Clean Marine Fuel: Integration of Co-pyrolysis Oil with High-Sulfur Fuel Oil

Dieni Mansur
Research Center for Chemistry, National Research and Innovation Agency, B.J. Habibie Science and Technopark

Hari Setiapraja
Research Center for Energy Conversion and Conservation, National Research and Innovation Agency, B.J. Habibie Science and Technopark

Oni Fariza
Research Center for Energy Conversion and Conservation, National Research and Innovation Agency, B.J. Habibie Science and Technopark

Aminuddin
Research Center for Process and Manufacturing Industry Technology, National Research and Innovation Agency, B.J. Habibie Science and Technopark

他

https://doi.org/10.5109/7326937

出版情報：Evergreen. 11 (4), pp.2959-2968, 2024-12. Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Japan
バージョン：

Clean Marine Fuel: Integration of Co-pyrolysis Oil with High-Sulfur Fuel Oil

Dieni Mansur[1,*], Hari Setiapraja[2], Oni Fariza[2], Aminuddin[3], Siti Yubaidah[2]

[1]Research Center for Chemistry, National Research and Innovation Agency, B.J. Habibie Science and Technopark, Serpong, South Tangerang 15314 Banten, Indonesia

[2]Research Center for Energy Conversion and Conservation, National Research and Innovation Agency, B.J. Habibie Science and Technopark, Serpong, South Tangerang 15314 Banten, Indonesia

[3]Research Center for Process and Manufacturing Industry Technology, National Research and Innovation Agency, B.J. Habibie Science and Technopark, Serpong, South Tangerang 15314 Banten, Indonesia

*Author to whom correspondence should be addressed:
E-mail: dien001@brin.go.id

(Received August 19, 2024; Revised November 6, 2024; Accepted November 12, 2024).

Abstract: The study investigated the production of pyrolysis oil by co-pyrolyzing palm fronds and waste-expanded polystyrene and then blending it with high-sulfur fuel oil (HSFO). This was considered one of the strategies to achieve the Sustainable Development Goal 7 (SDG-7) target of reducing emissions and HSFO consumption. The pyrolysis oil produced at 400 °C did not contain benzene, which is already restricted in fuel. The primary chemical compound in the pyrolysis oil was styrene, along with several other aromatic compounds, including ethylbenzene, toluene, α-methylstyrene, and various other aromatic hydrocarbons and oxygenates. The high hydrocarbon content in pyrolysis oil resulted in a high calorific value of 41.99 MJ/kg, low water content, and promoted the mixing of pyrolysis oil with HSFO. Additionally, pyrolysis oil had a very low sulfur content. The properties of the blended fuels showed that blending 5-10% of pyrolysis oil with HSFO resulted in a fuel that met marine fuel standards and provided several benefits, including reduced viscosity and lower sulfur content. Moreover, due to its lower viscosity, the blended fuel may require less energy to preheat before entering the engine, thus effectively improving fuel efficiency.

Keywords: Pyrolysis oil; Palm fronds; Waste-expanded polystyrene; Fuel oil

1. Introduction

The marine industry, which includes people and freight shipping, offshore operations, and fishing, is mostly powered by internal combustion engines. These engines, known for their powerful output, require a huge supply of marine residual fuel to operate properly. For transporting cargo solely, the demand might approach 640 thousand metric tons per day[1)]. The substantial rise in consumption creates significant challenges in regulating emissions, improving fuel efficiency, and exploring alternative fuel sources to fulfill the maritime industry's increasing demands while complying with sustainable development goals (SDG).

Central to the 2030 Agenda for Sustainable Development adopted by all United Nations Member States are the 17 Sustainable Development Goals (SDGs), which serve as a common framework for achieving peace and prosperity for both people and the planet, both now and in the future [2)]. One of them is SDG-7, which aims to achieve affordable, clean, sustainable, modern, and reliable energy, placing energy at the center of environmental and economic issues. By 2030, the targets include substantially increasing the share of renewable energy in the global energy mix and enhancing international cooperation to facilitate access to clean energy research and technology. One approach to this goal and target is using biofuels in the transportation industry. Biofuels are produced from biomass through biological, chemical, or thermochemical conversions, with biomass mostly derived from the organic waste of plants and animals[3)]. In this study, organic waste of oil palm fronds (PF) generated in palm oil plantations was processed through thermochemical conversion, specifically pyrolysis, to produce pyrolysis oil. The palm frond is plentiful in Indonesia and Malaysia, with an estimated 156.5 million tonnes and 59.3 million tonnes, respectively, in 2023, which aligns with the area of oil palm plantations in both countries[4)]. The oil palm fronds are combined with plastic waste, such as polystyrene, as a co-feed to reduce environmental waste. This process produced pyrolysis oil that contained compounds derived from biomass and

polystyrene that could be blended with fossil fuels. It also supports the concept of a renewable energy mix and clean energy technology that aligns with SDG-7 targets.

The International Maritime Organization (IMO) continues to emphasize the urgent need to reduce sulfur oxide (SO_x), nitrogen oxide (NO_x), and carbon dioxide (CO_2) emissions from ships engaged in diverse industrial operations. As a result, there is a rising effort to follow stringent regulations, which increases demand for low-sulfur petroleum fuels and other unconventional sources of energy[1),5),6)]. Therefore, researchers are exploring alternative fuels for heavy fuel oil (HFO) to reduce emissions and petroleum consumption[7)].

Various strategies have been implemented to address tightening exhaust gas and CO_2 emissions regulations. These include transitioning from high-sulfur fuel oil (HSFO) to low-sulfur fuel oil (LSFO), retrofitting vessels to run on liquefied natural gas (LNG), adopting biofuels, employing exhaust after-treatment technologies, installing sulfur scrubbers for HSFO use, integrating hydrogen usage, and converting to electric power[8-12)]. More holistic approaches such as enhancing vessel design, optimizing economic scales, and refining routing strategies are also being proposed to further reduce emissions[10)]. However, the primary challenge lies in the investment costs associated with implementing these measures[11)]. Even full life cycle analyses indicate that transitioning from HSFO to LSFO or marine gas oil still results in greenhouse gas emissions comparable to those from HSFO[10)].

Marine residual fuel used for large marine cargo vessels is heavy fuel oil (HFO) primarily derived from the residuum fraction of refined crude oil. The HFO mainly comprises high-molecular-weight aromatic and paraffinic hydrocarbons with boiling points above 350 ℃. They contain significant amounts of sulfur and are highly viscous[7)]. The geochemistry of some crude oils in Indonesia contains high levels of sulfur (> 0.5% wt.), which depends on the location of the formation process. In places containing clay-poor carbonate source rock, crude oil with high sulfur content will be produced[13)].

In order to prevent clogging in the supply line of the purifier, it is necessary to preheat the fuel oil to decrease its viscosity, which is powered by electricity from the generator[14)]. The residual fuel oils require heating to lower viscosity, even after blending with lower-viscosity components to achieve suitable flow and combustion characteristics. The expected higher costs for low-sulfur marine fuels, other forthcoming emission regulations, and the additional processing associated with HFO could provide a new market opportunity for biofuels, which have inherently low-sulfur content and the potential to reduce particulate matter (PM) emissions. Also, biofuels can reduce net CO_2 emissions due to carbon uptake from the atmosphere during biomass growth and play an essential role as a future marine fuel that is more renewable and lower in sulfur and other emissions[7)]. Pyrolysis oil, as one of the biofuels, is naturally low in sulfur[15)] and have been proven to decrease particulate emissions[6)]. One option to improve the utility of pyrolysis oil is to blend it with petroleum or other bio-based fuels to enhance their fuel properties[16)]. The pyrolysis oil was prepared in homogenous blends for biofuels in the marine industry[5)]. Difficulties may arise when attempting to create a mixture of pyrolysis oil and marine fuel since the pyrolysis oil is not homogeneous. This is due to the high levels of oxygen present in pyrolysis oil. In order to mix pyrolysis oil with marine fuel, it must undergo an upgrading process. One method of upgrading pyrolysis oil is through the co-pyrolysis process, which involves combining hydrocarbon materials with biomass[17)].

A study was conducted to produce pyrolysis oil by co-pyrolyzing palm fronds and waste-expanded polystyrene (EPS). The produced fuel was then blended with marine fuel oil. Previous studies have also blended petroleum diesel with pyrolysis plastic oil (10-50% by volume) derived from low-density polyethylene (LDPE)[18)] and hydroprocessing of waste plastics oil blended with HFO[19)]. Other examples included blending pyrolysis oil derived from biomass with butanol and biodiesel and/or marine gas oil[20),21)] and blending pyrolysis oil (5-30% by volume) derived from waste motor oil with gasoline[22)]. Two studies were conducted where heavy fuel oil was mixed with pyrolysis oil derived from lauan wood (2.5 – 10%) along with the addition of 0.2% surfactant[23)]. Another study mixed pyrolysis oil derived from dried sludge (20-80%) with the addition of tween 80 and span 80[24)]. However, no publications have found that mixing heavy fuel oil with pyrolysis oil from the co-pyrolysis process of plastic polystyrene and palm frond biomass. Therefore, this study compared the fuel properties of a mixture of marine fuel oil type HSFO with pyrolysis oil derived from co-pyrolysis of plastic polystyrene and biomass palm fronds with standard marine fuel. It is worth mentioning that no surfactant was added during the mixing process.

2. Material and methods

2.1 Material

Pyrolysis oil was prepared from palm fronds (PF) and real-world waste-expanded polystyrene (EPS) available in B.J. Habibie Science and Technopark, Serpong, South Tangerang, Banten, Indonesia. The palm fronds contained cellulose (31.40 wt.%), hemicellulose (21.15 wt.%), lignin (28.94 wt.%), ash (0.94 wt.%), and other extractives (7.86 wt.%)[25)]. The palm frond was cut, minced, dried, and sieved to produce a particle size of 10-14 mesh. The waste EPS was cut to around 10 x 5 cm^2 and pressed with a hydraulic press machine to make it denser. Moreover, HSFO, as a representation of marine fuel oil, was received from PT. Pertamina International, Indonesia.

2.2 Experimental procedure

Pyrolysis oil was produced using a co-pyrolysis process using the 8-liter volume capacity of a pyrolysis reactor,

consisting of a perforated stainless-steel basket as a feed container. The reactor had a condenser and two traps for catching the vapor from the co-pyrolysis process. A schematic diagram of the experimental pyrolysis setup is shown in Fig. 1. The PF and EPS with a weight ratio of 1:2 were put into the basket randomly and inserted into the reactor. The stainless-steel pyrolysis reactor was closed tightly. The process condition of co-pyrolysis is shown in Table 1. The condensable liquid products in a condenser and traps consisted of two separate phases: the oil phase and the aqueous phase. The oil phase hereafter is called pyrolysis oil (PO). Uncondensable fraction was called a gas product. After the process, the remaining solid in the reactor was called a char. The yield of pyrolysis oil, aqueous phase, and char was determined by comparing it with the total feed amount. The co-pyrolysis process was performed twice. The selection to use a PF: EPS ratio of 1:2 was based on the findings of earlier research, which resulted in a 64.67% pyrolysis oil. This percentage was higher than the figures obtained using a PF: EPS ratio of 1:1 and 2:1, which were 46.95% and 32.69%, respectively. The pyrolysis oil (PO) in some volume portions of 5% (PO 5), 10% (PO10), 20% (PO 20), and 30% (PO 30) were blended with HSFO at room temperature by mixing. The properties of pyrolysis oil, blended fuels, and HSFO were analyzed.

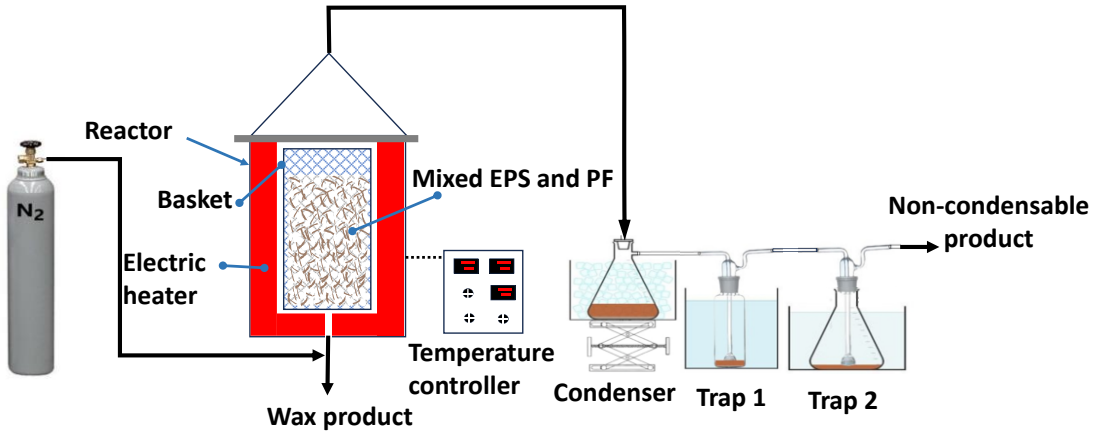


Fig. 1: A schematic diagram of the pyrolysis reactor (bench scale).

Table 1. Operating conditions and yield of the co-pyrolysis process.

Condition and yield	Co-pyrolysis Temperature (°C)	
	400	**500**
Heating rate (°C/min)	16.30	13.15
N_2 flowrate (ml/min)	15	15
Reaction time (h)	2	2
T condenser (°C)	0 - 5	0 - 5
T cold trap (°C)	(-10) – (-3)	(-10) – (-3)
Yield of products:		
Pyrolysis oil (wt.%)	56.38	53.91
Aqueous phase (wt.%)	6.66	8.78
Biochar (wt.%)	11.24	10.79
Gas + wax/ heavy tar (wt.%)	25.72	26.52

2.3 Characterization of the fuels

Characterization analysis was performed to identify the calorific value, moisture content, kinematic viscosity, density, total acid number, flash point, sulfur content, and chemical composition of the fuels.

2.3.1 The calorific value of fuels

The calorific value (higher heating value = HHV) was calculated by Dulong's equation (Eq.1)[26] based on the elemental content of carbon (C), hydrogen (H), nitrogen (N), oxygen (O), and sulfur (S) present in the samples. The Leco CHN 628 was used to measure the elements of C, H, and N. The O element was calculated by subtracting 100% and the sum of other elements. The elemental analysis data of the HSFO, the blended fuels, and pyrolysis oil samples are shown in Table 2.

$$HHV\ (MJ/kg) = 0.3383\ C + 1.443\ (H - (O/8)) + 0.0942\ S \quad (1)$$

Table 2. Elemental analysis data of HSFO, the blended fuels, and pyrolysis oil (PO).

Sample	Carbon (wt.%)	Hydrogen (wt.%)	Nitrogen (wt.%)	Sulfur (wt.%)	Oxygen (wt.%)
HSFO	85.33	11.01	0.02	2.958	0.68
PO 5	86.18	10.86	0	2.740	0.22
PO 10	86.38	10.68	0.02	2.628	0.29
PO 20	86.55	10.45	0	2.403	0.60
PO 30	87.06	10.18	0	2.073	0.69
PO	90.45	8.08	0	0.002	1.47

2.3.2 Moisture content of pyrolysis oil

The moisture content of pyrolysis oil was analyzed using a Karl-Fischer Moisture Titration MKC-501 (KEM, Japan) with a maximum measurement of 1000 ppm or 1%. For this analysis, Hydranal-coulomat CG catholyte reagent from Fluka Analytical (34840-50ML-R) was used, along with Hydranal-coulomat AG anolyte reagent from

Fluka Analytical (34836-500ML). Hydranal-water standard 1.0 (Fluka Analytical 34828-40ML-R) was used as the water standard. To perform the analysis, approximately 5 µl pyrolysis oil was taken using a micro syringe from Hamilton Co, Reno, Nevada, and then injected into the Karl-Fischer unit.

2.3.3 Kinematic viscosity and density analysis of fuels

The Anton Parr Stabinger Viscometer SVM 3000 was utilized to determine fuel density and kinematic viscosity. This was done at 5 °C intervals starting from 5 °C and going up to 100 °C. The process was carried out following the guidelines provided by ASTM D7042. The viscometer automatically calculated the viscosity and density of the fuels.

2.3.4 Total acid number (TAN) of fuels

The total acid numbers of pyrolysis oil, blended fuels, and HSFO were measured using an 848 Titrino Plus (Metrohm) following ASTM D664. For accuracy, 2.5 g of the fuels were analyzed in duplicate.

2.3.5 Flash point analysis of fuels

The flash point analysis used a Grabner Instruments Ametek Miniflash FLP Touch analyzer based on ASTM D6450-20.

2.3.6 Sulfur content analysis of oil product

The sulfur content analysis was performed by ASTM D4294 standard method using energy dispersive X-ray fluorescence spectrometry in petroleum and petroleum products. The pyrolysis oil was analyzed in its original state. HSFO and the blended fuels were diluted 50 times with hexadecane (anhydrous, ≥99%, Sigma Aldrich) to lower the sulfur concentration in the fuel.

2.3.7 Chemical composition of pyrolysis oil

The pyrolysis oil's chemical composition was analyzed using a gas chromatograph-mass spectrometer (GCMS-QP2010S Shimadzu). The instrument was plugged with a DB-5MS column (Agilent Technologies, Inc. 30 m x 0.25 mm x 0.25 µm), and helium was used as the carrier gas. The injector temperature was 300 °C, and the initial oven temperature of the column was 40 °C, which was maintained for 5 minutes. It was then raised to 300 °C with a rate of 5 °C/min and held for 13 minutes at 300 °C. The ion source temperature was 250 °C, and the interface temperature was 300 °C. Ionization energy was 70 eV, and the mass range was from m/z 28 AMU (atomic mass unit) to 600 AMU. The total flow was 101.5 mL/min, the column flow was 0.78 mL/min, and the linear velocity was 31.9 cm/s. The chemicals in the samples were identified by comparing the spectra and retention time of individual compounds with the authentic reference compounds stored in the mass spectral data library.

3. Results and Discussion

3.1 Effect of temperature on pyrolysis oil

The co-pyrolysis of PF and EPS was conducted at two different temperatures of 400 ℃ and 500 ℃, and the results are presented in Table 1. The table shows a higher yield of pyrolysis oil was obtained at 400 ℃ than at 500 ℃ due to a faster heating rate. This was mostly due to the decomposition of EPS, mainly hydrocarbon compounds. At 400 ℃, the decomposition of PF was relatively lower than that at 500 ℃, as evidenced by the lower yield of the aqueous phase, which was mostly composed of oxygenated compounds. This was supported by the higher char yield at 400 ℃. The yield of gas, wax, and heavy tar was determined from the mass balance because it was difficult to weigh a large enough reactor before and after co-pyrolysis.

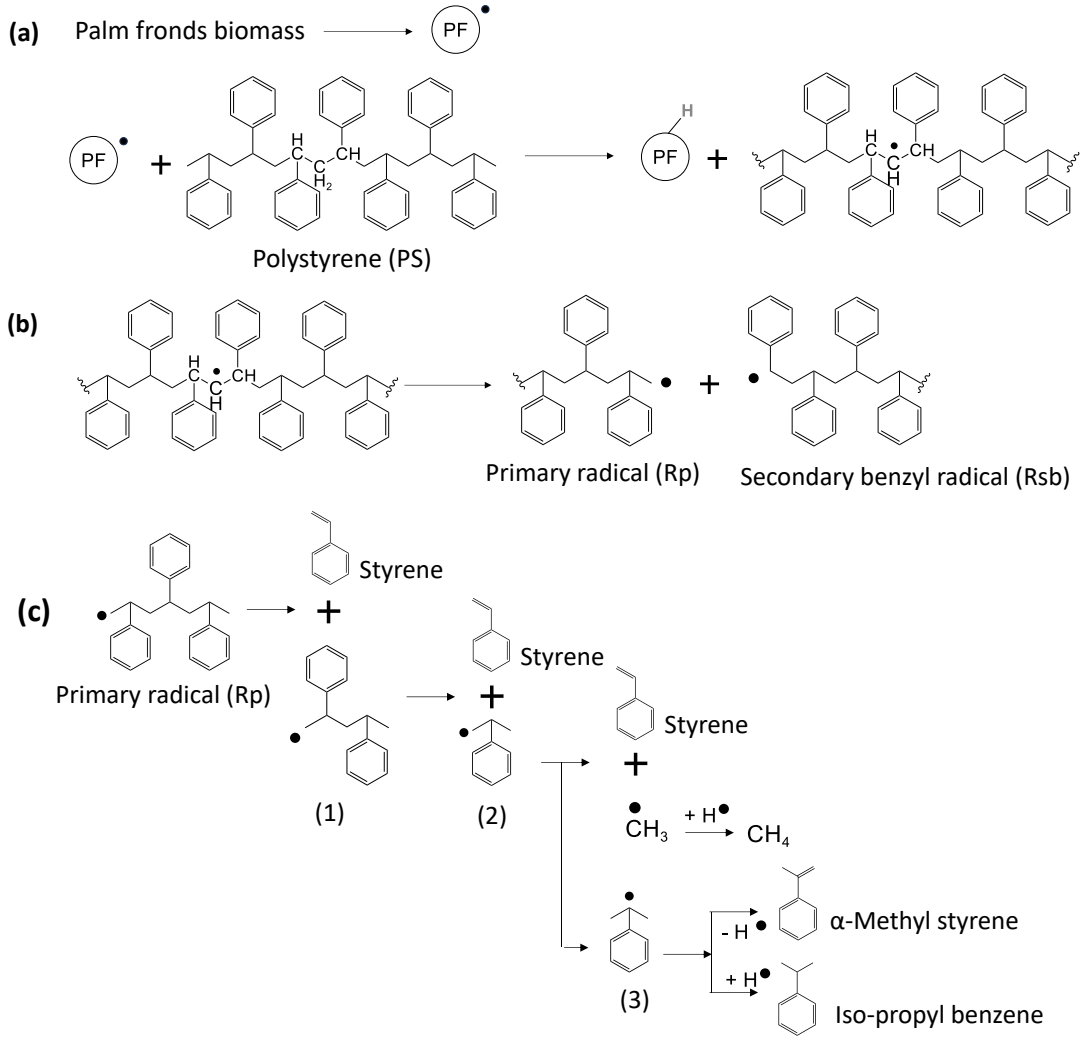
The pyrolysis oil composition was analyzed using GCMS; the results are presented in Table 3. The table shows that thermal cracking occurred excessively at 500 °C in the EPS structure, producing many benzene compounds. Benzene is a harmful chemical that can be found in fuel. The International Agency of Research on Cancer has categorized benzene as a Group I carcinogen. Exposure to benzene can result in genetic damage and many health problems, including decreased white blood cell and platelet counts, aplastic anemia, myelodysplastic syndromes, and leukemia. Because of its harmful effects, the federal government regulates the amount of benzene in gasoline. Refineries and importers are required to maintain an average of less than or equal to 0.62% benzene by volume[27),28)].

Table 3. Composition of pyrolysis oil as an effect of temperature of co-pyrolysis process.

Chemicals	Peak area (%)	
	400 ℃	500 ℃
Styrene	46.94	33.87
Ethylbenzene	18.21	6.76
Toluene	14.39	19.33
α-Methylstyrene	7.11	3.60
Benzene	-	18.66
Naphthalene	0.55	4.49
Phenanthrene	-	3.58
Other aromatic hydrocarbon	12.51	9.70
Aromatic oxygenate group	0.33	-

The pyrolysis oil produced at 400 °C did not contain benzene, but it contained approximately 50% styrene, as well as ethylbenzene, toluene, α-methylstyrene, naphthalene, phenanthrene, other aromatic hydrocarbons, and aromatic oxygenates. The chemicals contained in the pyrolysis oil were derived from the interaction of PF and EPS during thermal decomposition. In the initial stage of the co-pyrolysis process, the biomass (PF) components triggered radical formation[29)] to initiate the scission of the polymer (EPS) chain (Fig. 2 (a))[30)]. The thermal

decomposition of EPS began with an initiation reaction that led to two types of scission: random scission and chain-end scission (Fig. 2 (a)). The PS bond cleaved at the backbone C-C bond due to its lower bond dissociation enthalpy (BDE) compared to the C-C aromatic bond and C-H bonds at secondary and tertiary carbon atoms[31], which was illustrated in Fig. 2. A random scission produced a primary radical (Rp) and a secondary benzyl radical (Rsb) (Fig. 2 (b)). Also, chain-end scission formed a secondary benzyl radical (Rsb) and an unsaturated radical fragment (Ra). Styrene, ethylbenzene, toluene (methyl benzene), and α-methylstyrene were produced from the primary radical (Rp) and secondary benzyl radical (Rsb) during the propagation step with reaction mechanism was shown in Figs. 2 (c) and (d). The model of Rp and Rsb was limited to seven carbon atoms in the backbone. Formations of styrene, methane, α-methylstyrene, isopropyl benzene, toluene, styrene dimer, and ethylbenzene were derived from the breaking of the backbone carbon in radicals at the transition state, free radicals rearrangement, hydrogen atom abstraction, and dehydrogenation of the final radicals in every path[31]. Based on the reaction mechanism shown in Fig. 2, it was understood that the likelihood of styrene formation was higher than that of other compounds. This aligned with the findings of the pyrolysis oil analysis in Table 3. In Fig. 2, the flow of benzene formation was not apparent. Based on Table 3, when comparing the compounds in pyrolysis oil produced at 400 °C with those at 500 °C, it was predicted that benzene was produced from the breakdown of styrene, ethylbenzene, and α-methylstyrene due to the decrease in their values. Therefore, based on the analysis of the composition and yield of pyrolysis oil, the co-pyrolysis process at 400 °C was considered more effective. Thus, this fuel was blended with HSFO to find a suitable ratio that meets marine fuel standards.



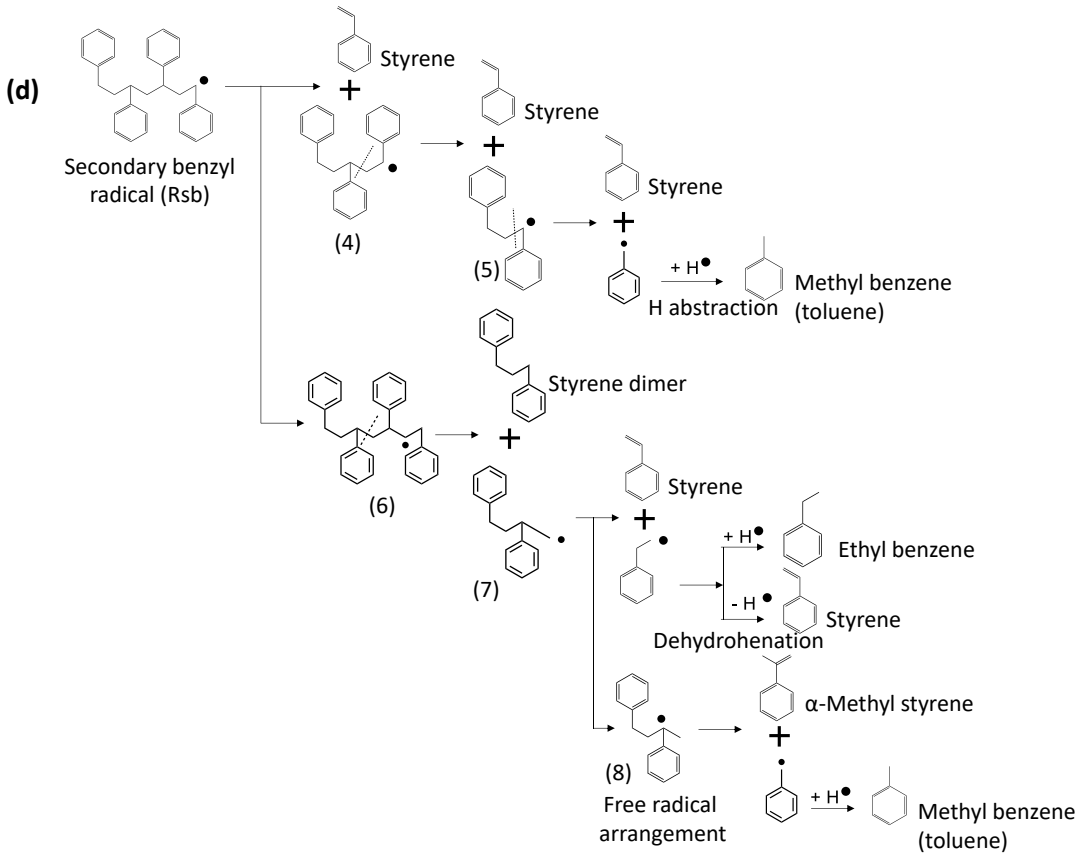


Fig. 2: Mechanism reaction for chemical production during propagation step of primary (Rp) and secondary benzyl radicals (Rsb). Modified from[31].

Table 4. The properties of blended fuels, pyrolysis oil, HSFO, and residual marine fuel.

Specification	Unit	Limit	RMG 180[#]	HSFO	PO 5	PO 10	PO 20	PO 30	PO
Kinematic viscosity at 50 °C	cSt	Max	180	106.98	62.02	39.33	17.93	9.60	0.86
Density at 15 °C	Kg/m^3	Max	991	956.0	954.9	953.7	952.2	950.4	943.9
Acid number	mg KOH/g	Max	2.5	0.05	0.25	0.48	0.98	1.69	5.52
Water	Vol %	Max	0.50	n.a	n.a	n.a	n.a	n.a	0.0925
Flash point	°C	Min	60	153.05	76.00	60.05	44.60	34.80	22.00
Sulfur	Mass %	Max	3.5%, or statutory requirement in SECAs	2.96	2.74	2.63	2.40	2.07	0.0024
Heating value	MJ/kg	At least	30	44.91	45.04	44.83	44.48	44.21	41.99

[#] R = residual, M = marine, G = specific product specifications, 180 = the maximum kinematic viscosity of the residual fuel; PO = pyrolysis oil, the number 5-30 refers to % volume of pyrolysis oil blending with HSFO. Example: PO 5 means 5% pyrolysis oil is blended with 95% HSFO. n.a = unavailable because we do not have a Karl Fisher volumetric unit. SECAs (sulfur emission control areas)

3.2 Effect of blending ratio of pyrolysis oil with HSFO on the fuel properties

In the determination of blended fuel that met marine fuel standards, a 5-30% volume of pyrolysis oil was blended with HSFO and analyzed. The pyrolysis oil was thoroughly mixed with HSFO. The pyrolysis oil primarily consisted of hydrocarbon aromatic compounds. HSFO contains asphaltenes, which are also aromatic in nature and have a high molecular weight[32]. As a result, the likelihood of asphaltene precipitation was very low. Table 4 provides a detailed comparison of blended fuels, pyrolysis oil, and HSFO in relation to residual marine fuel (RMF) based on the measurement test results elucidated in the previous sub-chapter. The kinematic viscosity of the fuels can be shown in Fig. 3. Kinematic viscosity indicates the degree of resistance a fluid offers to flow under the effect of gravity. When exposed to high temperatures, the fuel's oxidation process leads to an increase in kinematic viscosity. On the other hand, shear or dilution with unburned fuel decreases the kinematic viscosity of the fuel[33]. The decrease in kinematic viscosity is also due to the molecules in the fuel moving faster at higher temperatures, reducing the frictional forces between them. This allows the fluid to flow more easily. Tested HSFO

had lower viscosity compared to RMF as shown in Table 4. Blending pyrolysis oil (PO) with HSFO dramatically reduced the kinematic viscosity of the blended fuel because PO had a considerably lower viscosity than HSFO. The whole blending fuels of PO and HSFO could meet the RMF standard. Furthermore, the reductions in viscosity for blending of 5%, 10%, and 20% compared with HSFO were 42%, 63%, and 83%, respectively. Lowering the viscosity of the blended fuel could effectively improve fuel efficiency[34]. This finding was consistent with the study by Kim and Choi[35], which reported a viscosity decrease of roughly 50% using a 20% blend of palm oil and very low sulfur fuel oil. They also observed that the reduction in viscosity corresponds to a decrease in the optimal fuel temperature, which was directly proportional to the energy required to heat the fuel. Particularly, a noticeable viscosity drop caused a significant reduction in the energy needed for fuel heating[35].

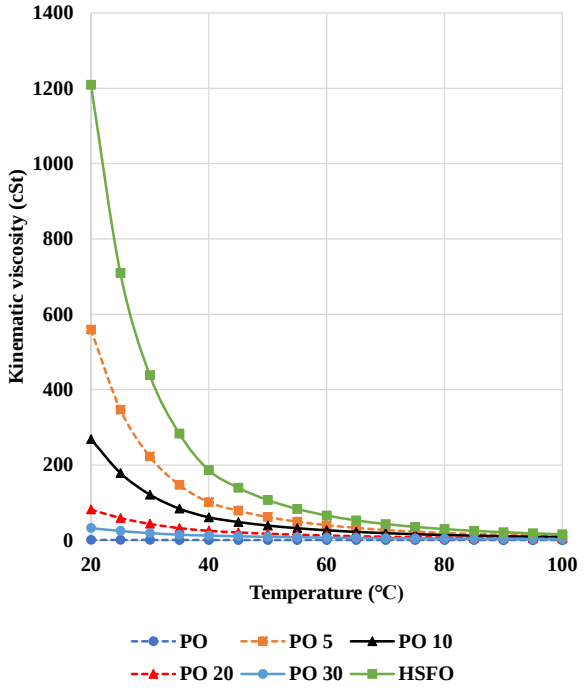


Fig. 3: Kinematic viscosity of the blended fuels compared to pyrolysis oil and HSFO.

The blended fuels and PO also met the RMF standard in terms of density. Fuel density is a key indicator of its ignitability and is closely linked to viscosity, particularly for residual fuels with low viscosity[36]. Figure 4 illustrates the density of the fuels measured within a temperature range of 5-100 °C. The density of fuels generally decreased with increasing temperature, as did the kinematic viscosity. According to the measurement results, a decrease in density for various blending ratios of 5-30% PO was less than 1%. Density is strongly related to the power and fuel consumption of the engine. Higher density often means more possibility for producing more power and lower consumption.

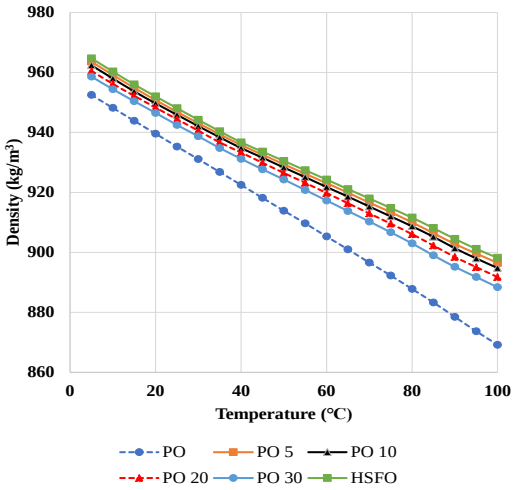


Fig. 4: Density of the blended fuels in comparison with pyrolysis oil and HSFO.

The acid number of fuel can be affected by the presence of acid compounds, which can damage engines and fuel injection equipment. According to Table 4, the maximum acid number for RMF based on ISO 8217 should be 2.5 mg-KOH/g[36]. The acid number of the blended fuel, PO 5-30, was less than 2.5 mg-KOH/g, even though the acid number of the PO was quite acidic at 5.52 mg-KOH/g. This acidity was due to acid compounds such as acetic acid[37], which were derived from PF. However, the presence of acid compounds in PO was minimal due to their small proportion compared to the identified hydrocarbon compounds, as shown in Table 3.

As a potential alternative fuel for marine energy, it is important to determine the water content of PO. The PO produced from co-pyrolysis of PF and EPS, the water content was significantly lower than that of standard RMF (0.3-0.5%). Thus, the utilization of PO as a marine fuel was not hindered by moisture content. However, in this particular study, the moisture content of the blended fuel could not be determined due to the limitations of the analysis instrument.

The flash point is the temperature at which a substance can produce flammable vapor in the air, indicating the fuel's combustibility[36]. Table 4 shows the results of flash point analysis of HSFO, blended fuels, and PO. Based on the table, the flash point value of PO was lower compared to RMF and HSFO, and this affected the flash point of the blended fuel. The study also found that blending 5-10% of PO into HSFO was acceptable compared to the standard RMF. As a result, the maximum blending ratio while considering acceptable storage and handling was 10%. The heating value is an important property for marine fuel because it is directly associated with power and fuel consumption. Table 4 shows the heating value of HSFO, blended fuels, and PO. The heating value of the PO was lower than HSFO, but it was still significantly higher than the minimum requirement by the standard RMF. Based on its heating value, the blending fuels and PO produced from co-pyrolysis of PF and EPS were acceptable as a

RMF with over 30 MJ/kg. As a result, 5-30% PO was blended with HSFO as marine transportation fuel complied with RMF requirements.

Based on Table 4, the sulfur content determined for RMF was 3.5% by mass. HSFO contained 2.96% sulfur, whereas PO only contained 0.0024% sulfur. Mixing 5-30% PO into HSFO could reduce the sulfur content by 0.22 - 0.89%. The more PO was mixed, the more the sulfur content in the blended fuel would be reduced. This reduction in sulfur content was greater than the reduction in sulfur levels in EBO (experimental blending oil), which was less than 0.2%. EBO was created by blending very low sulfur fuel oil and HSFO in mass ratios of 75:25, 50:50, and 25:75[38]. In terms of sulfur and nitrogen content, using pyrolysis oil is more profitable than using hydrothermal liquefaction (HTL) algae biocrude oil because the former has lower sulfur content compared to the latter, which contains high levels of nitrogen and sulfur. When HTL algae biocrude oil was used as a marine fuel, it caused a reduction in flash point and lower heating value (LHV), and an increase in NO_x and SO_x emissions, resulting in a significant increase in particulate matter (PM) emissions[39]. According to Table 4, taking into account properties such as viscosity, density, acid number, flash point, water content, heating value, and sulfur content of the blending fuel, the optimal blending ratio of PO into HSFO to achieve maximum engine power and minimum fuel consumption while reducing engine component damage was found to be 10%.

4. Conclusion

Production of 56.38 wt.% of PO from co-pyrolysis of PF and EPS was conducted, and the fuel was blended with HSFO. The results were compared to the standard RMF. It was found that blending up to 10% of PO with HSFO resulted in acceptable properties when used as marine fuel oil. The properties of the blended fuel, including kinematic viscosity (39.33 - 62.02 cSt), density (953.7 - 954.9 kg/m^3), acid number (0.25 - 0.48 mg KOH/g), flash point (60.05 - 76 ℃), sulfur content (2.4 - 2.63%), and heating value (44.83 - 45.04 MJ/kg) were determined. The blending of fuels provided benefits in terms of viscosity and sulfur content. Blended fuel can reduce the energy required for preheating before entering the engine and lower sulfur levels.

Acknowledgements

The authors acknowledge the facilities, scientific, and technical support from E-layanan sains (ELSA) Badan riset dan Inovasi Nasional (BRIN). This project received support from the Organization Research of Energy and Manufacturing, National Research and Innovation Agency No. 56/III.3/HK/2023, and the New Energy and Industrial Technology Development Organization of Japan (NEDO) with a Net Zero Emission theme No. 25/II.7/HK/2023. All authors declare that we have no conflict of interest.

References

1) S. Vedachalam, N. Baquerizo, and A.K. Dalai, "Review on impacts of low sulfur regulations on marine fuels and compliance options," *Fuel*, **310** 122243 (2022). https://doi.org/10.1016/j.fuel.2021.122243
2) U. Nations, "Transforming our world: the 2030 agenda for sustainable development," [Internet]. [cited 2024 Nov 4]. Available from: https://sdgs.un.org/sites/default/files/publications/21252030 Agenda for Sustainable Development web.pdf
3) S. Kufeoglu. Chapter 9: SDG-7 Afordable and Clean Energy in Emerging technologies Value Creation for Sustainable Development [Internet]. Springer Nature. 2022. 305–310 p. Available from: https://link.springer.com/chapter/10.1007/978-3-031-07127-0_9
4) M.R. Zakaria, F.M.A. Ahmad, H.S. Hafid, Y. Andou, and M.A. Hassan, "Practical role of oil palm fronds in Malaysia's sustainable palm oil industry," *Ind Crops Prod*, **222** 119753 (2024). https://doi.org/10.1016/j.indcrop.2024.119753
5) R.F. Galindo, L.A.B. Cortez, and T.T. Franco, "Ternary blends of renewable fast pyrolysis bio-oil, advanced bioethanol, and marine gasoil as potential marine biofuel," *Chem Eng Technol.*, **43** (8) 1530–7 (2020). https://doi.org/10.1002/ceat.202000082
6) E.C.D. Tan, T.R. Hawkins, U. Lee, L. Tao, P.A. Meyer, M. Wang, and T. Thompson, "Biofuel options for marine applications: Technoeconomic and life-cycle analyses," *Environ Sci Technol.*, **55** (11) 7561–70 (2021). https://doi.org/10.1021/acs.est.0c06141
7) M.D. Kass, B.L. Armstrong, B.C. Kaul, R.M. Connatser, S. Lewis, J.R. Keiser, J. Jun, G. Warrington, and D. Sulejmanovic, "Stability, combustion, and compatibility of high-viscosity heavy fuel oil blends with a fast pyrolysis bio-oil," *Energy and Fuels* **34** (7) 8403–13 (2020). https://dx.doi.org/10.1021/acs.energyfuels.0c00721
8) T. Lee, and H. Nam, "A study on green shipping in major countries: In the view of shipyards, shipping companies, ports, and policies," *Asian J Shipp Logist*, **33** (4) 253–62 (2017). http://dx.doi.org/10.1016/j.ajsl.2017.12.009
9) S. Nishio, T. Fukuda, A.Z.M. Fathallah, and H. Setiapraja, "Influence of palm biofuel for marine diesel engine on combustion and exhaust emission characteristics," *Mar Eng.*, **53** (3) 441–6 (2018). https://doi.org/10.5988/jime.53.441
10) A. Halff, L. Younes, and T. Boersma, "The likely implications of the new IMO standards on the shipping industry," *Energy Policy*, **126** 277–86. (2019). https://doi.org/10.1016/j.enpol.2018.11.033

11) A.R. Kim and Y.J. Seo, "The reduction of SOx emissions in the shipping industry: The case of Korean companies," *Mar Policy*, **100** 98–106. (2019). https://doi.org/10.1016/j.marpol.2018.11.024
12) G. Daniil and M. Boviatsis, "Evaluation of environmental impact assessment factors in maritime industry," *J Environ Sci Eng B.*, **11** (1) 18–23 (2022). https://doi.org/10.17265/2162-5263/2022.01.003
13) K.E. Peters, T.H. Fraser, W. Amris, B. Rustanto, and E. Hermanto, "Geochemistry of crude oils from eastern Indonesia," *Am Assoc Pet Geol Bull.*, **83** (12) 1927–42 (1999). https://doi.org/10.1306/e4fd4643-1732-11d7-8645000102c1865d
14) R. Martin, L. Castellano, A.A. Sami, M. Magomnang, and E.P. Villanueva, "Effects of viscosity and heat transfer on developed marine fuel preheating system utilizing diesel engine exhaust," *Mindanao J Sci Technol.*, **16** 211–30 (2018).
15) J. Klinger, D.L. Carpenter, V.S. Thompson, N. Yancey, R.M. Emerson, K.R. Gaston, K. Smith, M. Thorson, H. Wang, D.M. Santosa, and I. Kutnyakov, "Pilot plant reliability metrics for grinding and fast pyrolysis of woody residues," *ACS Sustain Chem Eng.*, **8** (7) 2793–805 (2020). https://dx.doi.org/10.1021/acssuschemeng.9b06718
16) A. Krutof and K. Hawboldt, "Blends of pyrolysis oil, petroleum, and other bio-based fuels: A review," *Renew Sustain Energy Rev*, **59** 406–19 (2016). http://dx.doi.org/10.1016/j.rser.2015.12.304
17) G. Radhaboy and M. Pugazhvadivu, "Properties of bio-oil produced by co-pyrolysis of Calotropis procera stem and waste polystyrene," A*IP Conf Proc.*,2225 (040003) (2020). https://doi.org/10.1063/5.0006401
18) M.S.N. Awang, N.W.M. Zulkifli, M.M. Abbass, S.A. Zulkifli, M.N.A.M. Yusoff, M.H. Ahmad, and W.M.A.W. Daud, "Effect of blending local plastic pyrolytic oil with diesel fuel on lubricity," *J Tribol.*, **27** 143–57 (2020).
19) V.L. Mangesh, P. Tamizhdurai, R. Vedavalli, S. Santhosh, R. Kumaran, N.S. Kumar, A.S. Al-Fatesh, P.K. Basivi, and G. Murali, "Maritime decarbonization: Alternate marine fuel from hydroprocessing of waste plastics," *Fuel*, **365** 131233 (2024). https://doi.org/10.1016/j.fuel.2024.131233
20) K.J. Chong and A.V. Bridgwater, "Fast pyrolysis oil fuel blend for marine vessels," *Environ Prog Sustain Energy*, **36** (3) 677–84 (2016). https://doi.org/10.1002/ep.12402
21) V. Sharma, A.K. Hossain, G. Griffiths, J.C. Manayil, R. Vinu, and G. Duraisamy, "Investigation of anaerobic digested pyrolysis oil and waste derived biodiesel blends as sustainable fuel for marine engine application," *Fuel*, **357** 129935 (2024). https://doi.org/10.1016/j.fuel.2023.129935
22) N. Patel, K.P. Shadangi, P.K. Kar, "Pyrolytic oil blended gasoline as future fuel: pyrolysis mechanism, fuel properties, and composition analysis," *Environ Sci Pollut Res*, **29** (57) 86400–17 (2022). https://doi.org/10.1007/s11356-022-19776-w
23) S.-S. Hou, W.-C. Huang, F.M. Rizal, and T.-H. Lin, "Co-firing of fast pyrolysis bio-oil and heavy fuel oil in a 300-kW_{th} furnace," *Appl Sci.*, **6** 326 (2016). https://doi.org/10.3390/app6110326
24) Y.-H. Kuan, F.-H. Wu, G.-B. Chen, H.-T. Lin, and T.-H. Lin, "Study of the combustion characteristics of sewage sludge pyrolysis oil, heavy fuel oil, and their blends," *Energy*, **201** 117559 (2020). https://doi.org/10.1016/j.energy.2020.117559
25) D. Mansur, E. Debora, Saepurahman, L. Hauli, W.D. Prasetyo, and Aminuddin, "Comparative study of thermal and catalytic pyrolysis of palm fronds over BEA zeolites extrudate," *AIP Conf Proc* **1** 2902 (2023).
26) S.A. Channiwala and P.P. Parikh, "A unified correlation for estimating HHV of solid, liquid and gaseous fuels," *Fuel*, **81** 1051–63 (2002). https://doi.org/10.1016/s0016-2361(01)00131-4.
27) Y. Zhou, K. Wang, B. Wang, Y. Pu, and J. Zhang, "Occupational benzene exposure and the risk of genetic damage: A systematic review and meta-analysis," B*MC Public Health*, **20** (1) 1–11 (2020). https://doi.org/10.1186/s12889-020-09215-1
28) A.N. Patton, M. Levy-Zamora, M. Fox, and K. Koehler, "Benzene exposure and cancer risk from commercial gasoline station fueling events using a novel self-sampling protocol," *Int J Environ Res Public Health*, **18** (4) 1–14 (2021). https://doi.org/10.3390/ijerph18041872
29) F.X. Collard and J. Blin, "A review on pyrolysis of biomass constituents: Mechanisms and composition of the products obtained from the conversion of cellulose, hemicelluloses and lignin," *Renew Sustain Energy Rev*, **38** 594–608 (2014). http://dx.doi.org/10.1016/j.rser.2014.06.013
30) V.I. Sharypov, N.G. Beregovtsova, B.N. Kuznetsov, L. Membrado, V.L. Cebolla, N. Marin, and J.V. Weber, "Co-pyrolysis of wood biomass and synthetic polymers mixtures. Part III: Characterisation of heavy products," *J Anal Appl Pyrolysis*, **67** (2) 325–40 (2003). https://doi.org/10.1016/s0165-2370(02)00071-2.
31) B. Karunarathna, J.D. Wanniarachchi, M.A.B. Prashantha, and K.K. Govender, "Enhancing styrene monomer recovery from polystyrene pyrolysis: insights from density functional theory," *J Mol Model*, **29** (8) 1–12 (2023). https://doi.org/10.1007/s00894-023-05661-x
32) K. Primerano, J. Mirwald, and B. Hofko, "Asphaltenes and maltenes in crude oil and bitumen: A comprehensive review of properties, separation methods, and insights into structure, reactivity and aging," *Fuel* **368** 131616 (2024). https://doi.org/10.1016/j.fuel.2024.131616.

33) A. Wolak, G. Zajac, and T. Słowik, "Measuring kinematic viscosity of engine oils: A comparison of data obtained from four different devices," *Sensors* **21** (7) 1–15 (2021). https://doi.org/10.3390/s21072530
34) Y. Zhang, Z. Ma, Y. Feng, Z. Diao, and Z. Liu, "The effects of ultra-low viscosity engine oil on mechanical efficiency and fuel economy," *Energies*, **14** (2320) 1-20 (2021). https://doi.org/10.3390/en14082320
35) J.S. Kim and J.H. Choi, "Feasibility study on bio-heavy fuel as an alternative for marine fuel," *Renew Energy*, **219** 119543 (2023). https://doi.org/10.1016/j.renene.2023.119543
36) C.W.C. Hsieh and C. Felby, "Biofuels for the marine shipping sector," *IEA Bioenergy* (2017). https://www.ieabioenergy.com/wp-content/uploads/2018/02/Marine-biofuel-report-final-Oct-2017.pdf
37) D. Mansur, S. Sugiwati, W.A. Rizal, R. Suryani, and R. Maryana, "Pyrolysis of cajuput (Melaleuca leucadendron) twigs and rice (Oryza sativa) husks to produce liquid smoke-containing fine chemicals for antibacterial agent application," *Biomass Convers Biorefinery*, **21** (0123456789) 1–14 (2021). https://doi.org/10.1007/s13399-021-01896-x
38) H.J. Ju and S.K. Jeon, "Analysis of characteristic changes of blended very low sulfur fuel oil on ultrasonic frequency for marine fuel," *J Mar Sci Eng.*, **10** (1524) 1-12 (2022). https://doi.org/10.3390/jmse10091254
39) F. Obeid, T.C. Van, E.J. Horchler, Y. Guo, P. Verma, B. Miljevic, R.J. Brown, Z. Ristovski, T. Bodisco, and T. Rainey, "Engine performance and emissions from fuels containing nitrogen and sulphur," *Energy Convers Manag X*, **14** (100179) 1-11 (2022). https://doi.org/10.1016/j.ecmx.2022.100179