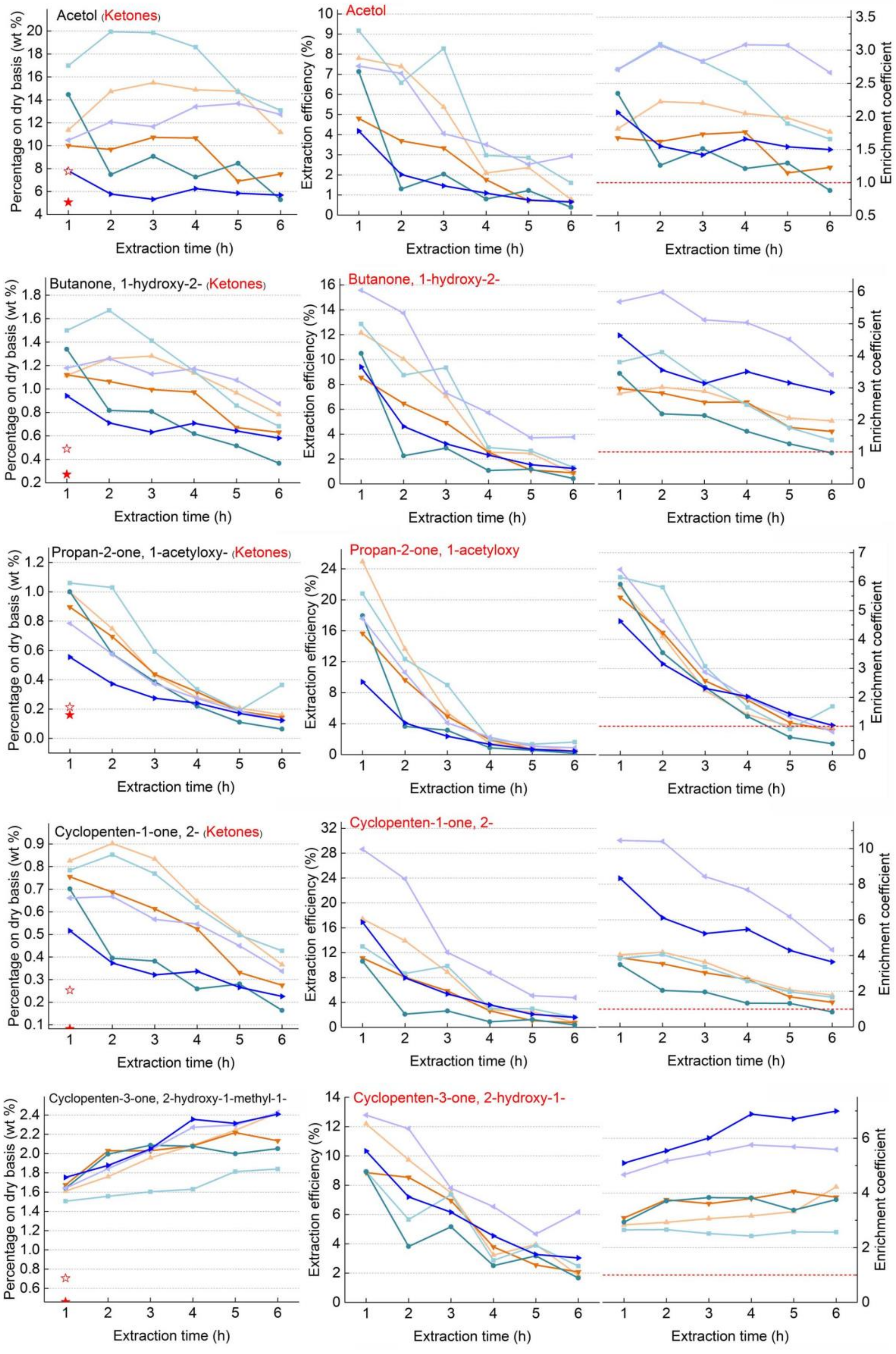


Figure 45: Extraction efficiency and enrichment coefficient of ketones from BTG oil.

4.4.4 Ketones

Ketones and their derivatives represent a main chemical group in bio-oils. Five ketones were selected for analysis: 1-hyroxypropanone (acetol), 1-acetyloxypropanone, 1-hyroxy-2-butanone, cyclopentenone, and 1-methyl-2-hydroxycyclopenteone. Most ketones in the pyrolysis liquid were present in low amounts (<1 wt%) except acetol, which had 5.6 wt% in PF oil, 8.2 wt% in TI-U oil, and 3.4 wt% in TI-L oil. At 150 bar, the extraction efficiency of acetol was 41.2% for PF oil, 17.2% and 22.9% for TI-U and TI-L oil. More acetol could be extracted from PF oil than from TI oil although TI oil showed a better enrichment effect. Besides acetol, 1-acetyloxypropanone in PF oil was also present in a high concentration of 6.0 wt% while 0.2 wt% were present in TI oils. The extraction efficiency of 1-acetyloxypropanone was as high as 87.4% for PF oil, 56.3% for TI-U oil, and 59.0% for TI-L oil. The enrichment coefficient also reached to 2.1, 7.6, and 6.0 for PF, TI-U and TI-L oil, respectively. The $scCO_2$ extraction of 1-acetyloxypropanone from different pyrolysis liquids gave the highest extraction efficiency among the non-aromatics. The extraction efficiency of other ketones varied between 41.2% and 55.9% for PF oil, 17.2% and 33.3% for TI-U oil, 22.9% and 47.1% for TI-L oil. The extraction efficiency of ketones from PF oil was higher than from TI oil which was attributed to the higher extraction yield of PF oil. The enrichment coefficient for PF oil was around 1 while for TI oil it is between 2.3 and 4.8, indicating that concentrations of ketones remained almost the same in the extracts from PF oil but increased to a large extent in the extracts from TI oil. Very few 1-acetyloxypropanone was detected in the residue with the distribution coefficient over 52.4. The distribution coefficient of other ketones was between 3.6-16.2.

The liquid CO_2 extraction efficiency of 1-acetyloxypropanone from PF oil reached 95.0% to 97.4% and for other ketones it was between 63.9% and 82.7%. The enrichment coefficient of liquid CO_2 extraction for all ketones was around 1.0. This means that most of the ketones were extracted with liquid CO_2 but their concentrations in the extracts did not change much. In liquid CO_2 extraction, the influence of the loading ratio was not obvious. Hexane showed poor extraction ability for acetol and 1-hydroxybutanone, while more than 50.0% of these two ketones were extracted with acetone. Hexane extraction efficiency of other ketones reached over 50.0%, leaving less residues that could be further extracted with acetone. Most of the ketones were not enriched in the extracts by solvent extraction. Higher loading ratios result in higher extraction efficiency with hexane but lower extraction efficiency using acetone.

The extraction efficiency and extraction coefficient of fresh BTG oil is shown in Figure 45. In fresh BTG oil, acetol accounted for 5.8 wt% and reached a maximum of 17.9 wt% in the extracts in the 6-hour extraction. Its enrichment coefficient remained above 1 and did not change much during the extraction process. But the extraction efficiency decreased with time due to the decreasing extraction yield. Low temperature led to a higher extraction efficiency of acetol while other factors such as carrier and aging were not important. Similar to acetol, the enrichment coefficient of 2-hydroxy-1-methylcyclopentenone did not change much with time. The enrichment coefficient was in the range of 2.4 to 7.0 with the highest value from aged BTG oil. Higher temperatures also enabled higher enrichment coefficients of 2-hydroxy-1-methylcyclopentenone. Except for these two ketones, low temperature always gave better extraction effects. The enrichment coefficient of other ketones decreased from around 6.0 to 1.0 with extraction time. Because of the decrease of the enrichment coefficients and extraction yield, their extraction efficiency also decreased quickly with extraction time.

In summary, the best extraction effects with different extraction methods showed 1-acetyloxypropanone with both a high extraction efficiency and a high enrichment coefficient. Concentration of ketones in the extracts from PF oil remained almost the same as in the original pyrolysis liquid. Most of the ketones in TI and BTG oils were enriched in $scCO_2$ extracts. It is interesting to note that different ketones showed different extraction profiles. Except for acetol and 2-hydroxy-1-methylcyclopentenone, the enrichment coefficients of other ketones decreased with the extraction time. Low temperature gives better extraction effects for most of the ketones while the carrier and aging are insignificant.

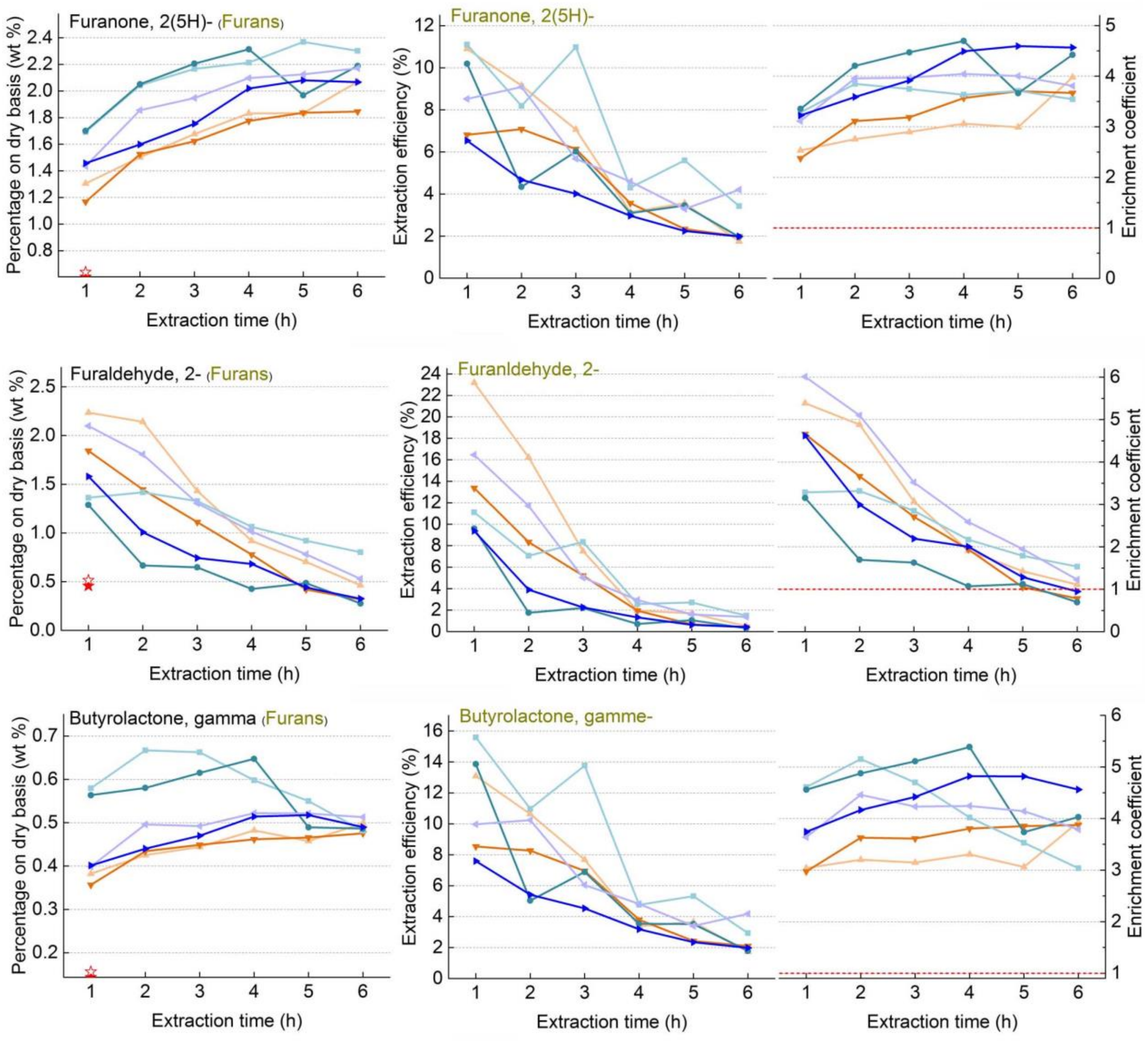


Figure 46: Extraction efficiency and enrichment coefficient of furans from BTG oil.

4.4.5 Furans

Furans belong to the main heterocyclic compounds in pyrolysis liquid and represent valuable platform chemicals. Furans selected for analysis are 2-furaldehyde (furfural), 2(5H)-furanone, and γ-butyrolactone. Among all furans, furfural had the highest concentration in pyrolysis liquid, namely 3.8 wt% in PF oil, 0.8 wt% in TI-U oil, and 0.9 wt% in TI-L oil. Its concentration in $scCO_2$ extracts from PF oil was slightly increased with an enrichment coefficient of 1.4 but largely increased when TI oils were used as feedstock. In this case, the enrichment coefficient reached 5.2 for TI-U oil and 3.2 for TI-L oil. The extraction efficiency of furfural was 59.7% from PF oil, 38.1% from TI-U, and 31.9% from TI-L. The $scCO_2$

extraction efficiency of furfural from PF oil was high but with a limited enrichment effect. In contrast, fast pyrolysis liquids with a relatively high amount of water like TI-U and TI-L oils showed high enrichment coefficients but low extraction efficiencies. The other two furans, 2(5H)-furanone and γ-butyrolactone had much lower content in pyrolysis liquids. Their $scCO_2$ extraction from different pyrolysis liquids was similar to that of furfural. The distribution coefficient of 2(5H)-furanone in PF oil was 0.7, showing that it was enriched in the residue. Concentration of all other furans in pyrolysis liquids was lower in the residue than in the extracts with the distribution coefficient of 1.4-31.2.

The $scCO_2$ extraction efficiency of furans from PF oil was higher with a higher oil loading ratio (100:80) compared to 100:40 but the enrichment coefficient was not influenced by the loading ratio. A slight influence of the loading ratio on liquid CO_2 extraction of furans from PF oil was observed. Furfural was extracted with hexane with an extraction efficiency of 31.7% for a loading ratio of 100:40 and 50.0% for a loading ratio of 100:80. The residue from hexane still contained a certain amount of furfural which was further extracted with acetone. 2(5H)-Furanone and γ-butyrolactone were not extracted with hexane but acetone proved to be a good solvent for the two furans. Although all three solvents are classified as non-polar, $scCO_2$, liquid CO_2 and hexane showed different extraction effect against furans.

The concentration of furfural in the $scCO_2$ extraction from BTG oil decreased with extraction time, leading to a decrease in the enrichment coefficient from 6.0 to 0.8 as shown in Figure 46. Together with the decrease in the extraction yield, the extraction efficiency of furfural decreased hourly from a maximum of 23.2% to a minimum of 0.3%. This indicates that the $scCO_2$ extracts obtained from different extraction stages had different concentrations while the influence of carrier, temperature or aging was insignificant. Different from furfural, the enrichment coefficient of 2(5H)-Furanone increased with the time while that of γ-butyrolactone remained almost unchanged during the whole process.

The enrichment coefficients of furans from TI and BTG oils were much higher than those from PF oil. The extraction of furans was complicated as different furans showed different extraction effects when different methods were applied. Their concentrations in the $scCO_2$ extracts also differed with different furan compounds. It was demonstrated that it is not possible to separate furans completely with one method. If one single furan was preferred to be extracted, a specific extraction methodology should be designed.

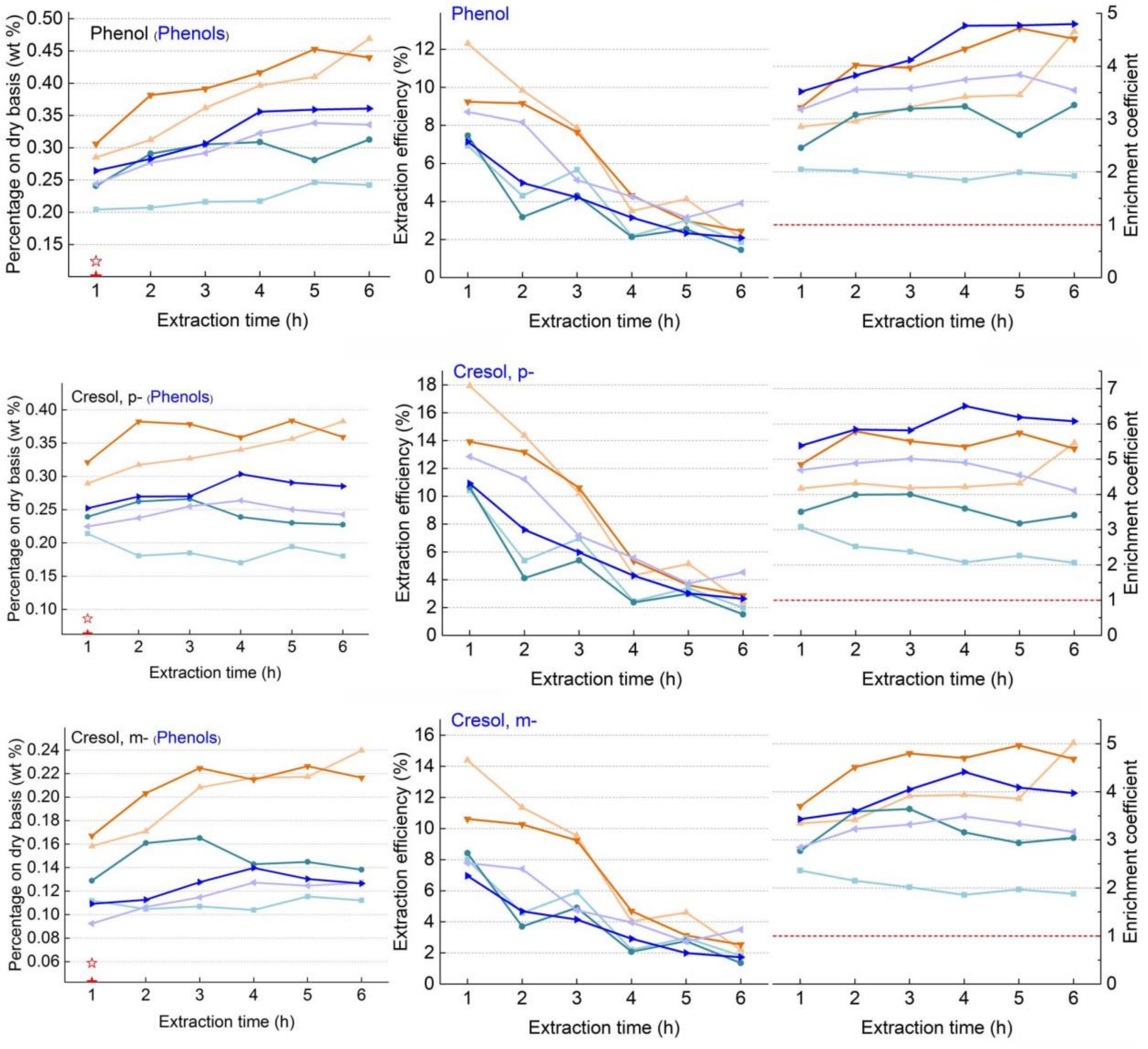


Figure 47: Extraction efficiency and enrichment coefficient of phenols from BTG oil.

4.4.6 Phenols

Phenols in pyrolysis liquid derive from the degradation of lignin. The production and utilization of monomeric phenols from lignin are of great interest. Phenols selected for analysis were phenol, *m*-cresol, and *p*-cresol. They were present in low concentrations (<1 wt%) in both slow and fast pyrolysis liquids. All phenols from PF oil showed a high extraction efficiency of over 50%. The extraction efficiency of *p*-cresol even reached 88.3%. The enrichment coefficient of phenols from PF oil was between 1.2 and 2.1 indicating a slight increase of concentration in the $scCO_2$ extracts. The extraction efficiency of phenols from TI oils was in the range of 37.5-53.2% but the enrichment coefficient was in the range of 3.9-7.2

demonstrating that the enrichment effect of phenols from TI oils was much better compared to PF oil. The concentration of *m*-cresol from PF oil was the same in the extract and residue. Other phenols had higher concentrations in the extracts with distribution coefficient of 1.8-12.8.

The extraction efficiency of phenols with liquid CO_2 was the highest compared to all other chemical groups, showing that liquid CO_2 had the best extraction effect on phenols. Similar to liquid CO_2, phenols could also be effectively extracted and enriched with hexane. The extraction efficiency of phenol by hexane was 76.5% and 92.2% for both oil loading ratios (100:40 and 100:80). Residual phenol was further extracted with acetone. Cresols were completely extracted with hexane because no cresols could be detected in the acetone extracts.

Phenols in BTG oil were present in low content (< 0.1 wt%). Their content increased to 0.2-0.4 wt% in the extracts showing enrichment coefficients in the range of 1.8-6.5. The concentration of phenols in the $scCO_2$ extracts remained almost constant with extraction time under different extraction conditions as shown in Figure 47. All the analyzed phenols showed similar extraction profiles. SiO_2 as carrier exhibited a slightly higher extraction efficiency than AC. The enrichment coefficients of phenols were higher at 80 °C than at 60 °C.

Although phenols had a low content in pyrolysis liquid, they could be effectively extracted with CO_2 and hexane. During the whole extraction process, their concentrations changed a little in the $scCO_2$ extracts. SiO_2 as a carrier could lead to a higher extraction efficiency while higher temperatures led to higher enrichment coefficients.

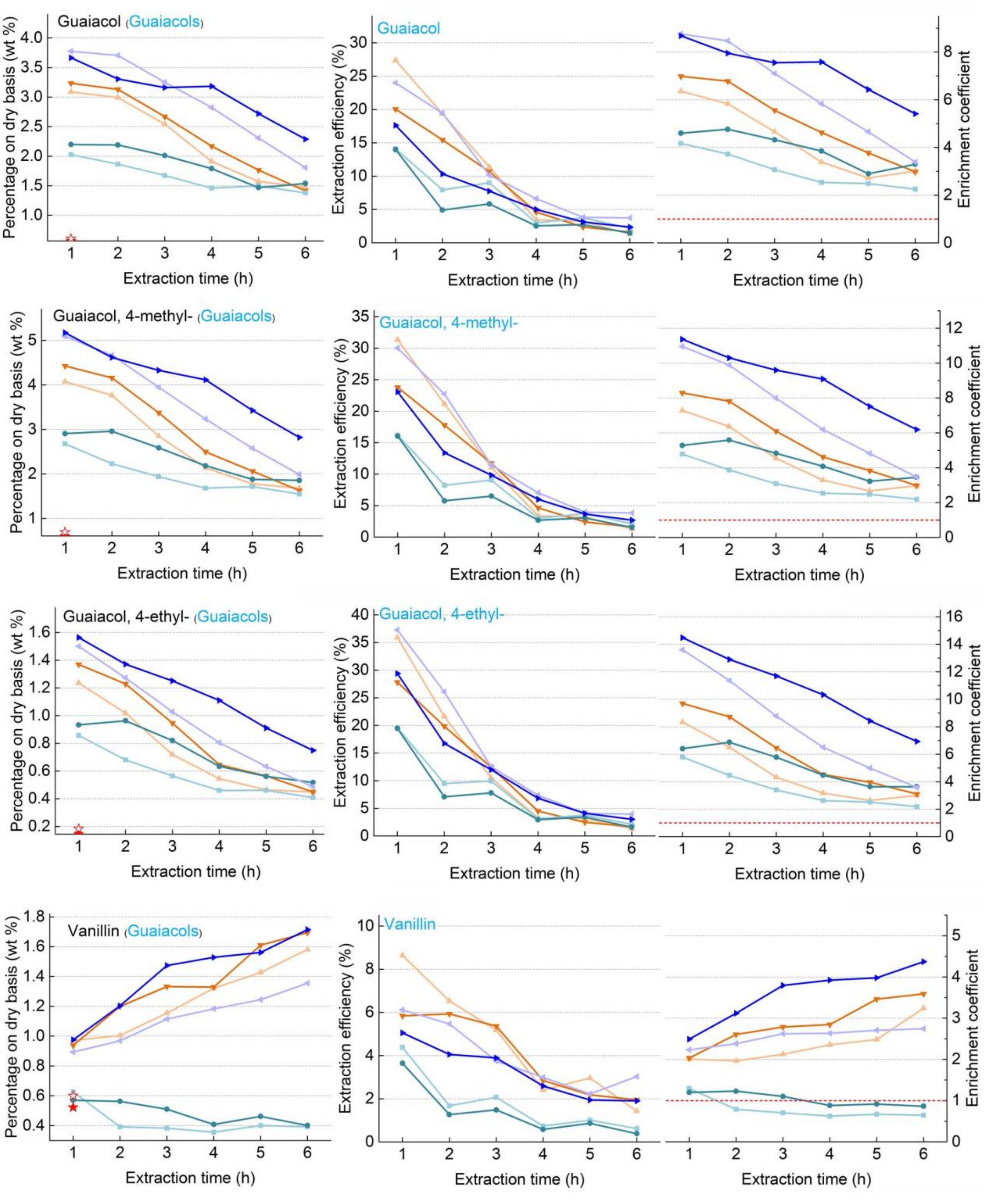


Figure 48: Extraction efficiency and enrichment coefficient of guaiacols from BTG oil.

4.4.7 Guaiacols

Guaiacols represent another aromatic chemical group derived from lignin. Their contents were higher than phenols. Three guaiacols were selected for analysis: guaiacol, 4-methylguaiacol, and 4-ethylguaiacol. Contents of guaiacol in PF oil, TI-U oil, TI-L oil were 2.1 wt%, 0.1 wt%, and 0.2 wt%, respectively. They were enriched to 3.7 wt%, 0.7 wt% and 1.0 wt% in the $scCO_2$ extracts. The extraction efficiency of guaiacols from PF oil was 75.6% while that of TI-U and TI-L oil it was 63.2% and 60.1%, respectively. The enrichment coefficients of guaiacols from TI-U and TI-L oil were 8.5 and 6.2, which means that guaiacol could be effectively enriched in the extracts and most of them could be extracted with $scCO_2$. Other guaiacols had lower concentrations but showed similar extraction effects as guaiacol. The extraction of 4-ethylguaiacol from TI-U oil gave the highest extraction efficiency of 83.1% and enrichment coefficient of 11.2. 4-Ethylguaiacol was not found in the residue of TI oils. Other guaiacols were in low concentrations in the residue with distribution coefficient of 10.2-62.2.

The extraction efficiency of guaiacols with liquid CO_2 was lower compared to phenols. Guaiacols were slightly enriched in liquid CO_2 extracts while the influence of oil loading ratio could be neglected. Guaiacols were completely extracted with hexane as no guaiacols were detected afterward in acetone extracts. The extraction efficiency with hexane was lower than 100% due to the fact that some guaiacols were adsorbed on SiO_2 and could not be removed neither with hexane nor with acetone.

Guaiacols were in low content in BTG oil in the range of 0.1-0.5 wt% but they were enriched to around 2-5 wt% in the extracts. Therefore, they had high enrichment coefficients with a maximum of 14.5. The enrichment coefficient of guaiacols decreased almost linearly with the extraction time as shown in Figure 48. The decrease of extraction yield and enrichment coefficient resulted in a quick decrease of extraction efficiency from around 30% to 2%. The main extraction of guaiacols was finished in four hours. Some exceptions were coniferyl alcohol, coniferyl aldehyde, and vanillin. Their contents increased with the extraction time and activated carbon as the carrier showed much lower extraction efficient. Guaiacols could be better extracted when SiO_2 as the carrier and high temperature was used for the process conditions.

4.4.8 Syringols

Syringols are aromatic degradation compounds from hardwood lignin. PF oil and TI oils were produced from beech wood while BTG oil was produced from pine, therefore syringols were only found in PF oil and TI oils. Similar to guaiacols, their derivatives were preferably substituted in *para* position by methyl, ethyl, propyl, allyl, and propenyl groups. Among the different derivatives, syringol had the highest concentration in pyrolysis liquids: 2.2 wt% in PF oil, and 0.4 wt% in TI oils. The enrichment coefficient of all syringols in PF oil was between 1.0-1.7, indicating that syringols could not be effectively enriched in the $scCO_2$ extracts when PF oil was used as feedstock. However, they were enriched in the $scCO_2$ extracts when TI oils were used with enrichment coefficients between 3.5 and 6.2. The extraction efficiency of syringols was in the range of 17.9-49.8%, which was slightly lower than that of phenols and guaiacols. As syringols are more polar than phenols and guaiacols, they show a lower enrichment coefficient with $scCO_2$ extraction. All the syringols in the residue were with lower concentrations than in the extracts with the distribution coefficient of 1.2-7.9.

The extraction efficiency of the main syringols from PF oil with liquid CO_2 was in the range of 1.3-1.6. The enrichment effect with liquid CO_2 was not very pronounced but better compared to the non-aromatic compounds. Hexane showed a higher enrichment of syringols in the range of 1.9-2.7. As with phenols and guaiacols, no syringols were detected in the acetone extracts. The extraction of phenols, guaiacols, and syringols with $scCO_2$ and hexane was influenced by the oil loading ratios. A higher oil loading ratio led to a higher extraction efficiency but lower enrichment coefficients.

5 Conclusions

Pyrolysis liquid produced from fast pyrolysis of lignocellulosic biomass has the potential for the production of renewable chemicals. It contains a considerable amount of bio-based platform chemicals such as acetic acid, hydroxyacetaldehyde, hydroxyacetone, furaldehyde, phenols, guaiacols, syringols, etc. The efficient separation and fractionation of pyrolysis liquid are challenging but important for its applications. Therefore, this research focuses on the fractionation of different pyrolysis liquids with supercritical carbon dioxide ($scCO_2$).

The pyrolysis liquids studied in this research work include PF oil (a by-product of a charcoal company), TI-U oil and TI-L oil (upper phase and lower phase of fast pyrolysis liquid self-produced at Thünen Institute), and BTG oil (a commercial product produced from BTG company). The preliminary $scCO_2$ extraction was done with PF oil, TI-U oil, and TI-L oil in the pressure range of 80-250 bar. With the conditions of 150-250 bar and 60 °C, the extraction yield for PF oil was 37.4-54.1 wt%, for TI-U oil it was 7.4-11.1 wt%, for TI-L oil it was 9.9-15.0 wt%. Water present in pyrolysis liquids has a negative effect on the extraction yield. It could be detected in the $scCO_2$ extracts but in much lower content. The total recovered mass of PF oil was 86.2-90.2 wt%, TI-U oil it was 83.9-87.1, and TI-L oil it was 75.4-79.6 wt%. The volatile components and those evaporated from the extracts contributed to the losses, which accounted for a significant portion of the mass balance. A condensation system with wash bottle filled with isopropanol and an activated carbon filter was developed to improve the mass balance. The total collected mass was increased up to 95.8 wt% when PF oil was used as feedstock.

The type of carrier material of pyrolysis liquids and the loading ratio are influencing factors in the $scCO_2$ extraction process. Different carrier materials were tested for the extraction of BTG oil: glass beads, silica gel (SiO_2), and activated carbon (AC). Glass beads showed the highest extraction yield with 15.5-21.6 wt%, compared to SiO_2 and AC with yields of 6.3-8.1 wt%. However, the absorption ability of glass beads was very low. Therefore, the systematic $scCO_2$ extraction of BTG oil was investigated with SiO_2 and AC (loading ratio 1:1) at different pressures (100, 200, 300 bar) and temperatures (60, 80 °C). The extraction yield was below 1.1 wt% at 100 bar, at 200 bar it was 6.4-13.1 wt%, at 300 bar it was 13.1-14.3 wt%. Under these experimental conditions, high pressure and low temperature led to higher extraction yield. The influence of temperature at 200 bar was significant but at 300 bar it was negligible. AC as the carrier gave less extracts and residues but more off-gases.

The $scCO_2$ extracts were collected hourly in a six hours run so that the extraction curves could be monitored. The extraction rate of BTG oil at 100 bar was constant but the yield was very low (< 1.5 wt%). At pressures > 200 bar, the extraction yield was largely increased and the extraction rate decreased with the extraction time. Hence, the $scCO_2$ extraction process is in conformity with the broken and intact cell model where the initial extraction period is dominated by dissolution and the later extraction period is dominated by diffusion.

Acids are the most abundant chemicals in fast pyrolysis liquids. The extraction efficiency of acids from PF oil reached more than 50 wt% but was below 26 wt% for the fast pyrolysis liquids. The enrichment coefficient was in the range of 0.7-2.6. Acids can be enriched in the $scCO_2$ extracts but with limited selectivity. However, it can be improved by applying low temperature, high oil loading ratio, and short extraction time. Hydroxyacetaldehyde was present in high amounts in fast pyrolysis liquids (1.9-6.8 wt%) and its enrichment coefficient increased with extraction time from 0.7-5.9. The extraction efficiency was in the range of 26.8-51.6 wt%. The carrier type was the most important factor that influences the enrichment effect of aldehydes. Ketones are a main chemical group with various derivatives in pyrolysis liquids. Ketone molecules with different structures showed different extraction profiles. The extraction efficiency of ketones from BTG oil was in the range of 0.2-28.6% and the enrichment coefficient was in the range of 0.6-10.5. The extraction effect can be improved by applying low temperature. Phenols are in low concentration in pyrolysis liquids (< 1 wt%). The enrichment coefficient of phenols from BTG oil was between 1.8 and 6.5. The concentration of phenols in the extracts remained almost constant during the six hours run. The $scCO_2$ extraction showed a good enrichment effect of guaiacols with a maximum enrichment coefficient of 14.5. The enrichment coefficient of guaiacols decreased almost linearly with the extraction time and the extraction efficiency decreased accordingly from 35.9% to 1.3%. Syringols were only present in PF oil and TI oils. Syringols in PF oils could not be effectively extracted. They had enrichment coefficient between 1.0-1.7 while in TI oils it was between 3.5-6.2.

The $scCO_2$ extraction process can separate pyrolysis liquids into different fractions without solvent removal. Most of the light bio-oil compounds can be enriched in the $scCO_2$ extracts. The properties of pyrolysis liquids and extraction process parameters significantly influence the yield and composition of the extracts. Selective extractions can be achieved by choosing proper conditions so that the target chemicals can be highly enriched in the extracts. To obtain pure chemical compound from pyrolysis liquid through $scCO_2$ extraction still remains challenging. In future work, both the $scCO_2$ extracts and the residue which is rich in carbohydrates should be used as feedstocks to develop further purification processes to produce pure chemical compounds.

Pyrolysis liquids from biomass are mixtures of several hundred organic compounds with various functional groups. The exploitation of pyrolysis liquid through extraction of value-added compounds is hardly successful with one single method. Different separation methods should be combined to achieve a feasible separation of target chemicals. Furthermore, the feedstock and pyrolysis process should be carefully controlled to produce more specific pyrolysis liquids. Pre-treatment of the pyrolysis feedstock, selective fast pyrolysis, and proper separation of pyrolysis liquid are the three most important factors in the pyrolytic conversion of biomass. Fast pyrolysis liquids are going to be commercial and compete with petroleum only when the mentioned three factors are efficiently improved.

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