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著者(和文)	TarnpradabThanyawan
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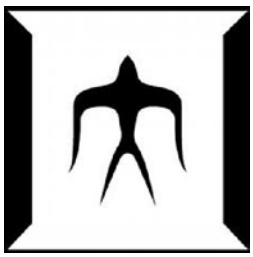
PHYSICAL TAR CLEANING SYSTEM COMBINING OIL ABSORPTION WITH OIL REGENERATION AND CHAR ADSORTION FOR BIOMASS GASIFICATION PROCESS

Thanyawan TARNPRADAB

Supervisor: Professor Kunio Yoshikawa



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Thanyawan Tarnpradab

ABSTRACT

Tar is the main problems for utilizing synthesis gas in biomass gasification technology, which condenses and blocks in downstream applications resulting in engine breakdown. This research is aimed to develop physical tar removal by both absorption and adsorption. The capacity of vegetable oil, waste cooking oil and char was investigated to estimate the periodic time for changing new absorbent and adsorbent, respectively. Then, the study for improving the tar removal performance has been done. Deteriorated oil was regenerated to recover tar removal performance. Both the filtration and the centrifugal sediment technique for oil regeneration were conducted. Finally, the commercial gasification test by utilizing the combination of vegetable oil with a regeneration unit and char, as physical tar cleaning unit, was done as well as its detail study on important phenomena. This research helps improving tar removal reliability for biomass gasification.

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Chapter 1

Introduction

1.1 Background

The energy security is the challenging issues due to growing concerns of energy depletion, energy demand and climate change. Up until now, the global primary resources for producing electricity has been fossil fuels such as natural gas, petroleum, coal and so forth, where these limited resources will be momentarily exhausted and taken millions of years by geological processes to create them again as shown in Figure1.1. It means fossil fuels are non-renewable energy resources, which is not able to be replaced within human timescales. In the meantime, growth of the world population dramatically rises the energy demand and consumption year by year, which is necessary for economic growth, country development or other living features. Furthermore, fossil fuel utilization increases the amount of carbon dioxide (CO_2) in the atmosphere. There are numerous reports and researches on natural disasters linked to the climate change [1-3]. To overcome these problems, renewable energy is now playing an important role in place of fossil fuels. It is the technologies for producing heat or electricity without burning fossil fuels and being constantly renewed such as solar energy, wind energy, geothermal energy, hydropower energy and bioenergy [4]

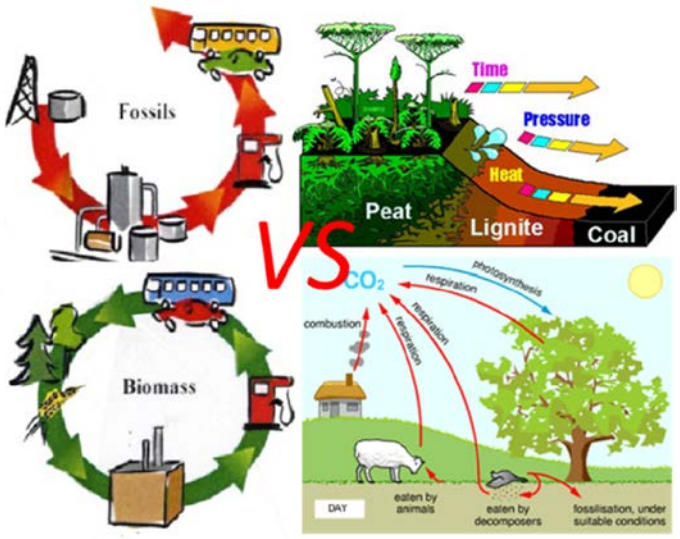

Figure1.1: Comparing Life-Cycle Carbon as energy resources from fossil fuel and biomass

Bioenergy is one of the more interesting candidates as a renewable energy resources. There is no CO_2 emission released to the atmosphere because of its carbon neutrality. CO_2 and water are converted by solar energy, and then, turned into sugar and flour in the plants. Thus, bioenergy utilization is useful for carbon recycling by the photosynthesis process as shown in Figure 1.1.

Biomass is one of bioenergy resources. There is a definition of biomass given by the National Renewable Energy Laboratory, The U.S. Department of Energy [5].

"Biomass is organic matter available on a renewable basis. Biomass includes forest and mill residues, agricultural crops and waste, wood and wood wastes, animal wastes, livestock operation residues, aquatic plants, fast-growing trees and plants, and municipal and industrial wastes"

Thus, biomass utilization is useful for carbon recycling in the photosynthesis process. For woody biomass such as woody crops, agricultural or forest residues and algae, there are three main components: cellulose, hemicellulose and lignin in different proportion. Table 1.1 shows compositions of some types of biomass [6, 7].

Table 1.1: Compositions of some biomass type [6, 7]

Type of biomass	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Other (%)
Softwood[a]	41	24	28	7
Hardwood[a]	39	35	20	7
Wheat straw[a]	40	28	17	15
Rice straw[a]	30	25	12	33
Bagasse[a]	38	39	20	3
Oak wood[b]	34.5	18.6	28	
Pine wood[b]	42.1	17.7	25	
Coconut shell[b]	24.2	24.7	34.9	
Almond shell[b]	24.7	27	27.2	

[a] Other refer to organic compounds such as starch and inorganic material such as salts, minerals and water

[b] Lignin was measured as acid-insoluble lignin, % cellulose= %glucose×0.9, and %hemicellulose = (%galactose + %mannose) × 0.9 + (%xylose + %arabinose) × 0.88

- **Potentials to utilized biomass for energy generation in South-east Asia and Thailand.**

Southeast Asia Region consists of eleven countries; Myanmar, Thailand, Laos, Cambodia, Vietnam, Malaysia, Singapore, Indonesia, Philippines, Brunei, and East Timor as shown in Figure1.2. Most of the countries in this region are the top producers of agricultural products e.g. rice, sugar cane, palm oil, coconut and rubber. Every year, more than 120 million tons of waste crop in South-east Asia e.g. rice husk, rice straw, bagasse, palm oil waste, and coconut shells are generated [8]. As one of the most important rice-producing and exporting region of the world, over 100,000 rice mills operated in Indonesia, Philippines, Malaysia, Thailand, and Vietnam produce approximately 19 million tons of rice husks annually, which has a potential for power generation of around 16,720 MW [9]. In addition, over 34 million tons of bagasse annually generated from sugar mills in Philippines, Indonesia, Thailand and Vietnam, representing the maximum power generation potential of around 11,407 MW [9]. Indonesia and Malaysia are the world's biggest palm oil producer. They produce more than 27 million tons of residues which may generate approximately 11,693MW [9].

Biomass is able to be the crucial energy resources in Thailand as well because Thailand is rich in agriculture and forest resources. It was reported that the total agricultural waste was 61 million tons in 1997 in which 41 million tons of biomass residues (or 426×10^9 MJ of energy) was unutilized [10]. Thus, it can be utilized for replacing the fossil fuels. The summary of biomass residues during agricultural activities in 2004 is shown in Table 1.2 [11]. Although over 70 million tons of biomass residues were generated in 2004, the comprehensive utilization rate of them was also very low, where just about 30% of biomass residues was utilized. The unused residues was abandoned or improperly

managed, which cause the environmental issue such as water pollution, air pollution, global warming and human heath harmful. For example, burning agricultural waste in the open field (open-air burning), which is the easiest and cheapest way to eliminate waste, is estimated to produce 40% of carbon dioxide (CO_2), 32% of carbon monoxide (CO), 20% of particulate matter, and 50% of polycyclic aromatic hydrocarbons (PAHs) released to the atmosphere, which cause smoke, greenhouse gases, highly toxic carcinogenic pollutants.

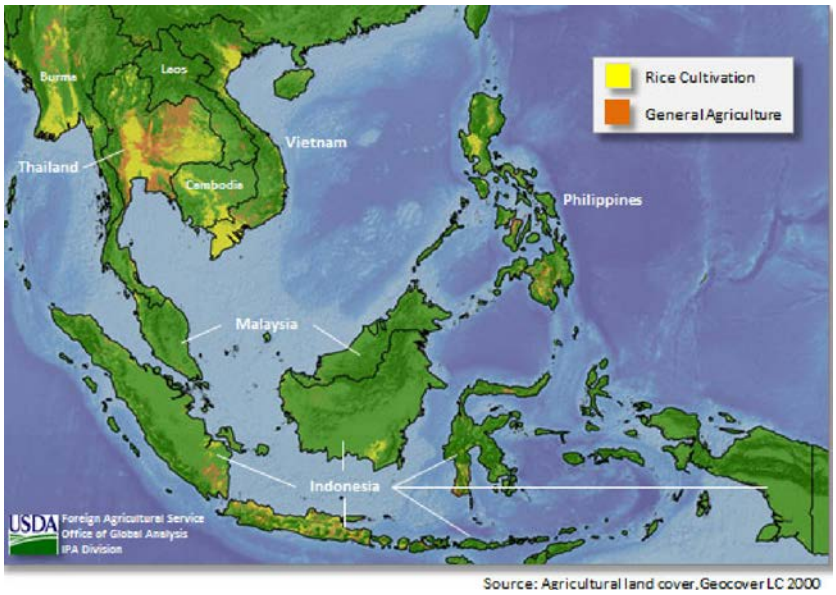

Figure1.2: Distribution of agricultural lands in Southeast Asia region

Table 1.2: Biomass residues from rice, sugar cane and palm oil in 2004 (Unit: 1,000 tons per year)

Biomass	Production	Residue	Crop-residue ratio	Amount	Surplus availability factor	Unused residue
Sugar cane	70,101	Bagasse	0.291	20,399	0.207	4,223
		Trash	0.302	21,171	0.986	20,874
Rice	26,841	Rice husk	0.230	6,173	0.493	3,044
		Rice straw	0.447	11,998	0.684	8,207
Palm	4,903	EFB	0.250	1,226	0.584	716
		Fiber	0.147	721	0.134	97
		Shells	0.049	240	0.037	9
		Fronds	2.604	12,767	1.000	12,767
Total				**74,695**		**49,936**

- **Biomass conversion technologies**

There are two main techniques to convert biomass energy that is biochemical and thermochemical. Biochemical techniques consist of two main process; fermentation and anaerobic digestion. For fermentation, it mainly converts the plant's glucose into a bioethanol which is rather difficult for lignocellulose biomass, while cellulose and hemicellulose can be converted to sugars, but lignin still remain as non-fermentable fraction. For anaerobic digestion, it directly converts organic materials to biogas by using bacteria and microorganism. It is widely used in industries. Anaerobic digestion is the natural biological degradation process in the absence of air (oxygen-free

atmosphere) to digest from biomass to biogas products such as methane (CH_4), carbon dioxide (CO_2), nitrogen (N_2), hydrogen (H_2) and hydrogen sulfide (H_2S). These biogas products can be utilized for electricity generation, transportation fuel and thermal energy production same as natural gas. However, biochemical techniques have some difficulties on feedstock variability, expensive and specific cellulosic enzymes, microorganism requirement, low biofuel yield and expensive pretreatment cost [12, 13]. Thermochemical techniques are more feasible for energy transformation, higher yield production and more compatible with existing technologies utilized for fossil fuel than one previously mentioned. There are various thermochemical conversion pathways of biomass including combustion, gasification and pyrolysis [14]. Biomass combustion is a thermal decomposition of lignocellulose biomass in the presence of sufficient amount of gas agent, where the biomass fuel is burned completely. The chemical energy stored in biomass is converted to heat or electricity. Combustion produces hot gases at the temperature around 800°C -1000°C. It is possible to burn any type of biomass where 50% of moisture content is limited. There are wide ranges of combustion plant scale from very small (domestic heating) to large scale (power plant). The conversion efficiencies of biomass combustion power plants range from 20-40%. For pyrolysis, it is the biomass conversion process in the absence of air. The products consist of liquid bio-oil, solid char, and fuel gases. For gasification, it is the conversion of biomass into combustible gas by partial oxidation of biomass at high temperatures (800°C -900°C). The producer gas can be burnt directly or utilized in engine. The main technology of biomass utilization is summarized in Figure 1.3.

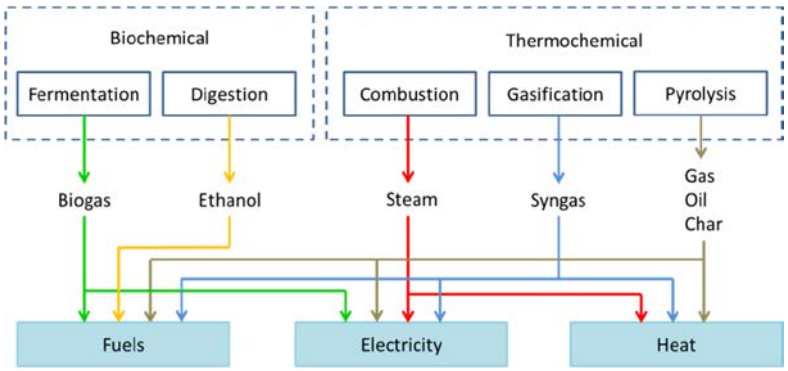

Figure1.3: Biomass conversion technologies and end-use application

- **Biomass gasification history**

Gasification was first used commercially in the 1800s for heating and lighting in industries and residence [15, 16]. At the beginning of the 20th century, the gasification technology was not widely demonstrated since the gas utilization systems were relatively complicated and insecure compared to combustion. During World War II, the interest in gasification was revived because of inadequacy of fossil fuels. Gasification was utilized in many applications such as fuel vehicles, fuel for industrial and residential heating and lighting.

- **Biomass gasification process**

During biomass gasification process, the solid carbonization materials are heated up with gasification agents e.g. air, oxygen, steam, carbon dioxide, or two or more mixture of these gasifying agents to produce gaseous fuel in partial oxidation condition. The combusible product fuel is called “synthesis gas” or “syngas” which consists of

hydrogen(H_2), carbon monoxide(CO), methane (CH_4) and some carbon dioxide (CO_2). The other by-product in gasification process are char, water, soot, and tar. Regarding tar, it was reported as the obstacle of biomass utilization because tar aerosols contained in synthesis gas will condense in the downstream process. The gasification process can be divided into four process zones; drying, pyrolysis, oxidation and reduction as shown in Figure1.4.

In the drying process, biomass is dried by the thermal energy obtained from the oxidation process up to 150°C for complete moisture removal. After that, the pyrolysis takes place. Between 200°C and 280°C, carbon dioxide and acetic acid evolve. The large quantities of tar and gases containing carbon dioxide are mainly produced from 280°C to 500°C in the pyrolysis process. From 500°C to 700°C, the gaseous products are little, however, hydrogen is produced in this range. Approximately 5%-25% by weight of solid fraction which cannot devolatile during the pyrolysis is called as “char”. In the oxidation process, the main product of this step is the thermal energy, which is necessary for the whole process, while other oxidation reaction products are the mixture of CO, CO_2, and H_2O (g). Finally, the reduction process is the step involving the reaction of all the products in the preceding stages (pyrolysis and oxidation). The reduction temperature is the key parameter of the overall process and is used to determine the characteristic of char and the synthesis gas, which is summarized in Figure1.5.

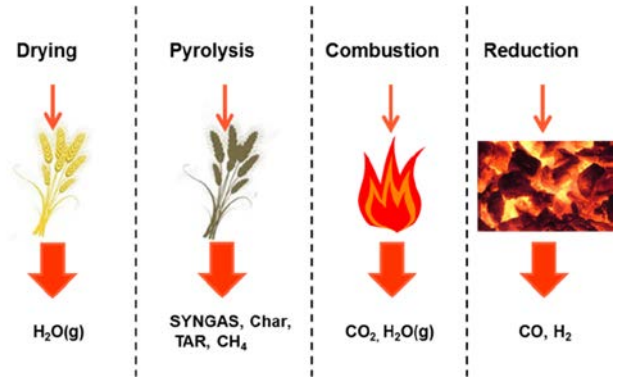

Figure 1.4: Main stage of gasification process [17]

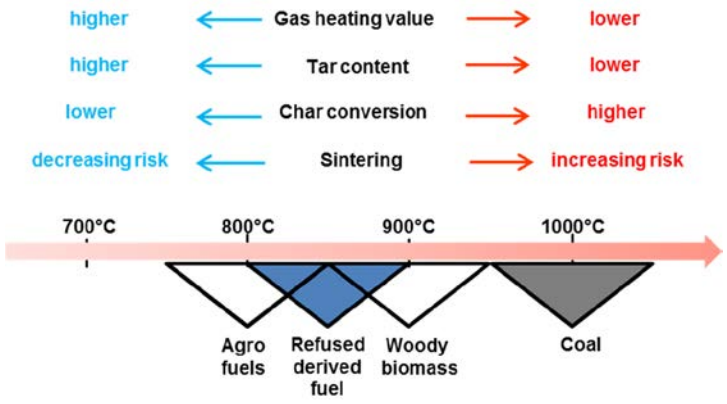

Figure1.5: Influence of the temperature change on the critical process characteristics

The main reaction in the gasifier consists of exothermic rections (gasification or combustion with oxygen) and endothermic reactions (gasification with carbon dioxide or steam). For minor reactions normally associated with

the gasification process are the gasification with hydrogen, the water gas shift reaction and the methanation. The major and minor reactions occuring in the gasifier is summarized in Table1.3. The quality and quantity of the synthesis gas depends on the type of the gasifier used, the operation conditions (temperature, residence time, size of feedstock and moisture content of feedstock). For example, higher operation temperature results in a higher cold gas efficiency and higher carbon conversion. However, the opeation temperature is limted by the ash agglomeration and the ash melting point.

Table 1.3 Major and minor reactions in biomass gasification[18]

Major reaction		$\Delta H°_{298}$**(kJ/mol)**	**Name**
$C + 1/2O_2 = CO$	**R1**	**-110.5**	partial oxidation reaction (or gasification with oxygen)
$C + O_2 = CO_2$	**R2**	**-393**	complete oxidation reaction (or combustion with oxygen)
$C + CO_2 = 2CO$	**R3**	**+172**	Boudourd reaction (Gasification with carbon dioxide)
$C + H_2O = CO + H_2$	**R4**	**+131.4**	Water gas reaction (Gasification with stream)
Minor reaction		$\Delta H°_{298}$**(kJ/mol)**	**Name**
$C + 2H_2 = CH_4$	**R5**	**-74.8**	Hydrogasification reaction (Gasification with hydrogen)
$CO + H_2O = CO_2 + H_2$	**R6**	**-40.9**	Water gas shift reaction
$CO + 3H_2 = CH_4 + H_2O$	**R7**	**-205**	Methanation

- **Gasifier design**

There are three types of conventional gasifier: the fixed bed gasifier, the fluidized bed gasifier and the entrained flow gasifier which are shown in Figure 1.6.

The fixed bed gasifier (updraft and downdraft) is the oldest and simplest type of gasifiers, which is known as the moving bed gasifier. The advantage of the fixed bed gasifier is a high carbon conversion, a long solid residence time, a low velocity and a low ash carry over. The feedstock is fed from the top of the gasifier and then preheated, dried, devolatilized, gasified and finally combusted towards the bottom of the gasifier. The position of the exiting gas strongly affects the quality of the synthesis gas.

The fluidized bed gasifier is divided into two types: the bubbling bed type (BFB) and the circulating type (CFB), depending on the velocity of the fluidization medium in the gasifier. The gas velocity in the BFB is 2 m/s, while in the CFB it is between 5 m/s and 10 m/s. The biomass is mixed with inert bed material, where the drying, the pyrolysis and the gasification occur in a bed. The behavior of inert bed during the gasification process is like a fluid behavior. Silica sand is the mostly used as a bed material. The maximum operating temperature is limited by the melting point of the bed material and generally operated between 800ºC and 900ºC. The weakest point of the fluidized bed technology emerges when biomass contain high amount of ash and alkali metals.

The entrained flow gasifier is well known for the coal gasification process, however, not so effective for the biomass gasification process. According to high operation temperature (1200ºC-1500ºC), it leads to molten ash formation of biomass. In order to prevent the slag problem, biomass pre-treating process is required.Moreover, it

requires a feedstock in the powder form, where fine powder crushing process is a very costly process in terms of energy.

Warnecke [19] summarized advantages and disadvantages of each gasifir design as shown in Table1.4

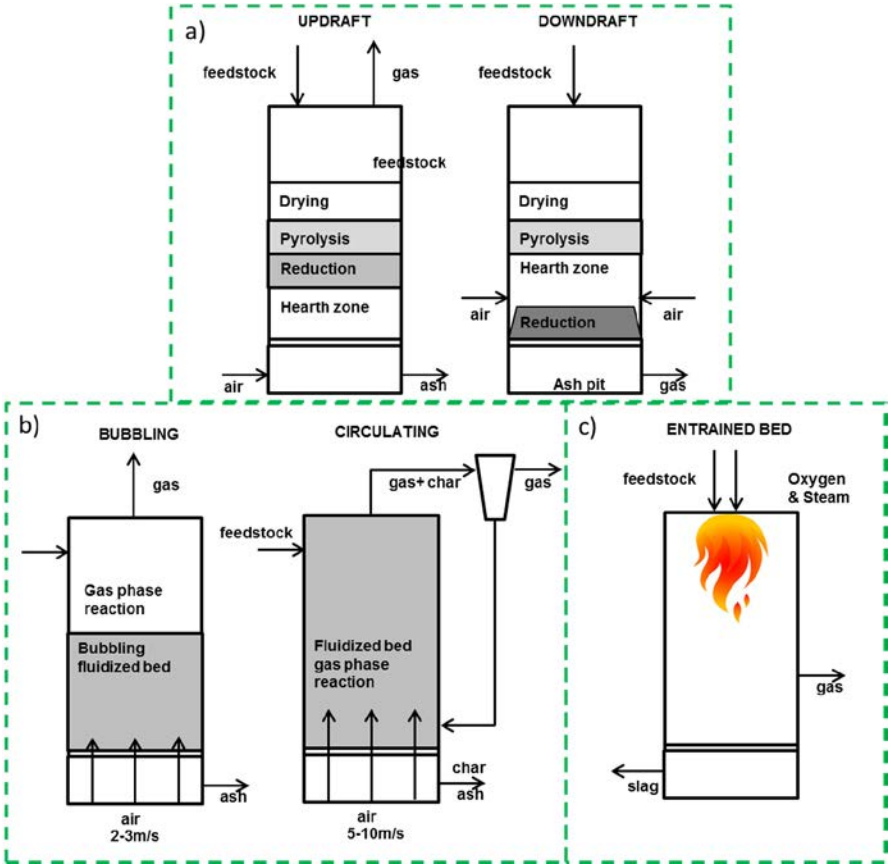

Figure1.6: Gasifier design: a) fixed bed gasifier, b) fluidized bed gasifier and c) entrained flow gasifier

Table1.4: Advantages and disadvantages of different gasifier design

Type	Advantages	Disadvantages
Updraft	• Simple construction • High thermal efficiency • High carbon conversion • Usable with high ash content feedstock	• High tar content • Limited for scaling up
Downdraft	• Simple construction • High carbon conversion • Usable with high ash content feedstock • Low tar content	• Low moisture content feedstock required • Limited for scaling up
Bubbling Fluidized	• High gas-solid mixing • Moderate tar content • High conversion efficiency • Potential for scaling-up	• High ash content • Ash molten problem in some feedstock
Circulating Fluidized	• High carbon conversion • Moderate tar content • High conversion efficiency	• High ash content • Ash molten problem in some feedstock

	• Potential for scaling-up	• High energy consumption
Entrained Flow	• Potential for scaling-up • Low tar content	• Particle size limits • Large amount of carrier gas • High particle load

- **Synthesis gas characteristics**

The quality of the synthesis gas depends on two main parts: the quality of the feedstock and the operation conditions. The quality of the feedstock consists of biomass components, the energy content, the bulk density, the moisture content, the size, the ash content and the slagging characteristics. According to major biomass components (cellulose, hemicellulose and lignin), it is found that the pyrolysis reaction of cellulose and hemicellulose is much faster than lignin, which is more difficult to decompose as its weight loss occurs in the wide temperature range (160°C -900°C) and its solid residue amount is very high (40 wt.%) [20]. For the gas yield, hemicellulose produces the highest carbon dioxide (CO_2) yield, cellulose produces the highest carbon monoxide (CO) yield and lignin produces the highest hydrogen (H_2) and methane (CH_4) yield as summarized in Table 1.5. Other is the moisture content of biomass. Generally, drying biomass to 10%-20% moisture content is considered as the optimum for minimizing the size and the cost of the entire gasifier plant [21]. Too much load of moisture in the biomass has several negative impacts on the process. Firstly, it requires higher energy consumption for vaporization of the moisture leading to the lower operating temperature of the gasifier, the synthesis gas yield and the synthesis gas calorific value. Secondly, the volumetric flow rate of the synthesis gas is risen due to the water vapor contained in the synthesis gas resulting in the requirement of larger downstream equipment such as the piping system, cyclone, vessels and so forth, which increase the investment cost. Lastly, there is a reduction of the synthesis gas volumetric heat capacity due to water vapor, where the synthesis gas is progressively harder to burn as the moisture content is increased. In addition, although the feedstock particle size is not directly influential to the gasification performance, the feedstock heat-up speed decreases as the particle size increases. Some gasifier types have a limitation of the feedstock size strictly. A smaller biomass size can give a benefit to some gasifier types, however, investment and operating cost increases with the feedstock size reduction. The dust content depends on the fuel type, the gasifier type and the intensity of the load where the gasifier should not produce more than 2–6 g/m^3 of dust [22]. The tar content depends on the composition of biomass and the operation temperature of the gasifier. For ash and slagging, it was also reported that these may cause the fouling especially in high mineral components of biomass e.g. silica, potassium and chlorine. However, slagging and fouling can be minimized by keeping the gasification temperature low enough to prevent the ash agglomeration.

Table 1.5: Yield of gas product from three components pyrolysis [20]

Sample	Gas production yield (milli mol /g-biomass as received.)					
	H_2	CO	CH_4	CO_2	C_2H_4	C_2H_6
Hemicellulose	8.75	5.37	1.57	9.72	0.05	0.37
Cellulose	5.48	9.91	1.84	6.58	0.08	0.17
Lignin	20.84	8.46	3.98	7.81	0.03	0.42

The gasification conditions such as the temperature, the gasification agents and ER are reported as the key parameters of the synthesis gas quality. The operation temperature strongly affects the gas composition, the tar concentration, the reaction rate and the ash build-up. The gasification at a low temperature results in low CO and H_2 contents and a high tar content in the synthesis gas [23]. High temperature operation produces a synthesis gas with high CO and H_2 contents and a low tar content. However, the operating temperature was limited by the ash melting

temperature especially for high ash content biomass. The gasification agent is an important parameter which reacts with biomass and convert it to the synthesis gas. Usage of air results in a low heating value synthesis gas because air contains nitrogen. The Increase of the H_2 concentration in the synthesis gas was achieved by utilizing steam with air but the addition of steam reduces the thermal efficiency of the gasification process. Carbon dioxide also acts as a gasifying agent to react with carbon to produce carbon monoxide. As for the equivalence ratio (ER), the higher ER induces more oxidation in the gasifier and thus causing a low calorific synthesis gas, while lower ER results in a higher calorific synthesis gas and a higher tar yield. The efficiency of the gasification system increases until reaching the optimum ER (0.25) and then decreased at a higher ER.

1.2 Biomass synthesis gas tars

1.2.1 Tar generation

There are many definition of biomass synthesis gas tars reported in the literature [24].

- "Organics produced through thermal or partial oxidation of any organic material are called tars"
- "Tars are a complex mixture of secondary and tertiary product (mostly aromatics) from the thermal decomposition or partial oxidation of organic material"

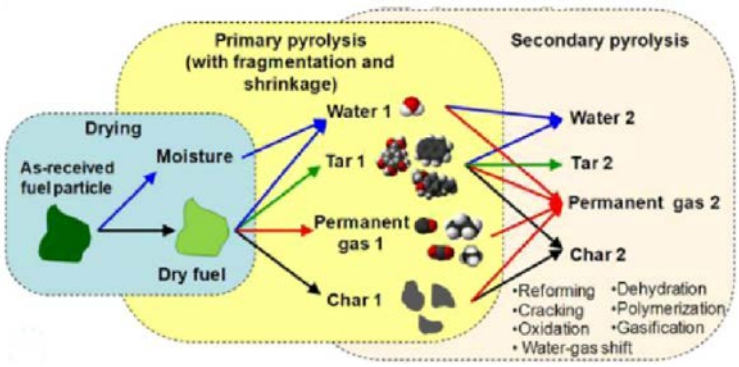

Figure1.7 Thermal decomposition of biomass in the inert atmosphere: drying, primary pyrolysis and secondary pyrolysis [25]

Tar formation is occurred by the breaking of solid carbonaceous substance of biomass as shown in Figure1.7. The primary tar is produced during the pyrolysis step and mainly depends on the biomass gasified. The primary tar produced from the pyrolysis of cellulose and hemicellulose components contains high amount of oxygen atoms. Therefore, the primary products from cellulose and hemicellulose components are oxygenated organic compounds e.g. alcohols, aldehydes, ketones, carboxylic acids, heterocyclic aldehydes, etc.[26], while products from lignin is mainly considered as precursor for PAH formation e.g. phenols, cresols, catechols, guaiacols, etc. due to their natural aromatic form [27]. In the oxidation step, the temperature rises above 500°C. Primary tars were oxidized resulting in more gas and secondary tar formation. The secondary tars are alkylated mono- and di-aromatics such as pyridine, furan, dioxins and thiophene [28]. At the temperature over 800°C, tertiary tars e.g. benzene, naphthalene, phenanthrene, pyrene and benzopyrenes are formed. The tertiary tars appear when the primary tar completely converted into the secondary tar. A possible simplified mechanism of the tar formation [29] is shown in Figure 1.8.

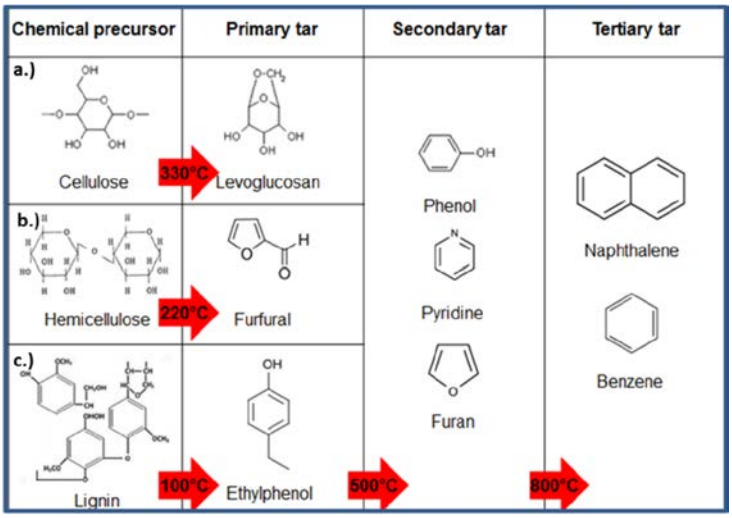

Figure1.8: Simplified mechanism of tar formation from: a) Cellulose[29] b) Hemicellulose[26] and c) Lignin[25, 27]

1.2.2 Compositions of tars

According to the Energy Research Center of the Netherland (ECN)[24], tar consists of various kind of organic aromatic ring hydrocarbons, which can be classified into five classes based on the composition, the delectability, the water solubility and the condensation behavior of the individual compounds[30] as summarized in Table1.6.

Table1.6: Tar type classification[30]

Tar classification	Definition
Class 1	**GC undetectable tar**: It contains heavy poly-aromatic hydrocarbon, which is more than 7 rings. It could be called heavy tar or gravimetric tar as well.
Class 2	**Heterocyclic compounds**: It is highly water soluble hydrocarbon, e.g., phenol.
Class 3	**Aromatic compounds**: It is one-ring aromatic hydrocarbon, which does not cause condensation and solubility problem, e.g., benzene, toluene, xylene, styrene.
Class 4	**Light poly-aromatic compounds**: It is two and three rings aromatic hydrocarbon , which condense at relatively high concentration at moderate temperature, e.g., indene, naphthalene, phenanthrene and anthracene.
Class 5	**Heavy poly-aromatic compounds**: It is from four to seven rings aromatic hydrocarbon, which condense at low concentration at high temperature, e.g., pyrene, fluoranthene, chrysene.

In this study, the gravimetric tar, benzene, toluene, phenol and naphthalene were selected as the model of tar compounds.

1.2.3 Acceptable limitation of downstream application

The acceptable tar concentration in the biomass synthesis gas depends on each downstream application required. Some downstream applications like combustion do not require any limitation of the tar concentration in the synthesis gas because tars can be burnt together with the synthesis gas. In this case, tar content increases the heating value of the synthesis gas [31]. For example, synthesis gas can be utilized as the fuel in the boiler or kiln for the thermal energy recovery. However, some applications require the limit of the tar content, for example, the

synthesis gas utilization as the fuel in the internal combustion engines for power generation purpose or as the feedstock for the chemical production like ethanol, methanol, hydrocarbons and so forth[32].

In this study, the purpose of the synthesis gas utilization is mainly focused on the power generation in internal combustion engines. While the synthesis gas is compressed in the internal combustion engines, it results in higher partial pressures of tar, which cause the condensation of tar [33]. In order to prevent and avoid an accumulation and condensation of tar in this process, it is recommended that the tar concentration is limited from 50 – 100 mg/Nm^3 [24]. Therefore, it is necessary to investigate the effective tar removal methods considering both simple and economic aspects.

1.3 Tar removal techniques for biomass synthesis gas

There are two main techniques for tar removal depending on the location of the tar removed. The primary methods eliminate tar inside the gasifier, whereas the secondary methods eliminate tar outside the gasifier as shown in Figure 1.9.

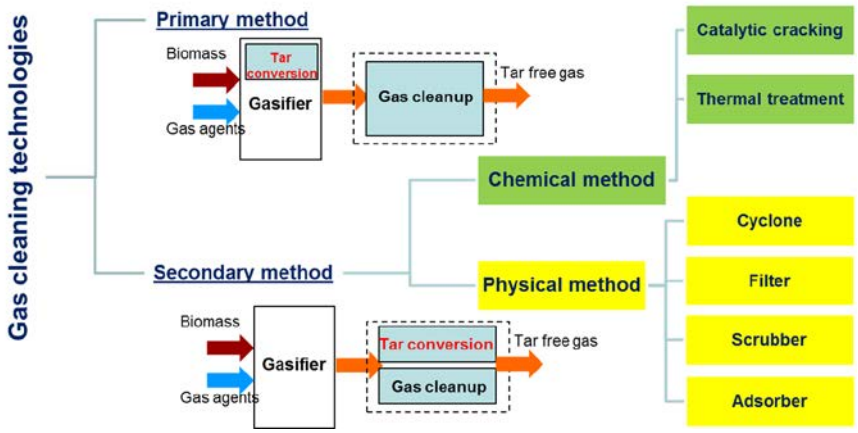

Figure1.9: Comparison of the primary and secondary measures for gas cleaning

1.3.1 Primary methods of tar removal

Primary methods of tar removal consist of biomass feedstock selection, the gasifier design, the operating conditions (the temperature, the equivalent ratio, the gasifying agent and the residence time) and the catalyst utilization. The gasifier design and the operating conditions play an important role in all aspects. The decision of these parameters relies on the gasifier type used.

For biomass feedstock selection, as aforementioned, the major biomass components constitute of cellulose, hemicellulose and lignin. Yu et al [34] found that lignin produces the highest tar yield, where phenol is mainly generated, while the lowest tar yield is cellulose. Cellulose and hemicellulose primarily produces benzene, toluene, ethylbenzene and xylene isomers. Because of the highest tar yield by lignin, the biomass feedstock which has high proportion of lignin should be carefully handle in regards to the control of the tar content during the gasification process.

For the gasifier design, the tar content which is mainly produced in the pyrolysis zone, is higher in the case of the updraft gasifier compared with the downdraft gasifier due to the difference of the direction of the gas flow through the gasifier. The gas flow of the updraft gasifier passes through the pyrolysis and the drying zones, which are low temperature zones (80°C -200°C), while the gas flow of the downdraft gasifier passes though the combustion zone, which is a high temperature zone (>1,000°C) leading to the thermal cracking and oxidization of tar. In the case of the fluidized bed gasifier, it normally operates at a high temperature (600°C -900°C). A typical tar concentration can be ranged as follows; 10,000-150,000 mg/Nm^3, 2000-30,000 mg/m^3 and 10-6000 mg/m^3 for the updraft, the fluidized bed and the downdraft gasifiers, respectively [35].

It was reported in the sawdust gasification in a fixed bed type gasifier that the tar concentration decreased corresponding with the increase of the temperature[36]. The significant amount of oxygenated organic compounds such as phenol, cresol and benzofuzan were produced only at the temperature below 800°C, while the aromatic hydrocarbons such as benzene, naphthalene and phenanthrene were destructed only at the temperature above 850°C. Yu et al. also investigated the effect of the temperature on the tar formation of birch wood in a free-fall reactor and found that the tar concentration were reduced more than 40% when the operating temperature was increased from 700°C to 900°C[37]. Similarly, the oxygenated organic, 1-ring and 2-ring aromatic compounds also significantly reduced with the increase of the temperature. A higher temperature is effective for reducing the tar compounds, however, there are several influential factors which limit the operating at a high temperature, for example, the gas heating value, char conversion and the sintering risk [38].

The increase of ER decreases the tar concentration, however, the gas yield and the gas heating value are also reduced. The amount of supplied O_2 is increased by increasing ER, which promotes the degree of combustion and results in a higher gasification temperature. According to Kinoshita et al.[36], the overall tar concentration was reduced by about 30% when ER was increased from 0.22 to 0.32 at 700°C. All phenol were disappeared at the ER of 0.27, however, the concentration of benzene and naphthalene increased.

For a gasifying agent, different gasifying agents such as air, steam, steam-oxygen and carbon dioxide (CO_2) have been studied. The common gasifying agent utilized is air, however, there is some operational limitation when selecting the ER value. The steam gasification is free of nitrogen content and enhances the hydrogen production by the water gas reaction. Herguido et al.[39] reported the effect of the steam-biomass ratio (SB) on the steam gasification. The yields of hydrogen and carbon dioxide were increased by 60% and 20%, respectively, while carbon monoxide was decreased by 25% when the SB ratio was increased from 0.5 to 2.5. There was no change in methane and C_2 fractions (C_2H_2, C_2H_4, C_2H_6). Furthermore, the tar yield is markedly decreased from 8% yield at 0.5 SB to almost 0% at 2.5 SB. However, the calorific value was decreased due to the reduction of carbon monoxide. The steam gasification is an endothermic reaction so it requires heat supply in the process and the process design will be complex. Thus, steam-oxygen gasifying agent is developed to provide a necessary heat in the process. Aznar et al.[40] reported that 85% of the total tar was removed when the steam-oxygen to biomass ratio (gasifying ratio: GR) was increased from 0.7 to 1.2. Both steam and steam-oxygen gasifying agents have the same advantage for hydrogen-rich gas production. Finally, the carbon dioxide gasifying agent is also very attractive due to its presence in the gasification atmosphere. Kirtania et al.[41], reported the spruce and coconut shell char gasification under the entrained flow condition in carbon dioxide atmosphere and found that almost no tar component was observed during CO_2 gasification at above 1,000°C.

The residence time has an influence on the tar transformation as well. Although it has a small effect on the tar yield, it significantly affects the tar composition due to the tar decomposition. Heavy tar contained in the synthesis gas can be cracked to lighter tar or synthesis gas by the thermal cracking reaction in the long free board zone gasifier.

For the catalyst utilization, it is the method to directly mix catalyst with biomass for tar removal. The catalysts are able to accelerate the rate of the gasification and the secondary reactions resulting in the reduction of the tar content in the synthesis gas. One of the potential catalysts as an active bed additive is Ni-based catalyst. It was reported as the effective tar removal catalyst. Shen et al. [20], reported the tar removal by utilizing rice husk char-supported Ni-Fe catalysts with calcination and Ni catalysts without calcination. Tar produced from biomass in 800°C pyrolysis process could be removed by 92.3% and 93%, respectively under the optimized condition.

Although primary methods are considered to be the best approach for the tar removal, they cannot reduce the tar concentration to the acceptable level for the internal combustion engines and are difficult to control.

1.3.2 Secondary methods of tar removal

According to the drawback of the primary methods, the secondary methods are more efficient and easier to control. There are several designs of the external gas cleaning units by the secondary methods, for instance, the chemical removal design and the physical removal design. The chemical removal designs are related to using high temperature or catalyst to convert heavy tar molecules into the burnable gas or lighter tar molecules, whereas the physical removal designs are related to using the mechanical methods to trap or capture the tar contained in the synthesis gas, for example, cyclone, filter, electrostatic precipitator, spray tower, scrubber and adsorber. Although there are many reports on tar removal efficiency by using chemical methods, which found that it was very effective for tar removal, they are not economical because of the expensive price of catalysts by the catalytic cracking and additional energy consumed by the thermal cracking. Therefore, the physical removal designs are considered as the most economical and simple operating system with a high tar removal efficiency. They can be categorized into the wet system (spray tower and scrubber) and the dry system (cyclone, filter, electrostatic precipitator and adsorber).

For the wet system, scrubbers are widely used for treating the pollution gas and controlling the particle matter. Dust and impurities are removed by the inertia impaction, the interception and the diffusion principle depending on the particle diameter[42], while the liquid phase tar is removed by the dissolve likes principle and condensation[43]. Previously, there were few researchers conducting the experiments of tar and VOC removal comparing water and organic liquids as scrubber medium. Since most tars are hydrophobic substances, they are capably dissolved in hydrophobic absorbents. It was reported that water, which is generally used for pollution gas cleaning processes, is not suitable for tar removal purposes. Water has a lower solubility of tar compounds than oily materials, quickly reaches the saturation point of absorption and causes the secondary pollution (highly toxic and carcinogenic) [44-47]. Moreover, washed water requires a waste water treatment process to remove organic compounds and inorganic residuals before using in the water recirculation process or disposing to the environment. On the other hand, oil scrubbers can provide a waste-free facility because, after the tar removal process, washed oil containing tar can be burned in boilers to recover the thermal energy. In addition, oily materials were reported as a more suitable scrubber medium than water. Phuphuakrat et al. found that the absorption efficiency of the gravimetric tar of oily material and water can be ranked as vegetable oil > engine oil > water> biodiesel oil > diesel oil, which recommended that vegetable oil should be selected as absorbent[43]. For VOCs removal efficiency, Ozturk and

Yilmaz reported that waste lubricant oil has a removal efficiency as high as the fresh vegetable oil. However, according to the cost of the absorbent, waste oil is much more competitive and effective for utilizing on a commercial scale [48]. Paethanom et al. compared tar removal performances between vegetable oil and waste cooking oil (WCO), which was the waste from household and restaurants. It was found that the tar removal efficiency was reduced by 7.2% when using WCO. In addition, increase of the turbulent mixing improved the tar removal efficiency to 89.8% and 81.4% by using 1000 rpm vegetable oil scrubber and 750 rpm WCO scrubber, respectively[49]. The massive of waste oil in industries such as waste lubricant and hydraulic can be utilized for tar removal as well.

Normally, for tar absorption technique using a scrubber, heavy tars and other solid particle can easily accumulate in absorbent, which leads to reduction of the tar removal performance and shorten the absorbent lifetime. Therefore, in this research, in order to deal with these problems, the optimization of the operating condition of the oil scrubbing will be firstly considered especially focusing on the temperature effect. The operating temperature affect the scrubbing oil characteristic, for instance, the density, the viscosity, the interfacial tension and the residence time. Then, the lifetime of scrubbing oil will be considered to predict the timing for changing to the new scrubbing oil. Finally, in order to prolong the absorbent lifetime, the regeneration of the deteriorated oil by the filtration and the centrifugal sedimentation techniques will be studied to reduce the use of make-up absorbent and the production of the deteriorated oil.

For the dry system, it is efficient particularly to remove tar in the vapor phase. Among various techniques of the dry system, an adsorber is the most convenient, easy to operation and design. Previously, there were few researchers conducting experiments of tar removal by adsorbers. It was found that the specific surface area of the adsorber has a large influence on the tar adsorption. Then, there is a comparison of various adsorption materials such as activated carbon, biomass, synthetic porous cordierite and waste char (WC) for tar removal. Phuphuakrat et al. studied the adsorption efficiency of porous materials for the tar removal and found that activated carbon performed the best adsorption efficiency due to the highest specific surface area [50]. However, because of the cost of adsorbents, waste char (WC), a by-product of the process, was studied. It was found that the pyrolysis temperature has a strong influence on the char produced. Thus, 800°C was the most favorable pyrolysis temperature to produce char for the tar adsorption due to both high specific area and fixed carbon content [51].

However, the tar adsorption techniques by the adsorber is not appropriate to adsorb solid and liquid phase heavy tar. Therefore, in this research, a scrubber will be installed for heavy tar removal, and then other tars in vapor phase will be adsorbed by the waste char adsorber. The lifetime of waste char will be considered as well to predict the timing for changing to the new waste char.

1.4 Objective of the present study

As mentioned above, the challenge of biomass gasification utilization for elecitricity generation is development of biomass tar removal techniques. In this research, the primary objective is to develop the technical and scientifical tar removal method on both qualitative and quantitative aspects employing the physical tar removal methods in order to achieve the acceptable limitation of the tar content for utilizing the synthesis gas in electricity generation. Therefore, the tar elimination technique was scoped in terms of the economical, simple and reliable gas

cleaning system and potential to implement in commercial gasification plants. Starting with waste resorces utilization, three kinds of waste from household waste oil, industrial process waste oil and gasification process char have been used as cleaning medium. This study intends to provide the useful data for designing the gas cleaning unit, including the appropriate operating conditions and improvement of the absorbent and adsorbent performance so as to optimize the effective tar removal processes. Finally, for prolong the lifetime of the scrubbing material, the used oil regeneration was conducted by both the filtration and the centrifugal sedimentition techniques.

This thesis is divided into two sections; 1) Lab scale tar removal by the physicle technique and devolopment system for prolonging tar removal performance of the medium and 2) Commercial scale implementation : Demonstration in 650 kW_{th} BFB gasifier.

1.5 Outline of the thesis

The content of this thesis has been divided into six chapters as below.

Chapter 1: Background and literature review

In this chapter, the general information about the biomass potential as energy resource, the conversion technology, biomass gasification technology, biomass tar formation, problems of biomass tar, and development of gas cleaning techniques are introduced, respectively. Then, the advantages and disadvantages of the chemical and physical methods for tar removal are reviewed. Special attention has been paid to the physical method for tar removal in the biomass gasification process. Furthermore, the classification of tar and tar measurement method are also reviewed. Finally, the objectives and originality of this research are stated.

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Chapter 2: Influences of the operating conditions of oil scrubber on tar removal performance from biomass gasification synthesis gas

In this chapter, tar removal technique using an oil scrubber is investigated in terms of the absorbent selection and the effect of the temperature on the viscous and high viscous fluid. Vegetable oil is utilized for comparing the gravimetric tar removal efficiency of the waste oil from household (waste cooking oil) and the waste oil from industry (waste lubricant oil). The tar removal efficiency of all absorbents is discussed in terms of the chemical properties of the absorbent and the physical properties (or hydrodynamic properties) of the absorbent. Finally waste cooking oil is recommended as a low cost adsorbent with a high tar removal efficiency

Chapter 3: Utilization of waste materials in combination of absorption and adsorption techniques for tar removal capacity improvement

In this chapter, tar is removed by using the absorption technique combined with the adsoption technique. Waste utilization for tar removal is highlighted in this chapter. The absorbent and the adsorbent are waste cooking oil and biomass char, respectively. The investigation on their capacity and removal efficiency for tar is performed, where the key parameters in this study are decided by the breakpoint and saturation point in the breakthrough curve graph.

The breakpoint is the point at which the deterioration of the absorbent (or adsorbent) starts and the changing to the new absorbent (or adsorbent) is required, while the saturation point is the point at which the passage of time has not an influence on the tar removal efficiency. In addition, in order to maintain the tar cleaning performance, the optimum periodical change of both the absorbent and adsorbent is discussed for the scaling up gas cleaning design.

Chapter 4: Improvement of the biomass tar removal capacity of scrubbing oil regenerated by mechanical solid-liquid separation

In this chapter, the combination of the bubbling type scrubber with the oil regeneration system is evaluated for treating the biomass gaseous tar in order to prolong the absorbent lifetime and reduce the waste oil produced after reaching its saturation. Tar is also continuously introduced into the canola oil scrubber. The regeneration of oil is done by using the filtration and the centrifugal sedimentation techniques. The temperature and the speed of the centrifuge is controlled at 30°C and 10k rpm, respectively which is the optimum speed for separating the suspended contamination of biomass tar in the post-processed oil. Oil is regenerated at every 135 minutes during 10 hours. The comparison of non-regenerated oil and the regenerated oil (the filtration and the centrifugal sedimentation techniques) is discussed in the term of the tar removal capacity and efficiency.

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Chapter 5: Tar removal performance by physical methods in a BFB gasification plant

Oil absorbent with the regeneration unit and wasted char adsorption are successfully developed for tar removal in previous chapter. In this chapter, a commercial scale 650 kWth BFB gasification of rice husk with a physical gas cleaning system is conducted at the operational conditions of the bed temperature of 800°C and the air equivalence ratio of 0.35. The gas cleaning system consists of five main parts: a ceramic filter, an air cooler, two water coolers, a venturi scrubber, and a packed bed adsorber. A major emphasis of this work is placed on an effective tar reduction system that utilizes palm oil with the regenerative unit by the filtration technique as an absorbent and saw dust and mixture of gasified char - saw dust as an adsorber, respectively. The tar concentration and the removal efficiency in each points of the gasification system and the gas cleaning system are stated. The thermodynamic analysis is performed to investigate the energy balance, the carbon balance, the carbon conversion efficiency and the cold gasification efficiency.

Chapter 6: Conclusion and recommendation

This chapter summarizes the important concluding remarks of this thesis. In view of these, some recommendations are also proposed to improve the tar removal performance.

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Chapter2

Influences of the operating conditions of oil scrubber on tar removal performance from biomass gasification synthesis gas

2.1 Background

Water-based scrubber has been widely used as the most common system for biomass syngas cleaning process, which has been utilized for the exhaust gas treatment in various industries. There were various types of water-based scrubber for tar removal [1-3]. Khummongkol et al.[1] reported 70% of tar was removed by water-based wet impinger units, where higher tar removal performance could be achieved by series of wet impingers. Bhave et.al [2] developed a water-based scrubbing system, which combined wet and dry-packed bed scrubbing sections in a single unit. The tar and particulate removal efficiency of the packed bed scrubber varied from 70% to 90%, while water base venturi scrubber shown the most effective in removal of tars and particulate [3]. However, these previous work mentioned above had several drawbacks, which more research works were required.

The severe problem by using water-based scrubber for biomass tar removal is the healthcare concerns and waste water treatment cost. Wash-water could be a secondary pollution source (highly toxic and carcinogenic), which essentially requires waste water treatment facility to remove organic compounds (tar as a mixture of several acidic, basic and neutral compounds) and inorganic residuals (ammonia, chloride, etc.)[4-6] before recycling that water in the recirculation process or disposing it to environment. However, this facility requires high installation and running costs[7]. Other drawback is that water, which is the hydrophilic substance, is low solubility of tar compounds and short absorbent life[8].

According to the “Like dissolve likes” principle, the hydrophobic substances could likewise dissolve hydrophobic absorbents. Thus, to remove tars which were mainly hydrophobic substances, scrubbing medium used must have similar hydrophobic properties. We found that oil was an interesting scrubbing medium because it was hydrophobic and waste-free material. Additionally, after being used in the tar removal process, wash-oil (post-processed oil) could be utilized in boilers to recover its energy. However, a few studies have been reported. According to oil based gas washer (OLGA) technology, Boerrigter et al.[9] reported the concentrated tar reduction in synthesis gas from 7000 to 50 mg/Nm^3. Nonetheless, the details of oil types were not provided. Heymes et al.[10] studied an efficient organic solvent for the removal of VOC compound. They stated the effective characteristic of absorbent for VOCs removal was high absorption capacity, low viscosity, high diffusion coefficient which regulates absorption kinetics, low vapor pressure to avoid loss of solvents. In addition, Phuphuakrat et al.[11] reported that the water scrubbing showed just 32% of the tar removal efficiency due to the ability of water to absorb only the hydrophilic tar. The recommended scrubbing medium was vegetable oil which showed the highest tar removal efficiency of around 60% among various oily materials.

For cost competitive absorbent, waste oil was an interesting medium for wet gas cleaning. According to the increase of used cooking oil from household, restaurants and industries, these caused a big environmental problem i.e. refused water, polluted soil, etc. because a major part of them were illegally dumped into rivers or landfill[12]. Finally, it became a cause of human health harms which was commonly poured down to the drain as waste. For this

reason, Paethanorm et al.[13] utilized vegetable oil and waste cooking oil for comparing tar removal efficiency. It was found that the tar removal efficiency of vegetable oil was higher than waste cooking oil by 7.2%. Additionally, the turbulent mixing could improve the tar removal efficiency from 63.6% to 89.8% when vegetable oil scrubbing was employed. Similarly as waste cooking oil, waste lubricant or hydraulic oil in industries were generated due to maintenance works or connector leakage[14]. It is quite unclear how massive waste industrial oil is treated especially in developing countries. Therefore, reused waste oil of both waste cooking oil and waste lubricant oil for treating biomass tar is one of interesting options as competitive absorbent in commercial gas cleaning.

The influencing factor on the tar removal efficiency is not only the type of absorbents, but also the operation temperature. The operating temperature affects the fluid properties such as the density, the viscosity, the interfacial tension and the gas hold-up[15-18]. The viscosity is a measure of the resistance offered by a fluid to flow. Krisnangkura et al.[19] reported the viscosity can be considered as the integral of interaction forces of molecules. When heat is applied to fluids, molecules can then slide over each other more easily making the liquid to become less viscous. The effect of the temperature on the kinematic viscosity of liquids can described by means of the Arrhenius equation($\mu = \mu_0 e^{\frac{E_\mu}{RT}}$). For the interfacial tension, it was the force acting at the interface of two liquids or between a liquid and a solid or between a liquid and a gas. Esteban et al. & Phankosol et. al [20, 21] reported that the interfacial tension of various plant-based oil decreases with the increase of the temperature. Kaldonski et.al.[22] also reported that the lubricant oil has the same tendency as the plant-based oil. Because the interfacial tension of oil is reduced as the solvent temperature increases, the increase in the temperature enhances the wettability and increases the effective interfacial area, which leads to a high mass transfer. The effect of the temperature on the gas holdup was reported by Pohorecki et al.[23], who determined the hydrodynamics of N_2 in cyclohexane under an elevated temperature and found that the gas holdup increased, whereas the Sauter-mean bubble diameter decreased with the temperature increase due to the decrease of the liquid surface tension.

Therefore, in this chapter, an investigation on the tar removal performance by palm oil, waste cooking oil and waste lubricant oil as low cost competitive oily medium in a wet bubbling bed scrubber was conducted. Moreover, the effect of the absorbent temperature was also studied for improving the tar removal efficiency of the scrubber unit[13].

2.2 Materials and setup

2.2.1 Materials

The feed material for biomass tar generation was Japanese cedar which was obtained from Maiwa Kogyo Co. Ktd., Kanazawa, Japan as shown in Figure 2.1a). Japanese cedar was prepared by crushing and sieving with the mesh size of 0.5 to 1mm and dried in an oven at 105°C for 12 hours in order to remove the moisture content in the raw feedstock. The ultimate and proximate analysis results of the Japanese cedar are shown in Table2.1

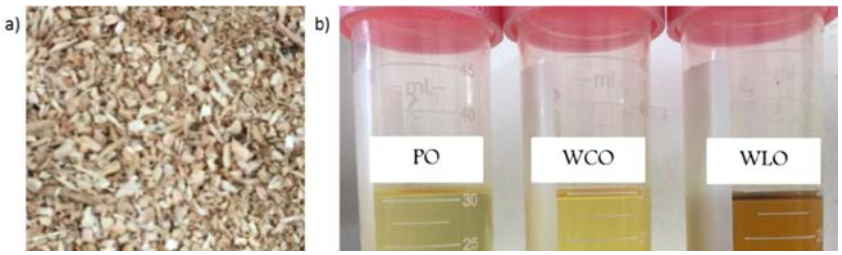

Figure 2.1: a) Feedstock: Japanese cedar b) Absorbents: PO, WCO and WLO

Three kinds of absorbents, palm oil (PO), wastes cooking oil (WCO) and waste lubricant oil (WLO) were utilized to treat synthesis gas as shown in Figures 2.1b). PO was purchased from Fareast Service Company, Ginowan, Okinawa, Japan. WCO was obtained from Best Trading Company, Atsugi, Kanagawa, Japan. The crude waste cooking oil was collected from restaurants where vegetable oil was used for cooking. As the pretreatment of the WCO, 200 liter of the collected waste cooking oil was mixed and held for one day. The residue at the bottom of the tank was removed to get rid of any contaminants and sediments. WLO was leaked oil from the pressing machine. The WLO was obtained from SRIC, Saraburi, Thailand, which was pretreated as the same as WCO. The ultimate and proximate analysis results of absorbents are shown in Table 2.1. The viscosity of the scrubbing oil was measured by the viscometer (TV-SES Model, Thomas Kinetic Viscosity Bath) which is shown in Figure2.2. The density and the kinematic viscosity of absorbents are summarized in Table2.2. The chemical compositions of absorbent oils are shown in Table 2.4 which were obtained by Gas Chromatography – Mass Spectrometry (GC-MS). The preparation of fatty acid methyl ester (FAMEs) was carried out according to modified ISO method [24], while the WLO was prepared according to the modified method reported by J.A.Hiltz.et.a [25]. More details of the analysis setup are explained in appendix A.

Table2.1: Ultimate and proximate analysis results of the Japanese cedar, PO, WCO, and WLO

Parameters	**Ultimate analysis (wt% dry and ash free basis)**					**Proximate analysis (wt% dry basis)**		
	C	H	O	N	S	Volatile matter	Fixed carbon	Ash
Japanese cedar	50.4	6.3	43.2	0.1	<0.1	84.1	15.6	0.3
PO	77.3	11.3	11.4	0.0	0.0	100	0	0
WCO	77.5	11.6	10.8	0.1	0	100	0	0
WLO	85.8	14.1	0	0.1	0	100	0	0

Figure 2.2: Experimental setup used to measure the viscosity of scrubbing fluids in the temperature range of 30°C-60°C by TV-SES Model, Thomas Kinetic Viscosity Bath

Table2.2: The density and the kinematic viscosity of the PO, the WCO, and the WLO in the temperature range of 30°C-60°C

Temperature(°C)	Density(g/cm^3)			Viscosity(mm^2/s)		
	PO	WCO	WLO	PO	WCO	WLO
30	0.90	0.88	0.86	47.5	50.5	98.2
40	0.90	0.88	0.86	32.9	35.1	56.0
50	0.90	0.87	0.85	24.0	25.5	36.6
60	0.89	0.87	0.85	18.1	19.1	24.6

2.2.2. Experimental setup

The synthesis gas generation part diagram is illustrated in Figure.2.3. It consisted of a screw feeder, a pyrolyzer and a N_2 cylinder tank. Dried Japanese cedar was packed in the feeder and the continuously controlled feed rate was 0.6 g/min. N_2 was used as a carrier gas with the flow rate of 0.8 l/min. An external heat source was supplied by an electric heater. The pyrolyzer was a fixed bed type made from a SUS306 tube with the diameter of 30 mm and the length of 280 mm. The temperature of the pyrolyzer was set at 800°C. Before conducting the experiments, the pyrolyzer was kept at the temperatures of 800 °C for 30 minutes with an air supply. Then, when the feeder started, the supplied air was switched to N_2. Japanese cedar was converted into synthesis gas, tar and char. After the operation of the feeder for 15 minutes, the synthesis gases were introduced to the sampling line. It consisted of the bypassed line and the gas cleaning line which were connected in parallel. The bypass line was used to sample the synthesis gas to measure the tar concentration before the scrubbing, while the gas cleaning line was used to sample the treated synthesis gas to measure the tar concentration after the scrubbing. Finally, the synthesis gas was introduced to the tar sampling unit.

For gas cleaning, the wet scrubber unit consisted of a 500 ml Woulff glass bottle scrubber with three thread necks sealed, a magnetic stirrer, and a temperature controlled bath as shown in Figure 2.4. 500 ml of scrubbing oil was supplied to the scrubber. The speed of the magnetic stirrer was set at 1,000 rpm, which were the optimum speeds of each oil, by a digital magnetic stirrer machine [13]. The temperature controlled bath was adjusted from 30°C to 60°C by the temperature controller. The absorbent temperature was recorded by a data logger at every 15 minutes for 60 minutes of the experiment.

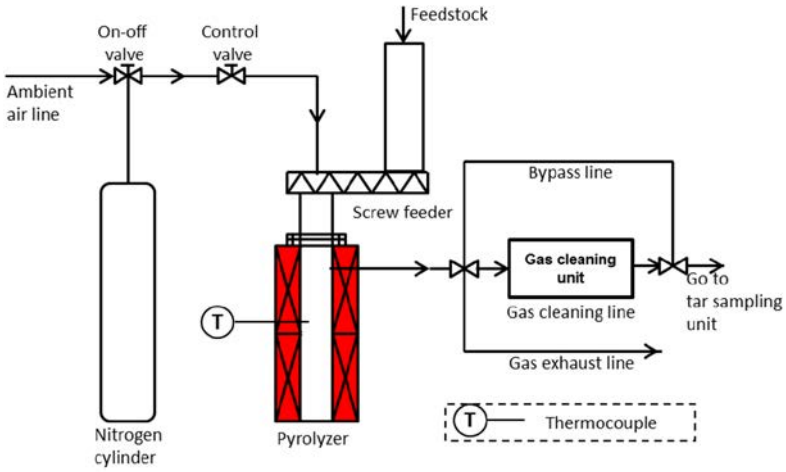

Figure 2.3: The process flow of the experimental setup

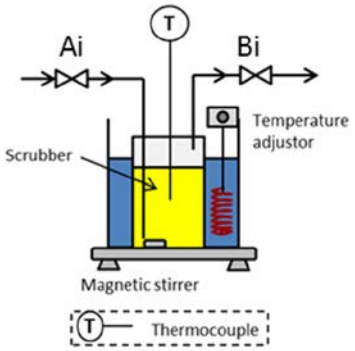

Figure 2.4: The process flow of the gas cleaning setup

2.3 Sampling and analysis method

Tar was sampled by both the wet and dry methods for measuring the gravimetric and the light tar concentrations in the synthesis gas, respectively. The details of the tar measurement method used in this research are described below.

2.3.1 Wet method for gravimetric tar measurement

According to the guideline for the sampling and the analysis of gravimetric tar and particles in biomass producer gases [26, 27], the wet method is the method to separate tar from the synthesis gas by using the principle of tar condensation at a low temperature. The procedure of the sampling method is shown in Figure 2.5. The sampling gas with the controlled volume flow rate of approximately 1 l/min was passed through the sampling unit. The wet method consisted of 10 impinger bottles connected in series. 100 ml of IPA and tar was dissolved in each impinger bottle. The total amount of IPA solution was 1,000 ml per experiment. The impinger bottles were put in the mixture of salt, water and ice bath. The temperature of the bath was controlled at 3°C by an electric cooler. The tar sampling was conducted for 60 minutes. After that, tar was separated from IPA by filtering and evaporating by a rotary

evaporator in a water bath with the temperature set at 40°C. The residue was defined as the heavy tar or the gravimetric tar which was measured by the weight.

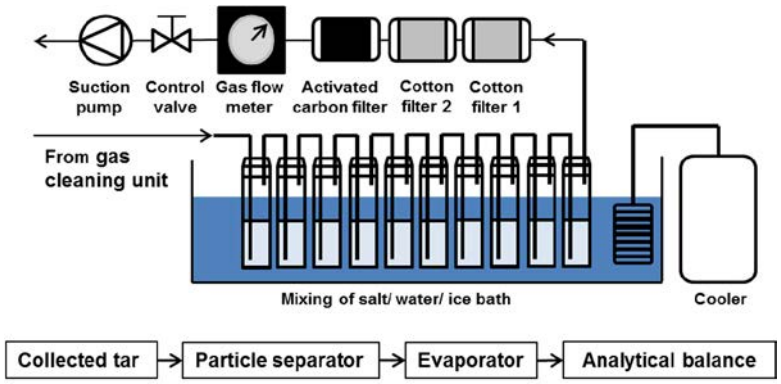

Figure 2.5: Schematic diagram of the wet sampling and the flow measurement method

2.3.2 Dry method for light tar measurement

For the dry method, the light tar concentration was measured by series of charcoal tube (containing 150 g of activated carbon) and silica gel tube (containing 780 mg of silica gel) purchased from Sibata Scientific Technology Ltd as shown in Figure 2.6. 0.5 l/min of the synthesis gas was sampled for 3 minutes. The sampling was started after the start of the feeder for 60 minutes, where A_i means the gas sampling at the inlet of the scrubber and B_i means the gas sampling at the exit of the scrubber. After finishing tar sampling, a gas chromatography flame ionization detector (GC-FID) was utilized to detect light tar compounds and their concentrations. Carbon disulfide and acetone were used as solvents for charcoal tube and silica gel tube, respectively.

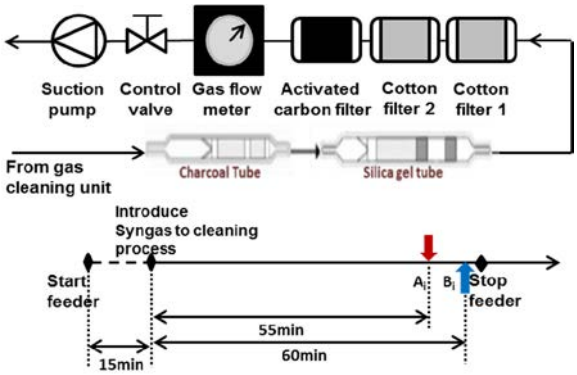

Figure 2.6: Schematics of the dry method for the light tar sampling and the analysis method

2.4 Experimental procedure

In this experimental setup, the summarized conditions of each experimental run are shown in Table 2.3. The scrubber unit was installed between the reactor and the gas sampling line as can be seen in Figure 2.3. For the tar analysis, 500ml of three kinds of hydrophobic absorbents (PO, WCO and WLO) were contained in a two neck flask

scrubber with the fixed turbulence mixing speed of 1000 rpm. The investigation was done by changing the absorbent temperature (30, 40, 50 and 60°C).

Table2.3: Initial experimental setup condition and experimental conditions of each experiment run

Parameters	Run1	Run2	Run3
Initial experimental set up			
Feedstock		Japanese cedar	
Feedstock size(mm)		0.5-1	
Feedstock rate(g/min)		0.6	
Carrier gas		Nitrogen	
Carrier gas rate(l/min)		0.8	
Pyrolyzer (°C)		800	
Experimental condition of each run			
Scrubber volume(ml)		500	
Absorbent(type)	PO	WCO	WLO
Scrubber stirring speed(rpm)	1000	1000	1000
Absorbent temperature (°C)		30, 40, 50, 60	
Tar measurement method		wet and dry	
Sampling time(min)		60	

2.5 Results and discussion

Results of each experiment were reported in terms of the tar removal efficiency which was calculated using the equation 2.1.

$$\text{Tar removal efficiency} = \frac{Tar_{in} - Tar_{out}}{Tar_{in}} \times 100 \qquad (2.1)$$

Where Tar_{in} is the tar concentration before the scrubbing and Tar_{out} is the tar concentration after the scrubbing.

2.5.1 Comparison of the tar removal efficiency of vegetable oil (PO) and low-cost competitive solvents (WCO, WLO)

The gravimetric tar concentration in the synthesis gas was 27.5 g/m^3, which was introduced to the 500 ml oil scrubber. The scrubbing temperature was set at 30°C and the temperature data was recorded at every 15 minutes for the experimental period. The magnetic stirrer was set at 1000 rpm. The gravimetric tar concentration after the scrubbing unit was reduced to 4, 5.8 and 11.7 g/m^3 by using palm oil, waste cooking oil and waste lubricant oil, respectively as shown in Figure 2.7.

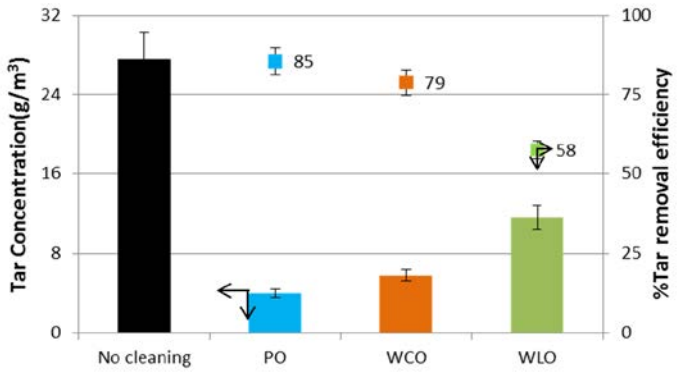

Figure 2.7: Comparison of the tar removal efficiency of vegetable oil (PO) and low-cost competitive solvents (WCO, WLO)

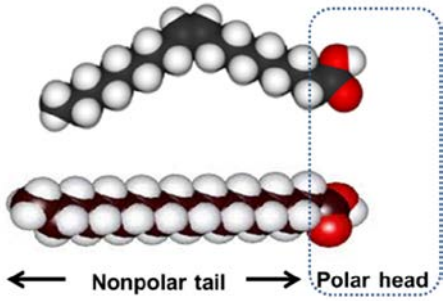

Figure 2.8: Polarity in vegetable oil structure

According to the completely different chemical components in the plant oil and the lubricant oil as summarized in Table 2.4&2.5, the plant oil is composed of fatty acids esterified with glycerol, which contains O-element (-ROOH). The primary components of PO are 43.3% of the palmitic acid, 4.8% of the stearic acid, 24.3 % of the oleic acid and 2.7 % of the linoleic acid, respectively, while the components of WCO are similarly as the palm oil which are 11.7% of the palmitic acid, 7.4% of the stearic acid, 47.6 % of the oleic acid and 17.7 % of the linoleic acid, respectively. The polarity of the carboxyl group in the palmitic acid, the oleic acid and other components in the plant oil shown in Figure 2.8 is the hydrophilic which is able to dissolve in the hydrophilic substance like water, while a long chain hydrocarbon called nonpolar tail is the hydrophobic which is able to dissolve in the hydrophobic substance. Thus, vegetable oil is able to dissolve both polar and nonpolar substances. The degree of the polarity is decreased by increasing their nonpolar tail structure. In contrary, the mainly compositions of WLO were basically long chain alkanes (C_nH_{2n+2}), which are hydrophobic substances as summarized in Table 2.5. Therefore, WLO mainly dissolves a nonpolar substance.

Table2.4: Chemical composition of plant oil (PO and WCO) determined by GC-MS (*Solubility and their properties data are available to the public at website: http://www.ncbi.nlm.nih.gov)

Systematic Name	*Solubility in water(mg/L)	*Chemical formula	*Molecular weight	*BP (°C)	*MP (°C)	PO (%wt)	WCO (%wt)
Other	-	**-**	**-**	**-**	**-**	**24.9**	**22.5**
Palmitic acid	0.04(25°C)	$C_{16}H_{32}O_2$	**256**	**351**	**62.9**	**43.3**	**11.7**
Stearic acid	0.597(25°C)	$C_{18}H_{36}O_2$	**284**	**361**	**69.3**	**4.8**	**7.4**
Oleic acid	0.0115(25°C)	$C_{18}H_{34}O_2$	**282**	**360**	**13**	**24.3**	**47.6**
Linoleic acid	0.159(25°C)	$C_{18}H_{32}O_2$	**280**	**230**	**-5**	**2.7**	**17.7**
Linolenic acid	0.124(25°C)	$C_{18}H_{30}O_2$	**278**	**231**	**-16.5**	**0**	**0**

Table2.5: Chemical composition of WLO determined by GC-MS(*Solubility and their properties data are available to the public at website: http://www.ncbi.nlm.nih.gov)

Systematic Name	*Solubility in water(mg/L)	*Chemical formula	*Molecular weight	*BP (°C)	*MP (°C)	WLO (%wt)
Octacosane	Insoluble	$C_{28}H_{58}$	**394**	**431**	**64**	**26.1**
Heptacosane	Insoluble	$C_{27}H_{56}$	**380**	**270**	**60**	**20.6**
Heneicosane	Insoluble	$C_{26}H_{52}$	**296**	**356**	**40.5**	**4.2**
Pentacosane	Insoluble	$C_{25}H_{52}$	**352**	**401**	**53**	**1.8**
Tetracosane	Insoluble	$C_{24}H_{50}$	**391**	**230**	**52**	**6.5**
Docosane	Insoluble	$C_{22}H_{46}$	**310**	**368**	**44**	**0.8**
Heneicosane	Insoluble	$C_{21}H_{44}$	**296**	**356**	**40.5**	**5.5**
Eicosane	Insoluble	$C_{20}H_{42}$	**282**	**342**	**36.6**	**6.1**
Nonadecene	Insoluble	$C_{19}H_{38}$	**266**	**329**	**23**	**5.3**
Octadecane	Insoluble	$C_{18}H_{38}$	**254**	**316**	**28**	**1**
Other	Insoluble	-	**-**	**-**	**-**	**22.1**

In this study, PO was the best scrubbing oil. The result showed that tar removal efficiency of plant oils (PO and WCO) was about 2 times higher than WLO. As mentioned above, a lot of O-element in their components in plant oils which is called as the polar head slightly increased the polarity degree for dissolving polar substances. Therefore, more polar tar was absorbed, whereas their nonpolar tail well-dissolved nonpolar tar. The long chains of the nonpolar tail or a high molecular weight of their compounds showed the positive effect for the overall tar solubility because a higher molecular weight resulted in a higher van der Waals force between the oil and tar molecules. Therefore, plant oils can remove both non-polar and polar tars.

For WCO, the results showed a slight decrease of the tar removal efficiency compared to PO. The decreasing of tar removal efficiency can be explained by the following reasons. Firstly, there is a reduction of O-element from 11.4%wt of PO to 10.8%wt of WCO as shown in the ultimate analysis results. After a deep frying process, the chemical components of vegetable oil were also changed. The GC-MS results also showed the increase of the unsaturated fatty acid which decreased the van der Waal interaction force between the oil and tar molecules. Secondly, there was a formation of high molecular weight of polymer [28, 29] during a deep frying process. The formation of high molecular weight polymers increased the oil viscosity as shown in Table 2.2. The viscosity was increased from 47.5 mm^2/s for PO to 50.5 mm^2/s for WCO. This increase of the viscosity of WCO means that the fluid resistance (drag force) was increased, which reduced the mass transfer rate. Finally, some contaminants in WCO which cannot be eliminated by the pretreatment process may have negatively acted. The contaminants in WCO disturbed and obstructed the absorption mechanism resulting in the reduction of the tar absorbability.

For WLO, the composition was long chain Alkanes and included some additives such as oxidation inhibitors, detergent dispersants, corrosion inhibitors, rust inhibitors, antifoam agent, anti-wear agent, viscosity index improvers and pour point depressants [30]. A major difference between plant oils and waste lubricant oil was O-elements (the carboxyl group in plant oils). As previously mentioned, tars are composed of nonpolar tars and polar tars. Therefore, the hydrophobic components in WLO can well dissolve the non-polar tars only from the synthesis gas, but it could not dissolve polar tars. Moreover, the viscosity of WLO shown in Table 2.2 was higher than PO and WCO, which limited the mass transfer rate. Therefore, the tar removal efficiency of WLO was the lowest in this study. For improving the tar removal efficiency by using WLO, it can be done by viscosity reduction as will be discussed in the following part.

2.5.2 Effect of the operating temperature on the tar removal efficiency

The other influencing factor for the tar removal efficiency was the absorbent temperature, which had a strong effect on the tar absorption. In this study, the operating temperature of plant oils (PO, WCO) and WLO were set at 30, 40, 50 and 60°C for investigating the gravimetric tar removal efficiency. The absorbent temperature was controlled by a temperature adjuster. The results are shown in Figure 2.9.

For PO, the gravimetric tar removal efficiency slightly decreased in proportion to increasing the temperature. The best operating temperature in this study was 30°C. The gravimetric tar was reduced to 4 g/m^3, which was 85% tar removal efficiency. Although the increase in the operation temperature results in the positive side of the mass transfer rate (i.e. decrease the viscosity of a fluid, decrease the interfacial tension and increase the gas holdup), these experiment results proved that, in a low viscous fluid, increasing the temperature of the scrubbing oil had a negative effect not only for the light tar but also for the gravimetric tar removal efficiency due to the gas stripping[31]. Moreover, the increase of the temperature reduced the retention time and the van Der Waals force between the tar and oil molecules because the energy added eliminated this weak bonding.

For WCO, the gravimetric tar removal efficiency showed similar tendency as PO according to its low viscosity characteristic. The optimum condition was at 30°C. The gravimetric tar was reduced to 5.8 g/m^3 which is 79% tar removal efficiency.

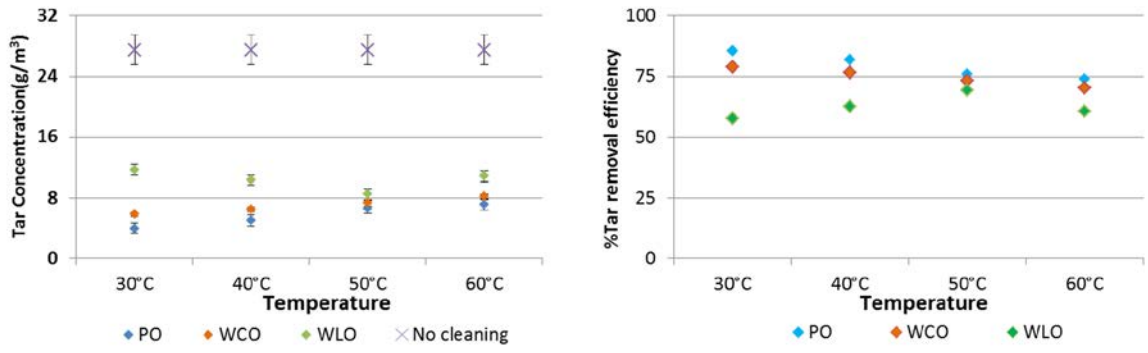

Figure 2.9 Temperature effect on the tar removal efficiency of vegetable oil (PO) and low-cost competitive solvents (WCO, WLO)

For WLO, which was a high viscous fluid, the gravimetric tar removal efficiency increased when the increase of the temperature from 30°C to 50°C, then, decreased above 50°C. As a result, the best temperature for operating WLO scrubber was 50°C, where the gravimetric tar could be reduced to 8.5 g/m^3, which was 69 % removal efficiency. For a high viscous fluid, increasing the temperature reduced the oil viscosity, minimized the thickness of the interface layer between the liquid phase and the gas phase and increased the diffusion rate of gases tar into the liquid phase. The reduction of the viscosity reduced the resistant of the fluid motion, which effectively reduced the portion of the leaked gas in the cleaning process compared to at 30°C. Another positive effect was the reduction of the interfacial tension resulting in the increase of the wettability and increased the effective interfacial area for removing tar. For bubble formation, bubble becomes smaller and more uniform when the temperature is increased[23]. These improvements of the contacting surface area and the contacting time for tar absorption resulted in the increase of the gravimetric tar removal performance. Nevertheless, above 50°C, the tendency of tar removal performance was similar to PO and WCO due to the tar desorption. Therefore, using WLO as a scrubbing liquid requires the external heating to improve the kinetic properties.

Comparing the tar removal efficiency at various operating temperatures of plant oils (PO, WCO) and waste lubricant oil (WLO), the plant oils showed the higher gravimetric tar removal efficiency according to the advantage of the polar tar removal by the oxygenated functions in plant oils. This clearly shows that the solubility has more influence for tar removal than the hydrodynamic properties. At the adsorbent temperature over 60°C, the viscosity of WLO was almost the same as those of plant oils (PO, WCO) as shown in Table 2.2. The increase of the absorbent temperature was effective for only the high viscous fluid (WLO), while there was an opposite effect for the low viscosity fluid (PO, WCO) when the absorbent temperature was increased. Finally, WCO clearly showed a good absorbent performance being competitive to PO due to a higher tar removal efficiency than WLO.

Light tar measurement was conducted to confirm the trend of desorbed tar. Synthesis gas was generated and introduced to 500 ml of oil scrubber at 30°C and 60°C. The major concentration of biomass light tar, which were benzene, toluene, phenol and naphthalene, were investigated before and after PO, WCO, and WLO scrubber. Light tar removal performance is shown in Figure 2.10. Naphthalene and phenol were completely absorbed in PO, WCO, and WLO scrubber because of two reasons. Firstly, the inlet concentrations of naphthalene and phenol were of less proportion. Secondly, the evaporation temperatures of naphthalene and phenol are higher than benzene and toluene. In case of benzene and toluene, increasing temperature dramatically decreases the light tar removal performance. WLO showed poor absorption performance for benzene and toluene at 60°C due to tar desorption. On the other hand, 100% of phenol and naphthalene were removed at the exit of the oil-based scrubber as shown in Figure 2.10.

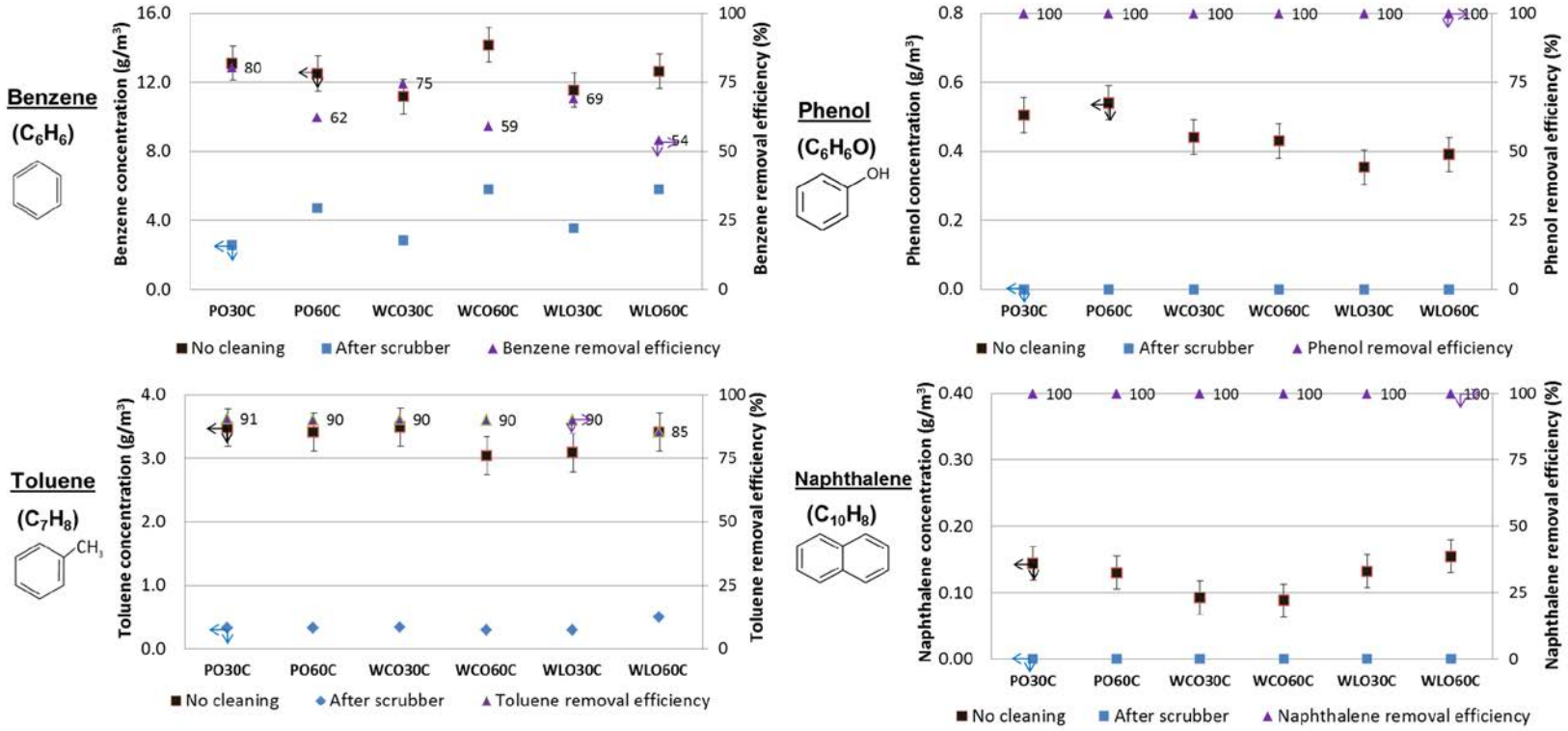

Figure 2.10. Temperature effect on the light tar removal efficiency of vegetable oil (PO) and low-cost competitive solvents (WCO, WLO)

2.6 Conclusion

For preventing unpredictable breakdown of machines in downstream application in the biomass gasification process, tar contained in the synthesis gas must be removed, especially the gravimetric tar. In this study, the simple method for tar removal by the wet gas cleaning with the consideration of the type and the kinetic characteristics of absorbents were investigated. For the absorbent type, new oil and waste oil were utilized. For the absorbent kinetic characteristics, four different operating temperatures were studied for the gravimetric tar removal. This research is aimed to study the solubility of the scrubbing oil by upgrading the kinetic absorption properties with the change of the operating temperature and the possibility for using waste oil in a scrubber as a cost competitive absorbent. The results could be concluded as follow.

1. OH element in PO and WCO improved the dissolution property of the polar tar which increased the global tar removal performance, while the polar tar could not be effectively removed by WLO.

2. For the absorbent kinetic characteristics, the improvement of the kinetic absorption by optimizing the solvent temperature could increase the gravimetric tar removal performance of WLO from 58% to 69% at 50°C, however, there was no improvement in the light viscosity oil (PO and WCO).

As a result, PO was recommended due to the highest tar removal performance, while WCO was recommended as a low cost scrubber medium with a high tar removal performance.

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Chapter 3

Utilization of waste materials in combination of absorption and adsorption techniques for tar removal capacity improvement

3.1 Background

The products from biomass pyrolysis and gasification processes are synthesis gas, tar and bio-char, where yields of each product depend on the process condition as mentioned in Chapter 1. The by-product bio-char is useful in many applications such as soil amendment, sorbent for contaminant reduction in soil and water, fuel cell system, raw materials for making activated carbon and gas adsorbents[1]. The physical properties, chemical properties and characteristic of bio-char depend on many main key factors such as the heating rate, the operation temperature, the gas agents and the residence time. Meyer et.al.,[2] summarized the char product yields in varies process type which 12-16% and 10% remained from the fast pyrolysis and gasification process, respectively. Fu et.al.[3] reported the effect of the temperature on char structural features of maize stalk, rice straw, cotton straw and risk husk. It was found that increasing of the operation temperature (700-900°C) resulted in the reduction of the char yield, but the increase of the surface area and the pore volume, while Guerrero et. al,[4] reported the influence of the temperature and the heating rate on the structure of rice husk and rice husk char. The SEM (scanning electron microscope) photomicrograph and the BET (Brunauer, Emmett and Teller) surface area clearly showed that no major morphological changes was found during the devolatilization at a high heating rate because of its high thermal resistance due to a high silica content.

For the tar removal purpose, most studies utilized chars as a catalytic conversion [5-9]. Abu El-Rub et.al.[5] reported the comparison of tar (model tar compounds) conversion by biomass chars with other catalysts, where biomass char was the highest naphthalene conversion among the low cost catalysts used. Park et. al.[7] conducted the primary tar reduction by hot char particles in a fixed bed gasifier. The mass yield of tar was reduced to 24.8%, 13.7% and 7.7% by the pyrolysis, the thermal cracking and the hot char particles, respectively. However, it contributed the soot or coke formation over the surface of char, which leaded to the loss of micro-pores that provided the active sites [8, 9]. On the other hands, few researchers conducted on chars for tar adsorption. For air pollution control, e.g. inorganic gases and VOCs in the finishing industrials, activated carbon is a most widely used medium because it is very effective, readily available and long lasting[10-12]. Das et.al.[13] reported the effect of the temperature, the VOC concentration, the gas flow rate and the BET surface area on the removal of VOC by activated carbon fibers. The results showed that a high temperature, a high concentration, a high gas flow rate, and a low BET surface area leaded to a low VOC removal. Phuphuakrat et.al.[14] investigated a low temperature packed bed for tar removal using three absorbents (activated carbon, woodchip and synthetic porous cordierite). The results showed that the activated carbon showed the best adsorption performance for light aromatic hydrocarbon tars and light PAH tars, while wood chip was recommended for practical utilization. For cost competitiveness, Paethanom. et. al.[15] proposed rice husk char as a cost-free adsorbent for gravimetric tar removal purpose. The effect of the pyrolysis

temperature (600, 800, and 1000°C) on the tar removal efficiency of the rice husk char was investigated. The results showed that 87.5% of the gravimetric tar could be removed by the char pyrolyzed at 800°C, which was the most favorable char for the tar adsorption, while the char pyrolyzed at 600°C had less fixed carbon content and that pyrolyzed at 1000°C had very low specific surface area.

As discussed in Chapter 2, the wet gas cleaning by the oil scrubber mainly eliminated the gravimetric molecular weight tar. However, some amount of tar still remained in the synthesis gas due to low removal performance of bubbling bed scrubber. A high porosity and adsorbability of residue char is advantageous for further gas cleaning, which was conducted on previous research in our laboratory. Combining the absorption (vegetable oil scrubber) and adsorption (char bed) technique improves almost 7% of gravimetric tar removal efficiency[16]. For scaling-up, the combination of 1 liter of sunflower oil scrubber with 41 grams of chestnut wood char in an adsorption bed could achieve 97.6% gravimetric tar removal efficiency in the lab-scale and, finally, the combination of15 liters of sunflower oil scrubber with 922 grams of chestnut wood char in an adsorption bed could achieve 98.7% gravimetric tar removal in the pilot-scale over 30 minutes of the test duration[17].

Even if the combination unit was well-achieved for tar removal, the crucial point which should be considered in the next step is the life-time of absorbents and adsorbents which shall determine the timing for changing these absorbents and adsorbents in order to maintain their tar removal performances and to prevent breakdown of downstream machines. Therefore, in this chapter, the tar removal capacity of WCO (waste cooking oil) and RHC (rice husk char) were investigated. WCO is considered as an absorbent, which was recommended in Chapter 2 as a high tar reduction and low cost absorbent. RHC is considered as a residue from the gasification process with a high porosity. The tar removal capacity of the WCO absorbent was analyzed by both the wet and dry tar collection methods using the cleaning unit 1 (CU1), and the tar removal capacity of the RHC adsorbent was also analyzed by both the wet and dry tar collection methods using the cleaning unit 2 (CU2).

3.2 Materials and setup

3.2.1 Materials

In this chapter, rice husk was used as a feed material which was obtained from the Siam Cement Public Company Limited, Thailand. It was crushed and sieved with the mesh size of 0.5 - 1 mm as shown in Figure 3.1a). Then, it was dried in an oven at 105°C for 10 hours in order to eliminate its moisture content.

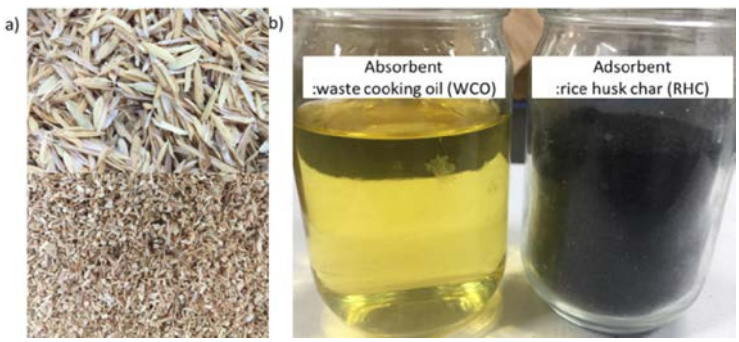

Figure 3.1: a) Feedstock: rice husk, b) Absorbents: WCO and Adsorbent: RHC

In the absorption unit, WCO was used as an absorbent as shown in Figure 3.1b) which was obtained from Best Trading Company, Atsugi, Kanagawa, Japan. In the preparation process, WCO was put in a 200 liter tank and left for one night for particle and impurity sediment to deposit at the bottom of the tank. Then, 10 liters of the oil at the bottom of the tank was drained to remove such impurities. Finally, it was heated and depressurized to 65°C and 0.095 MPa respectively so as to remove moisture content in WCO. Its density and kinetic viscosity was 0.88 g/cm³ and 53 mm²/s, respectively, at 27°C.

In the adsorption unit, RHC was by product from rice husk gasification process. Rice husk was supplied at the top of the reactor. The reactor was set at 800°C by the external heat source. The residue of this process was called as RHC as shown in Figure 3.1b). Table 3.1 describes the ultimate and proximate analysis results of rice husk, WCO and RHC, respectively.

Table3.1: Ultimate and proximate analysis of the rice husk, WCO, and RHC.

Parameters	Ultimate analysis (wt% dry and ash free basis)					Proximate analysis (wt% dry basis)		
	C	H	O	N	Cl	Volatile matter	Fixed carbon	Ash
Rice husk	32.2	4.3	62.3	0.8	<0.4	59.7	11.9	28.4
Waste cooking oil(WCO)	77.5	11.6	10.8	0.1	0	100	0	0
Rice husk char(RHC)	16.9	0.6	82.23	0.2	<0.07	13.5	13.9	72.6

3.2.2. Experimental setup

The synthesis gas generation part consists of a feeder, a pyrolyzer, a reformer and an air cylinder tank as shown in Figure 3.2. Dried biomass was packed into the feeder and was fed continuously with the feed rate of 0.6 g/min. Air was used as a carrier gas with a flow rate of 0.8 l/min in order to control the equivalent ratio to 0.35. An external heat source was supplied by electric heaters for both the pyrolyzer and the reformer. The pyrolyzer was a fixed bed type made from a SUS306 tube with the diameter of 30 mm and the height of 280 mm. The temperature of the pyrolyzer was set at 800°C. The reformer was also made from SUS306 tube with the diameter of 25 mm and the height of 1300 mm. The temperature of the reformer was set at 800°C for the thermal cracking of tar. Before conducting the experiments, both the pyrolyzer and the reformer were kept at the temperature of 800 °C for 30 minutes with supplied ambient air. After that, the feeder was started, and then, feedstock was pyrolyzed and converted into biochar and synthesis gas containing tar. In order to prevent the condensation of tar, synthesis gas containing tar aerosol flowing out from the pyrolyzer was introduced into the reformer in order to decompose the easily condensable tar. Finally, the synthesis gas was introduced into the gas cleaning unit and the tar sampling unit after the start of the operation of the feeder for 15 minutes.

In this chapter, the gas cleaning process was conducted by two units. The first cleaning unit was called CU1 which consisted of a bubbling scrubber and a digital magnetic stirrer. A total of 500 ml of WCO was contained in a three-neck flask scrubber with 750 rpm of the turbulence mixing speed controlled by a digital magnetic at 27°C as shown in Figure 3.3 a) while the temperature inside the scrubber was recorded at every 15 minutes during the experimental period. Another cleaning unit was called CU2 which consisted of a series of scrubber and a packed bed adsorber. The scrubber was similarly set as CU1. For packed bed adsorber, a total of 30 grams of RHC was packed in the cylinder bed of the diameter of 50mm and the height of 250 mm at the room temperature as shown in Figure 3.3 b).

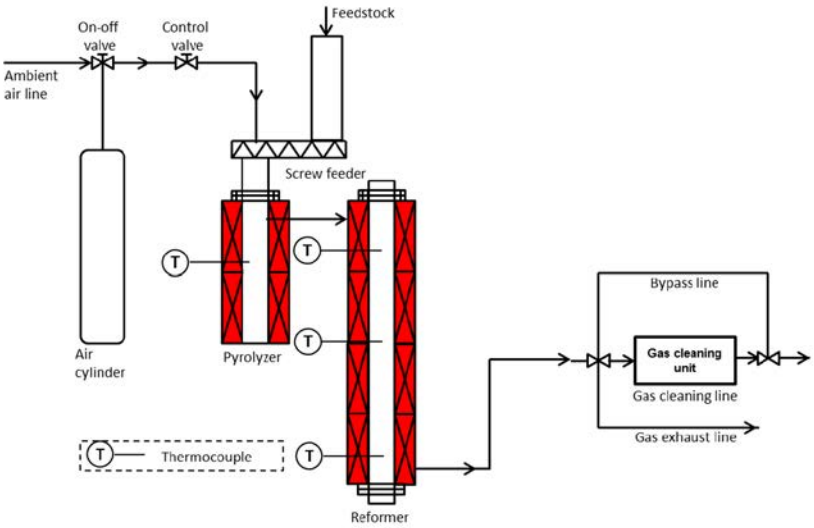

Figure 3.2: The process flow of the experimental setup

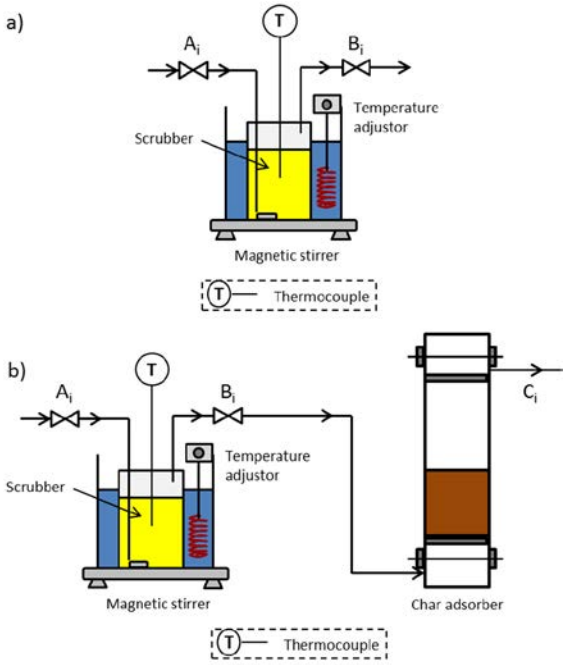

Figure 3.3: The process flow of the gas cleaning setup a) WCO scrubber (cleaning unit No.1 or CU1), b) WCO scrubber and RHC adsorber (cleaning unit No.2 or CU2)

3.3 Sampling and analysis method

Both the wet and the dry methods were employed to analyze the amount of tar in the synthesis gas with different purposes. The wet method was used for analyzing the complex high to medium weight tar. The gravimetric tar was measured by the weight. The dry method was used for analyzing PAH in the synthesis gas and GC-FID was utilized to analyze the contaminant in the synthesis gas. The details of both methods in this research are described as follows.

3.3.1 Wet method for gravimetric tar measurement

The wet method was the method separating the tar from synthesis gas by using the principle of tar condensation at a low temperature[18]. The procedure of the sampling method is shown in Figure 3.4. The wet method consisted of 10 impingers connected in series. Tar was dissolved in 100 ml of IPA which is non-polar solution and good dissolving medium contained in each impinger. The total of IPA solution was 1000 ml per experiment. The first six impingers were installed in the mixture of salt, water and ice bath with the temperature of around 1-3°C. The others were installed in the IPA bath with a cooling device to keep its temperature at -22°C. The tar sampling was done for 60 minutes. After that, tar was separated from IPA by filtering and evaporating by a rotary evaporator in a water bath whose temperature was set at 40°C. The residue was defined as the heavy tar or the gravimetric tar which was measured by the weight.

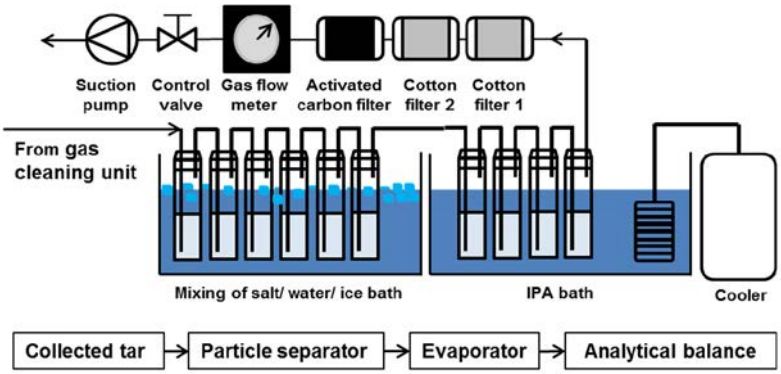

Figure 3.4: Schematic diagram of the wet sampling and the flow measurement method

3.3.2 Dry method for light tar measurement

The dry method was used for analyzing the light tar. The procedure of the sampling method is shown in Figure 3.5. The experimental equipment consisted of a 6 mm ID charcoal tube (containing 150 g of activated carbon) connected in series with a 8 mm ID silica gel tube (containing 780 mg of silica gel) purchased from Sibata Scientific Technology Ltd. The charcoal tube with a good adsorbing performance for non-polar organic compounds was used to measure benzene, toluene, styrene and naphthalene. The silica gel tube with a good adsorbing performance for polar organic compounds was used for measuring phenol and so on. The sampling line was connected with a cotton filter, an activated carbon filter, a gas flow meter and a suction pump.

The light tar was sampled at the constant flow rate (0.5 l/min) for three minutes. It was repeatedly sampled every 60 minutes at the same position. There were three positions for this measurement: point A (before entering the scrubber), point B (after exiting from the scrubber or before entering the char bed), and point C (after exiting from the char bed). After finishing the tar sampling, a gas chromatography flame ionization detector (GC-FID) was utilized to

detect light tar components and their concentrations. Carbon disulfide and acetone were used as solvents for the charcoal tube and the silica gel tube, respectively. Additional details of dry type tar sampling and analysis have been described in our pervious paper[19]

3.3.3 Flow measurement method

Both the wet and the dry tar measurement methods employed the same procedure for the gas flow rate measurement. The gas flow rate measurement equipment consisted of a cotton filter, an activated carbon filter, a gas flow meter, an adjustable control valve and a suction pump connected in series. It was installed after the tar measurement unit as shown in Figures 3.4 and 3.5.

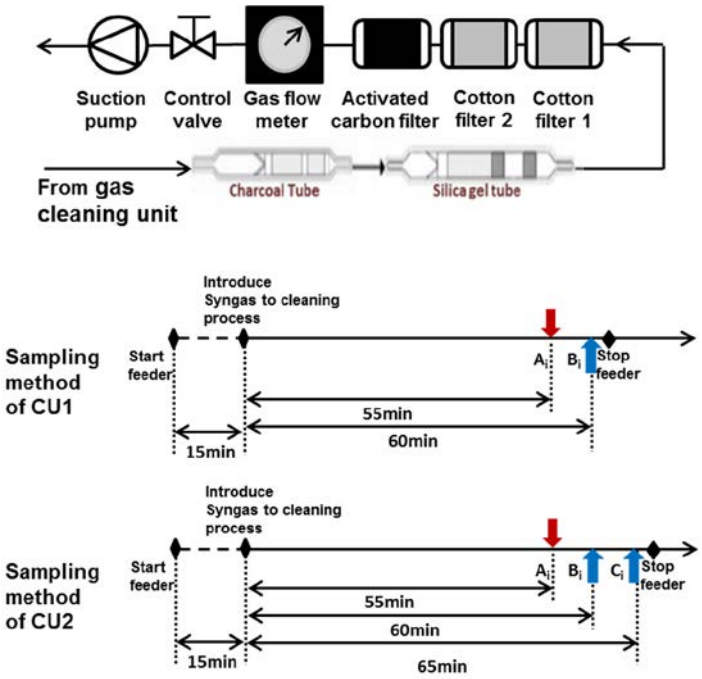

Figure 3.5: Schematic diagram of the dry sampling and the flow measurement method

3.4 Experimental procedure

3.4.1 Capacity analysis of WCO

The cleaning unit No.1 or CU1 was used for the WCO capacity analysis. After the synthesis gas was passed through CU1, the remaining tar was collected by both the wet and the dry methods. For the wet method, in the first three hours, tar was sampled at every 20 minutes. After that, tar was sampled at every 60 minutes for 10 hours. For the dry method, the light tar was sampled at every 60 minutes for 10 hours. The experimental procedure is shown in Table 3. 2.

3.4.2 Capacity analysis of RHC

Cleaning unit No.2 or CU2 was used for the RHC capacity analysis. The experimental procedure was the same as the WCO capacity analysis procedure as shown in Table 3.2.

Table 3.2: Initial experimental setup condition and the procedure of WCO and RHC capacity analysis

Parameters	Capacity analysis of WCO			Capacity analysis of RHC	
	Run 1-1	Run1-2	Run 1-3	Run2-1	Run 2-2
Initial experimental set up					
Feedstock			Rice husk		
Feedstock size(mm)			0.5-1		
Feedstock rate(g/min)			0.6		
Carrier gas			Air		
Carrier gas flow rate(l/min)			0.8		
Pyrolyzer(°C)			800		
Cleaning unit setup					
Absorbent	WCO	WCO	WCO	WCO	WCO
Volume (ml)	500	500	500	500	500
Mixing speed (rpm)	750	750	750	750	750
Adsorbent	-	-	-	RHC	RHC
Mesh size (mm)	-	-	-	0.5 – 1.0	0.5 – 1.0
Amount (g)	-	-	-	30	30
Gas flow rate (lph)	78	78	30	78	30
Measurement method	Wet method	Wet method	Dry method	Wet method	Dry method
Experimental duration (min)	20	60	60	60	60

3.5 Results and discussion

3.5.1. WCO absorption performance and capacity

- **Gravimetric tar removal capacity of WCO absorption**

In this study, the absorbent temperature inside the scrubber was set at 30°C. The tar removal mechanism stemmed from the condensation and dissolution of gaseous tar. The tar condensation took place when the absorbent temperature was lower than the tar dew point. The tar dissolution could be explained by the “like dissolve like" principle: the relationship between the solute and solvent is vital in determining the solubility (strong solute-solvent attraction implies larger solubility), where polar solutes dissolve in polar solvents, non-polar solutes dissolve in non-polar solvents, and polar solutes do not dissolve in non-polar solvents. WCO was chosen as a tar absorbent because it can remove both non-polar and polar organic compounds of biomass gaseous tar as mentioned in Chapter 2. Furthermore, WCO has other appropriate properties such as low evaporation rate, having no corrosive agents, availability, low price, low viscosity, non-toxicity, chemical non-reactivity and low freezing point. In this experiment, a total of 57 g/m³ of the gravimetric tar generated from rice husk gasification were continuously introduced into WCO scrubber over the 10-hour experiment period. Almost 90% of the gravimetric tar was removed from the synthesis gas in the first 20 minutes of the experiment as presented in Figure 3.6. While the absorption capacity continuously decreased proportionally to the time. In the first hour of the experiment, the performance slightly dropped from 88% in

the first 20 minutes to 80% in one hour. After the experiment was conducted for two hours, the tar removal efficiency decreased to only 68.2%. Finally, the tar removal performance dropped to 25.3% after finishing 10 hours of the experiment.

In this study, there were two essential points for the analysis; the saturation point (the point at which the tar removal efficiency does not change so much with time) and the breakpoint (the point at which the deterioration of WCO starts and the change to new WCO is required). From Figure 3.6, it can be seen that the absorption capacity was continuously reducing until reaching its saturation point in 7^{th} of the experiment which is 28.5% of the tar removal efficiency. In 8^{th}, 9^{th} and 10^{th} hour of the experiment, the tar removal efficiency was 28.3% 24.9% and 25.3%, respectively. Between 7^{th} and 10^{th} hour of the experiment, the difference percentage of the tar removal efficiency was only 3.2%. Therefore, 7^{th} hour of the experiment was the saturation point of WCO in this study, where the removed tar stemmed from the condensation of low-dew-point tar. The breakpoint from the breakthrough curve, there was a large change of the performance from 100 minutes to three hours in the experiment. A total of 11.5%, 1.2%, 7.1% and 7.5% of the percentage of the tar removal efficiency were different in every 20 minutes from this period of the experiment which, in total, was 27.3% of the performance drop indicating that it was the timing that WCO reached the breakpoint and should be changed to the new one. In the first period of the experiment which was between 20 minutes to 100 minutes, the total drop of the tar removal efficiency was only 8.3%. Therefore, it can be seen that WCO reached the breakpoint in the second hour of the experiment due to the huge percentage drop in this period (11.5% from 100 minutes to two hours). It illustrates that WCO was able to absorb tar at 46.15 g-tar/m³-synthesis gas which was around 80.6% of the tar removal efficiency on the average in the first two hours of the experiment. The formula for calculating the amount of tar removal and its performance is shown in Equations 3.1 and 3.2, respectively, where $f(x)$ and $g(x)$express the polynomial equation derived from the inlet and outlet data respectively and x is the experimental period (minute). The amount of tar removed and the tar removal efficiency is calculated and summarized in Table 3.3.

$$m_{tar,r} = \int_0^{600} f(x)dx - \int_0^{600} g(x)dx \qquad \text{Equation 3.1}$$

$$\eta_{tar} = \frac{\int_0^{600} f(x)dx - \int_0^{600} g(x)dx}{\int_0^{600} f(x)dx} \times 100 \qquad \text{Equation 3.2}$$

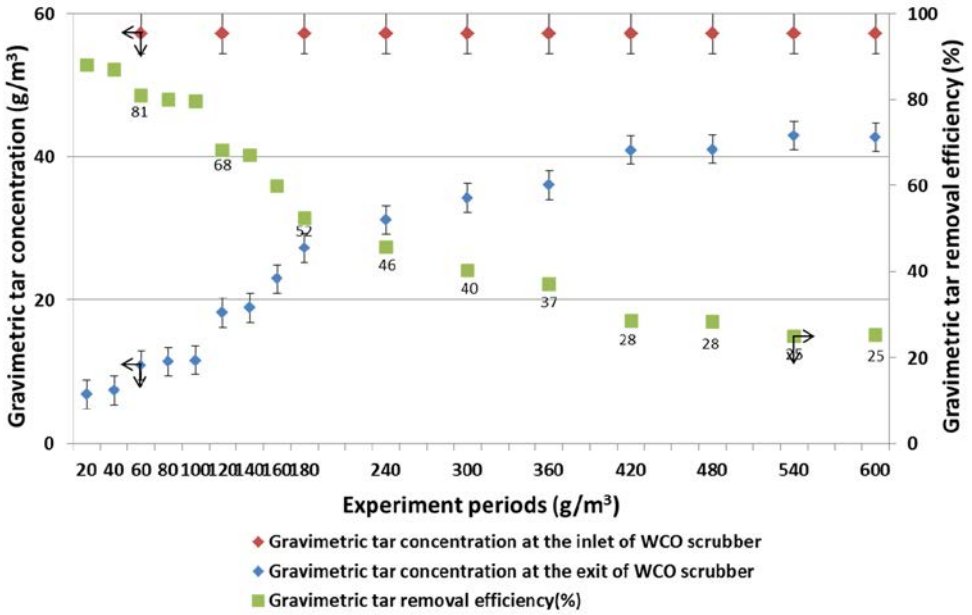

Figure 3.6: Gravimetric tar removal performance of WCO over 600 minutes

Table 3.3: Gravimetric tar removal performance of WCO for 10 hours of experiment

Experimental time (min)	Accumulative volume of the cleaned synthesis gas(L)	Tar removal amount (g/m³)	Tar removal efficiency (%)
20	26	50.37	88.0
40	52	49.79	87.0
60	78	46.31	80.9
80	104	45.79	80.0
100	130	45.60	79.7
120	156	39.03	68.2
140	182	38.35	67.0
160	208	34.30	59.9
180	234	29.99	52.4
240	312	26.07	45.5
300	390	23.00	40.2
360	468	21.19	37.0
420	546	16.29	28.5
480	624	16.18	28.3
540	540	14.26	24.9
600	780	14.51	25.3

During the absorption process, tar particles and other impurities were condensed and dissolved in WCO. The passage of time caused impurities, aerosols, dust and tar to accumulate in the WCO scrubber, leading to saturation of WCO. There were no impurities in the WCO scrubber at first. Then, the synthesis gas containing tar passed through the WCO scrubber continuously, the absorption mechanism of which is shown in Figure 3.7. It can be seen that there were a lot of available absorption area at the beginning. Hence, most of impurities were absorbed in the WCO scrubber, resulting in high tar removal efficiency. After that, tar removal efficiency decreased. This resulted from three main factors: the decrease of available absorption area, the increase of the fluid friction force, and the increase of desorption. The available absorption area was reduced by tar and other impurities accumulated in WCO. Consequently, the less available absorption area remained and the less amount of gaseous tar was removed. Moreover, the other impurities accumulated in WCO increased the viscous force (the hydrodynamic drag force) [20-

23]. This led to the increased portion of un-scrubbing gas. The tar desorption occurred at the interfacial area, where the rate of desorption increased with the reduction of available absorbent area. The tar in WCO whose dew point was very low had a tendency to desorb repeatedly. Finally, when there was no available absorption area, WCO reached the saturation point. After that, the tar removal of WCO could only be explained by the condensation effect.

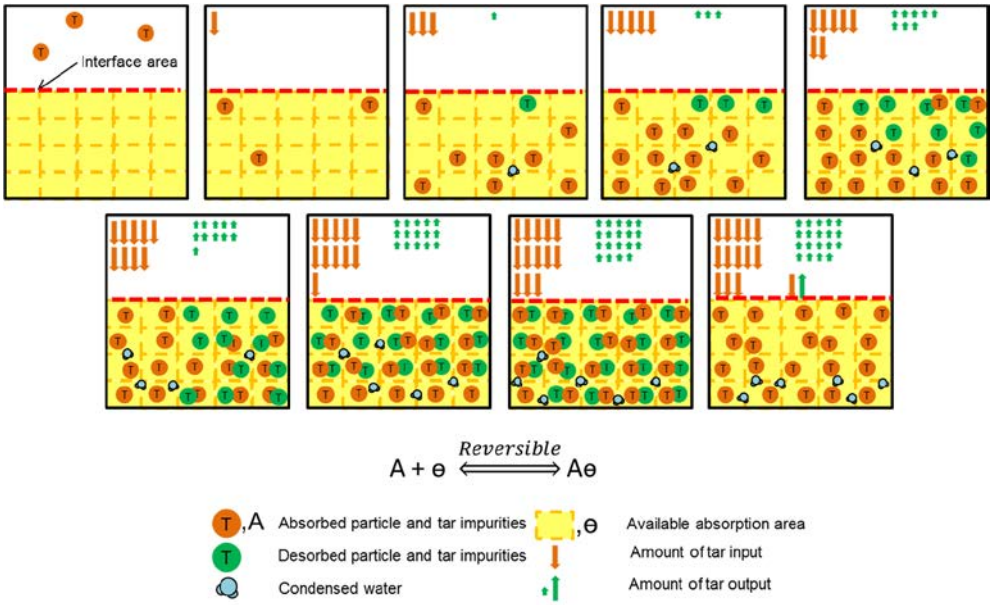

Figure 3.7: The absorption mechanism of WCO scrubber

- **Light tar removal capacity of WCO absorption**

The performance of WCO for removing one ring aromatic hydrocarbons and others which consist of the light tar were also studied. Benzene, toluene, phenol, and especially naphthalene showed good absorbability result by WCO as shown in Figure 3.8. Phenol and naphthalene were specifically concerned in this experiment due to direct changing from the gas to the solid phases at the ambient temperature leading to clogging and blocking inside of the piping and fitting system. Throughout the 10-hour experiment, the phenol and naphthalene removal efficiencies by WCO was relatively high, 85% and 87.5% on the average, respectively. However, considering the WCO capacity for gravimetric tar removal, the performance of light tar removal was important in the first two hours. In this experimental period, the phenol and naphthalene removal efficiency of WCO was 94.1% and 94.6% on the average, respectively. The removed amounts of other light tars and the removal efficiencies of them are calculated and summarized in Table 3.4.

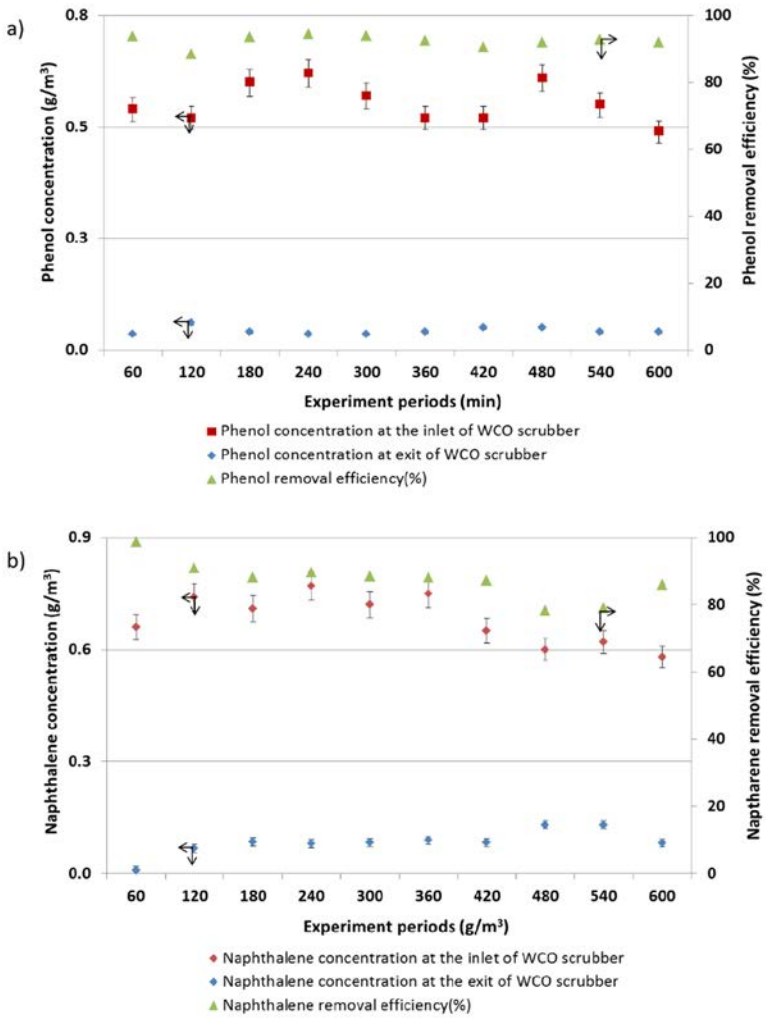

Figure 3.8. Light tar removal performance of WCO over 600 minutes: a) Phenol b.) Naphthalene

Table 3.4: The average light tar removal performance of WCO for the first two hours of the experiment

	Tar removal amount (g/m³)	Tar removal efficiency (%)
Benzene	15.44	74.1
Toluene	3.33	82.5
Phenol	0.78	94.1
Naphthalene	1.32	94.6

- **WCO scrubber designing**

Based on Table3.4, how to maintain the tar absorption capacity of WCO constantly by using the breakthrough curve of the gravimetric tar removal capacity will be discussed here for designing the scrubber. The tar mass balance was used for determining the suitable flow rate of WCO as shown in the following calculation:

Experiment

Tar mass balance;

$$m_{tar,t} = m_{tar,o} + m_{tar,wco} \quad [g]$$

Tar removal capacity;

$$C_{tar} = \frac{m_{tar,wco}\,[g]}{V_{wco}\,[L]} \quad \text{[g-tar/L-WCO]}$$

Tar removal efficiency;

$$\eta_{tar} = \frac{m_{tar,wco}\,[g]}{m_{tar,t}\,[g]} \times 100\% \quad [\%]$$

Scale-up

Tar removal amount;

$$m_{tar,wco} = \eta_{tar} \times m_{tar,t} \quad [g/h]$$

Tar contained in synthesis gas after cleaning;

$$m_{tar,o} = m_{tar,t} - m_{tar,wco} \quad [g/h]$$

Minimum flow rate required of WCO;

$$Q_{wco} = \frac{m_{tar,wco}\,[g/h]}{C_{tar}\,[g/L]} \quad [lph]$$

For the designing of the scrubber, the most important consideration is to maintain the tar absorption performance at the recommended level depending on the downstream application and the cleaning system[24] . From the experiment, we have observed that the heavy tar reached the breakthrough point before the light tar. Therefore, the data used for the calculation are limited in the first two hours of the experiment. The breakthrough curve illustrates that WCO was able to absorb tar at 14.4 g-tar/L-WCO which was the capacity to keep 80% tar removal efficiency on average.

3.5.2. RHC adsorption capacity

- **Gravimetric tar removal capacity of RHC adsorption**

Biochar, which is a residue from the gasification processes, can be utilized as an adsorbent of tar due to its high porosity. The gravimetric tar was not entirely removed by the bubbling scrubber. Therefore, the tar removal performance of the RHC combined with the WCO scrubber in the cleaning unit was also studied. The formula for calculating the amount of tar removal and its tar removal efficiency is the same as the formula for WCO scrubber as shown in Equations 3.1 and 3.2. The amount of tar removal and the tar removal efficiency were calculated and summarized in Table 3.5. CU2 performed better for heavy tar removal than CU1 in the first seven hours as shown in Figure 3.9 and Table 3.5 because some of the remaining gravimetric tar at the exit of the WCO scrubber was adsorbed by RHC adsorber leading to better gravimetric tar removal performance. However, due to the tiny pore size of RHC, it was not appropriate to use for gravimetric tar removal. After 7th hour of the experiment, the performance of CU2 was lower than CU1. This is because when pores of RHC were saturated by adsorbing both gravimetric and light tars, RHC lost the adsorption ability. Moreover, some of the gravimetric tar and light tar adsorbed by RHC had a tendency to vaporize easily resulting in lower performance of CU2 than CU1 finally.

Although RHC was not so effective for gravimetric tar removal, the increase of the gravimetric tar removal efficiency by RHC was between 2.3% and 4.6% in the first three hours, however, continuously dropped after fourth hours of the experiment. This means that pores of RHC adsorbed some of heavy tar and light tar. However, tar accumulation adsorbed in RHC decreased the specific surface area of RHC for adsorption until reaching the saturation point. It can be seen that after 8th hour of the experiment, RHC was deteriorated for tar removal completely

shown by the lower performance of CU2 compared to CU1. Therefore, it can be summarized that the breaking point of RHC for gravimetric tar removal was at third hour and the saturation point was at 8th hour.

Considering that the light tar reached the breakthrough point before the heavy tar, the data after the first two hours of the experiment was analyzed. The calculation of RHC adsorption amount was done by the difference of the amount of gravimetric tar removed between CU2 and CU1. Therefore, RHC was able to adsorb gravimetric tar with the capacity of 1.78 g-tar/m³ -synthesis gas which was around 3.1% of the increase of the gravimetric tar removal efficiency on average in the first two hours of the experiment. Details of RHC heavy tar removal is described in Table 3.5.

Table 3.5 Comparison of the gravimetric tar removal performance between CU1 and CU2 for 10 hours of the experiment

Experimental time (min)	Accumulative volume of the cleaned synthesis gas (L)	WCO and RHC		WCO		RHC	
		Tar removal amount (g/m³)	Tar removal efficiency (%)	Tar removal amount (g/m³)	Tar removal efficiency (%)	Increase of tar removal amount (g/m³)	Increase of tar removal efficiency (%)
60	78	47.62	83.2	46.31	80.9	1.32	2.3
120	156	41.26	72.1	39.03	68.2	2.23	3.9
180	234	32.61	57.0	29.99	52.4	2.62	4.6
240	312	27.89	48.7	26.07	45.5	1.82	3.2
300	390	24.21	42.3	23.00	40.2	1.21	2.1
360	468	22.15	38.7	21.19	37.0	0.96	1.7
420	546	17.34	30.3	16.29	28.5	1.05	1.8
480	624	14.88	26.0	16.18	28.3	-1.30	-2.3
540	540	13.45	23.5	14.26	24.9	-0.81	-1.4
600	780	14.71	25.7	14.51	25.3	0.20	0.5

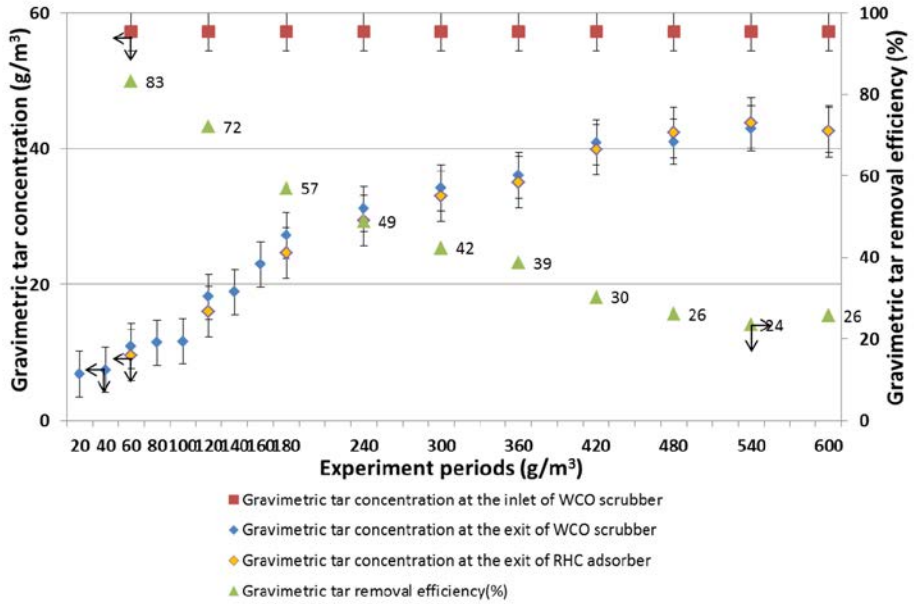

Figure 3.9 Comparison of gravimetric tar removal performance between CU1 and CU2 over 600 minutes of experiment

- **Light tar removal capacity of RHC adsorption**

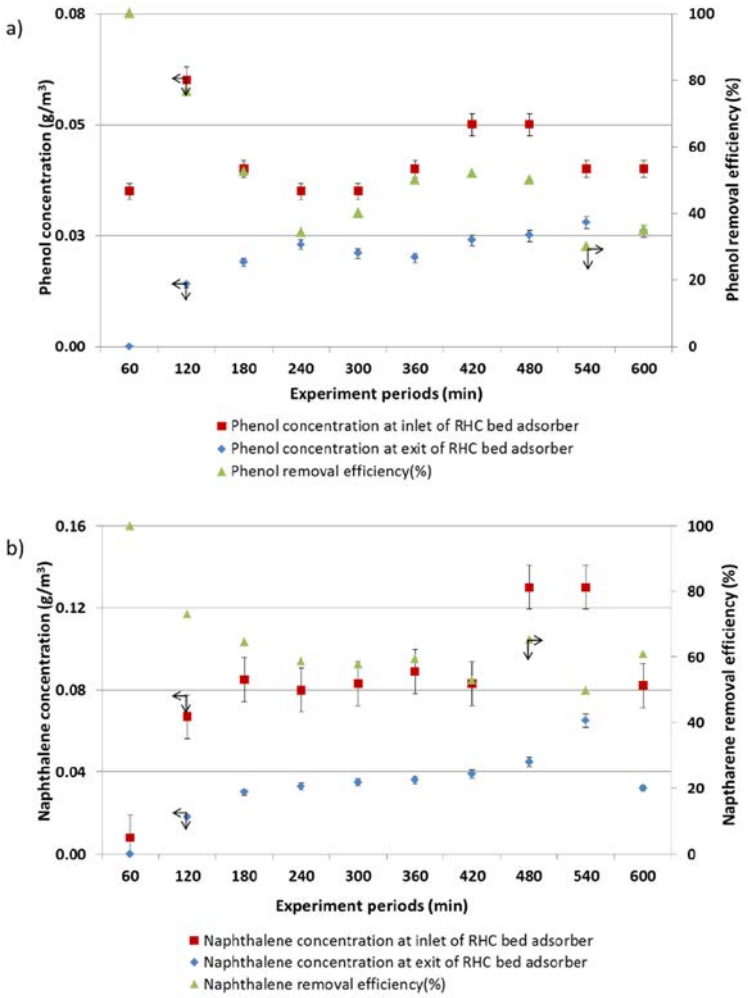

Figure 3.10: Light tar removal performance of RHC over 600 minutes a) Phenol, b) Naphthalene

As aforementioned, the objective to utilize RHC is mainly to capture the light tar (benzene, toluene, phenol and naphthalene). It was found that RHC(800°C) slightly contained an abundance of surface functional groups (e.g. hydroxyl group (-OH, Si-OH), C-H stretching of alkanes, C=O stretching of aromatic groups, C=C stretching of alkenes and aromatic, carboxyl-carbonate, CHOH stretching of alcohol group, Si-O-Si, and Si-H), which was analyzed by Fourier-transform infrared (FT-IR) spectroscopy [25, 26]. The adsorption mechanisms of RHC were controlled by the specific surface area, the micro-porosity and the interfacial force between RHC and tar molecules. The breakthrough curve and the removal efficiency of benzene, toluene, phenol and naphthalene are shown in Figure 3.10. For phenol removal, RHC well adsorbed phenol compared to benzene and toluene. The oxygen function groups (-OH, C-O, and C=O) of RHC could interact with phenol via the hydrogen bond. Moreover, the strong electron-donating ability of the hydroxyl group made the aromatic ring of phenol a π-electron rich system, as shown in Figure3.10b. As a consequence, the aromatic rings of different phenol molecules were easy to form π-π stacking interactions and offer a multilayer adsorption [27]. In the first two hours of the experiment, the performance of phenol removal decreased from 100% to almost 70%. After that, the removal efficiency remained constant at around 60%. The naphthalene removal by RHC also showed a high removal efficiency according to its electrostatic attraction [28,

29]. In the first two hours of the experiment, the performance of naphthalene removal decreased from 100% to 73.3% and decreased to 62.9% in the third hour. After that, the removal efficiency remained constant at around 60%. It can be concluded that the breakpoint of RHC for phenol and naphthalene removal was at the first two hours. The performance of RHC for naphthalene removal was 76.0% on average. The amounts of other light tar removal and their removal efficiencies are calculated and summarized in Table 3.6.

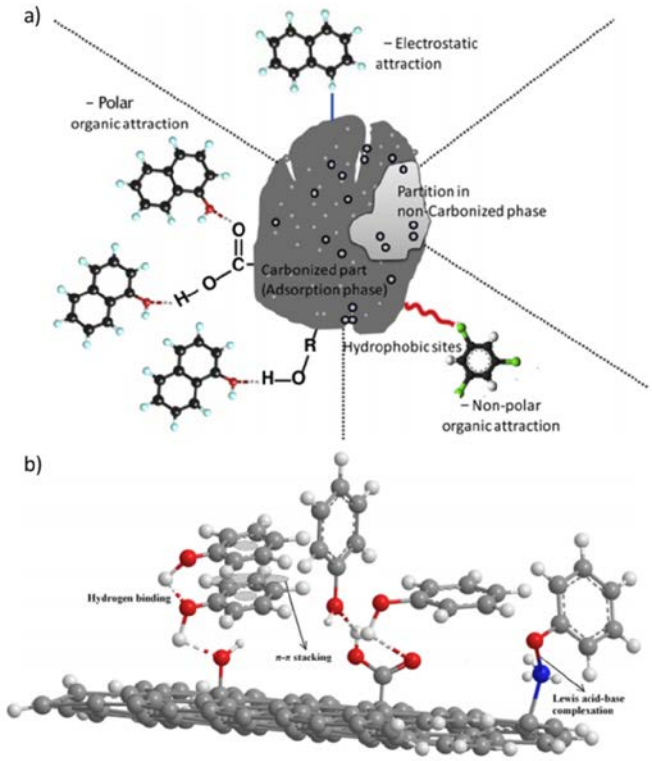

Figure 3.11a) Postulated mechanisms of the interactions of RHC with polar and nonpolar light tar [28] b) The interactions between phenol and the functional groups on the surface of biochar [27]

Table 3.6 Average of gravimetric and light tar removal performance of RHC for the first two hours of the experiment

	Tar removal amount (g/m^3)	Tar removal efficiency (%)
Gravimetric tar	2.23	3.9
Benzene	0.86	15.8
Toluene	0.08	11.4
Phenol	0.03	69.1
Naphthalene	0.06	76.0

- **RHC bed designing**

Based on Table 3.6, how to maintain the naphthalene adsorption capacity of RHC constantly by using the breakthrough curve of naphthalene removal capacity will be discussed here for designing the RHC bed. Mass balance of naphthalene was used for determining the amount of char required for naphthalene removal and the appropriate lifetime for changing to new char as shown in the following calculation.

Experiment

Naphthalene mass balance;

$$m_{nap,t} = m_{nap,o} + m_{nap,RHC} \quad [g]$$

Naphthalene removal capacity;

$$C_{nap} = \frac{m_{nap,RHC}\ [g]}{m_{RHC}\ [g]} \quad [g\text{-Nap/g-char}]$$

Naphthalene removal efficiency;

$$\eta_{nap} = \frac{m_{nap,RHC}\ [g]}{m_{nap,t}\ [g]} \times 100\% \quad [\%]$$

Scale-up

Naphthalene removal amount;

$$m_{nap,t} = m_{nap,t}\ [g/h] \times t_d \quad [h]$$

$$m_{nap,o} = \eta_{nap} \times m_{nap,t} \quad [g]$$

Naphthalene contained in synthesis gas after cleaning;

$$m_{nap,o} = m_{nap,t} - m_{nap,RHC} \quad [g]$$

Minimum required of RHC;

$$m_{RHC} = \frac{m_{nap,RHC}\ [g]}{C_{nap}\ [-]} \quad [g]$$

According to the naphthalene adsorption capacity data of RHC obtained from the experiment, it was found that RHC was able to adsorb naphthalene with the capacity of 0.15 mg-naphthalene/g-char to have 76% of the naphthalene removal efficiency. These data can be used for determining the amount of RHC and the changing period in order to operate the scale-up unit stably.

3.6 Conclusion

Two types of tar; the gravimetric tar and the light tar, were mainly concerned for determining the operating conditions of the WCO scrubber and the RHC adsorber. The objective of this study was to know the timing for periodic changing of these absorbent and adsorbent in order to maintain their tar removal performance and prevent unpredictable breakdown of machines due to tar condensation. In this research, there were two essential points for the analysis; the saturation point (the point at which the tar removal efficiency does not change so much with time) and the breakpoint (the point at which the deterioration of WCO starts and the change to new WCO is required). WCO was mainly used for heavy tar removal due to its non-polar characteristics. 7th hour of the experiment was the saturation point of WCO in this study as the percentage of difference of tar removal efficiency was only 3.2% between 7th hour and 10th hour of the experiments, while the breakpoint was within 2 hours of the experiment due to the large percentage drop of the tar removal efficiency which was 27.3% from 1 hour 40 minutes to 3 hours. According to the breakpoint data, 1 litter of WCO can absorb 14.4 g of tar with 80% removal efficiency.

On the other hand, RHC bed which was connected downstream of the WCO scrubber in series was mainly used for light tar removal due to its high porosity. The breakpoint of RHC for naphthalene removal was at the first 2 hours and reached the saturation point in 8th hour. According to the breakpoint data, 1 g of RHC can remove 0.15 mg of naphthalene with 76% of the removal efficiency. In addition, RHC also adsorbed gravimetric tar of 48.8 mg-tar/g-waste char with 3.1% increase in the removal efficiency on the average.

These data are useful for designing the gas cleaning unit in regards to the amount and the period of change of absorbent and adsorbent for the optimum utilization in scale-up or commercial applications. The author recommends that, in a commercial-scale design, the breakthrough point will be limited by the synthesis gas cleaning requirement of downstream facility. For utilizing as fuel in gas engine, the gravimetric tar concentration of treated synthesis gas should be less than 0.1 g/m^3. The higher tar removal efficiency could be achieved by series of bubbling type scrubber, packed bed scrubber or venturi scrubber with char adsorption unit.

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Chapter4

Improvement of the biomass tar removal capacity of scrubbing oil regenerated by mechanical solid-liquid separation

4.1 Background

The mechanisms of biomass heavy and light tar removal in a scrubber can be described by two main principles that are the condensation and the dissolution by oil, which is considered as the effective biomass tar removal solvent according to Chapters 2 and 3. Nevertheless, the increase of the heavy tar, particles and other contaminated loads accumulated and suspended into scrubbing oil solvents by the passage of time generate the viscous resistive force against the solvent flow, which is known as the hydrodynamic drag and also give less interaction between the synthetic gas and the scrubbing oil molecule by theirs blocking[1-3]. As mentioned in Chapter 3, the method to maintain the tar removal performance of the wet scrubbing system can be achieved by periodic making-up of new oil in the scrubber[4]. However, it requires make-up oil and massive new oil will be consumed and waste scrubbing oil also will be generated. Therefore, it is not economical and environmentally friendly process. To solve these problems, regeneration of waste oil would be the ideal solution for sustainable gas clean-up process establishment. The limitation of the solid contamination loads in the post scrubbing oil, which decreases the tar removal performance of the scrubbing oil, must be concerned [4]. Therefore, to upgrade and prolong the absorbent lifetime called as the regenerated absorbent is one of the interesting targets to reduce waste in the process and increase the reliability of the wet gas cleaning unit.

One possibility to regenerate oil is to remove the impurities stored in the deteriorated oil. The mechanical separation methods of solids from liquid or liquid from liquid by the filtration and the centrifugal sedimentation are wildly used to purify liquid media in many industries such as wastewater, drinking water, pharmaceutical, chemical, food, agriculture and mining industry[5-8]. Thus, the tar removal capacity recovery of the scrubbing oil is a challenge in the next step of this research, which was conducted by the filtration and the centrifugation sedimentation for separating micro-particles of biomass tar economically.

As for the filtration, it is a size based separation. The insoluble solids suspended in the scrubbing oil is trapped and removed by the filter medium, where the solid have to be larger than liquid molecules. There are four groups of driving forces to separate solids and liquids that are gravity (screening), vacuum (deep bed filtration), pressure (cake filtration) or centrifugal forces (cake filtration)[9]. For the gravity driving force, a screen filter is utilized to trap the solid particles. The hydrostatic head of liquid is a driving force for this filtration. The solid particles can be passed through or retained on the screen depending on the aperture size of the screen material. For the vacuum driving force, a sand filter or other media filters are utilized to trap the solid particles. It normally consists of silica sand, anthracite coal garnet or other granular materials. The solid particles are trapped by this filter at 5 – 30 m/h of the liquid velocity. Normally, downward flow of this filter under vacuum is utilized. For the pressure driving force, it utilizes hydraulic or mechanic pressure to force the liquids pass through a membrane where the solid particles will be trapped. The centrifuge driving force is similar to the gravity driving force. However, the centrifugal forces are utilized to

accelerate the driving force for the filtration (100 to 2500 times larger than the gravity force). Among the four driving forces, the most commonly and simply used one is the deep bed filtration. Waste treatment processes also utilize this method for the solid-liquid separation. In addition, there are four mechanisms during the filtration[10]. It consists of the impingement, the straining, the entanglement and the attractive force. First, the solid particles are moved along the streaming flow and strike the filter medium by the impingement of each driving forces. After that, the solid particles are retained on the filter medium. Straining is occurred similarly to the sieving, where larger size particles cannot pass through the smaller pore sized filter medium. Entanglement occurs because particles entangle with the filter, while its size is smaller than filter pore size. Therefore, the smaller solid particles are able to retain within the filter medium by the entanglement. The attractive force is the reacted force between the retaining solid and the filter medium. The choice of the filter materials and the type of the filter units are the keys for the unit design in order to achieve the highest particle removal efficiency and lowest investment cost. The selection depends on the purpose of the filtration and the qualities. The recommended properties of the filtration mediums are the inert, the maximum passage of liquid, and delivering a clear filtrate at a suitable production rate. Coal, sand, wire screening, fabrics of cotton, wool and nylon are commonly utilized. However, there are some drawbacks of the filtration method. The experiment time has an influence on the filtration performance as the filter material continuously accumulate the separated solid particles until it will deteriorate, which can be inspected by the head loss increase. It requires a periodic cleaning of the filtration materials. The other limitations are irremovable solutes in solution and the difficulty to separate the chemical constitutes in the same phase. The residence time for separation of the suspension from oil was also concerned during implementation[11]. The filtration rate depends on the driving force, the pressure difference across the filter and the flow resistance.

On the other hands, the centrifugal sedimentation is a specific gravity base separation method. The conventional technique of this method stems from the gravity sedimentation. It is a physical process to remove suspended solid particles from liquids. The solid particles can be naturally removed by sedimentation depending on the size and specific gravity of those particles. The drawback of the gravity sedimentation is the required long time for the sedimentation because the specific gravities of components may not be much different. This leads to the development of the centrifugation technique, which utilizes the centrifugal forces to accelerate the sedimentation. The centrifugal sedimentation can separate irremovable or insoluble solid and immiscible liquid from the base liquid, where the solid part settles to the bottom chamber, while the lightest liquid part will be the top one and separated by their density[12, 13]. The greater the density differs, the faster the separation occurs. There are three main factors which have influenced on the centrifugal force that are the rotation radius, the rotation speed, and the particle mass. The advantages of the centrifugal sedimentation are a high performance, a low operating cost, the versatility, and the compact size[14].

Therefore, in this study, real tar produced from the pyrolysis of Japanese cedar was supplied to a bubbling scrubber. Canola oil without any additive was chosen as the absorbent in the bubbling scrubber with the magnetic stirrer speed of 1,000 rpm. 10hours (600 minutes) of the experiment was set to investigate the improvement of the tar removal performance by the oil regeneration. Moreover, the tar absorption capacity of canola oil with and without the regeneration was compared in the experimental period. The objective of this chapter is to investigate the possibility of enhancement of the tar removal capacity of the scrubbing oil by comparing the tar removal performance between non-regenerated oil and regenerated oil by the filtration and the centrifugation.

4.2 Materials and setup

4.2.1. Materials

Japanese cedar obtained from Maywa Company, Kanazawa, Japan was used as the feedstock to generate biomass tar as shown in Figure 4.1a). Firstly, the feedstock was prepared by crushing and sieving with the mesh size of 0.5 to 1mm. Then the feedstock was dried in an oven at 105°C for 12 hours in order to remove the moisture content in the raw feedstock. The ultimate and proximate analysis results are shown in Table 4.1.

As for the scrubbing material, canola oil was purchased from a Japanese convenient store which is shown in Figure 4.1b). The main ingredients were 60% and 40% of soybean and canola oil, respectively. Its density and the kinematic viscosity at 30°C scrubbing temperature was 0.9 g/cm^3 and 50.7cSt, respectively. The ultimate and proximate analysis of results are also shown in Table 4.1

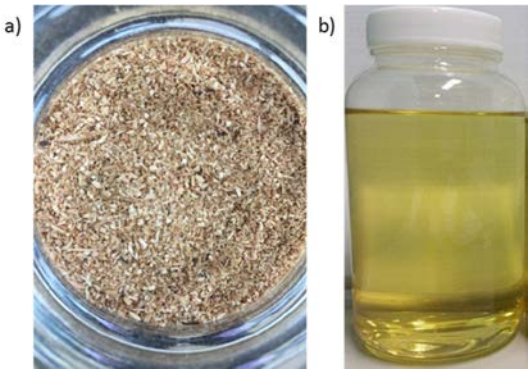

Figure 4.1: (a) Japanese cedar (b) canola oil

Table4.1: Ultimate and proximate analysis of the Japanese cedar and canola oil

Parameters	Ultimate analysis (wt% dry and ash free basis)					Proximate analysis (wt% dry basis)		
	C	H	O	N	S	Volatile matter	Fixed carbon	Ash
Japanese cedar	50.4	6.3	43.2	0.1	<0.1	84.1	15.6	0.3
Canola oil	77.5	12.7	9.6	0.2	0.0	100	0	0

4.2.2. Experimental setup

In this experiment, biomass tar was generated by the pyrolysis process. The tar generation equipment consists of a screw feeder, a pyrolyzer, an external heater and a nitrogen cylinder as shown in Figure 4.2. Pre-dried and crushed Japanese cedar was packed in the feeder and was fed continuously with the feed rate of 0.6 g/min. Nitrogen is used as a carrier gas with the flow rate of 0.8 l/min. The fixed bed pyrolyzer made from a SUS306 tube with the diameter of 30 mm and the height of 280 mm. The operation temperature was controlled by the external heater at 800°C. After the reactor reached the temperature of 800°C, the air was supplied without the feed material to combust irremovable remaining in the reactor for 20 minutes. Then it was switched from the ambient air line to the nitrogen line and the feeder was started. The screw feeder supplied the feedstock to the pyrolyzer which was

pyrolyzed and converted into char, synthesis gas, and tar. Before the synthesis gas was introduced to the sampling line, it was directly exhausted for 15 minutes to prevent unsteady state synthesis gas to be sampled. The sampling line consisted of the bypassed line and the gas cleaning line which was connected in parallel. The bypass line was used to sample the synthesis gas to measure the total tar concentration in it, while the gas cleaning line was used to sample the treated synthesis gas. Finally, the synthesis gas was introduced to the tar sampling unit.

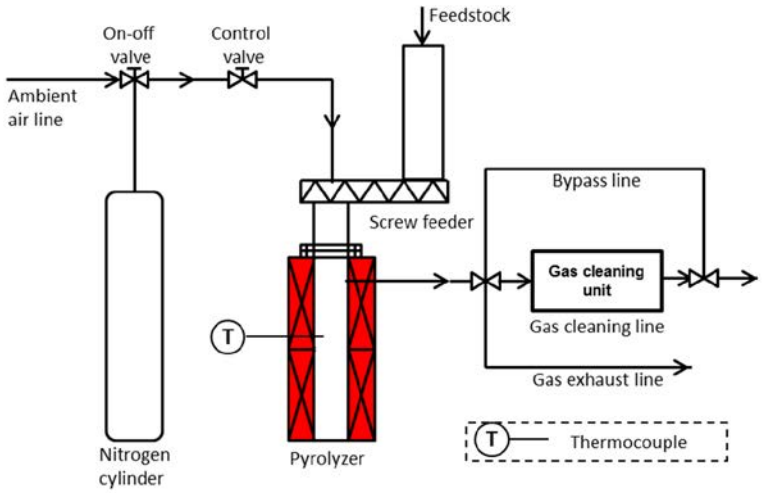

Figure 4.2: The process scheme of the experimental setup

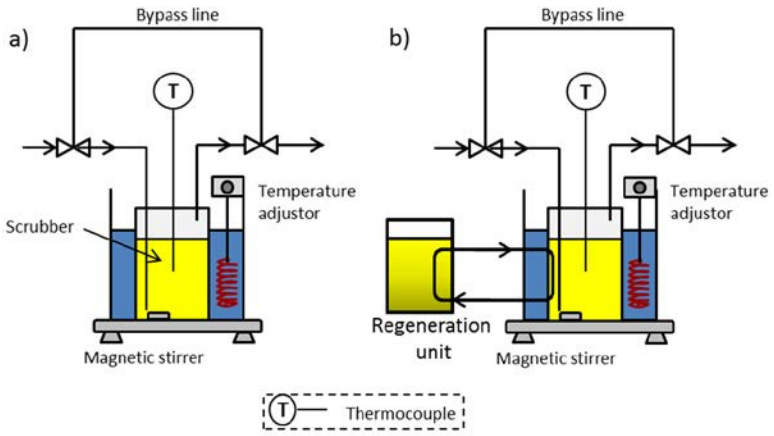

Figure 4.3: Schematics of the wet scrubber setup: (a) without the regeneration unit; (b) with the regeneration unit

For the gas cleaning process, the wet scrubber unit consisted of a bubbling type scrubber (500 ml Woulff glass bottle scrubber with three thread necks sealed), a magnetic stirrer, and a temperature controlled bath as shown in Figure 4.3a. 450 g (or 500 ml) of canola oil was contained in the scrubber. The magnetic stirrer was set at the speed of 1,000 rpm, while the temperature of the bath was controlled at 30°C. Without the regeneration unit operation, the cleaning unit was set as shown Figure4.3a. The wet scrubber combined with the regeneration unit is shown in Figure4.3b. In this cleaning unit, the oil used for 135 minutes in the scrubber was sent to the regenerative process by using the filtration and the centrifugal sedimentation techniques. For the filtration, it was done by a vacuum packed

bed filter composed of a packed bed filtration tower, a container and a vacuum pump as shown in Figure 4.4. The packed bed filtration tower contained 7cm, 3cm, 7cm and 3cm of the filter bed, the sand bed, the filter bed and the sand bed, respectively. Silica sand with the average size between 0.7-0.9 mm was used as a coarse media in order to prevent rapid increase of the pressure drop while the filter bed was used as a fine media in which the packed bed filtration tower can remove particles with the size greater than 30μm from the used oil. For the centrifugal sedimentation, the controlled condition was set at 30°C and 10,000 rpm for 10 minutes using the high speed refrigerated micro centrifuge model MX-160 as shown in Figure 4.5. This centrifugation condition effectively removed particles with the size less than 1μm. After that, the centrifuged oil separated to the upper layer and the lower layer zones. Only the upper layer zone of the centrifuged oil was recycled for re-utilization in the scrubber. Finally, the regenerated oil by both the filtration and the centrifugal sedimentation techniques was reused in the scrubber.

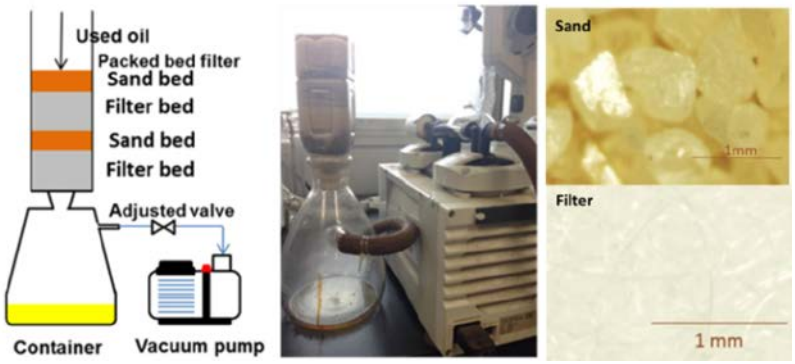

Figure 4.4: Schematics of the oil regenerative setup by the filtration technique

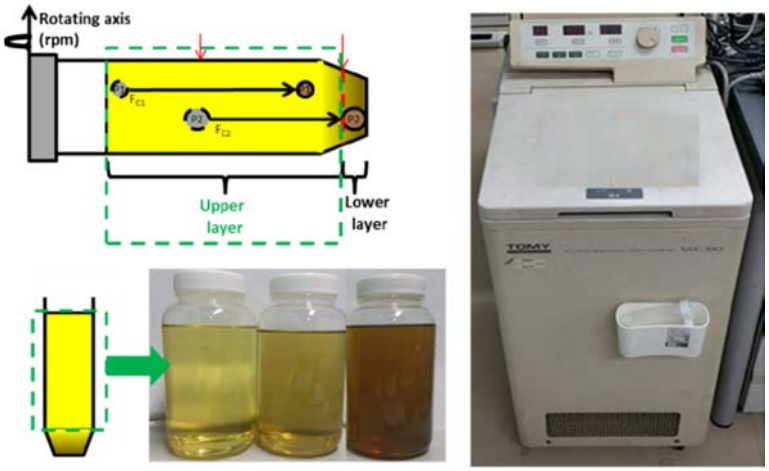

Figure 4.5: Schematics of the oil regenerative setup by the centrifugal sedimentation technique using the high speed refrigerated micro centrifuge model MX-160

4.3 Tar sampling and analysis method

Tar was sampled by both the wet and dry methods for measuring the gravimetric and the light tar concentrations in the synthesis gas, respectively. The details of the tar measurement method used in this research are described below.

4.3.1 Wet method for gravimetric tar measurement

The gravimetric tar was separated from the synthesis gas by using the principle of tar condensation at a low temperature as described in the ECN guideline[15]. The sampling line consisted of a series of 10 impingers and the flow control equipment, which were a gas flow meter, an adjustable valve and a suction pump as shown in Figure 4.6. Each impinger contained 100 ml of isopropanol and was set in a water bath controlled at the temperature of 3°C by a mechanical cooling device. A cotton filter tube and an activated carbon tube were connected to prevent the tar clogging in the flow control equipment line. 1 l/min of the sampling gas was controlled and measured for 15 minutes. Tar contained in 1000 ml of the post sampling IPA was separated by the filtering and the evaporating, and finally, the solid tar was measured by the analytical balance.

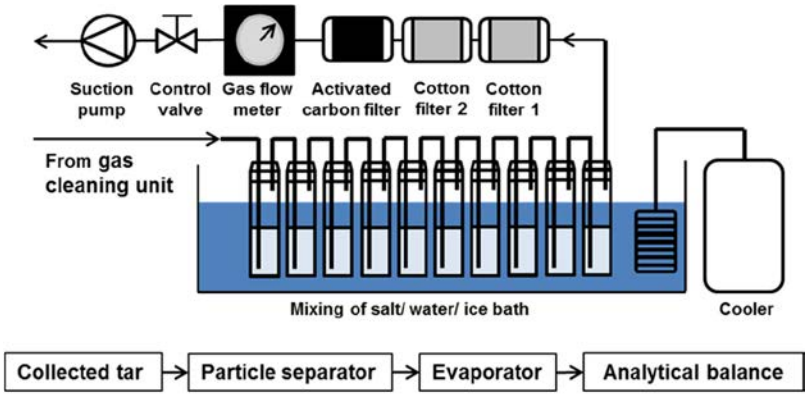

Figure 4.6: Schematics of the wet method for the gravimetric tar sampling and the analysis method

4.3.2 Dry method for light tar measurement

For the dry method, the light tar concentration was measured by series of charcoal tube (containing 150 g of activated carbon) and silica gel tube (containing 780 mg of silica gel) purchased from Sibata Scientific Technology Ltd as shown in Figure 4.7. 0.5 l/min of the synthesis gas was sampled for 3 minutes. The sampling was started after the start of the feeder for 15 minutes as shown in Figure 4.7., where A_i means the gas sampling at the outlet of the scrubber (treated synthesis gas) and B_i means the gas sampling at the inlet of the scrubber (untreated synthesis gas). After reach 135 minutes of the experiment, the used oil in the scrubbing process was supplied to the regeneration unit to be regenerated and reused in the scrubber. The light tar measuring method for the regenerated oil was similar to that which was mentioned previously. The measuring was conducted till 10 hours of the scrubbing period. After finishing tar sampling, a gas chromatography flame ionization detector (GC-FID) was utilized to detect light tar compounds and their concentrations. Carbon disulfide and acetone were used as solvents for charcoal tube and silica gel tube, respectively. Additional details of the light tar sampling and the analysis have been described in our pervious paper[16].

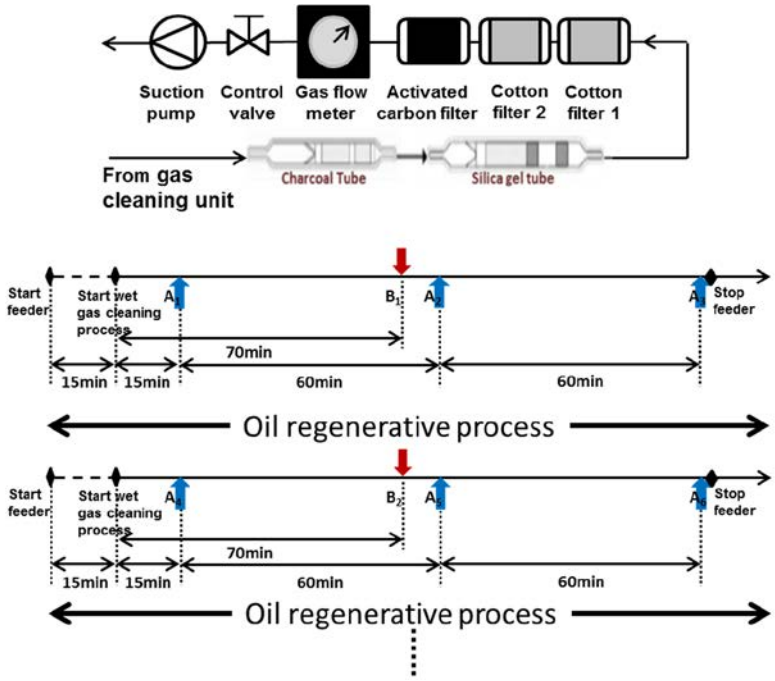

Figure 4.7: Schematics of the dry method for the light tar sampling and the analysis method

4.4 Experimental procedure

Initial experimental setup conditions and experimental conditions of each run are shown in Table4.2. In the 1st run, the scrubbing oil was continuously used for 10 hours (600 minutes) without the regeneration process, while, in the 2nd to 5th runs, the post scrubbing oil was repeatedly regenerated in every 135 minutes of operation by the filtration (2nd and 3rd runs) and the centrifugal sedimentation (4th and 5th runs) for 10 hours, where the regenerated oil was reused in the scrubber.

Table4.2: Initial experimental setup condition and experimental conditions of each experimental run

Parameters	RUN1	RUN2	RUN3	RUN4	RUN5
Initial experimental set up					
Feedstock			Japanese cedar		
Feedstock size(mm)			0.5-1		
Carrier gas			Nitrogen		
Carrier gas rate(l/min)			0.8		
Pyrolyzer (°C)			800		
Experimental condition of each run					
Absorbent			Canola oil		
Scrubber volume(ml)			500		
Scrubber stirring speed(rpm)			1000		
Scrubber temperature(°C)			30		
Regeneration technique	-	Filtration	Filtration	Centrifugal Sedimentation	Centrifugal sedimentation

Regeneration periods(min)	-	135	135	135	135
Tar measurement method	Wet	Wet	Dry	Wet	Dry
Operation period (hours)	10	10	10	10	10

4.5. Results and discussion

4.5.1 Gravimetric tar removal performance over 600 minutes of experiment period

According to their high portion of lipophilic compounds in biomass tars, it is well dissolved in oil. The canola oil ($C_{22}H_{42}O_2$), which composes of both lipophilic group and slightly hydrophilic group (-COOH), was used as the scrubbing medium for absorbing biomass tar. 30g/m^3 of the gravimetric tar in the synthesis gas was supplied to the scrubber. The results of the tar removal efficiency in each experiment were reported, which was calculated using the following equation.

$$\eta_{tar,removal} = \frac{m_{tar,in} - m_{tar,out}}{m_{tar,in}} \times 100 \quad (1)$$

Where $m_{tar,in}$ is the initial gravimetric tar concentration and $m_{tar,out}$ is the gravimetric tar concentration after the scrubbing.

- **Oil scrubber performance without the regeneration unit**

To maximize the oil utilization, minimize the oil replacement and maintain the tar removal efficiency, the breakthrough curve of canola oil and the tar removal capacity was investigated which is shown in Figure 4.8. For the gravimetric tar removal efficiency, the graph illustrates that, at the first 15 minutes, 98% of the gravimetric tar condensed and dissolved in the oil scrubber. However, the removal efficiency was reduced corresponding to the increase of the synthesis gas volume according to the accumulated contaminants in the scrubbing oil (e.g. gravimetric tar, soot and water) especially micro particles blocking the contacting area between the synthesis gas bubble and the oil. The increase of the solid particle content may reduce the turbulence level and the interface mobility. The increase of the solid concentration will enhance the gas bubble coalescence frequency and the interface area will decrease as was explained in Chapter 3[4, 17]. The gravimetric tar removal performance of canola oil is shown in Table 4.3. According to the breakthrough graph, canola oil reached the saturation point in the 7th hour of the experiment. This is because there is no significant change in the tar removal performance after that. After the 7th hour, the tar removal efficiency was almost constant at 29% which was due to the tar condensation at a lower temperature. The heavy tar with a low condensation point was condensed in the oil scrubber controlled at the temperature of 30°C. The breakpoint represents the starting deterioration point of canola oil for the gravimetric tar absorption at which the replacement of oil or oil regeneration is required for maintaining the tar concentration at an acceptable level. In this experiment, the gravimetric tar removal efficiency markedly dropped by 31% during 2nd to 4th hours. The point with this large efficiency drop can be defined as the deterioration point or the breakpoint of the absorbent. The tar removal mechanism of canola oil scrubber is similar to that discussed in Chapter 3.

Table4.3: Gravimetric tar removal performance of the oil scrubber without the regeneration unit for 600 minutes of the experiment period

Sampling time(min)	Accumulated volume of the cleaned synthesis gas(liter)	Tar removal amount (g/m^3)	Tar removal efficiency (%)
0-15	15	29.3	98
60-75	75	27.3	91
120-135	135	21.3	71
180-195	195	14.7	49
240-255	255	12.0	40
300-315	315	10.7	36
360-375	375	10.0	33
420-435	435	8.7	29
480-495	495	8.7	29
540-555	555	8.7	29
600-615	615	9.3	31

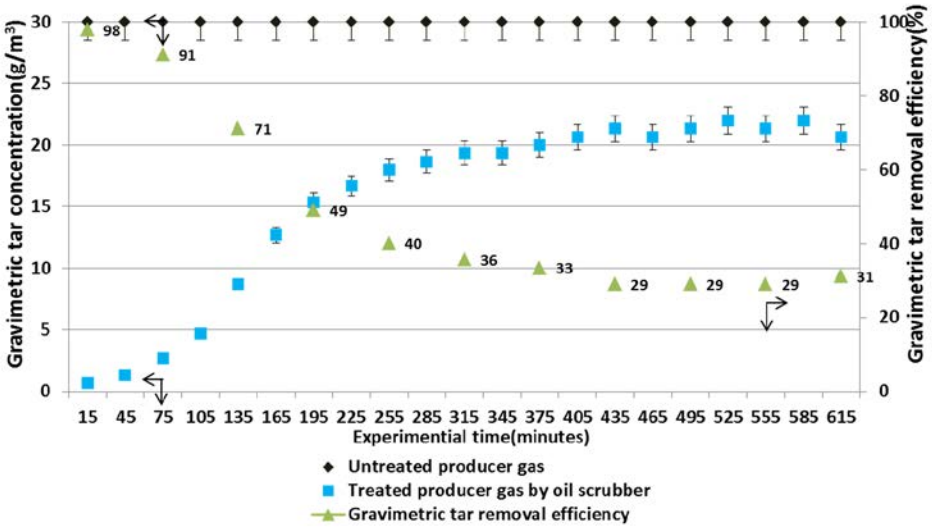

Figure4.8: The gravimetric tar concentration and the gravimetric tar removal efficiency over 600 minutes of the experiment period

- **Oil scrubber performance with the regeneration process by the filtration technique**

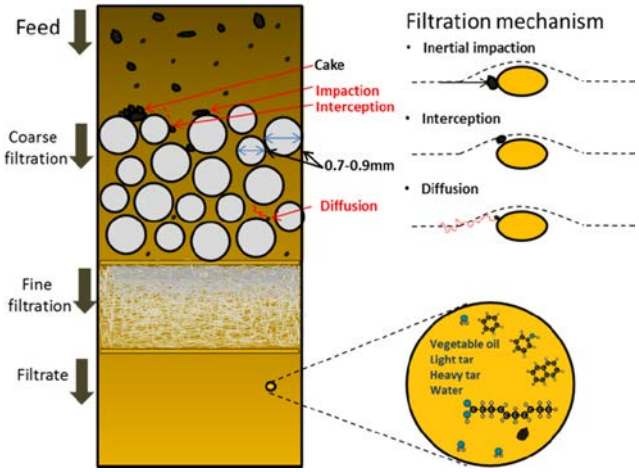

Figure 4.9: The filtration mechanism by sand and the polyester filter

For the regeneration of the used oil by the filtration technique, sand and the filter as previously mentioned were utilized in this study for trapping solid contaminants and let liquid absorbent passing through. The filtration mechanism is shown in Figure 4.9. The reduction of solid contaminants increases the contacting area in the filtrated oil, which increases the tar removal efficiency. Along 10 hours experiment, the scrubbing oil was totally regenerated 4 times at every 135 minutes by the filtration technique.

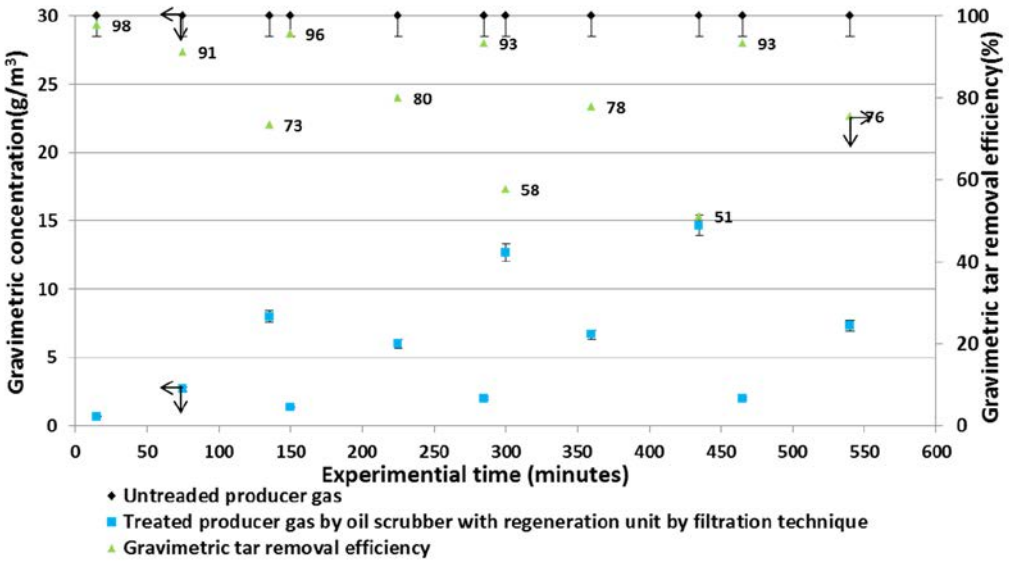

Figure 4.10: The gravimetric tar concentration and the gravimetric tar removal efficiency of the oil scrubber with the filtration unit over 600 minutes of the experiment period

At the beginning, the gravimetric tar removal efficiency of new canola oil was reduced with the increase of the contaminant accumulation, which was reduced from 98% to 73% in the first 135 minutes operation as shown in Figure 4.10. Tar was continuously accumulated in the scrubber as time went by. The increased tar concentration in

the oil scrubber resulted in the reduction of available absorption area, increasing the portion of tar leaving from the scrubber. For the 1st filtrated oil, the tar removal efficiency was recovered to 96%, increased by 23% compared to the efficiency before filtration. The filtration technique was proved to be capable of recovering the gravimetric tar removal efficiency of the scrubbing oil effectively. The absorption mechanism of the oil scrubber with the filtration unit is shown in Figure 4.11. Most of polymerized gravimetric tars were trapped by the filter membrane, resulting in the increase of available absorption area. Nevertheless, the filtration unit could not trap water. Similarly, the same tendency was shown by the 2nd, 3rd and 4th filtrated oil, which 35%, 42% and 44% of gravimetric tar removal efficiency of filtrated oil were markedly recovered after filtration. Comparing the new oil and the filtrated oil (1st, 2nd, 3rd, 4th) for 15 minutes operation, more than 90% of the gravimetric tar removal efficiency was maintained by filtrated oil as summarized in Table 4.4, while the gravimetric tar removal efficiency in average over 10 hours was 78%.

However, in the 4th filtration of the first 15 minutes of the experiment, the tar removal efficiency was slightly dropped by 7% compared to the new oil and the 1st filtration due to the deterioration of the filtration media. Both sand and the filters utilized need a periodic cleaning in order to steadily control the tar concentration after the scrubbing process and prevent the increase of the pump head loss.

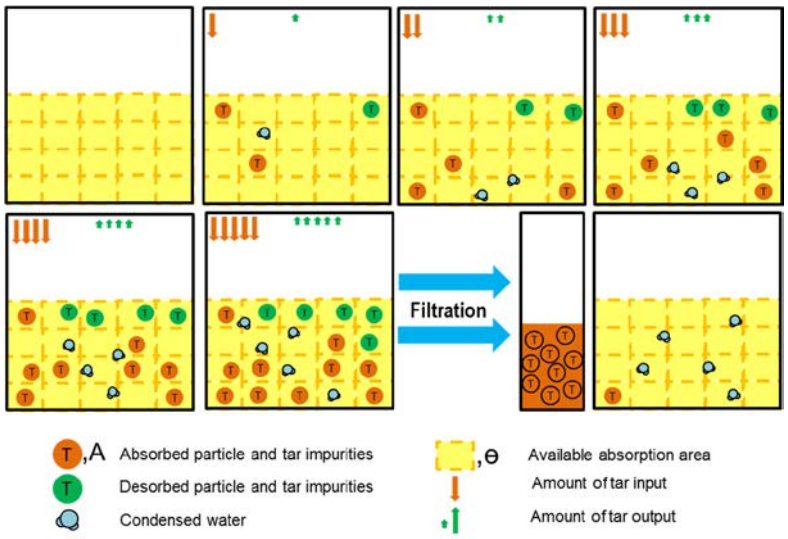

Figure 4.11: The mechanism of tar removal in the oil scrubber with the filtration unit over 600 minutes of the experiment period

Table 4.4: The gravimetric tar removal performance of the oil scrubber with the regeneration unit by the filtration technique for 600 minutes of the experiment period

Sampling time(min)	Accumulated volume of the cleaned synthesis gas(liter)	Tar removal amount (g/m^3)	Tar removal Efficiency (%)
0-15	15	29.3	98
60-75	75	27.3	91
120-135	135	21.3	73
135-150	150	28.7	96
195-210	210	23.3	80

255-270	270	17.3	58
270-285	285	28.0	93
330-345	345	22.7	78
390-405	405	15.3	51
405-420	420	28.0	93
465-480	480	22.7	76
525-540	540	14.0	47
540-555	555	27.3	91
555-615	615	22.0	73

- **Oil scrubber performance using canola oil with the regeneration process by the centrifugal sediment technique**

For the oil regeneration by the centrifugal sediment technique, the gaseous phase tar and contaminants were collected in the oil scrubber. These contaminants are small and suspended in oil which cannot be effectively separated by the gravitational sedimentation. Therefore, the centrifugal sedimentation of contaminants in the scrubbing absorbent is more appropriate to precipitate toward the bottom and remove from the system, which is faster than the gravitational one as shown in the equations 4.2&4.3.

$F_g = mg$ gravitational sedimentation force (4.2)

$F_c = mr\omega^2 = mr(2\pi N/60)^2 = m(0.011rN^2)$ centrifugal sedimentation force (4.3)

It can be seen that the gravitational acceleration (g), which is constantly at 9.81 m/s^2, has been replaced by the centrifugal acceleration ($0.011rN^2$). As previously mentioned that 10,000 rpm of the centrifugation speed was set for this study, this centrifugal sedimentation force (RCF) was about 9100 times larger than the gravitational force, which well separated the high-density substances. The high density solid and water contaminants were precipitated at the bottom and removed from the absorbent after the centrifugation. This lead to more absorption area and less particle obstacle to the contacting area in the centrifuged oil resulting in the increase of the gravimetric tar removal efficiency. The scrubbing oil regeneration was similarly repeated for 4 times in the regeneration unit as same as the filtration technique.

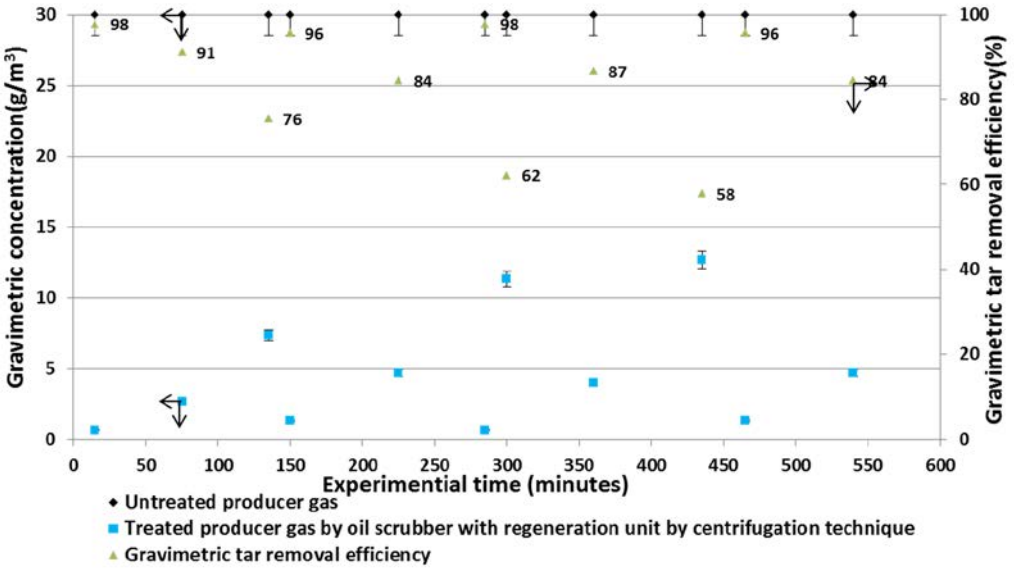

Figure 4.12: The gravimetric tar concentration and the gravimetric tar removal efficiency of the oil scrubber with the centrifugal sedimentation unit over 600 minutes of the experiment period

The trends of the gravimetric tar removal performance of the centrifugal sediment were similar to that of the filtration. The 1st centrifuged oil was able to recover the gravimetric tar removal efficiency from 76% to 96% as shown in Figure 4.12. The centrifugal sediment technique also effectively proved that it can recover the gravimetric tar removal efficiency as summarized in Table 4.5. The polymerized gravimetric tar, solid contaminants and water could be removed by the centrifuge, resulting in the increase of the available absorption area, as shown in Figure 4.13. For the 2nd, 3rd and 4th centrifuged oil, 36%, 38 % and 38% of the gravimetric tar removal efficiencies were distinctly improved after the centrifugal sedimentation. Almost 95% of the gravimetric tar removal efficiency was maintained by the centrifuged oil for the first 15 minutes after the centrifugal sedimentation as summarized in Table 4.5, while the gravimetric tar removal efficiency on average in 10 hours was 83%.

Nevertheless, in the 4th regeneration of the first 15 minutes of the experiment, the tar removal efficiency was slightly dropped by 5% compared with the new oil and the 1st regeneration oil due to the centrifugation limitation. The tiny and low-density contaminants will be retained in absorbent after the centrifugation and continuously accumulated in each centrifugation leading to the tar removal performance drop in the 4th regeneration[14]. Therefore, a longer centrifugal sedimentation time or a higher centrifugation force is required in order to maintain the tar removal efficiency.

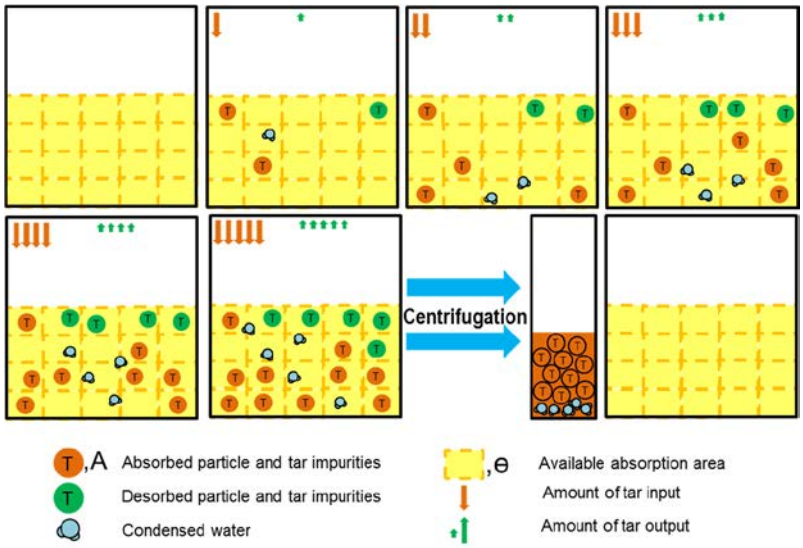

Figure 4.13: The mechanism of tar removal in the oil scrubber with the centrifugal sedimentation unit over 600 minutes of the experiment period

Table 4.5: The gravimetric tar removal efficiency of the oil scrubber with the regeneration unit by the centrifugal sedimentation for 600 minutes of the experiment period

Sampling time(min)	Accumulated volume of the cleaned synthesis gas(liter)	Tar removal amount (g/m^3)	Tar removal Efficiency (%)
0-15	15	29.3	98
60-75	75	27.3	91
120-135	135	22.7	76
135-150	150	28.7	96
195-210	210	25.3	84
255-270	270	18.7	62
270-285	285	29.3	98
330-345	345	26.0	87
390-405	405	17.3	58
405-420	420	28.7	96
465-480	480	25.3	84
525-540	540	16.7	56
540-555	555	28.0	93
555-615	615	24.7	82

- **Comparison of the gravimetric tar removal efficiency and the capacity between the oil scrubber without and with the regeneration unit by the filtration and the centrifugal sedimentation techniques over 600 minutes of the experiment period.**

The non-regenerated oil showed the lowest tar removal performance, where only 48% of the gravimetric tar could be removed on the average. Although the tar removal rate at the beginning of the experiment was absolutely high, the impurity accumulation in the absorbent have a high influence to obstruct the dissolution ability resulting in the continuous dropping of the tar removal efficiency as previously seen in the breakthrough curve graph. However, with the utilization of the regeneration unit, the tar removal efficiency was able to be improved to 78% and 83% on the average along the 10 hours experiment period by the filtration and the centrifugal sedimentation, respectively. The tar removal efficiency of the centrifugal sediment was higher than the filtration due to the deterioration of the filter media and the solid particle size limitation as shown in Figure 4.14 [18]. Irremovable micro solid particles (<30μm) have a tendency to pass through the filter media, which caused the lower gravimetric tar removal efficiency compared with the centrifugal sedimentation.

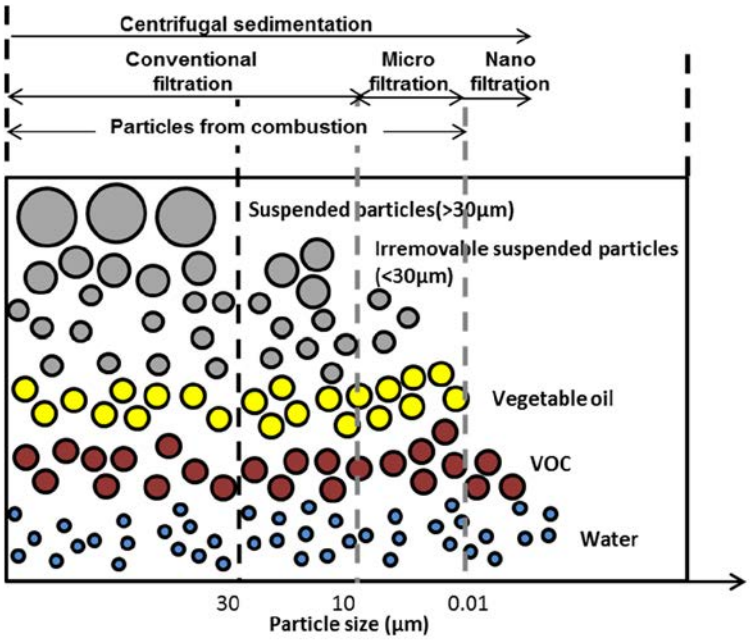

Figure 4.14: Solid-liquid separation characteristic

For the gravimetric tar removal capacity over 600 minutes of the experimental period, 1 liter of non-regenerated oil could absorb only 16.6 g of the gravimetric tar. However, the regenerated oil by both the filtration and the centrifugal sedimentation showed the effective improvement of the gravimetric tar removal capacity to 26.8 g and 28.8 g, which is 160% and 175% higher absorption capacity than the non-regenerated oil, respectively.

These results show an interesting fact that the regenerated oil by both methods showed much higher tar removal efficiency and capacity than the non-regenerated oil with the economical ability using the less absorbent medium for absorbing tar. In addition, the tar removal performance of the regenerated oil after each regeneration is not significantly changed compared to the new absorbent. Therefore, there is a possibility for utilizing regenerated absorbent longer than 10 hours without changing to the new absorbent.

4.5.2 Light tar removal capacity over 600 minutes of the experiment period

- **Light tar removal performance of the canola oil medium with the regeneration system using the filtration**

For the filtration technique, the filter mainly trapped the solid contaminants from the recycled oil, while letting the others pass through. The first positive side of the filtration technique was no significant improvement for the removal on single aromatic compounds. The concentrations of both benzene and toluene were not reduced after the filtration process as shown in Figures 4.15a&b, because the molecular size of both benzene and toluene are smaller than the canola oil molecule. These remaining benzene and toluene are not dangerous tar without causing a problem in the downstream process. In addition, some energy can be recovered from them to increase the heating value of the synthesis gas.

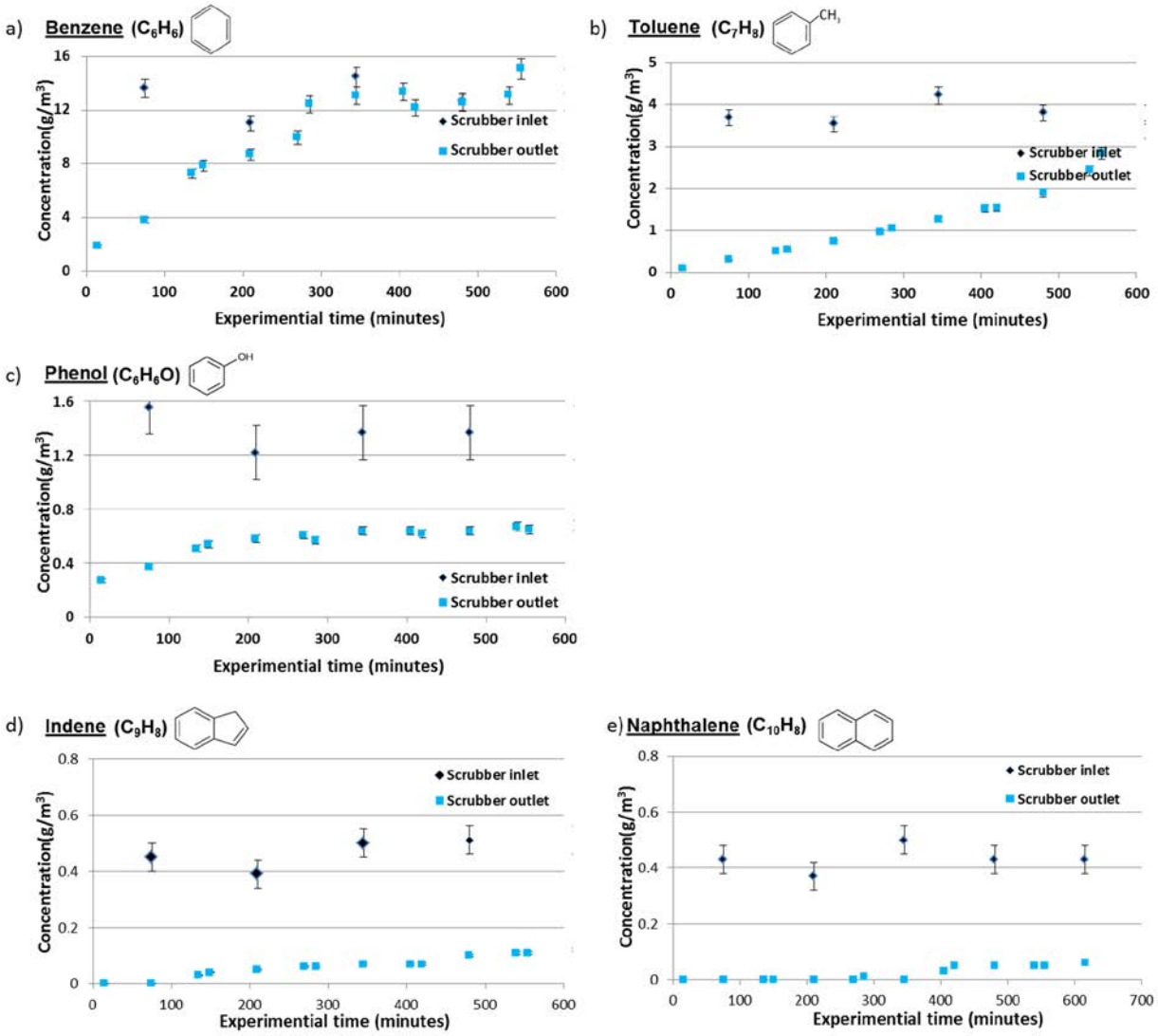

Figure 4.15: The light tar removal performance of the oil scrubber with the regeneration system by the filtration over 600 minutes: (a) benzene; (b) toluene; (c) phenol; (d) indene; (e) naphthalene

Another positive side of the filtration came from the irremovable water, which occurs during the condensation of the inherent moisture content in the synthesis gas during scrubbing. The accumulated water was increased by the increased treated gas volume. This accumulated water was the main cause of the improvement of the phenol removal efficiency according to the increase of the polar proportion in the absorbent after the filtration as shown in Figure 4.15c. Moreover, the vacuum filtration unit for the regenerated oil and the stirrer in the cleaning unit produced a homogenous emulsion status, which has been proved to improve the tar removal efficiency[19].

On the contrary, the filtration was not able to remove polyaromatic compounds. Most of indene and naphthalene were not eliminated after the filtration process as shown in Figures 4.15d&e. Therefore, the indene and naphthalene removal efficiencies were reduced by the time passage.

- **Light tar removal performance of the canola oil medium with the regeneration system using the centrifugal sedimentation**

The intermolecular attraction force between canola oil (mainly nonpolar solvent) and light tar (nonpolar solute), which is van der Waals force (London force), could be destroyed by the centrifugal force. Then some light tar components whose specific gravities are higher than canola oil, would be precipitated toward the bottom, while others still remain in the centrifuged oil.

According to Figures 4.16a&b, there was no significant improvement in the removal of single aromatic compounds. The concentrations of benzene and toluene increased with the increase of time because the centrifuged benzene and toluene, whose densities are lighter than canola oil, was returned to the scrubber together with the centrifuged oil. Irremovable benzene and toluene are also the advantages as previously mentioned.

The oil centrifugal sedimentation system also insignificantly improved the phenol removal performance as shown in Figure 4.16c, because all of the water was removed after the centrifugal sedimentation. The OH group in phenol (C_6H_5OH) is highly hydrophilic and is well absorbed in the emulsified oil[19] .

For polyaromatic compounds, the oil centrifugal sedimentation significantly improved the indene and naphthalene removal as shown in Figures 4.16d &e. The Indene concentration was reduced after the centrifugal sedimentation. The broken intermolecular of indene and scrubbing oil was precipitated at the bottom because its density was higher than canola oil resulting in the increase of the indene removal after the oil regeneration process. In addition, all of the naphthalene was removed during the 10 hours operation. This is a huge advantage because naphthalene, which is considered as the dangerous tar causing severe problems in a downstream application, is able to be completely removed by the oil centrifugation.

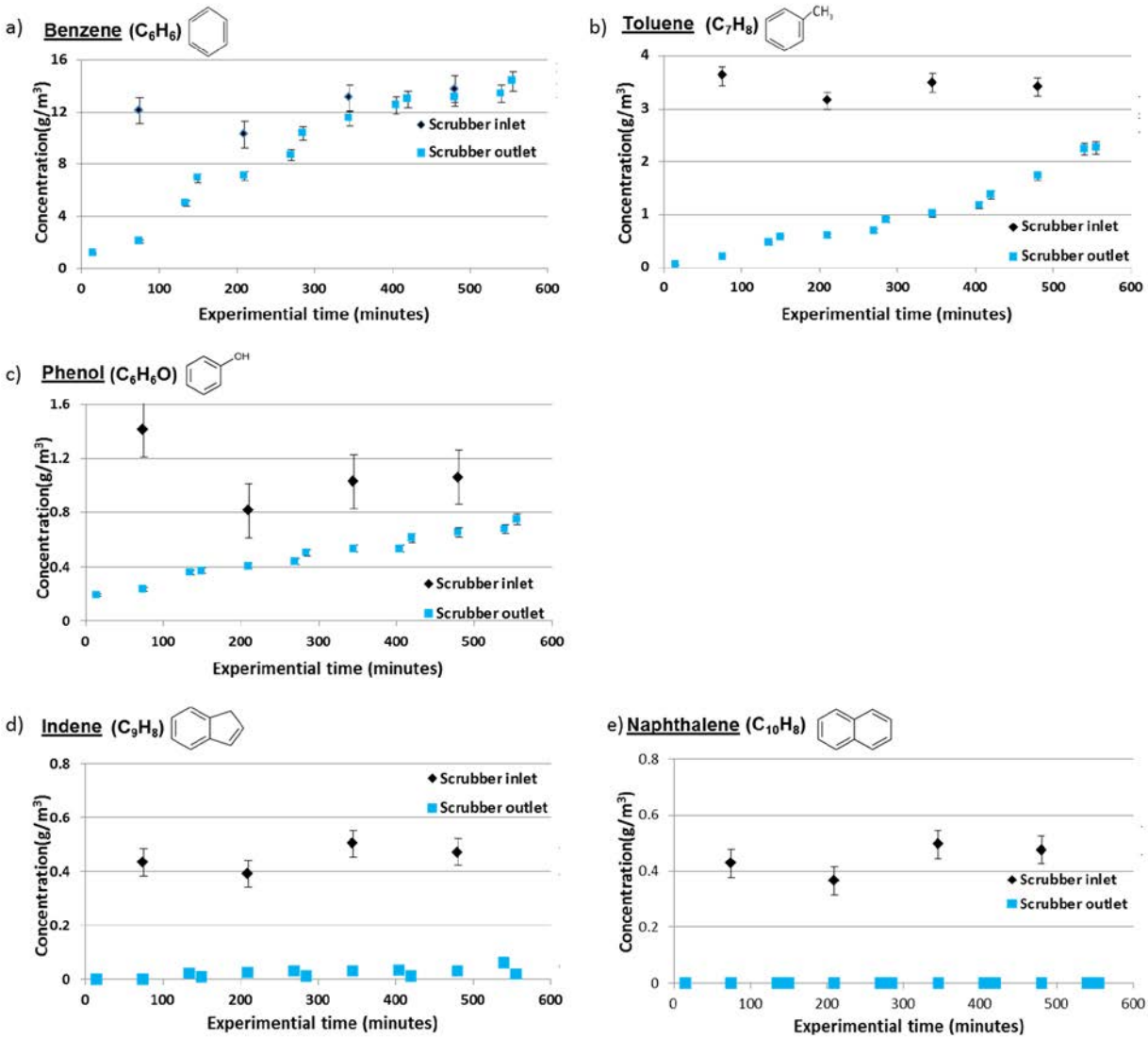

Figure 4.16: The light tar removal performance of the oil scrubber with the regeneration system using the centrifugal sedimentation over 600 minutes: (a) benzene; (b) toluene; (c) phenol; (d) indene; (e) naphthalene

4.5.3 Possibility of commercial scale implementation

According to the results of the gravimetric and light tar removal performance using both regeneration methods, the removal efficiency was recovered to mostly as the same as the new absorbent. However, the performance was not stable. It can be seen that the removal efficiency was very high in the first hour of the utilization, and then slightly decreased until reaching the breakpoint. This unstable removal performance may cause the drawback for the real implement in a commercial scale. Therefore, in order to prevent these obstacles, both the filtration and centrifugal sediment techniques should be improved by continuous regeneration methods. Without concerning the breakpoint of the absorbent, oil is continuously supplied to the regeneration unit, and then automatically return to the scrubber so that the impurities and tar will be continuously removed, which results in the stable tar removal performance of the oil scrubber.

4.6 Conclusions

The objective of this chapter was to investigate the tar removal efficiency and the capacity of the oil scrubber combining with and without the regeneration techniques by the filtration and the centrifugal sediment. Canola oil was used as an absorbent for testing on the laboratory scale. The synthesis gas containing tar produced by the pyrolysis of Japanese cedar was introduced into the oil scrubber along the 10 hours experiment period. There were three methods for treatment of absorbent at every 2 hours, which were 1) no treatment 2) treatment by the filtration 3) treatment by the centrifugal sediment. After cleaning in the scrubber, the remaining tar in the synthesis gas was measured by both the gravimetric (wet) and the light tar (dry) measurement methods.

For the gravimetric tar, only 48% of the gravimetric tar could be removed with 16.6 g tar absorbed in 1 L of oil along 10 hours without regeneration due to solid particle accumulation obstructing the oil absorbability. However, with the usage of the oil regenerative unit, the tar removal efficiency was able to be improved to 78% and 83% by the filtration and the centrifugal sediment, respectively. The tar removal capacity was shown to be increased to 160% and 175% by the filtration and the centrifugal sediment, respectively, compared to non-regenerated oil. The performance of the filtration was slightly lower than the centrifugal sediment because of the filter media deterioration and the solid particle size limitation.

For the light tar removal, both methods could not remove benzene and toluene, which could increase the synthesis gas heating value. The advantage of the filtration method was to increase the phenol removal efficiency due to water remained in the regenerated oil, while the centrifugal sediment could remove naphthalene completely along the 10 hours experiment.

In summary, this chapter shows attractive results for utilizing oil regeneration by both methods. The gravimetric tar removal performance and capacity markedly improved compared to non-regenerated oil. Moreover, there was no significant change of the tar removal efficiency after each regeneration compared to new oil. Therefore, there is a possibility for utilizing regenerated absorbent without changing it to the new one for a longer period of the operation.

4.7 Reference

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COMMERCIAL SCALE: TAR REMOVAL BY PHYSICAL TECHNIQUE

Chapter5

Tar removal performance by physical methods in a BFB gasification plant

5.1 Background

One of the major barriers for commercial scale gasifier implementation is unreliable gas cleaning process. The raw synthesis gas from a gasifier contains various type of solid and liquid contaminants depending on the operation condition and the type of the gasifier [1, 2]. These contaminants should be removed before utilization in downstream processes. Regarding the continuous development for tar removal system in Yoshikawa laboratory, physical removal techniques have been studied to improve the low cost gas cleaning unit and control tar concentration according to downstream operation requirements [3-12]. Physical techniques were proved as low cost and effective gas treatment methods in both laboratory and pilot scale gasification processes.

Regarding the minimum requirement of the tar concentration for internal combustion engines, particles (<10μm) and tar concentrations should be lower than 50mg/Nm^3 and 100mg/Nm^3, respectively [13]. The hot gas cleaning devices consist of cyclones and ceramic filters, which mainly remove solid particles. The operation temperature of the hot gas cleaning should be operated at a higher temperature than the tar dew point in order to prevent the tar formation and corrosion inside the devices. The cyclone is the first cleaning unit for the synthesis gas at the exit of a gasifier. Cyclones can be constructed by several materials such as metal or ceramic, which is resistant to high temperature gases, abrasive particles and corrosive gases. It mainly removes the particles contaminated in the synthesis gas by the vortex separation [14]. The dirty synthesis gas flows into the side-top of the cyclone leaded to a spinning motion. Particles are forced to sediment to the bottom by the centrifugal force because these particles have such a high inertia that they are not able to go along with the centrifugal stream line, which is tight curve, resulting in hitting onto the outside wall, and then falling to be removed at the bottom of the cyclone. At the bottom of the cyclone, the clean synthesis gas reverses to the inner core, and then leaves at the top of the unit [15]. However, there was a report that the fine particle removal efficiency by cyclones was low, which was 5% and 70% for 5 and 10 microns of particle size removal, respectively [16]. Therefore, they mainly eliminate fly ash and unburned carbon during gasification processes. In the ceramic filter, which can conduct the hot gas filtration, the particles are eliminated by the interception, the impaction, the diffusion and the gravitation settling, where the particle collection efficiency depends on the filter porosity [17]. The synthesis gas flows into a chamber and then the particles are trapped on the surface of candle filters, while the fine particles, whose size is smaller than the filter pore, escape along with the treated synthesis gas at the top of the unit. According to the passage of time, the particles will be accumulated on the filters. This formation results in plugging, erosion and weakening of the filter. The coupled pressure pulse was reported as the effective technique for preventing permanent residual built up [18, 19]. The particles formation will fall to the bottom of chamber by back pressure. Engstrom et al. [20] reported the hot gas ceramic filter operated at 350°C -400°C was achieved for over 2,000 hours of operation. There was no evidence of tar accumulation or tar blinding on the candle surface.

For the cold gas cleanup, it is a crucial process for treating the combustible gases from gasification processes especially the utilization as fuels for internal combustion engines and as feedstock for chemical production like methanol. It mainly reduces the synthesis gas temperature and treats the remained particles and tar contaminants by gas coolers, scrubbers or adsorbers. For gas coolers, most common indirect-cooling systems are air heat exchangers, where the cooling done by the free convection in shell and tube heat exchangers. Furthermore, the heat from the gas cooling process can be recovered. The heated air was supplied for drying the raw feedstock or utilizing as a gasification agent. In addition, the indirect-water cooling is also used while the cooling water need to cool down the temperature by cooling towers or cooling ponds. For scrubbers, water base scrubber was reported as low tar solubility, short absorbent life, high evaporation rate and high investment cost of waste water treatment plant [21, 22], while oil-based scrubber was reported as the proper cleaning unit for tar removal propose as aforementioned in Chapter 2. Finally, adsorber units are effective as the last units of the gas cleaning system, which mainly treat the escaped tars. However, most of heavy tar and particles are collected by scrubber units. More details of scrubbers and adsorbers were discussed in Chapters 2 and 3.

In this chapter, the knowledge and technique from the previous research were implemented in a commercial scale of 650 KW_{th} bubbling fluidize bed(BFB) gasifier. Biomass tar contained in the synthesis gas was primarily removed by thermal cracking reactions inside the reactor due to a long free board zone design. The remaining tar and other contaminants were removed and cooled by series of cyclones, ceramic filters, air coolers and water coolers. Finally, the combination of a venturi scrubber with a regeneration unit and a packed bed adsorber were utilized to maximize the tar removal performance and prolong the lifetime of the absorbent.

5.2. Materials and setup

5.2.1 Materials

Rice husk was supplied from a rice mill near SRIC Company, Saraburi, Thailand and used as feedstock for the fluidized bed gasification. The photograph of rice husk is illustrated in Figure5.1a, while the proximate and ultimate analysis are shown in Table 5.1.

Table5.1: Proximate and ultimate analysis of rice husk, palm oil, sawdust and gasified char

Materials	Rice husk	Palm oil	Sawdust	Gasified char
Proximate analysis (wt.%,wet basis)				
Moisture content	11	0	9	0.8
Volatile matter	58	100	74.2	15.1
Fixed carbon	15	0	13.9	14.2
Ash	16	0	2.9	70
Ultimate analysis(wt.%,dry basis)				
C	36	76.3	45.1	15.3
H	5	12.3	5.7	5.1
O	33	11.3	48.9	79.3

N	1	1	0.3	0.3
LHV(MJ/kg)	14.27	37.4	16.4	2.3
Density(g/cm3)@30°C	-	0.9	-	-
Viscosity(mm^2/s)@30°C	-	47.5	-	-
BET(m^2/g)	-	-	0	3.4

Figure 5.1: (a) Rice husk, (b) packed bed material sawdust and (c) gasified char

For the wet scrubber, the palm oil was selected as a scrubber medium for tar removal due to it is low cost, convenient utilization, and high availability. Palm oil was purchased from Morakot Industries Public Co Ltd., Thailand. Its density and kinematic viscosity at 30°C scrubbing temperature was 0.9 g/cm³ and 47.5 mm^2/s, and at 50°C scrubbing temperature was 0.9 g/cm³ and 24 mm^2/s, respectively. 50 L of palm oil was contained in a storage tank. The proximate and ultimate analysis results of palm oil are shown in Table 5.1. During the gas cleaning process, the 20 L/h of palm oil was trapped at the bottom of the storage tank to supply to the oil regeneration system, which consisted of 5 parallel filtration bottles (2 liter PET bottle size). After the regeneration, the regenerated oil was returned to the storage tank. The filtration medium made from the fine poly-filter (18 cm height) was contained inside in each bottle so as to filter the solid contaminant in the scrubbed palm oil. The poly-filter was replaced at each experimental run.

For the adsorbent unit, saw dust and mixed gasified char were utilized as porous materials. There were two adsorbent units connected in parallel for convenient switching between these two adsorbents. In the first run, sawdust with the BET surface area of 0 m^2/g was packed in the first packed bed adsorbent, while the 2nd run utilized mixed gasified char (sawdust and gasified char) in the second unit of the packed bed filter. The gasified char composed of unburned-carbon and fly ash which was collected by the cyclone. The BET surface area of the gasified char was 3.4 m^2/g. The ratio of the mixed gasified char was 50:50 in the packed bed volume. The inner diameter and

the height of the parallel packed bed adsorbers are 0.5 m and 0.84 m, respectively. The photos of sawdust and char are shown in Figures 5.1b) and c), and the physical and chemical properties are shown in Table 5.1.

5.2.2 Experimental setup

The BFB gasifier was designed by Siam Cement Public Company Limited (SCG), Thailand. The BFB gasifier consisted of the biomass feeding system and the reactor as shown in Figure 5.2. For the feeding, rice husk was first stored in two hoppers and then injected into the reactor via a controlled mass flow meter (260 kg/h) and three series of gear motors. The reactor is made of steel with the inner diameter and the height of 0.6 m and 9.50 m, respectively. Heat-resistant material was coated inside the reactor with a thickness of about 0.175 m. Air nozzles were installed at the bottom of the combustion chamber. Natural gas burner nozzle is located at the surface of the bed material. Biomass feeding was located at 1.32 m above the distributor plate level. Silica sand with the average size between 0.5 and 0.7 cm was used as a bed material with the bed height around 0.25-0.3 m allowing the heat absorption and the temperature stabilization inside the reactor. Five thermocouples (K-type) and three pressure gauges were installed for monitoring the temperature and the pressure inside the reactor. A pressure relief valve was installed at the top of the reactor to safeguard against the development of an extreme pressure at any stage of the operation. After rice husk was fed to the reactor so as to produce the synthesis gas, it was passed through the gas cleaning units or the flare. The detail of the cleaning system will be described in the following sub-section.

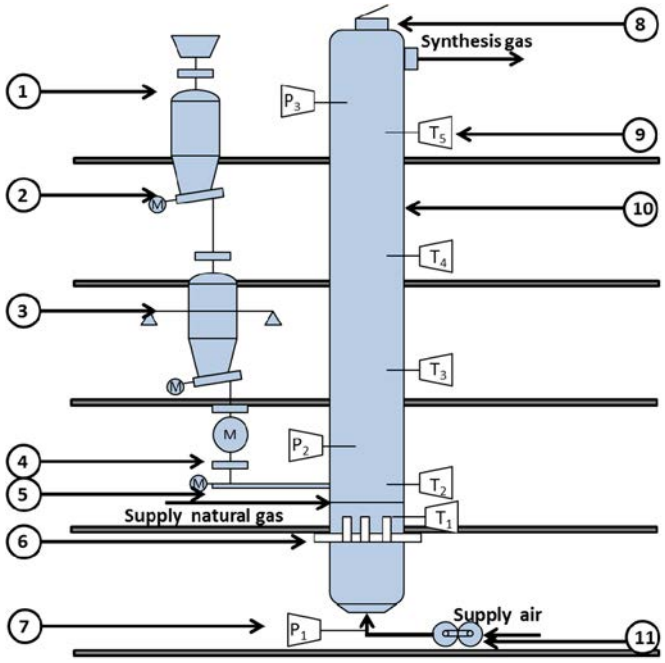

Figure 5.2 : BFB gasifier system : (1) hopper; (2) screw feeder and motor; (3) weight balancing; (4) air lock valve; (5) preheat system; (6) air distributor plate; (7) pressure transducers (P_1-P_3); (8) pressure relief valve; (9) thermocouples (T_1-T_5); (10) fluidize bed reactor; (11) force draft fan.

The gas cleaning system is shown in Figure 5.3. It consists of six main parts: (1) a cyclone (2) a ceramic filter, (3) an air cooler, (4) two water coolers (5) a venturi scrubber and (6) a packed bed adsorber. The synthesis gas

was delivered to the gas cleaning system by the induced draft fan installed before the venturi scrubber inlet. Firstly, the synthesis gas containing tar, dust and particles entered into the hot gas cleaning unit; the cyclone and the ceramic filter. The synthesis gas from the reactor was passed through the cyclone in order to eliminate unburnt carbon and ash before sending the synthesis gas to the ceramic filter. Then, the remaining dust and particles were trapped by the ceramic filter (candle filters). When dust and particles accumulation exceeded the maximum design pressure drop, nitrogen is supplied to force them falling at the bottom bin. The synthesis gas temperature inside the ceramic filter was around 500°C, which was cooled down to 450°C and subsequently to 60°C by the air cooler and the water coolers, respectively. High molecular weight tar was condensed and polymerized during these cooling processes, especially in the water cooler unit. After that, the synthesis gas entered into the venturi scrubber in order to reduce tar and remaining contaminants further. Palm oil was used as a scrubber medium due to its good tar absorbing characteristics. The operation temperature of the scrubbing oil was between 40° and 50°C. The liquid to gas ratio was 7.25 L/Nm^3 and the gas velocity at the oil spray was 67 m/s. With these scrubber design conditions, palm oil broke into tiny droplets resulting in improved removal of tar and dust. Finally, the synthesis gas entered into two parallel units of packed bed adsorbers. The first unit contained sawdust while the second unit contained mixture of sawdust and gasified char with 50/50 volume ratio.

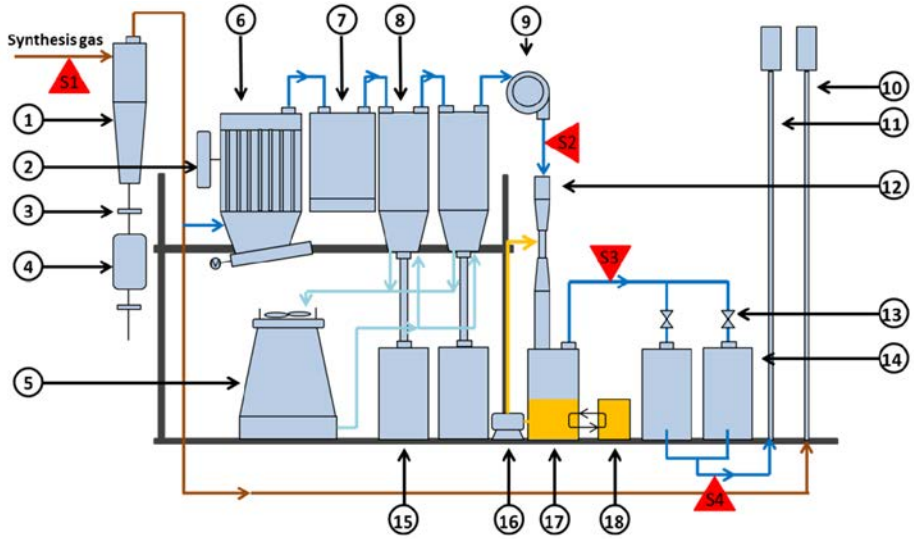

Figure 5.3 Gas cleaning facilities : (1) dust cyclone; (2) nitrogen tank; (3) air lock valve; (4) dust chamber; (5) cooling tower; (6) ceramic filter; (7) air cooler; (8) water cooler; (9) induce draft fan; (10) flare1; (11) flare2; (12) venturi scrubber; (13) on-off valve; (14) pack bed adsorber; (15) tar condensed container; (16) oil close loop pump; (17) oil storage tank; (18) regenerated oil system

5.3 Tar sampling and analysis method

Tar was measured after rice husk was fed for about two hours when the gasifier reached to a steady state. For tar sampling, four measuring points namely S1 (at the gasifier outlet), S2 (at the scrubber inlet), S3 (at the scrubber outlet) and S4 (at the adsorber outlet) were used as shown in Figure 5.3. The sampling was done in both the wet and dry methods in order to measure the majority of tar present in the producer gas. The wet method was

used for analyzing the complex high to medium molecular weight tar, while the dry method was used for analyzing the light tar compounds in the synthesis gas. The gravimetric tar was measured by the weight and GC-FID was employed to determine the concentration of the light tar compounds. The detail of the wet and dry tar measurement methods are given below.

5.3.1 Wet tar measurement method

The wet method was used according to the protocol for sampling and analysis of tar and particles in biomass producer gas. The procedure of the sampling method is shown in Figure 5.4. The sampling gas with the controlled volume flow rate of approximately 1 L/min was passed through the sampling unit which consists of 10 impinger bottles connected in series. Each impinger bottle contained 100 mL of IPA. In total, the volume of about 1000 mL IPA solution was used in each experiment. The impinger bottles were placed in an ice bath kept at 3±2°C and the tar sampling was conducted for about 15 minutes in each experiment. The sampling gas was primarily cleaned before passing through a gas flow meter, an adjustable valve and a suction pump by series of cotton filter tube and activated carbon tube. After that, the tar was separated from IPA by filtering and evaporating using a rotary evaporator in a water bath at the temperature of about 40°C as shown in Figure 5.5. The residue is defined as the heavy or the gravimetric tar which was measured by the weight.

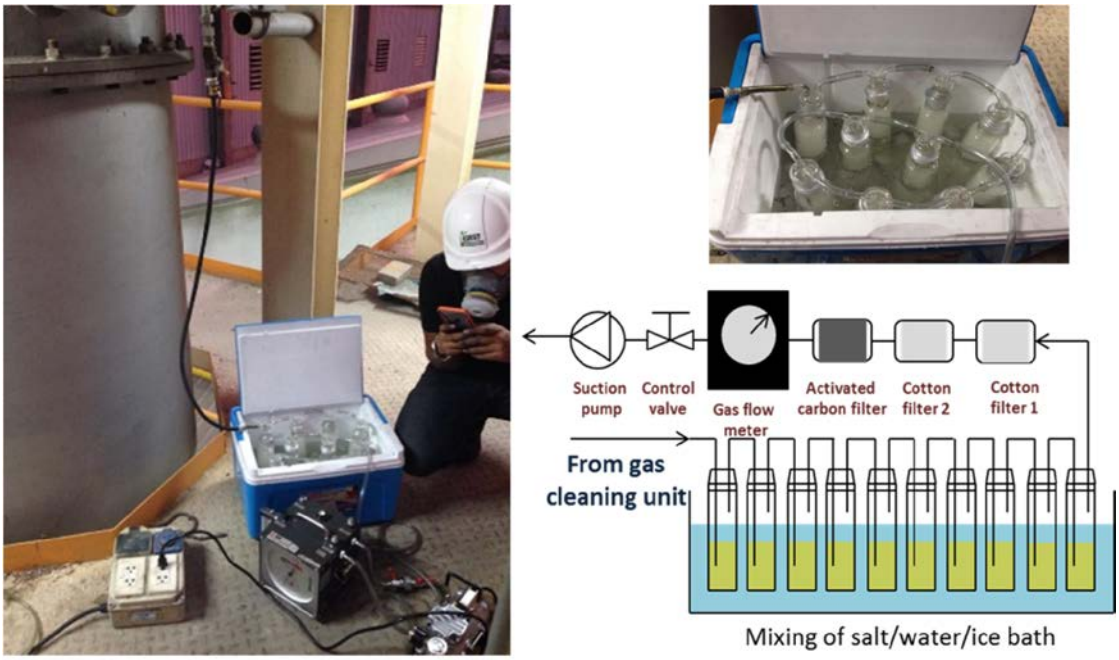

Figure 5.4: Schematic diagram of the wet sampling and the flow measurement method

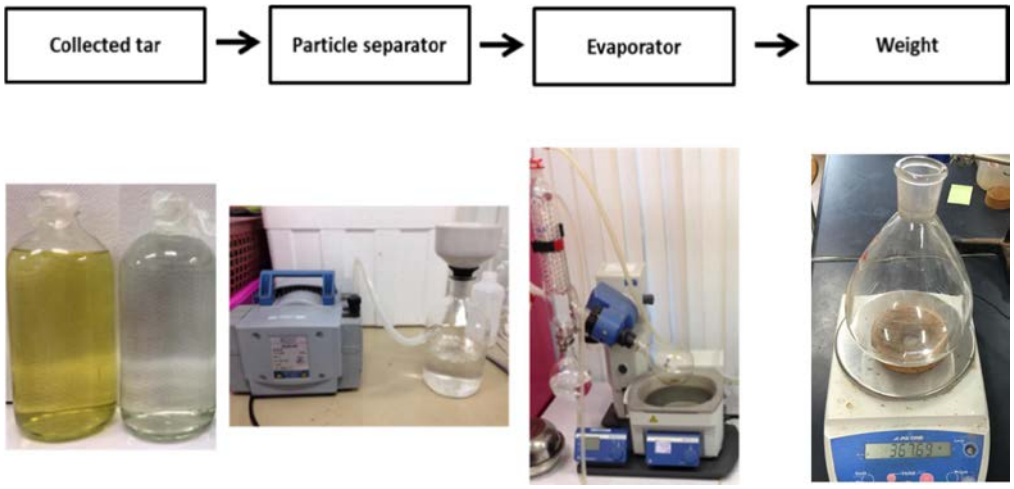

Figure 5.5: Gravimetric tar analysis process flow

5.3.2 Dry tar measurement method

The dry method was used for analyzing the light tar. The procedure of the sampling method is shown in Figure 5.6. The experimental equipment consists of 6 mm ID charcoal tube (containing 150 g of activated carbon) connected in series with 8 mm ID silica gel tube (containing 780 mg of silica gel) purchased from Sibata Scientific Technology Ltd., Japan. Charcoal tube which is well-absorbed for non-polar organic compounds was used to measure benzene, toluene and naphthalene, while silica gel tube, which is well-absorbed for polar organic compounds, was used to measure phenol. The synthesis gas containing the light tar was sampled at the flow rate of 0.5 L/min for 3 minutes. After the tar sampling by the dry method, the gas chromatography flame ionization detector (GC-FID) was utilized to detect the light tar compounds and their concentrations. Carbon disulfide and acetone were used as solvents for charcoal tube and silica gel tube, respectively. Details of the dry tar sampling and the analysis method was described elsewhere in a related pervious paper [23].

Figure 5.6: Schematic diagram of the dry sampling, the flow measurement method and the analysis facility

5.4 Experimental procedure

Before starting up the reactor, an induced draft fan was started to ensure there was no combustible gases inside the combustion chamber. This can be noticed at the smokestack when there is no exhaust smoke released. After that, fabric oil soaked with engine oil was set on fire and put in the combustion chamber. Natural gas and air were also supplied. As a result, the temperature in the gasifier increased to about 600°C at which silica sand started bubbling. The heating continued until T_1 and T_2 reached to 850 and 800°C, respectively. Finally, 260 kg/h of rice husk was fed to the reactor and natural gas supply was simultaneously stopped. The air flow rate was set in the range of 375-400 Nm^3/h in order to control the air equivalence ratio (ER) at 0.35. As the biomass feeding started, the temperature inside the reactor slightly dropped due to the influence of endothermic reactions. The synthesis gas was introduced into the gas cleaning system after about 2 hours of the operation when the reactor achieved the stable gasification temperature. The operation conditions and the experimental procedure are summarized in Table 5. 2. The tar removal performance by the cooling systems and the venturi scrubber with the regeneration unit were studied along 20 hours duration test in the first run. In the second and third runs, the combination with the packed bed adsorber were studied by sawdust and mixed gasified char, respectively, along 6 hours duration test.

Table 5.2: Operation condition and experimental procedure

Parameters	RUN1	RUN2	RUN3
Initial experimental set up			
Under bed temperature(°C)		800	
Bed temperature(°C)		850	
Bed material		silica sand	

Preheated fuel		natural gas	
Feedstock		rice husk	
Feed rate(kg/h)		260	
Air flow rate(Nm^3/h)		375	
Equivalent ratio		0.35	
Experimental condition of each run			
Ceramic filter temperature(°C)	500	500	500
Scrubber medium	Palm oil	Palm oil	Palm oil
Scrubber volume(L)	50	50	50
Liquid to gas ratio (L/Nm^3)	7.25	7.25	7.25
Scrubber temperature(°C)	45-50	45-50	45-50
Adsorber materials	-	Sawdust	Mixed gasified char
Adsorber temperature(°C)	-	30	30
Tar sampling method			
Gravimetric tar	Wet	Wet	Wet
Light tar	Dry	Dry	Dry
Operation period (h)	20	6	6

5.5. Results and discussion

5.5.1 20 hours duration test on series of gas cleaning: the cyclone, the air cooler, the water cooler and the venturi scrubber with the oil regeneration unit.

The gravimetric tar concentration in the exiting gas from BFB gasifier and in each gas cleaning sampling locations is shown in Figure 5.7. It can be seen that, before entering the cleaning devices, the synthesis gas contained approximately 11.77 g/Nm^3 of gravimetric tar at the exit of the gasifier. After that, the synthesis gas passed though the hot gas cleaning units and cooling units (cyclone, ceramic filter, air and water cooler, respectively), where 64% on the average of the gravimetric tar was eliminated. Then, the concentration of the gravimetric tar was reduced further to 0.57 g/Nm^3 (95% tar removal efficiency), when the gas passed through the venturi scrubber. The palm oil absorbent, which was utilized as a gas scrubbing medium, was trapped and regenerated for 7 times(20 L/h) by the filtration method along 20 hours of the operation. It was observed that the overall gravimetric tar removal efficiency by this cleaning system was 95%, 95%, 94% and 94 %, respectively. It can be seen that the regenerated oil showed a slight drop of the tar removal efficiency of about 2% along the 20 hours duration test. As mentioned in Chapter 4, the poly-filter perfectly filtered large size (> 30μm) contaminants. However, the tiny contaminants (<30μm) still remained and returned to the oil storage tank. These impurities were continuously accumulated. The non-regenerated oil contained a huge load of contaminants which obstructed the contacting area of absorption resulting in the decrease of the tar removal efficiency. The improvement of tar removal performance can be achieved by installing the fast and effective mechanical separator (increasing the oil filtration flow rate or using the centrifugal sedimentation technique) in order to continuously and efficiently remove the contaminants in the absorbent.

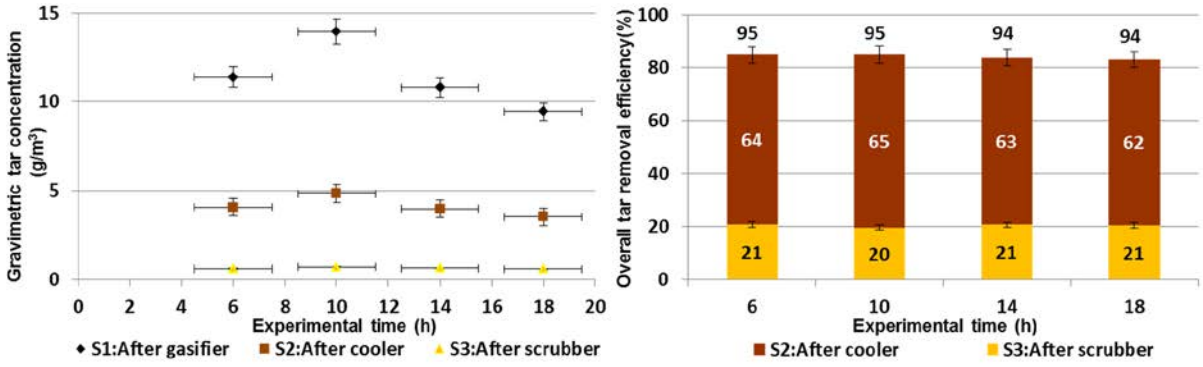

Figure 5.7: The gravimetric tar concentration and the overall tar removal efficiency in the exiting gas of BFB gasifier and in each gas cleaning sampling locations along the 20 h duration test

For the light tar removal, the results show that the cooling unit and the scrubber perfectly removed phenol and naphthalene contaminations. 100% of phenol was removed at the exit of the cooler while 100% of naphthalene was removed at the exit of the oil-based venture scrubber as shown in Figure 5.8.

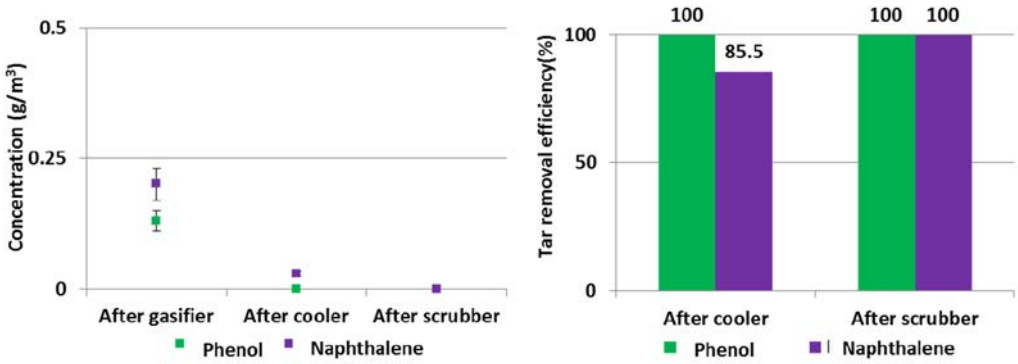

Figure 5.8: The light tar concentration and the removal efficiency in the exiting gas of BFB gasifier and in each gas cleaning sampling locations along 20 h of duration test

Although the hot gas cleaning unit, the cooling units and the venturi scrubber with the regeneration unit performed a very high gravimetric tar removal performance and perfectly removed dangerous light tars (phenol, naphthalene) along 20 hours, the remaining tar in the synthesis gas was still higher than the acceptable level for using in IC-engines. Therefore, the packed bed adsorber, which is low cost and effective tar removal unit, was required for removing the remaining gravimetric tar before supplying to IC-engines.

5.5.2 Comparisons on the tar removal efficiency of the gas cleaning series with the sawdust packed bed and the mixed gasified char packed bed.

Two kinds of adsorbent were investigated for determining the tar removal efficiency during 6 hours of operation. The synthesis gas was sampled at pre (S3) and post (S4) packed bed adsorbers by both the wet and dry methods.

The concentrations of the gravimetric tar at the inlet and outlet of the packed-bed adsorber are shown in Figure 5.9. When only packed bed unit was taken into consideration, sawdust as an adsorbent reduced 27% of the gravimetric tar from 0.6 g/Nm^3 to 0.46 g/Nm^3, while the mixed gasified char removed 83% of the gravimetric tar. This is because the specific surface area of the gasified char was much higher than that of sawdust. The BET surface area result is shown in Table 5.1 and the SEM micrograph of porous texture is shown in Figure 5.10. With the mixed gasified char packed bed adsorber, there was less than 0.1 g/Nm^3 of gravimetric tar remained in the synthesis gas which achieved the gas quality requirement for utilization in internal combustion engines. As a result of the overall gravimetric tar removal performance, 97% of the gravimetric tar was removed by using the sawdust packed bed adsorber, while the mixed gasified char line showed the gravimetric tar removal efficiency up to 99%.

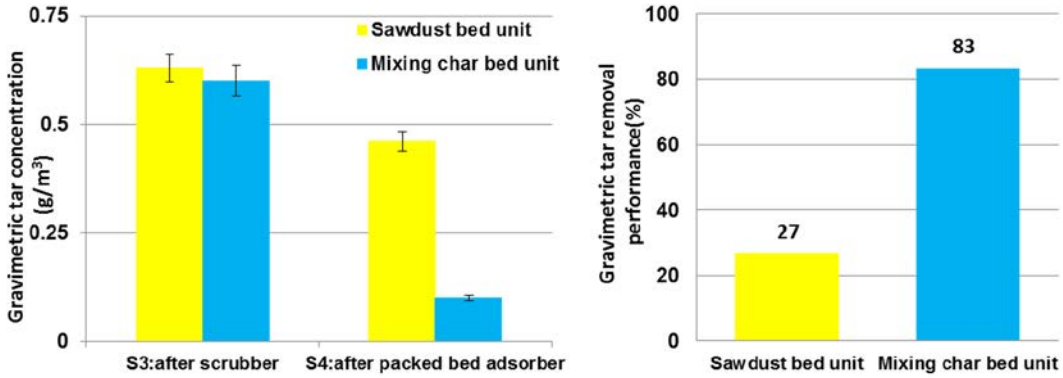

Figure 5.9: Comparison of the gravimetric tar removal capacity and the gravimetric tar removal efficiency of sawdust and the mixed gasified char in the packed bed adsorber

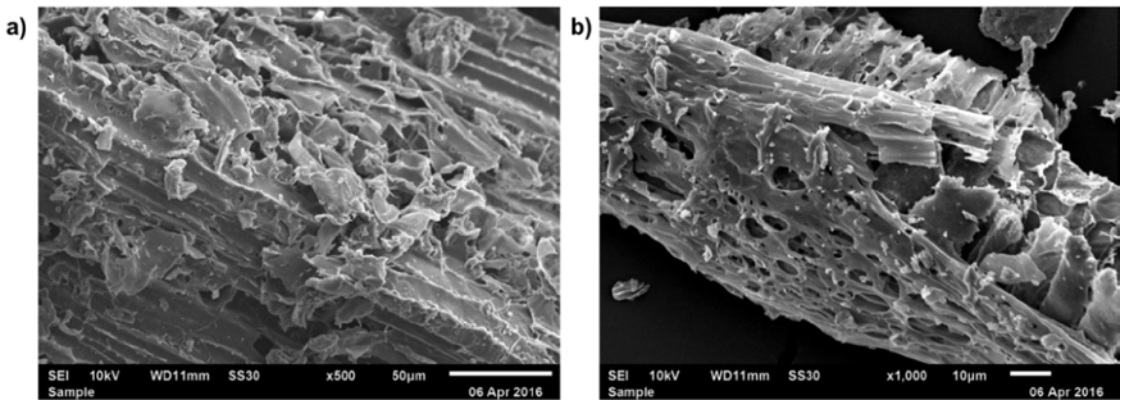

Figure 5.10: SEM micrograph of a) sawdust b) gasified char

5.5.3 Characterization of post cleaning wastes: scrubbing oil and solid adsorbent treatment

The palm oil utilized for 20 hours scrubbing clearly contained the gravimetric tar, fine particles and water as can be seen in Figure 5.11. Use of the poly-filter packed tower was not adequate for removing fine particles and water in the regenerated oil. These accumulated contaminates in the regenerated oil disturbed the absorption

mechanism which eventually led to low tar removal performance. The ultimate and proximate analysis of pre and post scrubbing oil is shown in Table 5.3. The moisture and ash content in the post scrubbing oil increased to 1.2% and 0.4% respectively. The possibility of improving the absorbability and the lifetime of the regenerated oil can be obtained by using the centrifuge in the regeneration system. The integrated centrifuge can also reduce the requirement of make-up oil. For the heat recovery, the degraded regeneration oil can be used as a fuel in the combustion process. The heating value of the pre and post scrubbed oil was not so different in 20 hours of experiment. The heating value of pre and post scrubbed oil was 37.4 MJ/kg and 38.4 MJ/kg, respectively.

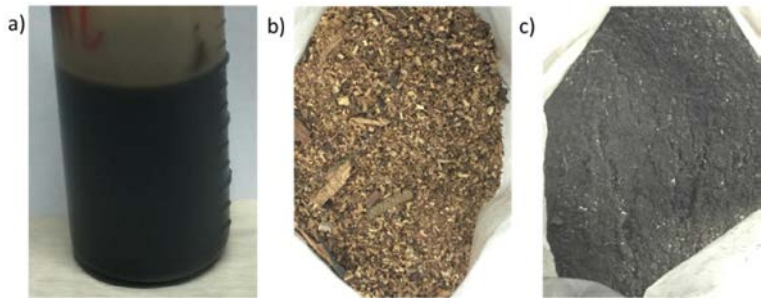

Figure 5.11: Post processed absorbent and adsorbent: a) oil b) sawdust and c) char

The ultimate and proximate analysis results of the pre and post adsorbent are shown in Table 5.3. The moisture content of the 6 hours post adsorbed sawdust decreased from 9 % to 5 %, while the gasified char increased from 0.8 % to 6.7 %. This means that the water adsorption of char was higher than sawdust. The volatile matter absorbed in sawdust during the 6 hours tar adsorption increased from 74.2 % to 81.3 %, while the that in gasified char increased from only 15.1 % to 57.8 %. It is clearly shown that the volatile matter adsorbed by char was more than that by sawdust. Moreover, the heating value of the sawdust and the gasified char after adsorption increased by 0.9 MJ/kg and 1.4 MJ/kg, respectively. However, sawdust has a lower tar absorbability compare with gasified char due to its lower BET surface area. It resulted in lower amount of tar adsorbed and lower heating value improvement.

Table 5.3: Comparison of the characteristics of oil, sawdust and gasified char in pre and post cleaning process

Sample name		C	H	O	N	HHV	LHV	MC	VM	FC	Ash
		(wt.%,dry basis)				MJ/kg		% as received			
Sawdust	Pre	0.451	0.057	0.489	0.003	17.6	16.4	9	74.2	13.9	2.9
	Post	0.478	0.054	0.461	0.006	18.5	17.3	5	81.3	8.1	5.6
Char	Pre	0.153	0.051	0.793	0.003	3.5	2.3	0.8	15.1	14.2	70
	Post	0.245	0.025	0.726	0.004	4.3	3.7	6.7	57.8	13.2	22.2
Oil	Pre	0.763	0.123	0.113	0.001	40.1	37.4	0	100	0	0
	Post	0.771	0.129	0.095	0.005	41.2	38.4	1.2	98	0.3	0.4

5.5.4 Mass and energy balance

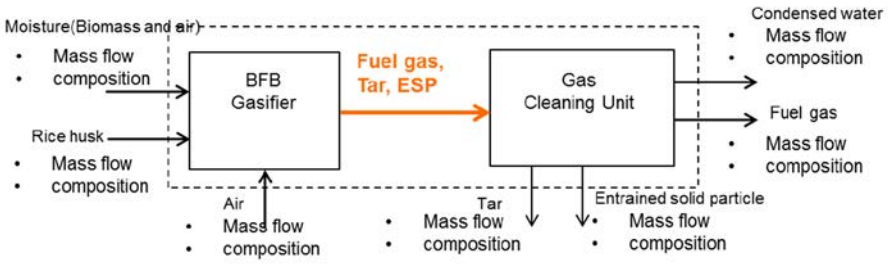

Figure 5.12: BFB gasifier mass flow diagram

Material Balance(kg/h)		
Mass In		%
Biomass	231	33
Air	474	67
Moisture	65	9
Total	705	100
Mass Out		
Dry gas	654	93
Tar	7	1
$ESP_{,cyclone}$	9	1
$ESP_{,ceramic\ filter}$	11	2
Moisture& $ESP_{,undetectable}$	25	4
Total	705	100

Energy Balance(MJ/h)		
Heat In		%
Biomass	4270	100
Total	4270	100
Heat Out		
Fuel dry	2309	54
Sensible heat loss	397	9
Tar	214	5
ESP	44	1
Moisture loss	82	2
Surrounding	1224	29
Total	4270	100

Performance Summary	
$\eta_{cold\ gasification}$ (%)	54
$\eta_{carbon\ conversion}$(%)	92

The mass and energy balances were used to analyze the input and output streams of the gasification process. The elemental compositions of the mass inputs composed of rick husk, air, and moisture (present in both biomass and air), while the elemental compositions of the mass outputs consisted of synthesis gas, tar and condensed water, and ESP (entrained solid particle) are shown in Figure 5.12. According to the air humidity, the moisture content of air was evaluated by using psychometric chart at 30°C and 60% of the relative humanity which was the average weather condition in Thailand during the experiment. The total dry-synthesis gas flow rate was calculated from the nitrogen mass balance of the entire gasification system. The volume of N_2 and other gases in the synthesis gas compositions were calculated based on the ideal gas law. The mass flow rate of ESP was weighted after the experiment in each run. The results revealed that 92% by mass of carbon input from dry rice husk converted into the synthesis gas, while 5% and 1% converted into tar and ESP, respectively. For the energy balance, 54% of energy in rice husk transferred into the synthesis gas that can be used for generating electricity, while 6% of the remaining energy stored in tar and ESP. The energy loss due to the gas cooling, radiation to the surrounding environment and moisture condensation in the synthesis gas was 9%, 29% and 2%, respectively.

5.6. Conclusion

This study discussed the physical gas cleaning system for tar removal of scaled-up rice husk gasification plant of 650 kW_{th} BFB gasifier. The results are summarized as below:

1. 95 % of the overall gravimetric tar was removed by the series of cyclone, ceramic filters, air cooler, water coolers, vegetable oil base venturi scrubber system (with the oil regeneration unit) along the 20 hours duration test.
2. 100% of naphthalene was removed by vegetable oil base venturi scrubber system (with the oil regeneration unit) along the 20 h duration test.
3. Even if dangerous light tars were perfectly eliminated by the series of cyclone, ceramic filters, air cooler, water coolers and the vegetable oil venturi scrubber, the gravimetric tar concentration at the exit (0.57 g/Nm^3) remained higher than the acceptable level for using in IC-engines (0.1 g/Nm^3). Therefore, we proposed a packed bed adsorber as low cost and effective tar removal unit to eliminate the remaining tar.
4. 97% of the gravimetric tar was removed by combining the venturi oil scrubber with the sawdust packed bed adsorber, while combining with the mixed gasified char performed 99% tar removal efficiency which achieved the synthesis gas quality requirement for IC-engines.
5. By this BFB gasifier , 54% of the biomass energy was converted to the raw synthesis gas.

5.7. Reference

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Chapter 6

Conclusion and recommendation

6.1 Conclusion

This research focuses on the tar removal efficiency and capacity based on the physical tar removal technique. It consists of two main parts: 1.) lab-scale: Tar removal by physical technique and process development, and 2) Scaling up: Demonstration in commercial scale biomass gasification plant. The physical gas cleaning techniques and developments were investigated based on the gasification temperature of 800°C, which is an operation condition of both the laboratory experiment and the scaling up plant.

In the lab scale experiment, the followings are investigated; 1) the best operating temperature for three kinds scrubbing medium, which are palm oil, waste cooking oil and waste lubricant oil, 2) the gravimetric and light tar removal performance (efficiency and capacity) during 10 hours experiment without the regeneration unit, 3) the gravimetric and light tar removal performance (efficiency and capacity) during 10 hours experiment with the regeneration unit (the filtration and the centrifugal sedimentation).

Firstly, the operating conditions of the gas cleaning unit are key parameters for improving and optimizing the tar removal efficiency. In this study, the primitive study was conducted based on the previous work in order to optimize the operating condition to utilize low-cost absorbents. Three kinds of scrubbing medium, which are palm oil, waste cooking oil and waste lubricant oil, were investigated for the gravimetric tar removal efficiency. The attention was paid on the absorbent temperature effect. The temperature was strongly affected the hydrodynamic of a Newtonian fluid and physical properties, e.g. the kinematic viscosity, the interfacial tension, the wettability (distribution ability) and the retention time. The results found that although the high absorbent temperature maximized the mass transfer rate of the high viscous fluid, the increase of the temperature contributed the channel of the stripping and the contacting time reduction for a low viscous fluid. Therefore, the increase of the temperature of palm oil and waste cooking oil could not improve the gravimetric tar removal efficiency due to the low viscosity characteristic, whereas it was effective for the waste lubricant oil. It was summarized that palm oil performs the highest gravimetric tar removal performance among three kinds of absorbent and waste cooking oil was recommended as low cost scrubber medium with a high tar removal efficiency, while waste lubricant oil requires the external heating for improving the tar removal efficiency.

There was an accumulation of tar aerosols and other contaminates in the scrubber by continuation of the cleaning, and these accumulated contaminants strongly affected the mass transfer between the gaseous tar and the scrubbing oil. The contaminants caused the increase of the viscosity, decrease of the turbulence level and the interface mobility resulting in reduction of the overall tar removal performance by continuation of the cleaning. Therefore, the next research was concerned on their tar removal capacity in order to predict the periodic change to the new oil to maintain the tar removal efficiency of the scrubber and to prevent breakdown of downstream machines. In addition, char, which is the by-product from the gasification process, was utilized to evaluate the tar removal

capacity as well. The tar removal capacity of the combination of waste cooking oil and char were investigated. The breakthrough curve was used to identify the appropriate period for replacing the absorbent and the adsorbent. Based on the breakpoint data, 1 litter of waste cooking oil can absorb 14.4 g of tar with 80% removal efficiency and 1 g of char can remove 0.15 mg of naphthalene with 76% removal efficiency. In addition, char also adsorbed the gravimetric tar of 48.8 mg-tar/g- char with 3.1% increase of the removal efficiency on the average. The results were utilized for scaling up in commercial plants

It was found that a huge amount of absorbent are required for maintaining the tar removal performance of the scrubber which is not economical and environmentally friendly system. The next step of this research work proposed the oil regeneration idea for recovering the tar removal capacity of the scrubbing oil. The overall tar removal efficiency was almost completely recovered by the filtration and the centrifugal sedimentation techniques. The tar and impurities contained in the absorbent were effectively removed by these methods. The experiments were conducted for 10 hours to compare the performance between the non-regenerated and the regenerated oil. The non-regenerated oil performed the lowest tar removal efficiency, which only 48% of the gravimetric tar could be removed on the average. Although the removal rate at the beginning of the experiment was very high, the impurities accumulation in the absorbent have a high influence to obstruct the dissolution ability resulting in continuous dropped of the tar removal efficiency. However, with the utilization of the regenerative unit, the tar removal efficiency was able to be improved to 78% and 83% on the average along 10 hours experiment period by the filtration and the centrifugal sedimentation, respectively. The tar removal efficiency of the centrifugal sediment was higher than that of the filtration due to the deterioration of the filter media and the removable solid particle size limitation. Irremovable micro solid particles (<30μm) have a tendency to pass through the filter media, which resulted in a lower recovery of the gravimetric tar removal efficiency.

Based on the successful lab-scale results, the gas cleaning system employing the physical tar removal methods by the combination of the palm oil scrubber and the filtration regeneration unit and the adsorber were implemented in a commercial scale facility. The 600kW_{th} bubbling fluidized bed gasifier with rice husk feedstock was utilized to study the tar removal capacity of the physical cleaning system. By the use of series of cyclone, ceramic filters, air cooler, water coolers, vegetable oil base venturi scrubber with the oil regeneration unit, stable tar removal during 20 hours operation with 95% of tar removal on the average was demonstrated. Combined with the adsorber, 97% tar removal efficiency on the average could be achieved by the sawdust packed bed adsorber, while 99% by the mixed gasified char pecked bed adsorber could be achieved meeting with the syngas quality requirement for IC-engines.

This research proved an effective and low cost gas cleaning system for treating biomass tar with a long period of the operation.

6.2 Recommendation

Many researchers in this field found that oil based scrubber was much more effective for treating biomass gases tar than water based scrubber. The oil based scrubber were reported as a high tar removal efficiency materials during high gasification temperature (>950°C). However, the reduction of tar removal efficiency was observed during low and medium operation temperature of gasification process (<800°C). In low and medium gasification temperature, there was mainly the primary tar produced. The tars, which decomposes from cellulose, hemicellulose and lignin,

mainly composed of phenolic ethers group (polar tars). On the other hand, these primary tars completely converted to larger polycyclic aromatic hydrocarbons (LPAHs), which were non-polar tars, at temperature higher than 900°C.

Therefore, the effective gases tar cleaning units should be designed based on the gasification condition. More researches on this topic has to be further investigated. The proposal method from this research is to remove heavy tar and light tar by oil scrubber with centrifugal sediment techniques to regenerate oil and char adsorber are suggested, respectively.

For the up-scale plant, Figure 6.1 shows the appropriated gas cleaning system for the BFB gasifier which showed a high tar removal performance. The BFB gasifier system in this research consisted of a cyclone, ceramic filters, an air cooler, water coolers, a vegetable oil based venturi scrubber and the packed bed adsorber, respectively. The centrifugation unit is proposed to replace filtration unit to prolong the operational time of oil-based adsorbent.

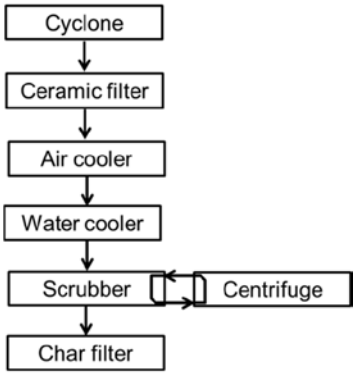

Figure 6.1: The flow diagram of the gas cleaning system

Appendix

Appendix A

Chemical components analysis method of oily materials

According to solvent properties, it strongly affected on tar removal performance. Few researchers recommended vegetable oil as suitable solvent for tar removal purpose due to hydrophobic property. Vegetable oil was classified as hydrophobic substance as a result of tar effectively absorbed by this solvent. On the contrary, lubricant oil which was also categorized as hydrophobic substance had low tar removal efficiency. As reported in chapter 2, the main difference of plant base oil and lubricant oil was the carboxyl group in vegetable oil, where more portions for the polar tars were absorbed. The longer chains of fatty acids are less soluble in water, while the shorter chains of fatty acids are more soluble in water. The rare study reported the comparisons on theirs component of absorbent analysis as this research.

Preparation method for plant base oil analysis

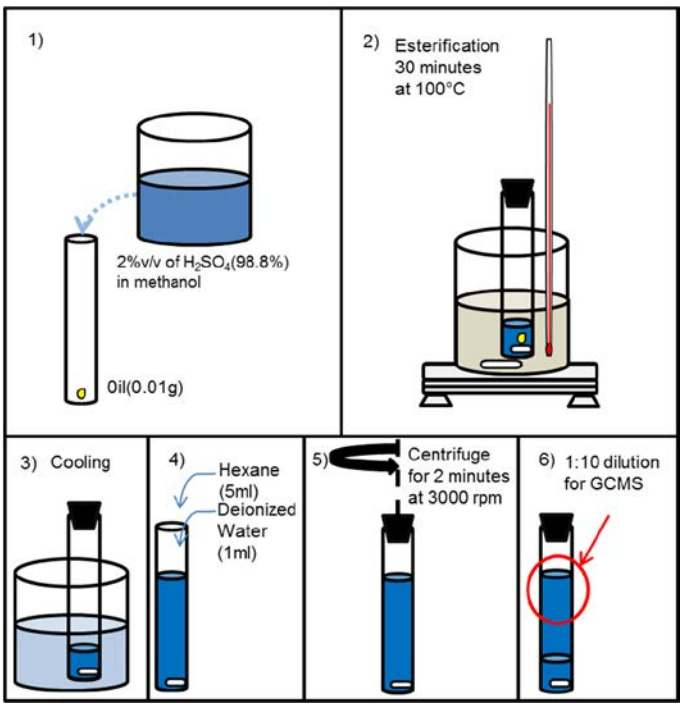

Figure A1: Preparation method of fatty acid methyl esters (FAMEs)

The chemical component analysis data of plants base oil which summarized in Table 2.4 was detected by GC-MS. The preparation of plants oil base analysis was followed the modified ISO method [1]. 0.01 g of the plants base oil was dissolved in 1 mL of solution. The solution was prepared by 2%v/v of 98.8% H_2SO_4 in anhydrous methanol. Esterification was performed by refluxing for 30 minutes at 100°C in tightly sealed Pyrex tubes. After

cooling at room temperature, 5mL of hexane was added followed by 1ml of deionized water, mixed gently and allowed to settle until the upper petroleum ether layer becomes clear by centrifuge (3,000 rpm for 2 minutes). The distinct upper layer of methyl ester in hexane was separated carefully in a capped vial and used for analysis. Then dilute the methyl ester in hexane 10 times for GCMS. 1µl of the hexane were injected into the chromatographic column and peaks were recorded for their respective retention time, areas by the data processor unit of GC. The preparation process was shown in Figure A1.

Preparation method for lubricant oil base analysis

While the chemical component analysis data of lubricant base oil summarized in Table 2.5. The n-hexane was used as a solvent. The lubricant oil was prepared according to the modified method reported by J.A.Hiltz.et.al [2]. The 100 times diluted lubricant oil in hexane was prepared for GCMS. 1µl of the hexane were injected into the chromatographic column and peaks were recorded for their respective retention time, areas by the data processor unit of GC.

Reference

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Appendix B

Optimization of centrifuge speed

10 hours of condensed and absorbed contaminants in oil scrubber from biomass pyrolysis was investigated as shown in Figure B1. For solid particles, 2µl of sampling oil was arranged in square appearance (0.5×0.5 cm^2) on glass plate and inspected by using microscope as shown in figure B3.

Figure B1: The post process oil

Centrifuged oil is defined as post process oil which was solid- liquid-liquid separated by centrifugation in different speed of centrifuge (5000, 10000, 12500rpm) for 10 minutes. During centrifugation, the temperature of centrifuge was set at 30°C. Centrifuged oil after centrifuge was shown in figure B2. For solid particle, microscope was investigated the size distribution and separation performance of contaminated in each speeds. 2ul was inspected into glass.

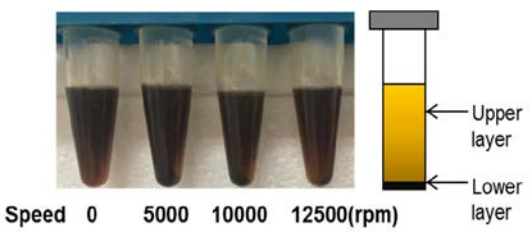

Figure B2: The pre and post centrifugation process oil

Contaminated particles in oil are irregular shape. The solid particle size from scrubbing biomass gases tar defines as statistical diameter which was obtained when linear dimension was measured by microscope. The optimum centrifuge speed was 10k rpm due to completely eliminated particle size larger than 1 micron as shown in figure B3.

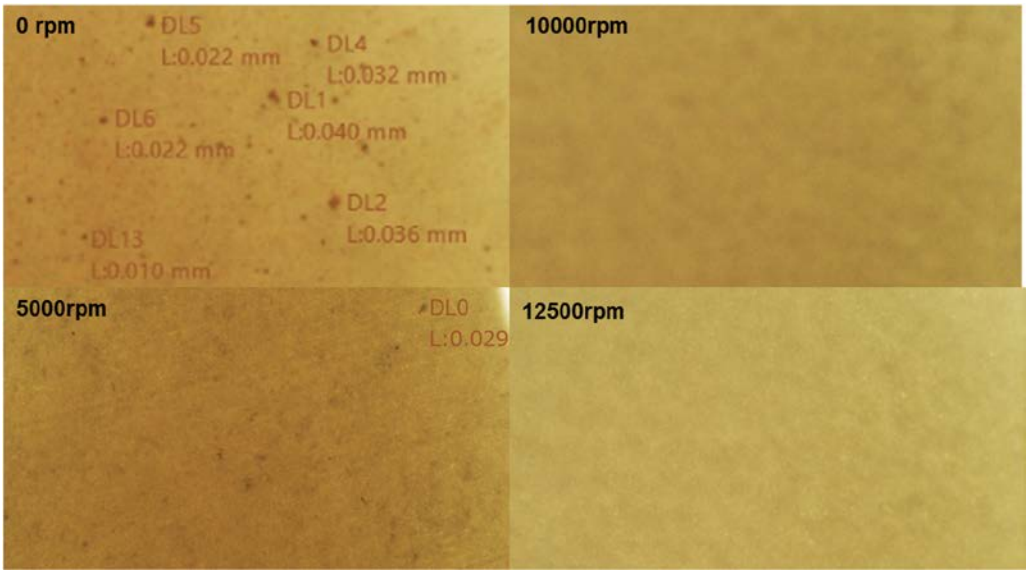

Figure B3: Microscopic images of suspension in upper layer of pre and post centrifuged oil

Appendix C

Figure C1: The photograph of 650 kW_{th} fluidized bed gasification facility at Siam Refractory Industry Co.Ltd. (SRIC), Thailand

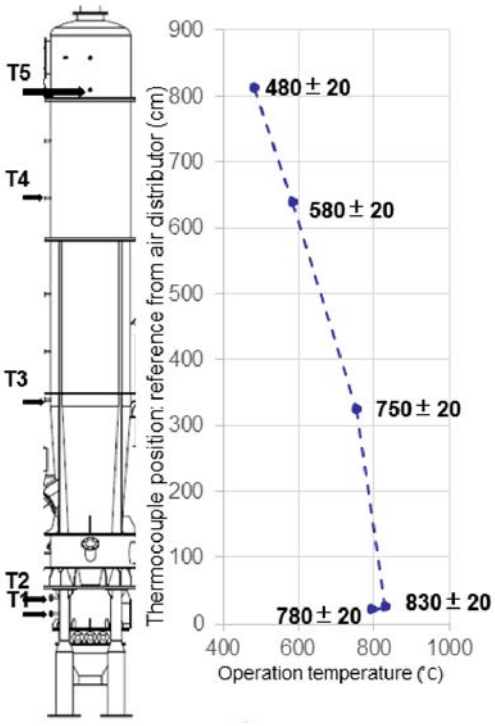

Figure C2: The temperature profile inside BFB gasifier

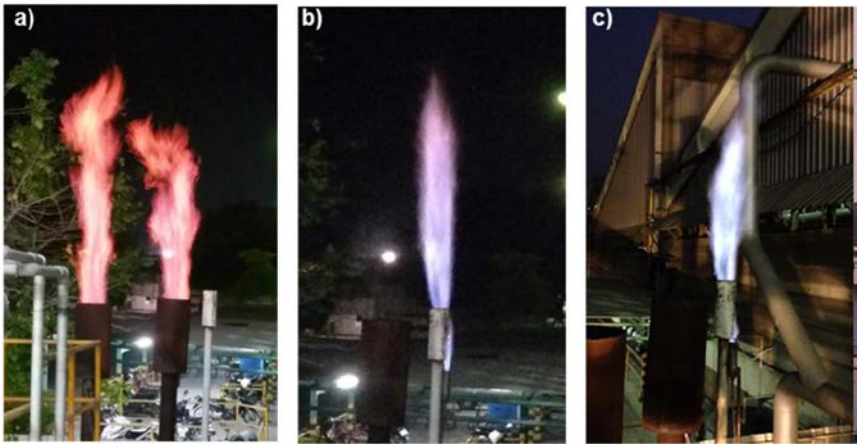

Figure C3: The flame color of syngas a) without gas cleaning process b) with gas cleaning process (adsorbent unit 1) c) with gas cleaning process (adsorbent unit 2)