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The Potential Use of Biomass (Sapindus Mukorossi) for Production of Valuable Products

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Abstract

Civilization has been improving since the beginning of humanity, utilizing all those natural resources. When natural resources are used as a source of any form of energy, called biomass. Some biomasses are generated from waste in the household. These kinds of products can be useful when they are treated with pyrolysis treatment, biological treatment and other thermal degradation processes. Biomass needs to be dried before going to the thermal process or pyrolysis process. According to analysis, when the time can vary significantly by 3, 6, 9, and 12 hours, temperature ranges of 150°C, 200°C and 250°C can be chosen. The temperature of the reactor can be chosen from 500°C to 550°C, which provides a great amount of bio-oil. The heating rate will vary between 5°C/min, 10°C/min and 20°C/min. These processes can convert the most unproductive products into real valuable products. Soapnuts (Sapindus Mucorossi) is considered as one of the most insubstantial biomasses that has been researched and executed in a limited manner, no other use than dumping. It is to be noted that 'Soap nuts' are a great source of bio-oil, biochar and biogas (Syngas) that can be converted by a fast pyrolysis process. A small amount of "Erucic" acid present in soap nuts which is absent to bio-oil produced by another biomass. This "Erucic" acid improved the quality and distinguish it from others as unique characteristic. Some waste management treatment has also been compared in this research. The yield from the pyrolysis process can produce not only bio-oil but also other beneficial chemical elements. The main focus of this research is on the bio-oil which is extracted from soap nuts (Sapindus Mucorossi). Overall comparison of the soap nut with other nonedible bio-oil from similar biomass is provided.

Index Terms: Bio-oil, Pyrolysis, Renewable energy, Soapnuts

Introduction

Fossil fuel is the source of world energy. Natural gas and fossil petroleum are the main sources of all engines. Industries and all kind of vehicles are highly depending on this source of energy. However, this energy source is limited and it will finish soon according to the present use of petroleum. The world is looking for the alternative of this energy source. Large amounts of wastes are generated daily in both households and industries. Developed countries are producing more solid waste compared to undeveloped countries [1]. These wastes can be used as an alternative to fossil fuel through some process. When this kind of commodity is used to produce energy, it is called "Biomass." Biomass is the residue of the plants and animals that can be used for energy production through different processes. Biomass is any kind of organic matter that can be used as an energy source [2].

There are four types of biomass, such as “wood and agricultural byproducts”, “solid waste”, “landfill gas and biogas” and “ethanol”. According to the research, 44 per cent of biomass energy is coming from wood and agricultural byproducts [2]. Solid waste can be used as the alternative of coal. One ton (2000 pounds) solid waste energy can be compared with 500 pounds of coal energy [2]. Landfill gas and biogas can be produced by the bacterial digestion which is very efficient and even environment friendly. The most important source of methane is farm debris and human waste. Ethanol is also a source of energy that is extracted through the fermentation of the sugars and starches found in plants.

Large amounts of solid waste are generated daily in both households and industries. Developed countries are producing more solid waste compared to undeveloped countries. Throughout North America estimated to produce 4.87 pounds per day per capita of solid waste, while Sub-Sahara African countries produce approximately 1.01 pounds per day per capita of solid waste [3]. Despite the large amount of solid waste generated by developed countries, they have an established technology such as Incineration, Heat Recovery from Incineration, Waste to Energy Incineration to treat these wastes [4]. According to the research [5], 90% of the total weight of the municipal solid waste (MSW) can be reduced through incineration. As much as 30% of carbon dioxide [5] emitted from the incineration of MSW. Thus, it is a big threat to the environment. Not only carbon dioxide (CO^2) but also other toxic gas and heavy metal emits during the incineration. The fly ash contains those heavy metals. In 2016, MSW incinerators in China released approximately 1.12 x 102, 2.96 x 103, 1.82 x 102, 3.64 x 104, 1.00 x 102, 7.32 x 103, 2.42 x 102, and 1.47 x 10 tonnes of cadmium (Cd), lead (Pb), chromium (Cr), zinc (Zn), nickel (Ni), copper (Cu), arsenic (As), and mercury (Hg) respectively [6]. Every day the amount of waste is increasing drastically from the day to day activities of the human. Daily generation of MSW of some South Asian countries [1] are given below:

Table 1: MSW generation rate (kg/capita/day) of some Megacities [1]

	Bangkok	Beijing	Hong Kong	Seoul	Singapore	Tokyo
MSW generation rate (kg/capital/day)	1.041-1.18	0.85-1.20	1.27-1.36	0.95-1.08	0.96-1.10	0.77-1.03

Table 2: MSW treatment of some South Asian countries [1]

MSW Management	Bangkok	Beijing	Hong Kong	Seoul	Singapore	Tokyo
Incinerated (%.wt.)	-	4	-	20	41	79
Incinerated (number of a plant)	14	2	-	35	5	21
Landfilled (%.wt.)	98	94	63	19	3	21
Recycled (%.wt.)	-	-	37	61	56	0
Composted (%.wt.)	2	2	-	-	-	-

Every day the world population is increasing. As a consequence, the total generation of MSW also increasing respectively. According to the Malaysian population growth, per day waste generation was 21,452 tonnes in 2002 [5]. In 2016, the per day waste generation was 32,939 tonnes [5]. From the statistical data, it is a matter of concern to process this high amount of MSW. In 2016, nearly 5% of the global emissions were produced from the solid waste management and the transportation process were included [7].

Singapore, America, and some other significant countries are using their solid waste as a power plant fuel in their thermal power plants. However, this process also produces some highly toxic gas and byproducts which have a negative impact on the environment. To eliminate this, there should be another phase after the combustion of the solid waste which will reduce carbon emissions and other toxic gases. To extract a useful product from the waste materials, scientists distinguish waste that can be transformed into useful products. Not all residual materials have the same significance. Some of the waste materials are incredibly dangerous for incinerating (e.g. battery, children's diaper). Therefore, before the solid waste is combusted, the waste needs to be inspected properly. There are some valuable materials, people are wasting just because less research has been done regarding it. These materials are not very expensive and not commonly used. People do not recognize the significance of these kinds of useful materials. Such goods may be overlooked in the village or rural area as debris from the forest. Soap Nut (Sapindus Mukorossi) is a kind of berry that grows in the lower foothills and mid-hills of the Himalayans, up to altitudes of 4000 feet [8]. India, Nepal and some parts of China are geographically the appropriate environments to produce soap nut.

Nowadays this soap nut (Sapindus Mukorossi) is getting popular to some of the cosmetic or beauty product manufacturing companies. Soapnut (Sapindus Mukorossi) is a particular type of berry that has substantial seeds. The juicy part of the fruit (flesh) is usually used for making soap and other aromatic products. The seeds are discarded or landfilled after the juicy portion of the fruit is extracted at the soap nut production and processing plant. However, the soap nut contains a high content of oils, i.e. 39 wt.%, making the seed a valuable product for bio-oil, beauty products, and bio-diesel production. Depending on the thermal treatment, which is called the drying phase, the yields can be enhanced. During the pyrolysis process, the maximum amount of moisture extracted from the feedstock gives a higher amount of bio-oil. Grinding the size of the feedstock plays a very important role in the optimum quantity of bio-oil extraction. The studies indicate that the 0.5-1.4 mm range is a better range for maximizing the output of bio-oil while maintaining the moisture content low [27].

The sorting process is ongoing, according to figure 2 below. In the first picture, flesh and seeds are divided as a sorting process. The second image gives a clear view of the internal portion of the seed. The third image provides a good view of the entire fruit. Nepal and China are the two main countries planting the soap nut in large scale due to the suitable climate producing good quality of soap nuts. The region of soap nut cultivation is given below.

Figure 1: Soap Nuts (Sapindus Mukorossi) [8]

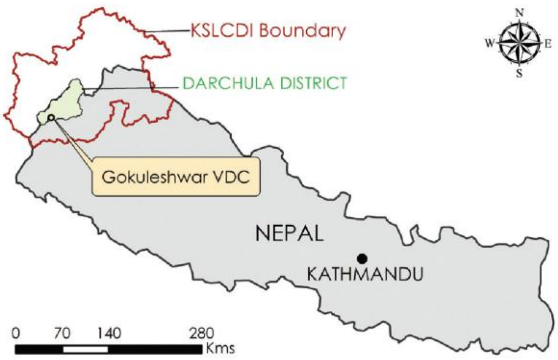

Figure 2: Soap Nut Production Region [8]

Useful products from the pyrolysis process

Biomass can be converted into many useful products by a fast pyrolysis process. As biomass, here we are using soap nuts. Fast pyrolysis process allows converting the biomass (Soapnuts) into bio-oil, bio-char and syngas. All these byproducts of the biomass (Soapnuts) can be used as organic substitutes of the chemical products. Bio-oil can be used as biofuel (biodiesel) in the power plant. Syngas is thus composed of hydrogen (H2), carbon monoxide (CO), methane (CH4), carbon dioxide (CO^2) and water (H2O) [10]. The heating value (calorific value) of the syngas comparatively lower than the natural gas. The syngas provides 8.02 MJ kg-1 [11] whereas natural gas can give 42-55 MJ kg-1. The lower calorific value is still sufficient for the power plant combustion as fuel and the drying process [12]. Biochar can be used as fuel of combustion chamber of the power plant and for pyrolysis process itself. The heating temperature of the bio-char is 23 MJ kg-1 (approximately) [10]. For the natural coal, removal of sulfur and other toxic elements (SOx, NOx) must be performed before combustion. Some of the power plants are using another treatment plant for the emitted smoke before releasing it into the environment. These processes are expensive and difficult to execute. On the other hand, biochar is free from this kind of toxic gases and byproducts. Bio-char can be used directly to the combustion chamber as fuel. Bio-char has a very good fertilizing characteristic. Biochar is an efficient adsorbent for both nutrients and organic pollutants, hence the existence of biochar in soils has been shown to improve water quality in studies of column leaching and field lysimeters, and the same is predicted for agricultural watersheds [12].

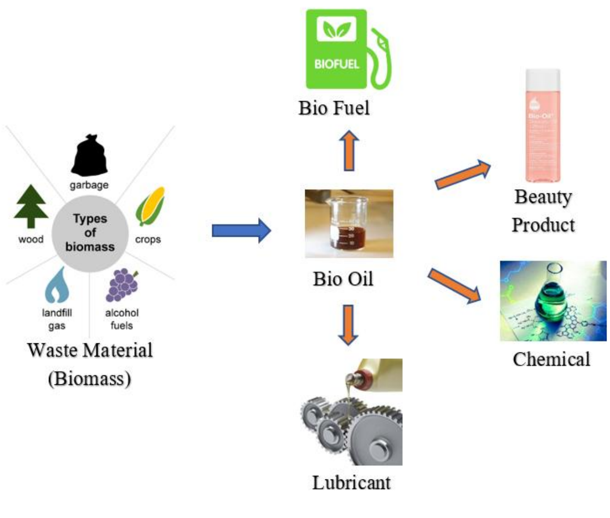

Figure 3: By-products of biomass

current Treatment of Biomass

According to the present condition of the waste, the world is facing a great problem. Day by day the amount of waste is increasing remarkably. The landfill is the most affordable way to dispose of solid waste but it has a significant impact on the environment. This trigger toxic releases of latching and methane. In addition to this method of waste management, there are other waste management processes, including gasification, pluralization, microwave pyrolysis, anaerobic digestion, bio-drying, gas plasma, in-vessel composting, mechanical biological heat treatment, and incineration [5].

Valuable products from the different treatment process

A. Incineration

Many countries burn the waste materials to access the waste disposed of. The incineration process allows for waste material to produce a lot of toxic gas. So, the procedure cannot be considered beneficial to the community. An incinerator is an enclosed chamber which can keep the heat lost during combustion operation, an incinerator is built with well-insulated material. By creating the gas treatment chamber with the incineration plant, toxic gas emission can be reduced. Incineration can be classified into two types: one is the combustor structure without recovering energy to generate electricity, while the other is built to recover energy, which is the conversion method called waste-to-energy (WTE) [5].

B. Gasification

In this process, municipal solid waste is directly changed into gasification. For the commercial gasification process, direct melting system (DMS) is the most efficient and suitable process.

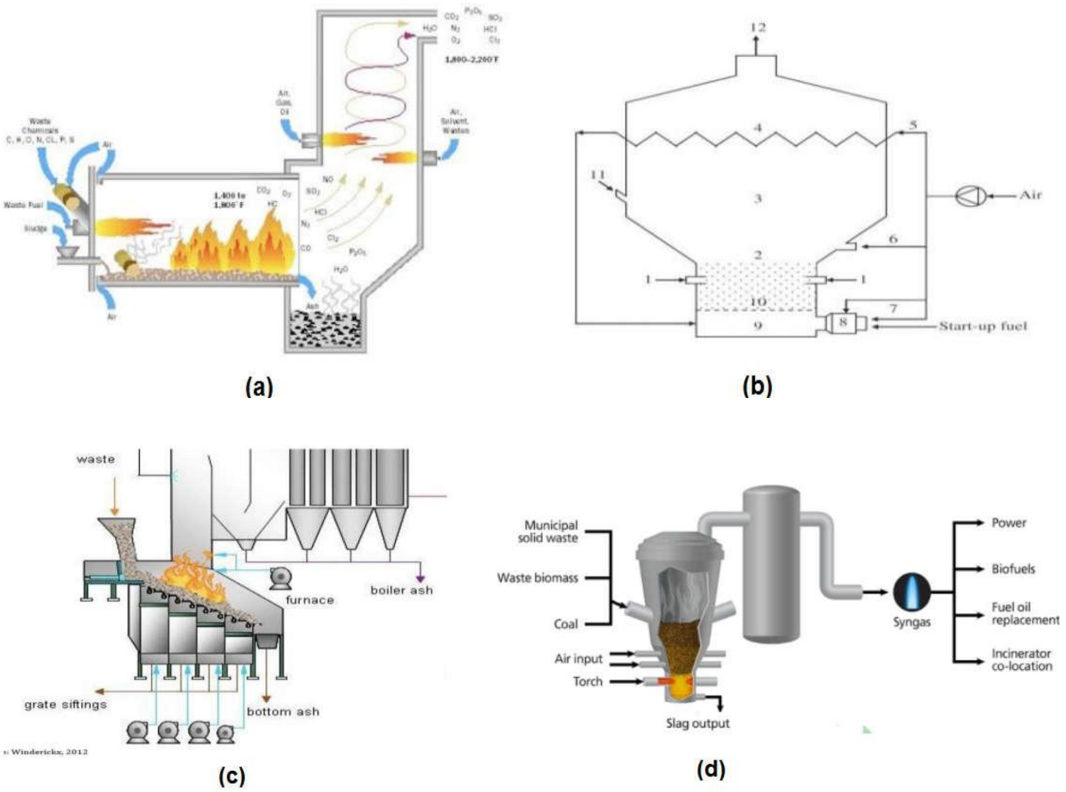

Figure 4: Waste Incineration Schematic [21]

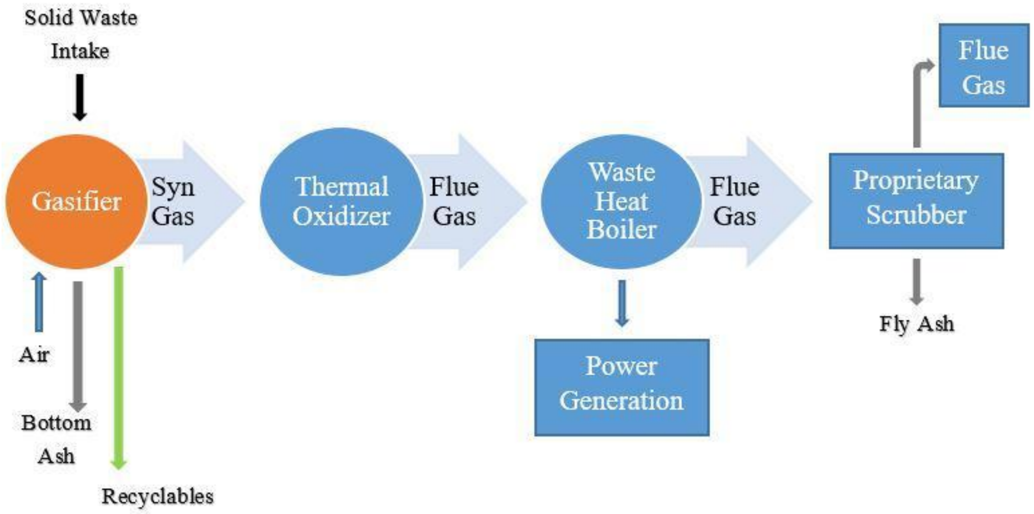

Figure 5: Process Flow Diagram of IET's Waste Gasification System [30]

Direct melting system (DMS) does not require any pretreatment for the municipal solid waste. Coke and limestone are mixed in this process as reducing agent and viscosity regulator accordingly. Limestone adjusts the viscosity of the melt and also it helps to discharge the sediment of the reactor from the clogging [14]. Reactor temperature reached from 1000°C to 1800°C [14]. According to the research, the lifetime of the landfill sites for MSW is assumed to be 18 years [14]. By using the gasification process, the lifetime of the landfill area can be increased remarkably. This process reduces the amount of the production of the municipal solid waste disposal at the landfill. By the heating process, 90% of the weight of the municipal solid waste (MSW) can be reduced [5].

C. Pyrolysis

Pyrolysis is one of the most well-known thermochemical processes capable of producing bio-oil, bio-char and combustible gasses (syngas) from any kind of the biomass. The slow pyrolysis is mainly used for biochar production, while the fast pyrolysis is used for bio-oil production, and the instant pyrolysis is used for bio-oil production, and the instant pyrolysis is used for gas production. The sluggish pyrolysis with a residence time of two hours operates in 4°C/min up to 400°C. The swift (or flash) pyrolysis operates at a constant temperature between 400°C to 600 C

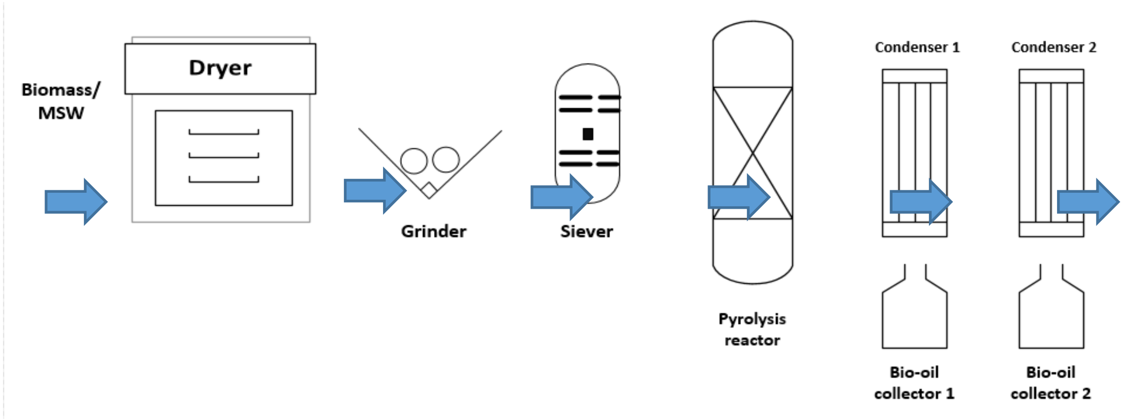

Figure 6: Biomass Pyrolysis Liquefaction Process [20]

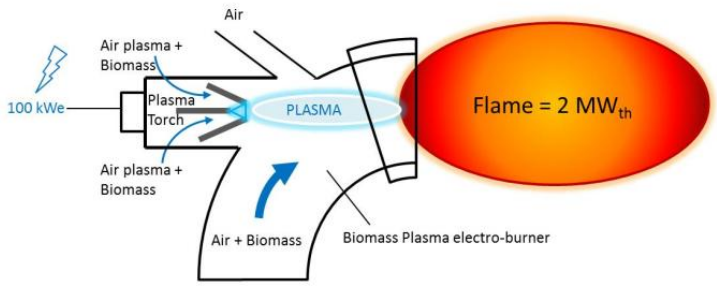

Figure 7: Plasma Pyrolysis process [28]

in just a few seconds, with a short residence time. The temperature of pyrolysis, size of MSW and heating rate were the main factors in biochar, bio-, and gaseous yields. The benefits of bio-application can be used in engines and turbines, as well as feedstock for refineries [5]. Microwave reactor can accomplish fast pyrolysis operation the same as the conventional reactor [7]. Microwave technology provides possibilities for regulating the internal temperature levels of large particles by the absorption of energy by dielectric loss beyond that can be done with heat or convection. [7]. The microwave pyrolysis reactor is capable of internal heating of the biomass particle because the heat generation is done as a wave instead of a flame. Higher temperature extracts a higher amount of yields while 10°C/s will yield the same productivity [7].

D. Plasma

Plasma treatment for the biomass or the waste materials is called plasma pyrolysis. Plasma pyrolysis is effective for the high calorific plastic waste into a valuable synthesis gas (syngas) [15]. This plasma process is very high thermal pyrolysis process which works from 50000 C to 100000 C [8]. This process is the most effective process to recycle high calorific and hazardous plastic products [15]. High temperature converts the plastic into hydrogen (H2), carbon monoxide (CO), methane (CH4), acetylene (C2H2), ethylene and other hydrocarbons [15]. Most of the produced gases are highly combustible and toxic. However, the gas treatment plant for this plasma *pyrolysis* project is a must. The calorific value of the produced gas is 43.5 MJ/kg which is very good as fuel [15].

E. Biological treatment:

The biological process to convert energy: Municipal solid waste has very high potential energy and fuel production capability. The biological treatment process can be divided into two ways. Aerobic and anaerobic treatment processes. Aerobic treatment is a fermentation process which is done at the presence of oxygen [16]. Whereas the anaerobic process is not performed without the presence of oxygen [16]. Both of the processes need microorganism to digest. Microorganism helps to digest the waste and convert into biogas. This biogas is highly combustible and it is mostly methane (CH4) [11]. The digestion helps to reduce the weight of the solid waste and converts into fertilizers for the cultivation [16]. Biogas can be used in the power generation process and even in the industry. Thermal treatment to energy: Pyrolysis and incineration are the thermal degradation of municipal solid waste to convert them into valuable products. By this process, biochar, bio-oil and biogas are produced. . Biochar can be used as combustible fuel and the conditioner for the soil to grow crops. Biogas can be used as combustion gas for the power plant and industry. This kind of process can be run from 3000 to 8000 C temperature depending on the materials [16]. The non-reactive atmosphere is needed for this kind of treatment process [16]. By this process, 90% of the total mass of the municipal solid waste can be reduced [5]. After this process, waste can be dumped into the landfill. High temperature melts the metals. Before dumping, metals will

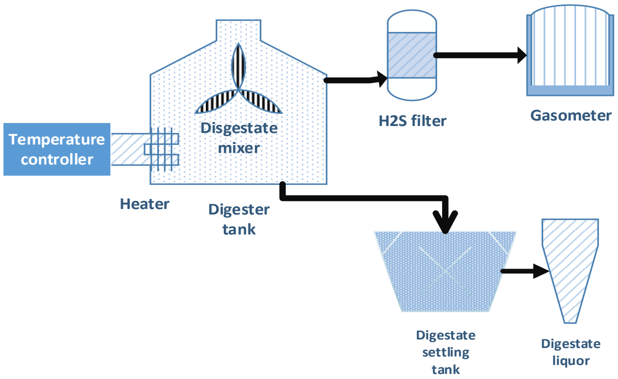

Figure 8: Biological Treatment [21]

be separated for the other use. Minimum environmental issues can be noticed by this treatment process. Plasma pyrolysis is the most advanced technology developed for the development of syngas by converting high calorific value plastic waste. There are two bio-products generated by state-of-the-art commercial plasma technologies: hydrogen-rich syngas used for electricity generation, and inert building materials.

Byproducts of Soap Nuts from the pyrolysis process

Soap nuts are the main waste materials produced from the soap production areas. Soap production factories are using the flesh of the soap nut fruits and the inlet nuts they throw as garbage. While other municipal solid wastes are using for the thermal degradation to produce bio-oil, biochar and syngas, soap nuts also can be used for the same treatment plant. Flow chart showing below gives a clear view of the entire process

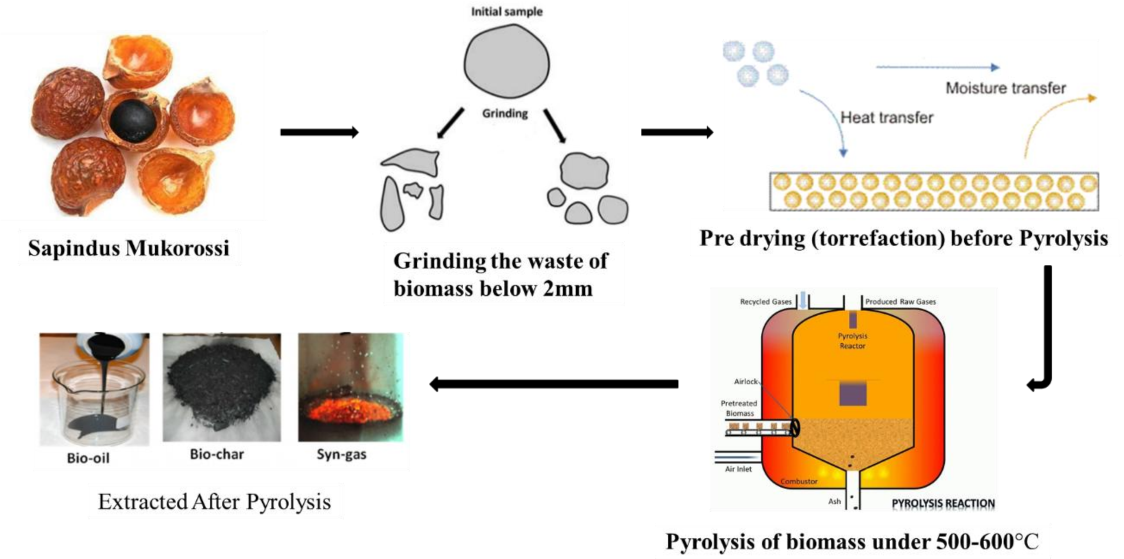

Figure 9: Pyrolysis process using soap-nuts (Sapindus Mukorossi)

Biodiesel production from bio-oil using soap nuts

Bio-oil is a dynamic mixture of water, char fines, and compounds (monomers, oligomers, polymers, or fragments) derived from cellulose, hemicellulose, and lignin macropolymers of biomass [9]. This bio-oil includes sugars, acids, alcohols, aldehydes, ketones, furans, esters, phenols, guaiacols, syringes, and multifunctional compounds, such as hydroxyacetic acids, hydroxyaldehydes, and hydroxyketones. These organic materials present in bio-oil are constantly reacting to move towards chemical equilibrium [9]. Because of this character of the bio-oil, it is difficult to store the bio-oil for a long period. Quality of the bio-oil depends on the moisture content of the feedstock and the drying process as well

Sugar, aromatic and sugar derivatives are the principal elements of the bio-oil which are highly polymerized [17]. As a consequence, it is difficult to store the bio-oil for some time. According to figure 6, bio-oil converts into two

phases by adding polar water [17]. One is a water-like phase and the other one is a paste-like phase. Water-like phase converts into “Platform Chemicals” and “Fuel Additive” by the acid-catalyst reaction. Platform chemicals consist of “Levulinic acid/ester” whereas fuel additive consists of “Ethers, acetals, esters” [17]. Main fuel production has occurred in the paste-like phase which gives 70 to 80 per cent of fuel [17]. Hydrotreatments of paste-like phase give these fuels and fine chemicals. Sugar and sugar derivative is called water-like phase. The aromatics and others are called paste-like phase. Both can be used for fuel production purposes. However, aromatics and others give more fuel by hydrotreatment process [17].

From the research, it is clear that the pyrolysis process has a good impact on the production of bio-oil as well as biodiesel (Table 3). Flashpoint, kinematic viscosity and calorific value give the clear property of the extracted oil.

Quality can be denoted by these parameters. A flashpoint for microwave pyrolysis process is 54°C [18].

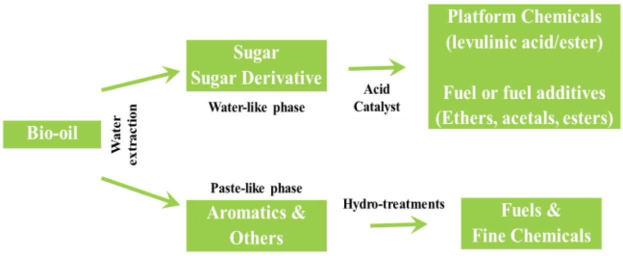

Figure 10: Bio-oil to fuel/chemical conversion steps [17]

Table 3: Yield quality comparison of soap nut (Sapindus Mukorossi) from different bio-oil extraction process [9], [17], [18]

Properties	Soxhlet extraction system	Microwave Pyrolysis	Solvent extraction method
Flash Point	1590 C	540 C	950 C
Kinematic Viscosity at 400 C	32.1 mm^2/s	36.7 mm^2/s	5.3 mm^2/s
Calorific Value	38 MJ/kg	22 MJ/kg	-

A flashpoint for "Soxhlet extraction system" and "Solvent extraction method" is 159°C [9] and 95°C [18] accordingly. From this data, it is clear that pyrolysis gives the better quality of the bio-oil than the other process. All these values can vary according to the environment and testing process.

Soapnut (Sapindus Mukorossi) and other similar nonedible oil are compared in the table-4. Most important parameters are compared in this table. According to the table, soap nut (Sapindus Mukorossi) is lighter than the "Madhuca Indica" oil and "Pongamia Glabra" oil whereas "Hevea Brasiliens" oil is lighter than the Sapindus Mukorossi oil. On the other hand, a viscosity of the "Hevea Brasiliens" oil is higher than the soap nut (Sapindus Mukorossi) oil. The calorific value of soap nut (Sapindus Mukorossi) (38 MJ/kg) also comparatively better than the other bio-oil. The acid value of the soap nut (Sapindus Mukorossi) is lower than the "Madhuca" and "Hevea" oil which is 15.6 mgKOH/g. Acid value depends on the cultivation, soil quality and preservation system of the seeds [9]. Flashpoint also giving a positive indication for soap nut (Sapindus Mukorossi). It has a lower flash point (159°C) than the other oil. Flashpoint depends on the procedure of the production of the biodiesel. Flashpoint can be varying by using extra chemical or the catalyst with the produced biodiesel. Production cost also can vary depending on the quality of the biodiesel

Table 4: Properties comparison of Sapindus Mukorossi oil with similar oil [9]

Properties	Units	Sapindus Mukorossi	Madhuca Indica	Pongamia Glabra	Hevea Brasiliensis
Density at 150 C	kg/m3	923	960	931	910
Viscosity at 400 C	mm2/s	32.1	24.58	26.06	66.2
Calorific value	MJ/kg	38	36.1	40.51	37.5
Acid value	mgKOH/g	15.6	38	1.21	34
Flash point	0 C	159	232	NA	198

Discussion

Soapnut (Sapindus Mukorossi) kernels contain a significant amount of oil (39 wt.%) that is much suitable for quality bio-oil production [8]. Normally diesel engines produce carbon monoxide (CO), unburnt hydrocarbons, particulate matter, and air toxics [18]. On the other hand, when diesel engines are powered by bio-oil, these kinds of toxic elements are not generated. Quality and the quantity of the bio-oil depends on the raw materials, de-moisturization techniques, particle size and the associated pyrolysis temperature as well as the heating rate. Not only the soap nut (Sapindus Mukorossi) but also other biomass (e.g. solid waste, crops husk) can be utilized instead of just burning. There is a significant effect of incineration on the atmosphere and living beings. Toxic gases and ash contaminate the air that causes respiratory disease. Toxins released from an incinerator stack into the atmosphere as well as fugitive pollutants can be accumulated on the ground near the incinerator and

therefore contaminate the local environment [23]. Open incineration cannot be the proper solution for solid waste. Pyrolysis can be the most effective and stable waste management which is more environmentally friendly. Not only waste management but also energy can be generated by this waste management system. Fast pyrolysis is a thermochemical conversion process at a moderate temperature (400-600°C) in which biomass is rapidly heated in the absence of an oxidizing agent with heating [24]. Before pyrolysis, moisture removal from the biomass is very important to get the best quality of yield. Hence, the gradient of temperature has an impact on the yield. The maximum removal of the moisture will give a better quality of yield. According to the analysis, 5°C/s, 10°C/s, 15°C/s and 20°C/s are chosen as effective temperature gradients. By the Karl Fischer method, oven drying took place at 135°C for 2 h, and oven drying at 125°C, 115°C, 105°C, or 95°C for increase the drying time from 1 to 24 h [25]. According to the analysis, temperature ranges of 150°C, 200°C and 250°C can be chosen if the time can differ significantly by 3, 6, 9, and 12 hours. At a pyrolysis temperature of 400°C, the oil yield was 34 per cent and, at a final pyrolysis temperature of 500-550°C, the oil yield was 38 per cent for the safflower seed [25]. However, with 89 wt%, the maximum methyl ester yield was obtained with 3 h reaction time at 60°C, catalyst 3.5 wt% and oil-methanol ratio 1:15 [18] for soap nut (Sapindus Mukorossi). It is apparent that soap nut (Sapindus Mukorossi) produces much better bio-oil content and the yield quantity is also much higher than the others by comparing the pyrolysis of different types of biomass product.

Conclusion

The current study sought to investigate the possible sources of bio-oil feedstock from soap nut (Sapindus Mukorossi) oil. It is proved that this tree seed has the potential capability to generate bio-oil as well as biodiesel by the means of fast pyrolysis. Fast pyrolysis is the thermal decomposition process of biomass and this thermal decomposition performs in the absence of oxygen. There are also some other thermal processes to produce bio-oil. All thermal processes are not called pyrolysis. However, based on the current trend of biomass treatment, incineration has operated to a matured technology. By moving forward improvement, now the next generation of technologies are here: Hybrid of pyrolysis (CO^2 reduction purpose) and Waste to Energy (WtE). Quality of the bio-oil depends on the moisture content and the size of the feedstock. The moisture content of the feedstock should be below 10% to get a better quality of the yield otherwise it will produce only water and some of the sludge will be in it. As a result, the feedstock drying process plays a vital role to produce a better quality of bio-oil, biochar and biogas (syngas). Slow pyrolysis process produces biochar whereas fast pyrolysis produces 60% of bio-oil out of total loading. According to this research, bio-oil from soap nut (Sapindus Mukorossi) is comparatively better & efficient than the other non-edible bio-oil.

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