CHARACTERIZATIONS OF BIO-ASPHALT USING PALM BIO-OIL FROM EMPTY FRUIT BUNCHES AND BETA CAROTENE

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by

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I hereby declare that all corrections and comments made by the supervisor(s)and examiner have been taken into consideration and rectified accordingly.

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ABSTRAK

Penyusutan sumber petroleum di muka bumi telah menarik minat penyelidik dalam menjalankan penyelidikan bagi menghasilkan bahan pengikut alternatif. Bio-asfalt dilihat berpotensi besar untuk menggantikan asfalt berasaskan petroleum kerana memiliki sifat reologi yang hamper serupa, sumber yang boleh diperbaharui, dan mesra alam. Dalam kajian ini, minyak sawit yang diperolehi daripada sisa tandan buah kosong (WBO) dan bio-minyak beta karotena (CBO) ditambahkan ke dalam pengikat asfalt konvensional pada kadar 5%, 10%, dan 15%. Sifat pengikat asfalt yang diubahsuai menggunakan bio-minyak dan dikenali sebagai bio-asfalt telah dikaji. Pada mulanya, sifat fizikal dan reologi pengikat bio-asfalt diuji dengan ujian penusukan, ujian titik pelembutan, ujian kelikatan putaran, ujian kemuluran, ujian graviti tentu, dan ujian perubahan jisim RTFO. Kemudian, ujian FTIR dan GC-MS dilakukan untuk mengenal pasti komposisi kimia dan kumpulan berangkap dalam kedua-dua bio-asfalt. Seterusnya, campuran bio-asfalt disediakan melalui kaedah Marshall untuk menentukan kandungan pengikat optimum (OBC) dan kesan bio-minyak terhadap sifat isipadu dan prestasi mekanikal campuran. Akhirnya, ciri perkhidmatan dinilai menggunakan ujian rendaman air statik dan ujian air mendidih. Penambahan bio-minyak menurunkan titik pelembutan, kelikatan, dan kemuluran, sementara meningkatkan penusukan, graviti tentu, dan kehilangan jisim selepas RTFO. Analisis FTIR menunjukkan keberadaan kumpulan fungsi WBO termasuk fenol, alkohol, keton, aldehid, dan asid karboksilik. Selain itu, analisis spektrum FTIR bagi kedua-dua bio-asfalt adalah hampir serupa berbanding asfalt konvensional. Berdasarkan ujian reka bentuk campuran Marshall, semua campuran asfalt memenuhi spesifikasi penentuan piawai JKR. Walau bagaimanapun, campuran 10% WBO bio-asfalt menunjukkan pretasi yang lebih baik dari segi sifat isipadu dan tingkah

laku mekanikal. Hasil ciri perkhidmatan menunjukkan bahawa campuran bio-asfalt yang diubahsuai mempunyai prestasi ikatan dan penyaduran yang lebih baik berbanding dengan campuran asfalt terkawal. Secara keseluruhannya, sifat campuran bio-asfalt WBO adalah setanding dengan campuran yang disediakan menggunakan pengikat asfalt konvensional. Oleh itu, penggunaan WBO dapat menghasilkan ciri standing atau lebih baik berbanding pengikat asfalt kawalan. Oleh itu, disarankan agar WBO digunakan sebagai bahan penggantian separa dalam penghasilan bio-asfalt manakala CBO digunakan sebagai bahan peremajaan dalam campuran asfalt terusia.

ABSTRACT

The depletion of petroleum resources around the world has sparked interest among researchers in looking for potential alternative binders. Bio-asphalt is eventually categorized as a high potential binder to replace petroleum-based asphalt due to its similar rheological properties, renewable resources, and environmental friendliness. In this study, the palm bio-oil derived from waste empty fruit bunches (WBO) and beta carotene bio-oil (CBO) were added into the conventional asphalt binder at 5%, 10%, and 15%. The properties of bio-asphalt made of WBO and CBO were investigated. Initially, the physical and rheological properties of bio-asphalts were assessed using penetration test, softening point test, rotational viscosity test, ductility test, specific gravity test, and mass loss after short-term aging process via rolling thin film oven (RTFO). Then, the FTIR and GC-MS tests were carried out to identify the chemical compositions and functional groups of both bio-asphalts. Furthermore, the asphalt mixtures were prepared via Marshall method to determine the optimum binder content (OBC), and the effect of bio-oil on volumetric properties and mechanical performances of asphalt mixtures was addressed. Finally, the service characteristics were assessed using static water immersion and water boiling tests. The addition of bio-oil results in a lower softening point, viscosity, and ductility, while increasing the penetration, specific gravity, and mass loss after RTFO. FTIR analysis shows the functional groups of WBO were mainly phenol, alcohols, ketones, aldehydes, and carboxylic acids. The FTIR spectra analysis of bio-asphalts was almost similar to the control asphalt. From the Marshall mix design, all asphalt mixtures meet the standard requirements of the JKR. The 10% WBO bio-asphalt mixture, on the other hand, outperforms in terms of volumetric properties and mechanical behavior. The service characteristics results show that the bio-asphalt mixtures have better bonding and coating performance as compared to the control asphalt mixture. In summary, the properties of WBO bio-asphalt are comparable to the conventional asphalt binder. Whereas the addition of WBO could produce comparable, if not superior properties to the control binder. As a result, it is recommended that WBO can be used as a partially replaced ingredient in the production of bio-asphalt, whereas CBO has a high potential for use as a rejuvenator in the improvement of the properties of highly aged asphalt mixtures.

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LIST OF SYMBOLS

C	Carbon Element
H	Hydrogen Element
O	Oxygen Element
N	Nitrogen Element
S	Sulphur Element
CO_x	Carbon Oxide
H_2O	Water
NO_x	Nitrogen Oxide
SO_x	Sulphur Oxide
G*	Complex Modulus
δ	Phase Angle
M	Mega
k	kilo
μ	Micro

LIST OF ABBREVIATIONS

ASSHTO	American Association of State Highway and Transportation Officials
ASTM	American Society for Testing and Materials
BSI	British Standards Institution
CBO	Carotene Bio-oil
CS	Control Sample
EFB	Empty Fruit Bunches
FTIR	Fourier-Transform Infrared Spectrometer
GC-MS	Gas Chromatography – Mass Spectrometry
HDO	Hydrodeoxygenation
HHV	Higher Heating Value
HMA	Hot Mix Asphalt
HTL	Hydrothermal Liquefaction
JKR	Jabatan Kerja Raya
MF	Mesocarp Fibers
MPOB	Malaysia Palm Oil Board
OBC	Optimum Binder Content
POME	Palm Oil Mill Effluent
PKS	Palm Kernel Shell
RV	Rotational Viscosity
R&D	Research and Development
RPM	Revolutions per Minute
RTFO	Rolling Thin Film Oven
SGC	Servopac Gyratory Compactor
USD	United States Dollar
USM	Universiti Sains Malaysia
VFB	Voids in Aggregates Filled with Bitumen
VMA	Voids in Mineral Aggregates
WBO	Waste EFB Bio-oil

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Asphalt binder or bitumen is a black, sticky and with high viscosity liquid. It has been widely used since 19^{th} century for many applications including highways, airport runways, sideways, carriageways and even sports area. Asphalt has become the most commonly used material for road construction and road repair due to its excellent ability to withstand stress and providing riding comfort.

The demand of bitumen has exponentially increased throughout the years due to the expeditious development. Bitumen is used to repair existing roads and to build new ones. Although roughly 5% by weight of asphalt binder is used during asphalt mixture production, but due to huge stretch of road networks in the world, the global asphalt binder market has an enormous need for road infrastructure (Gürer *et al.*, 2020). As a result, there was a rise in demand for substitute bituminous materials.

Green energy came to the minds of researchers in line with United Nations Sustainable Development Goals. In all sectors, including manufacturing, sustainability and circular economy are now guiding principles. In the building and construction industry, several sustainability ideas have been applied, especially in road pavement engineering. For instance, asphalt technologies have invented several approaches, known as hot or cold recycling techniques as well as warm or cold asphalt mixtures. Another sustainability approach applied in road pavement engineering is by using biomass materials for bio-asphalt production that can reduce the dependency on bitumen. It could be partially or fully replaced (Wen *et al.*, 2013; Yang *et al.*, 2013; Sun *et al.*, 2016).

Due to biomass energy accessibility and its environmental friendly, biomass sources had come to the mind of researchers (Wang *et al.*, 2020). Biomass material is a potential option because bio-oil can be generated, and it has much similarity as bio-oil. There are a variety of biomass sources can be used to produce bio-oil globally such as algae (Abdul *et al.*, 2019), switchgrass (Yue *et al.*, 2017), corn stover (Yang *et al.*, 2017), swine manure (Fini *et al.*, 2011, 2012; Mills-Beale *et al.*, 2014; Wang *et al.*, 2020), waste wood resources (Yang *et al.*, 2013; Yang *et al.*, 2014; Gürer *et al.*, 2020; Ingrassia *et al.*, 2020), and waste cooking oil (Wen *et al.*, 2013; Sun *et al.*, 2016; Zahoor *et al.*, 2021) . Particularly in Malaysia, lots of biomass waste are left over when extracting palm oil such as the mesocarp fruit fibers (MF), palm kernel shells (PKS), palm oil mill effluent (POME) and not forgetting the empty fruit bunches (EFB). These palm oil wastes could be a biomass sources for producing bio-oil especially the EFB (Abdullah and Gerhauser, 2008; Pogaku *et al.*, 2016; Yiin *et al.*, 2016; Abdullah *et al.*, 2017; Rosli *et al.*, 2017; Chang, 2018).

Throughout the years, it has been discovered that much research has been conducted in the search for a modifier or substitute for the asphalt binder. However, there has been no or very little study on bio-asphalt utilising palm oil empty fruit bunches. As palm plantation in Malaysia has created a lot of biomass waste, it is suggested that EFB could be used to produce palm bio-oil in advancing the bio-asphalt. Thus, in this experimental study, palm bio-oil is produced from waste EFB (WBO) and beta carotene bio-oil (CBO) were used to partially replaced the bitumen at 5, 10, and 15% by weight of the asphalt binder. On the other hand, the physical and rheological properties of bio-oil asphalt are being tested.

1.2 Problem Statement

Bitumen is a by-product of crude oil refining. Crude oil is the largest energy resource in the world, and the world's energy consumption is mostly depending on it. However, several challenges emerged when bitumen is a non-renewable resource, the increase in crude oil consumption, and the fluctuations of crude oil prices (Razek and Michieka, 2019; Maghyereh and Sweidan, 2020; Mensi *et al.*, 2020; Lin and Bai, 2021). As Malaysia is one of the oil producers, Petroliam Nasional Berhad, known as Petronas, produce and handle crude oil production. Recently, the price of crude oil fell from USD116 per barrel in the year 2014 to USD50 by December of the same year and it is estimated the price will continue to fall until USD38 in year 2015 (Mohd *et al.*, 2018). Besides, the oil consumption and production are increasing every year, however researcher has warn that the conventional petroleum will probably reach its peak within the next 15 years and then begin its decline (Minniear, 2000). Figure 1.1 provides the comparison between the world liquid fuels consumption and production.

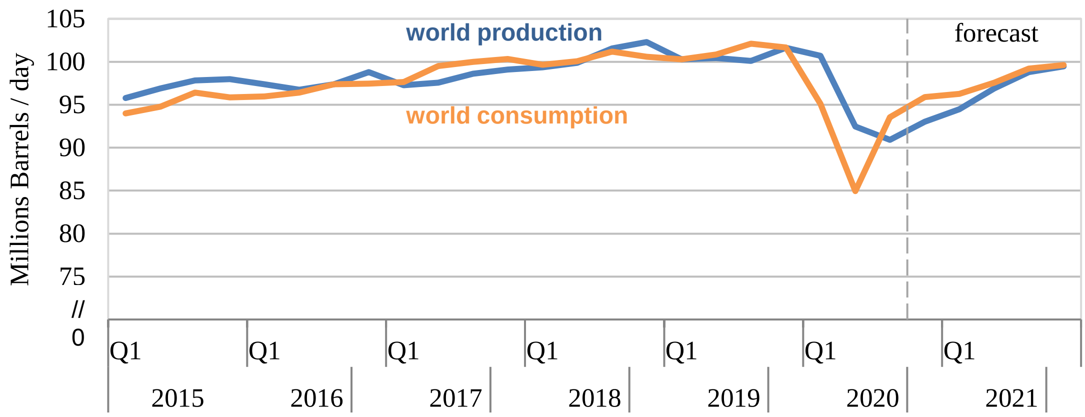

Figure 1.1: World Liquid Fuels Production and Consumption Balance.
(Source: *Short-Term Energy Outlook - U.S. Energy Information Administration (EIA)*)

To address these challenging problems, industries and researchers had done extensive work, looking for suitable material to replace or substitute traditional binder. Therefore, the need for substitute materials for conventional asphalt binder is at urge.

On the other hand, due to the rise of palm trees plantation, mickle of biomass materials are created, hence causing landfill issue. From research, the quantity of biomass waste from oil palm industries recorded at almost 91,000 kilotons, EFB recorded as the second highest of wastes with 18,022 kilotons. Currently, EFB is burnt and used as fertiliser and mulch in plantations and, is use for power and steam utilization of palm oil mills. However, lots of fine ash and greenhouse gases are produced in such way and discouraged by the Department of Environment Malaysia. Hence, further investigation and research on sufficient utilization of EFB was conducted. For instance, it is suggested that palm oil EFB could be a good alternative to produce bio-oil then replace with bitumen to produce bio-asphalt (Abdullah *et al.*, 2011; Geng, 2016).

1.3 Objectives

The objectives of this experimental study are:

1. To determine the physical, rheological, and chemical properties of bio-asphalt binders derived from empty fruit bunches and beta-carotene.
2. To determine the optimum binder contents, volumetric properties and mechanical performance of bio-asphalt mixtures.
3. To investigate the service characteristics and coatability of palm bio-asphalt binders derived from empty fruit bunches and beta-carotene.

1.4 Scope of Work

The purpose of this experimental study was to develop a new bio-asphalt using biomass waste from palm oil empty fruit bunches (EFB) and beta-carotene from palm oil. The research starts with the preparation of raw materials which comprises granite as aggregate, a binder with penetration grade 60/70, the EFB undergo pre-treatment through pyrolysis to obtain palm bio-oil derived from waste empty fruit bunches (WBO) and palm cooking oil as beta-carotene bio-oil (CBO) obtained from the market. The physical, rheological, and chemical properties of the bio-asphalt were carried out prior to ensuring it meet the minimum requirement of the current asphalt used in road construction. The WBO and CBO were added into asphalt at 5, 10, and 15% by weight, hence producing six specimens of bio-asphalt. Several binder tests were conducted, including penetration test, softening point, ductility test, mass loss test, rotational viscosity test, and specific gravity test. The Gas Chromatography – Mass Spectrometry (GC-MS) and Fourier Transform Infrared Spectrophotometer (FTIR) was conducted to assess the physicochemical properties of asphalt binders. Next, the asphalt mixtures were prepared through Marshall method to determine the effect of bio-oil on the volumetric properties, Marshall stability, flow, stiffness, and optimum binder content (OBC). As for asphalt mixture service characteristics, water boiling and static water immersion tests were conducted to determine the coatability of asphalt binders. The performance and service characteristics of bio-asphalt mixtures were examined.

Lastly, the suitability of using WBO and CBO in development of bio-asphalt was discussed.

1.5 Significance of Study

The significance of this study is to maintain and preserve the sustainability of road construction materials. Alternative binder for road pavement engineering is important as the crude oil price keep on fluctuating and its depletion source. Besides, EFB is a solid waste produced by palm oil industry. If the solid waste is not properly disposed, it may impair the surrounding environment. Hence, a sustainable waste management system is required to tackle the waste. One of the suggestions is to utilize EFB waste in bio-oil production. It is because EFB is rich in plant nutrients and organic in origin. By utilizing the EFB waste from palm oil industry, it could probably lower the depletion rate on natural resources. Once the performance of bio-asphalt mixture derived from EFB is affirmative, the overall cost of road construction could positively reduce. Besides that, the dependency of imported bitumen would reduce as well. Hence, the sustainability of road construction materials could be maintained and preserved.

1.6 Dissertation Outline

This thesis consists of five chapters include introduction, literature review, methodology, results and discussion and lastly, conclusions and recommendations. A wide range of systematic experimental works were carried out to achieve the objective of this research.

Chapter 1 described the background of the study, problem statement that related to current issues, objectives to be achieved throughout the research study, scope of work, significance of this study, and dissertation outline.

Chapter 2 included a series of literature review of past research findings on application of bio-oil, sources and methods of bio-oil production, R&D of bio-asphalt in different countries, performance evaluation of the asphalt binders and mixtures prepared with bio-asphalt and the benefits of bio-asphalt.

Chapter 3 discussed the steps of the experimental works. It illustrates the materials used and method of preparation of the asphalt binders and asphalt mixtures. It also explains the specific testing procedures conducted in this study.

Chapter 4 presented the results and discussion of the tests conducted. The collected laboratory data was analysed and illustrated in figures and tables. The results and discussion in this chapter consists of binder physical and rheological properties, physicochemical analysis, volumetric properties and mechanical performance of asphalt mixtures, optimum binder content, and service characteristics of asphalt mixtures.

Chapter 5 concluded the results and discussion from chapter 4. Recommendations were given for further research on bio-asphalt.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Over exploitation on earth resources due to the continuity of urbanization worldwide has led researchers to explore renewable resources. It is one of the biggest challenges in the 21st century for researchers to secure ever-lasting renewable materials and develop sustainable technologies for the unceasing demand for energy without any significant effect on the environment. Ever since the 19th century, the Second Industrial Revolution created a vast opportunity for petroleum, replacing the machinery powered by hydro and steam in First Industrial Revolution. Petroleum production is further increase in demand with the invention of the automobile in the early 20th century. Today, United States produces about 6.8 billion barrels of oil annually (*National Geographic Society*, 2018). Fossil fuels are still on large dependencies for many sectors and technologies. The world's energy consumption is sustained by extracting fossil fuels for rapid industrialization. Besides, the extraction of fossil fuels contributing to environmental issues such as climate change due to a huge amount of CO_2 emission into the atmosphere (Masjuki *et al.*, 2013). As fossil fuels are non-renewable resources, alternative methods should be taken to sustain development in the future.

In recent years, one of the suggestions for renewable energy is from biomass materials. Biomass materials are defined as any hydrocarbon materials that consist of carbon, hydrogen, oxygen, nitrogen, and some with a little portion of sulphur. With different conversion processes and conditions, biomass can be transformed into char, liquid, and gas forms (Sutrisno and Hidayat, 2018). The liquid product after the conversion process is called bio-oil. Bio-oil is a dark brown and almost free-flowing liquid. It is almost similar to the petroleum extracted from the deep earth, and it is a complex mixture of high-oxygenated hydrocarbon.

This chapter presented a wide range of topics related to bio-oil. This included the application of bio-oil, source of bio-oil for production, method of production of bio-oil, research and development of bio-asphalt in different countries, production of bio-oil from palm oil-based materials, performance evaluation of the asphalt binders and mixtures prepared with bio-asphalt, and short-term and long-term benefits of bio-asphalt.

2.2 Application of Bio-oil

Bio-oil is a liquid fuel produced from solid biomass through thermochemical processes. Bio-oil is considered a green fuel because it generates fewer greenhouse gases. Bio-oil increases its applicability in many sectors, such as replacing petroleum fuel in power, heat generation, and transportation. However, bio-oil is highly oxygenated, highly corrosive, thermal instability, and high viscosity. Therefore, due to its poor properties, pre-treatment on bio-oil is required for direct use. Table 2.1 shows the flow chart for the application of bio-oil.

2.2.1 Bio-Asphalt

Asphalt or bitumen has been widely used in the flexible pavement due to its viscoelastic properties. The fluctuation of the price of asphalt and its environmental effects led researchers to discover alternative binders (Rahman *et al.*, 2014; Aziz *et al.*, 2015). An alternative binder such as bio-asphalt is derived from biomass material. It may decrease the usage of asphalt in three different ways; direct alternative binder (100% asphalt replacement), asphalt extender (25% to 75% asphalt replacement), or asphalt modifier (<10% asphalt replacement) (Raouf and Williams, 2010). The application of bio-asphalt in road pavement has been utilized due to its renewable feature. The development and application of bio-asphalt in the paving industry help lower road construction costs, enhance road performance, and protect the environment. (Rahman *et al.*, 2014)

Ingrassia *et al.* (2020) investigated the chemical, morphological and rheological characteristics of bio-binders mixed with 50/70 bitumen. The wood bio-oil was added partially to replace a certain amount of bitumen at 0%, 5%, 10%, and 15% by weight. Numerous tests were carried out. The study illustrated that mixing of wood bio-oil into 50/70 bitumen gave a softening effect. In terms of performance, wood bio-oil improved the low-temperature behaviour and fatigue resistance compared to control bitumen. However, the tendency of permanent deformation increased. These findings show favourably to the bio-binders to be implemented in road pavements.

Wen et al. (2013) prepared bio-asphalt mixtures using waste cooking oil. The binder and mixture tests were conducted in this study to determine the possibility of waste cooking oil as an asphalt modifier. Waste cooking oil was added partially at different percentages (0, 10, 30, and 60%) by weight. The binder tests, which include constant shear loading tests and multiple stress creep and recovery tests, the resistance to rutting and fatigue were declined with bio-asphalt. On the other hand, the addition of bio-asphalt in the HMA mixture boosts its resistance to thermal cracking but lowers resistance to fatigue cracking and rutting.

Aziz et al. (2015) and Raman et al. (2015) presented a literature review on the application of bio-oil as an alternative binder. In both reviews, they recognized that bio-oil application could improve the quality of asphalt mixture with a certain percentage of asphalt replacement. Raman et al. (2015) suggested that strategic management is important, especially when decomposing and utilizing biomass, as it will promote bio-oil as renewable sources in asphalt mixtures.

2.2.2 Transportation Fuel in Automotive Industry

Sustainable transport fuels produced from biomass is an alternative and effective way to reduce the consumption of conventional fuels and environmental issues of using fossil fuels. Throughout many kinds of research, fast pyrolysis was a promising thermochemical process in producing bio-oil that could probably convert it into potential renewable fuels (Perkins *et al.*, 2018). However, the properties of bio-oil such as low heating value, high acidity, high water content, high oxygen content, and storage stability were the drawbacks that bio-oil could not be directly used as an alternative fuel (Imran *et al.*, 2018). As an example, Table 2.1 shows the comparison between the properties of palm bio-oil and petroleum fuel. The common compound found in bio-oil via pyrolysis were hydrocarbon, acids, alcohols, aldehydes, phenols, esters, ketones, and aromatics compounds. Hydrocarbon is an organic compound that favourable in fuel application, but carbonyl and acids were the high oxygen-containing compounds that are not favourable in fuel application (Chang, 2018; Imran *et al.*, 2018).

Table 2.1: Comparison Between Properties of Palm Bio-oil and Petroleum Fuel (Source: Sukiran *et al.*, 2009; Abdullah *et al.*, 2011)

Physical Properties	**EFB Bio-oil**	**Petroleum Fuel**
Water content, wt%	18.74	0.1
Elemental analysis, wt%		
C	49.80	85.2
H	7.98	11.1
O	40.29	1.0
N	1.93	0.3
S	0	2.3
HHV, MJ/kg	21.41	42.94
Density, kg/m^3	900	940
Viscosity, cP@25°C	-	180
pH	2.7	-

In order to apply bio-oil as transportation fuel, several upgrading processes were required. For instance, catalysts cracking (Imran *et al.*, 2018), emulsions (Jiang and Ellis, 2010), and hydrodeoxygenation (HDO) (Owen and Morgan, 1998; Gollakota *et al.*, 2016; Hu and Gholizadeh, 2020). Imran et al. (2018) reviewed the effect of catalysts on bio-oil. From the study, microporous zeolites had the best performance in efficient deoxygenation and molecular weight reduction on the pyrolysis product. However, some shortcomings include decreasing organic phase yield in bio-oil and catalysts deactivation caused by coke deposition. Besides, the high-water content in bio-oil cannot be easily isolated, causing immiscibility with fossil fuels. To overcome this inferiority, Jiang and Ellis (2010) investigated the method of emulsifying bio-oil with biodiesel. The findings used 4% by volume of octanol surfactant, initial bio-oil/biodiesel ratio of 4:6 by volume, 15 minutes mixing time, 1200 rpm stirring intensity, and emulsifying temperature at 30°C produced a stable bio-oil/biodiesel mixture. This method is one way to obtain a suitable fuel portion from bio-oil to use as a supplement in transportation fuel.

The evaluation for renewable transport fuel production is in full swing. Unfortunately, the inferior properties of bio-oil caused the bio-oil cannot be directly used as a transportation fuel or fuel supplement. Thus, several upgrading processes are required before commercializing. Rapid development on biofuel production could change the dependency on conventional fossil fuels. Using sustainable transportation fuels would convert the current transportation system into a more renewable and sustainable transportation system.

2.2.3 Heat and Power Generation

Bio-oil from pyrolysis of biomass can be a potential alternative for replacing petroleum fuel or diesel in some immobilized applications, including boilers, furnaces, gas turbines, and diesel engines for heat and power generation. Bio-oil can be used in direct burning, co-firing, or upgrading (Bridgwater, 2012; Hu and Gholizadeh, 2020). Using bio-oil as fuel replacement has several benefits. One of the most benefits is reducing environmental issues. The gases produced by the combustion of bio-oil could probably reduce air pollution compared to conventional fuel combustion. The low emission of these gases is due to the low nitrogen and sulphur content in most of the biomass (Hu and Gholizadeh, 2020). Hou et al. (2016) showed significant reductions of NO and SO_2 emissions with 2.6% and 7.9%, respectively, using 2.5% bio-oil and 97.5% heavy fuel oil in a 300-kW_{th} furnace.

Bio-oil can be used through direct burning, particularly for heat production in the boiler. At Red Arrow Products pyrolysis plant, USA, the commercial swirl burner used bio-oil for heat generation, and it operated for more than 10 years. The combustion of bio-oil happened in a 5MW_{th} swirl burner. Not only combustion of bio-oil, but the swirl burner also used the biochar and syngas for heat production. The first large-scale combustion of bio-oil in Europe was carried out at Arsta District Heating Plant in Sweden. Their $9MW_{th}$ boiler was used to combust the bio-oil from different origins, originally designed for fossil fuel combustion. Satisfactory combustion performances were obtained for bio-oil replace fossil fuels from the large-scale boiler (Lehto *et al.*, 2014; Hu and Gholizadeh, 2020). Valtion Teknillienen Tutkimuskeskus company (VTT) in Finland tested different grades of bio-oil in a test boiler of $4MW_{th}$ heat output level. They suggested that little modification on the conventional boiler was required for the combustion of bio-oil. They also concluded that proper handling and pumping of bio-oil, clean nozzle, and certain optimum adjustments could increase the efficiency (Oasmaa *et al.*, 2008).

Bio-oil can be directly used in gas turbine and diesel engines for power generation with or without any modification on the combustor. Juste and Monfort, (2000) conducted a study on the combustion of bio-oil and bio-oil with ethanol mixtures in an unmodified gas turbine combustor. Under certain operation conditions, a mixture of 80% bio-oil and 20% ethanol had the same combustion performance as JP-4. However, there was a decrease in the range of efficient combustor operation in terms of fuel/air ratio and load parameter compared to standard fuel. Strenziok, (2012) conducted an experimental work of combustion of bio-oil on a small commercial gas turbine with a rated electric power output of 75kW. The experiment's outcome showed the possibility of burning bio-oil as a second fuel in dual-fuel mode and two separate nozzles. Van De Beld et al. (2013) carried out experiments using a one-cylinder diesel engine with 20kW capacity to monitor the performance of different fuels. The fuel injection system was modified using non-corrosive stainless steel to feed five different fuels, including pyrolysis oil, emulsified bio-oil, PO-Ester, Mild HDO, and Blend. Pyrolysis oil was successfully combusted when the air inlet temperature was at 100-120°C and 40°C with an engine compression ratio of 17.6 and 22.4, respectively. However, the combustion of pyrolysis oil released higher CO and lower NO_x gases comparing to diesel, biodiesel, and vegetable oils. Generally, the four upgraded bio-oils were easier to combust as compared to pyrolysis oil.

Brammer et al. (2006) conducted an assessment on commercializing bio-oil in the heat and power market of Europe based on their commercial attractiveness. Bio-oil applications were compared to conventional fuels for the same output of heat and power. The data was collected from 14 European countries, including Italy, Netherlands, Denmark, Greece, Austria, Spain, Belgium, Finland, France, Germany, Ireland, Norway, Portugal, and United Kingdom. The most economically competitive assessment recorded in ascending order were heat applications, combined heat and power (CHP) applications, and electricity applications. Boiler in heat applications had the highest economic competitiveness followed by inner-combustion engine and Rankine cycle for CHP across Europe.

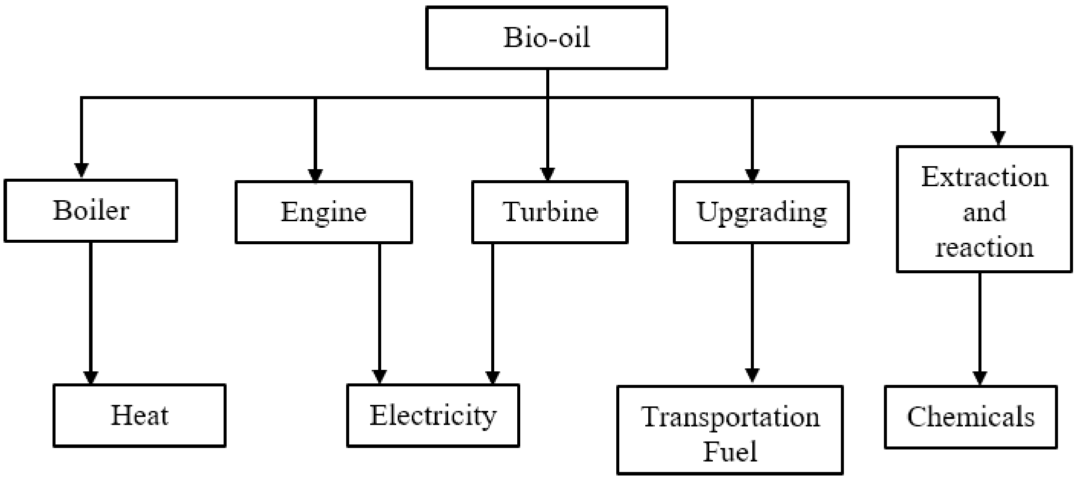

Figure 2.1: Application of Bio-oil (Source: Bridgwater et al., 1999)

2.3 Source of Bio-Oil for Production of Bio-Asphalt

With the world population keeps on rising every year, the world energy consumption correspondingly increases. Thus, the development of sustainable sources is being focused on meeting future needs. Bio-oils/biofuels are attractive, sustainable energy to substitute the current petroleum fuels as they have wide applications. Bio-oils are derived from biological and natural sources, unlike fossil fuels formed by the decomposition of plants and animals after many years. The sources of bio-oil production mostly rely on plants, agricultural residue, algae, crops, and even manure. Bio-oils are categorized into three different groups: first generation, second generation, and third generation. Table 2.2 shows the type of bio-oils and their corresponding feedstock. First-generation bio-oils are mostly derived from food crops. However, first-generation bio-oils are not reliable as their feedstock is mostly human food. Second-generation bio-oils are the most generated and been researched. They are produced from non-food crops, including food wastes, agricultural residue, wood wastes, waste cooking oil, and animal manure. Food crops are only used in producing bio-oil when they fulfilled their purpose. For instance, wheat straw from wheat production and empty fruit bunches after palm oil extraction. Third-generation bio-oils are relatively new. They are based on aquatic biomass such as algae, seaweed, and microbes. Algae is widely used in this category, and it has large potential due to its short cultivation period. However, algae have one fatal drawback; it requires a huge amount of phosphorus and nitrogen for growth which would cause environmental issues (Dahman *et al.*, 2019; Zhang and Zhang, 2019).

Table 2.2: Type of Bio-oils and Their Corresponding Feedstock (Source: Zhang and Zhang, 2019)

Class	Biomass	Generation
Edible feedstock	Starch (wheat, barley, corn, potato); sugars (sugarcane); oil crops (rapeseed, soybeans, sunflower, palm, coconut, used cooking oil, animal fats)	First
Non-food based	Forest and forest residue; agricultural residue (corn stover, straw grass, rice husk, EFB); energy crops (jatropha, cassava, miscanthus); municipal solid waste (wood waste, paper waste); animal manure	Second
Aquatic biomass	Microalgae; seaweed; microbes	Third

2.3.1 Crop Residues as Feedstock

Crop residues are referred to the materials that are left in the agricultural field after harvested. Crop residues are lignocellulosic materials, content components of cellulose, hemicellulose, and lignin. Thus, they have a large potential as a renewable energy source. From a study, approximately 4.0×10^9 Mg of crop residues were produced throughout the world in a year. By assuming the fuel value of crop residues per Mg was around 2 barrels of diesel, the estimated energy value of crop residues worldwide was around 7516×10^6 barrels of diesel. As shown in Figure 2.2, among the crop residues produced worldwide, 75% was contributed by cereals (rice, corn, wheat millets, etc.), 25% was contributed by legume, oil seeds, sugarcane, and tuber crops. Among the crop residues produced from cereals, Asia is the largest contributor with 63.8% (Lal, 2005; Bhattacharyya and Barman, 2018).

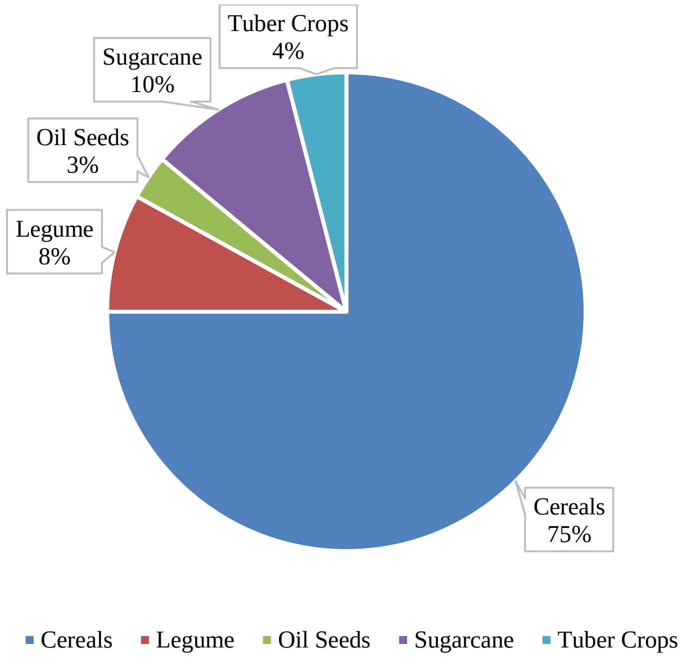

Figure 2.2: Relative Contribution of Different Crops on Residue Production (%) in the World (Source: Bhattacharyya and Barman, 2018)

After realizing the benefits of crop residues as a renewable energy source, researchers actively conducted experiments on crop residues that could be used directly or produce liquid fuels through certain processes (Ali *et al.*, 2019). Bao et al. (2020) studied the effect of corn residue bio-oil and wood waste bio-oil on the rheological properties of polymer modified asphalt. The polymer modified asphalts used were styrene-butadiene-styrene (SBS) and waste rubber powder. After several tests conducted, they concluded that the bio-asphalt derived from wood waste had a better performance as compared to bio-asphalt derived from corn residue. Another research was conducted on the bio-asphalt made from corn residue and castor oil residue. From their results, the bio-asphalt derived from corn residue had better rutting resistance performance. Besides, it increased the moisture susceptibility, whereas bio-asphalt derived from castor oil had no adverse effects on moisture damage resistance. However, they concluded that both bio-asphalt could be used as asphalt substitutes (Dong *et al.*, 2018). Raman et al. (2015) studied the effect of EFB bio-oil on the penetration index and softening point index. They concluded that the addition of EFB bio-oil subsequently softened the asphalt while maintaining the temperature susceptibility.

Crop residues are potential materials to be used as renewable energy under the thermochemical process. Using crop residues as renewable energy is beneficial, such as lowering anthropogenic greenhouse gases and securing energy supply. However, harvesting crop residues should be appropriate. Several effects, including soil nutrient availability, soil organic matter, water erosion and runoff, wind erosion, soil water availability, etc., should be considered to ensure crop residues can be sustainably harvested and used as renewable energy (Wortmann *et al.*, 2012).

2.3.2 Urban Wastes as Feedstock

Urbanization has resulted in massive waste generation. These wastes are defined as urban wastes. Urban wastes including solid waste, plastic waste, paper waste, tins and metals waste, organic waste, municipal solid waste, etc. Urban waste generation is increasing every year, and it was expected to double by 2045 (Noor *et al.*, 2020). Roughly 150 million tons of municipal solid wastes were disposed of by European households. It was estimated that around 44 million tonnes of household and garden waste would be available in 2030 as feedstock for advanced biofuels in European countries (Chris Malins *et al.*, 2014). Urban wastes are potential materials to be converted into bio-oil through conversion processes (Gaeta-Bernardi and Parente, 2016; Jiang *et al.*, 2017).

Researchers conducted several studies on the use of bio-oil derived from urban wastes as asphalt modifiers or substitutes. Yang et al. (2013) used three different types of waste wood bio-oils: the original bio-oil (OB), de-watered bio-oil (DWB), and polymer-modified bio-oil (PMB), in producing asphalt binder. These three bio-oils were added into base asphalt PG 58-28 at 5% and 10% by weight. They concluded that the waste wood bio-oils reduced the rotational viscosity of origin asphalt binder and probably reduced the mixing temperature of asphalt mixture. Besides, it also enhanced the high-temperature performance. Ingrassia et al. (2020) discussed that the wood bio-oil was suitable to be used as an asphalt substitute for road applications without affecting their workability. Yang et al. (2014) studied the asphalt mixture performance with the blending of wood bio-oils. From the findings, the fatigue performance was significantly improved with the addition of wood bio-oil. Hence, it was suggested that bio-oils produced from waste wood resources could be used as a modifier in conventional asphalt.

Mahssin et al. (2021) investigated the potential of using bio-oil derived from food waste as an alternative composite of asphalt binder. The results showed that the liquefied food waste product was suitable to mix with asphalt due to its thermal stability and high viscosity. Besides, there were no substantial changes in the modified binder's physical properties and storage stability. Chen et al. (2019) analysed the properties of bio-oil from food waste produced from hydrothermal liquefaction. The higher energy density and combustibility of liquefaction bio-oil from food waste showed it was suitable to substitute fossil fuel.

Wen et al. (2013) and Sun et al. (2016) produced bio-oil from waste cooking oil and used it as an alternative binder. Both groups of researchers concluded that the addition of bio-oil gave good compatibility. However, the addition of bio-oil decreased the stiffness and resistance of deformation in both binder and mixture. However, Wen, Bhusal and Wen, (2013) concluded that all the bio-asphalt mixtures passed the minimum requirement set by AASHTO.

Wu and Montalvo (2021) reviewed waste plastics in asphalt mixtures either by the dry or wet method. From the review, the modified asphalt mixtures showed better engineering performance, including stiffness, rutting resistance, and fatigue resistance with the addition of waste plastic.

Utilizing urban wastes, including food waste, waste wood, waste cooking oil, and waste plastics, alternative binders are discussed above. As urban waste management is currently facing the landfill issue, converting urban wastes into useful bio-oils could solve the issue.

2.3.3 Other Sources

Besides urban wastes and crop residues as bio-oil feedstock, other biomass materials have also been used by researchers to produce quality bio-oil and used as alternative binders. For instance, algae, swine manure, and switchgrass are potential biomass materials as bio-oil feedstock.

Algae is a potential feedstock in bio-oil production, generally a third-generation biofuel (Dahman *et al.*, 2019). Algae can be categorized into microalgae and macroalgae. Microalgae as bio-oil feedstock presented many benefits, including higher growth rate, non-conflict with human food, and higher production rate. Audo et al. (2015) conducted a study on *Scenedesmus* species microalgae residue bio-oil as road binder. The microalgae bio-oil was produced through hydrothermal liquefaction. Although the bio-oil had different chemical composition from the conventional binder, it had similar viscoelastic properties.

Further study was required to confirm the suitability of microalgae bio-oil as an alternative road binder. Abdul et al. (2019) reviewed the potential of algae biomass as renewable sources through applicable conversion processes in Malaysia. From the study, algae as bio-oil feedstock had many advantages and could be a reliable alternative for clean energy in the future. They suggested that hydrothermal liquefaction was the most suitable conversion process compared to pyrolysis. This was because pyrolysis required a pre-treatment process. Chailleux et al. (2013) concluded that the microalgae-based road binder was feasible. This was because the microalgae bio-oil showed similar rheological properties as conventional asphalt.

Another potential feedstock that is used to generate bio-oil is manure. Presently, researchers investigated the use of swine manure bio-oil in the application of road construction. The advantages of swine manure bio-binder include reducing environmental pollution caused by the pile-up of swine manure and decreasing the need for swine manure management. Fini et al. (2012) studied the swine manure bio-binder from the hydrothermal process. The bio-modified binder (BMB) improved low-temperature properties. With polyphosphoric acid (PPA) added into BMB, the intermediate and high-temperature performance was enhanced. Wang et al. (2020) studied the effect of different pyrolysis conditions on the performance of the swine manure bio-binder. They partially replaced the conventional asphalt with swine manure bio-oil at 15%. Several physical and rheological properties tests on swine manure bio-binder were carried out. The results concluded that the most suitable temperature and reaction time was 550°C and 1s. These optimum conditions were made based on the yield of bio-oil and the performance of the bio-binder. Fini et al. (2011) and Beale et al. (2014) studied the possibility and characteristics of swine manure bio-oil as an alternative binder. From the findings, both groups of researchers found that swine manure bio-binder was a promising alternative binder for partial replacement of conventional asphalt.

2.4 Methods for Production of Bio-Oil

Biomass can be used through direct burning; by other choices, biomass can be transformed into liquid or gaseous. This liquid generated is called bio-oil. There are several ways for bio-oil production, basically categorized into two groups: thermochemical conversion and biochemical conversion. Thermochemical conversion is the process of heating biomass in the absence of oxygen to produce a mixture of gas, liquid and solid. Thermochemical conversion comprises torrefaction, liquefaction, pyrolysis, gasification, and combustion. On the other hand, anaerobic digestion is one of the examples of biochemical conversion. A clear flowchart of thermochemical conversion of biomass is shown at Figure 2.3. In this subtopic, only the pyrolysis and liquefaction processes are discussed. This is because a thermochemical conversion has a superior ability to convert most of the lignocellulosic biomass into useful bio-oil (Geng, 2016).

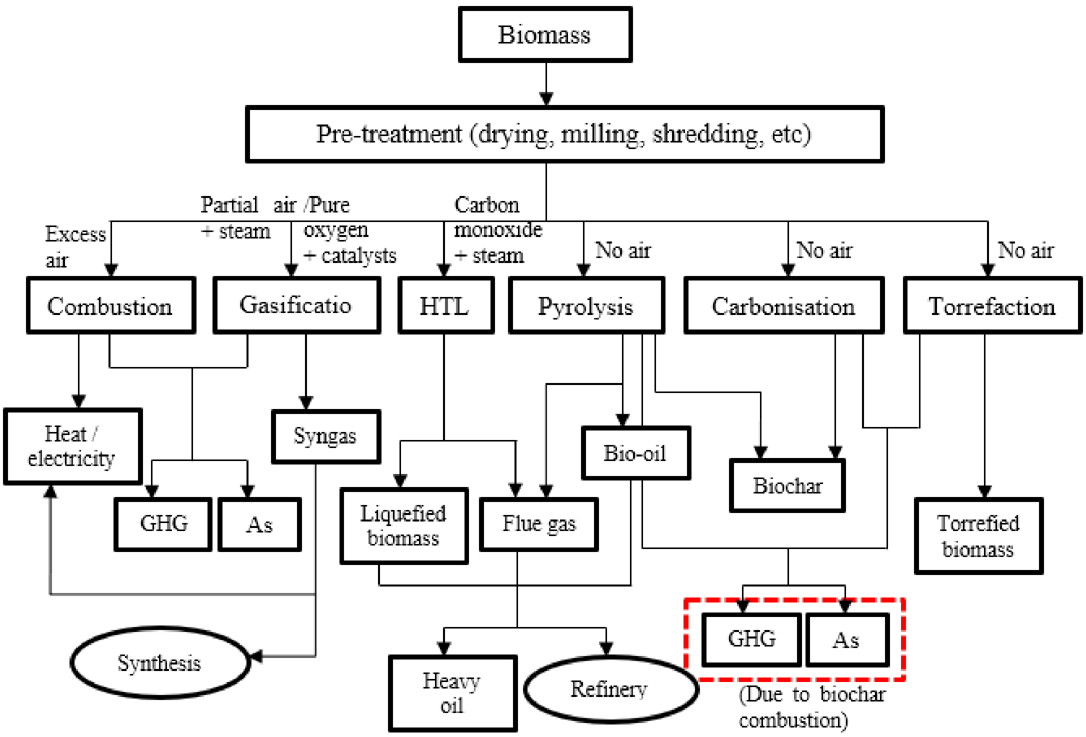

Figure 2.3: Biomass Thermochemical Conversion Pathways
(Source: Verma *et al.*, 2012)

2.4.1 Pyrolysis

Pyrolysis is a typical and remarkable thermal decomposition process occurred in the absence of oxygen and water. It is a remarkable process due to its potential to convert all types of biomasses into valuable bio-oil for the industrial sector. The pyrolysis process normally heats the biomass materials at atmospheric pressure and in a high-temperature range between 400°C to 700°C. Biomass pyrolysis techniques are divided into slow pyrolysis and fast pyrolysis. Slow pyrolysis normally has longer feedstock residence time and lower heating rate, for example, 30°C/min and 50°C/min, vice versa for fast pyrolysis (Zhang and Zhang, 2019). In the pyrolysis process, higher temperature and longer vapour residence time favour producing syngas, while lower temperature and longer vapour residence time increase char production and moderate temperature and short vapour residence time are optimum conditions bio-oil production. Table 2.3 shows the product distribution from different modes of the thermochemical conversion process. Figure 2.4 shows the schematic diagram of pyrolysis system.

Table 2.3: Typical Product Yields Obtained by Different Thermochemical Conversion Process of Wood (Source: Anthony V. Bridgwater, 2004)

Process	Conditions	Liquid	Gas	Char
Fast pyrolysis	Moderate temperature, short vapour residence time	75%	12%	13%
Carbonisation	Low temperature, very long vapour residence time	30%	35%	35%
Gasification	High temperature, long vapour residence time	5%	10%	85%