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Research Article

Investigation on Yield of Natural Rubber to Bio-Crude Oil from Hydrothermal Liquefaction Process

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Abstract:
Hydrothermal liquefaction (HTL) requires the presence of water and potentially some catalyst to convert biomass straight to bio-crude oil. In this study, the raw natural rubber is converted to bio-crude oil by the hydrothermal liquefaction process. Experiments are conducted in the autoclave reactor sized of 100 mL at various temperatures ranged between 325-400 °C, with water to natural rubber mass ratios of 1:1 to 5:1, and reacting times of 30-75 minutes. From the investigation, it was found that the highest bio-crude oil yield of 71.4 wt% can be obtained at temperatures of 350 °C, water to natural rubber mass ratios of 4:1, and reacting time of 60 minutes. From the Fourier transform infrared spectroscopy analysis, the major components of the bio-crude oil compound contain high carbon and hydrogen contents which are similar to fossil crude oil in generals. Therefore, it is suggested the synthesis of liquid fuel by the liquefaction process of natural rubber in Thailand is feasible and could be one of the energy potential in the near future.

Keywords: *Hydrothermal liquefaction, Raw natural rubber, Bio-crude oil*

1. Introduction

In the early 20th century, biomass from crops and trees was used as a starting material to produce dyes, solvents, or synthetic fibers. In addition, biochemical and chemical research was promoted to study the production of biofuels from biomass. The thermochemical liquefaction of biomass is the process that has generated the most interest in recent years since it generates higher energy density, requires a shorter reaction period, and can be applied to a wider range of materials [1, 2]. Hydrothermal liquefaction (HTL) is one of the thermochemical process which converts biomass into bio-crude oil at subcritical water condition [3, 4]. Typical operating temperature and pressure are 260–350 °C and 8–20 MPa respectively. At lower temperatures, hydrothermal carbonization is favoured, while at higher temperatures, especially above the critical point of water, favours gasification. One of the most important advantages of this technique is that it can use raw material with high moisture content without the need for pre-drying. Therefore the drying energy and time in preparation the raw material is saved. This process is carried out by introducing water at high temperatures and high-pressure conditions (i.e. steam) to induce the decomposition of long-chain polymers of carbon, hydrogen, and oxygen into small-chain petrochemicals (monomers) [5, 6]. The product generated by this process is called bio-crude, which is equivalent to the renewable oil since it is an energy-dense intermediate that can be upgraded to a variety of liquid fuels [7]. The HTL technique uses the specific characteristics of compressed hot water [8, 9].

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Throughout the HTL process, the biomass undergoes a series of depolymerization reactions such as hydrolysis, dehydration, or decarboxylation, giving rise to insoluble products such as bio-crude oil or bio-carbon. Furthermore, additional byproducts are also composed, including gases (such as CO_2, CO, H_2, or CH_4) and soluble organic compounds (primarily acids or phenols) [2, 10]. Example from reports on bio-oil production costs. Francis et al. analyze the strategy of sawdust waste management via its pyrolysis into bio-oil, with a major focus on economics. The price of the producible bio-oil varied widely between \$9.90/kg and \$4.65/kg for a payback period between 2 and 6 years [11].

It is well know that natural rubber is a very important compound in automobile tires. Usually, the automobile tire consists of 40–52.2% of natural rubber [12, 13]. As an alternative energy, researchers or some industries have already successfully converted damaged tires to crude oil with a high calorific value either by pyrolysis or hydrothermal process. For example, Zhang et al. [14] used a hydrothermal process for damaged tires and showed that the calorific value of oil obtained under optimal conditions was 44.09–45.09 MJ/kg. The heating value of the product is close to the heating value of oil derived from petroleum fuels such as diesel (44.8 MJ/kg) [15]. Natural rubber is an organic polymer compound consisting of isoprene and polyisoprene (C_5H_8), along with small amounts of other impurities and water [16]. Thailand is one of the major producer of natural rubber in the world, which produces around 693 ton/year of raw rubber sheet [17]. Sometime, the supply is much over the demand and forces to a very low price in the market. One possibility to give a value-added to the natural rubber is to find the new path way for higher value product such as bio-oil or bio-fuel. Therefore, this research aims to investigate the yield of bio-crude oil from hydrothermal liquefaction process of natural rubber. Effect of variables, which are temperature solvent/material mass ratio, and reacting time on the resulting product yield are examined. Also, the functional group of C-H of the resulted bio-crude oil (BCO) is analysed. So far, there is no available literature discussing on the depolymerization of natural rubber to bio-crude oil using the hydrothermal liquefaction technique, especially the natural rubber sample from Thailand.

2. Experimental Setup

2.1 Raw Material

The natural rubber (NR) or raw sheet used in this study was obtained from the rubber sheet in Det Udom District in Ubon Ratchathani Province, Thailand. The rubber tree is PRIM 600 strain which is the post popular strain grown in Thailand. Then, the raw sheet was cut into small cubes sized 3-5 mm as shown in Fig. 1. Thermogravimetric analysis (TGA) of this NR was analyzed and used to characterize the natural rubber and design for the experimental temperature ranges. Also, the ultimate and proximate analysis of the NR were carried out to realize the initial properties of this raw material and estimate the possible results.

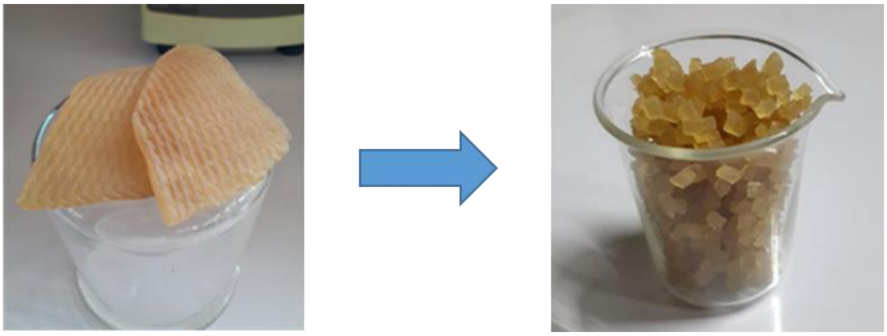

Fig. 1. Small pieces natural rubber or raw sheet as raw material.

2.2 Experimental Methods

The HTL testing was carried out in a batch Ni-alloy reactor with a volume of 100 mL and an inner diameter of 25 mm. Reactor is heated by a 3.0 kW electric heater and its temperature is automatically controlled by the temperature switch. The built-in pressure sensor was also used to monitor and detected the overpressure release and also provided feedback on the operating pressure [18]. The schematic of the HTL reactor and its instrumentation are shown in

Fig. 2. Initially, to conduct the experiment, the natural rubber was weighted and mixed with the water (deionized water). Then, nitrogen gas was used to purge the reactor for 5 minutes, and fill to set the beginning pressure at 0.2 MPa. Them the reactor is heated at a heating rate of 10 °C/min, in all experiments, resulting in a spontaneous pressure increase to the range of 6.0–15 MPa.

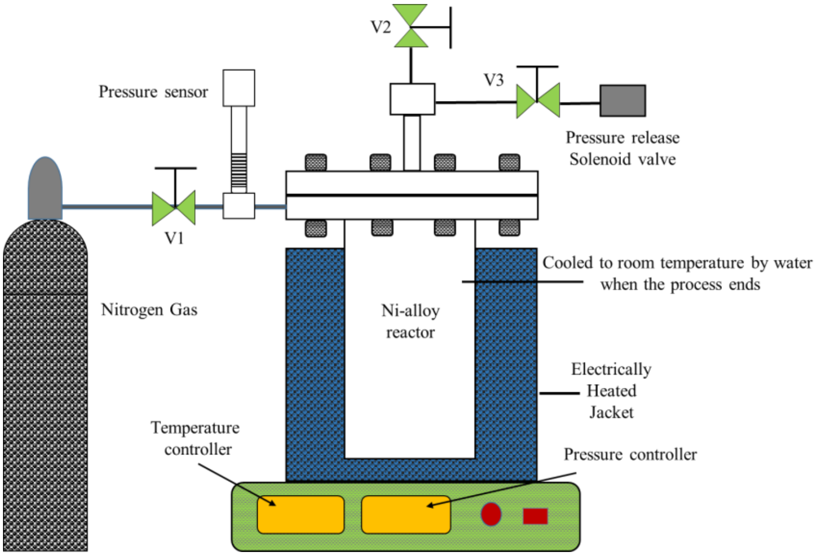

Fig. 2. Schematic of the experimental setup for production

When the reaction ended, the reactor was quickly cooled to near room temperature by putting in a water tub. After that, release gas in the reactor leaves freely without being analyzed. Moreover, dichloromethane (DCM) was utilized to extract bio-oil from the solid residue and subsequently washed onto the inner surface of the reactor. The products in liquid and solid forms were taken out of the reactor and then distinguished through the process of filtration. Afterwards, the reactor was cleansed using 100 mL of DCM to remove any residual reaction products that could be adhering to the inner surface of the reactor. The water-based product was isolated from the DCM solution through the use of a separatory. Ultimately, the solid remains resulting from the filtration and DCM processes were subjected to dehydration at 105 °C for a duration of 12 hours. Weighing each component of the product was conducted to determine the yield, as illustrated in Fig. 3, depicting the steps of the separation process. The conversion and BCO yields were calculated according to Eq. (1)-(3), respectively.

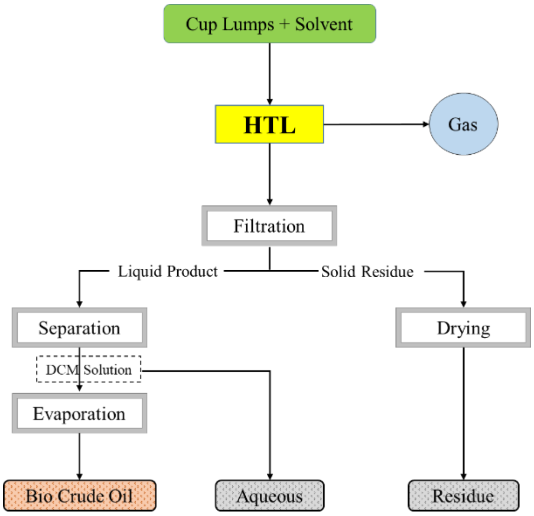

Fig. 3. Bio oil and residue separation procedure diagram

$$Yield_{oil}\,(\%) = \frac{W_{oil}}{W_{NR}} \times 100 \tag{1}$$

$$Conversion\,(\%) = \left[1 - \frac{W_{SR}}{W_{NR}}\right] \times 100 \tag{2}$$

$$Yield_{Wsp+Gas} = \left[1 - \frac{W_{oil} + W_{SR}}{W_{NR}}\right] \times 100\% \tag{3}$$

The determination of yield involved the utilization of Eq. (1) to ascertain the proportion of solid fuel transformed into liquid and gaseous products as dictated by Eq. (2). Additionally, the quantification of the yield of the water-soluble product W_{sp} was conducted through its separation from the dichloromethane (DCM) solution, employing a separatory funnel by Eq. (3).

2.3 Feedstock and Product Analysis

A CHNS/O analyzer model 2400 was utilized to perform an elementary analysis of the feedstock or raw material. The proximate analysis of the feedstock was carried out using the standard methods, ASTMD 3173 and ASTMD 3175. The Rigaku Thermo Plus 2 TG-DTA TG8120 model was utilized for conducting the thermogravimetric (TGA) analysis. The objective of this analysis is to investigate the bio crude oil composition. Product differentiation was achieved using the CHNS-628 apparatus from LECO Corporation, employed for elemental (CHNS) analysis to determine the carbon, hydrogen, nitrogen, and sulfur contents in the bio-crude oil samples. Additionally, the Thermo Scientific Nicolet 6700 FT-IR Spectrometer was utilized for Fourier-transform infrared (FTIR) spectroscopy, scanning the samples across the range of 450 to 4000 cm^{-1} with an 8 cm^{-1} resolution.

3. Results and Discussions

3.1 Characterization of Feedstock

Proximate and ultimate analyses analysis of raw material is essential for information on chemical composition and composition. Table 1 shows the proximate and ultimate analysis of the sample natural rubber. The proximate analysis consists of volatile matter, fixed carbon, ash, and moisture content. In determining the total volatile matter, From Table 1, it can be seen that the volatile matter in the natural rubber is very high being at 98.83% while the fixed carbon ash and moisture contents in natural rubber are very low which are 0.06%, 0.18%, and 0.93% respectively. Moreover, in the ultimate analysis it shows that the natural rubber consists of high hydrocarbons as it is pure poly-isoprene. The carbon and hydrogen contents in natural rubber have been estimated to be 85.46% and 10.92% respectively. High amounts of carbon and hydrogen have a positive effect on the high heating value (HHV) of the bio-crude oil. From these properties, the natural rubber is very promising and suitable as potenial raw material for the production of liquid bio-crude oil.

Table 1: Proximate and ultimate analysis of natural rubber

Characteristic	**Amount**
Proximate analysis (wt%)	
Volatile matter	98.83
Fixed carbon	0.06
Ash	0.18
Moisture content	0.93
Ultimate analysis (wt%)	
Carbon	85.46
Hydrogen	10.92
Nitrogen	0.37
Oxygen	3.22
Sulfur	0.03
HHV (MJ/kg)	43.46

* CHN: Application note No. 203-821-485 According to the LECO method.,
S: Application note No. 203-821-466 According to the LECO method.

3.2 Thermogravimetric Analysis (TGA) of Raw Material

The thermogravimetric analysis (TGA) was performed to get an overview of the thermal behaviour of the raw material. As shown in Fig. 4, the thermal degradation of natural rubber begins at approximately at 50 °C, and this is followed by a distinct decomposition phase occurring within the temperature range of 200 to 400 °C. According to this test results, more than 95% of natural rubber was degraded or mass lost within the temperatures of 400 °C. TGA analysis indicates that there is a high mass loss at temperatures between 325–400 °C, which indicates the optimum temperature for increasing the conversion efficiency of natural rubber into liquid products. The same study has been reported by Ahmad et al. [19]. The technique has been effectively utilized to convert natural rubber into liquid fuels.

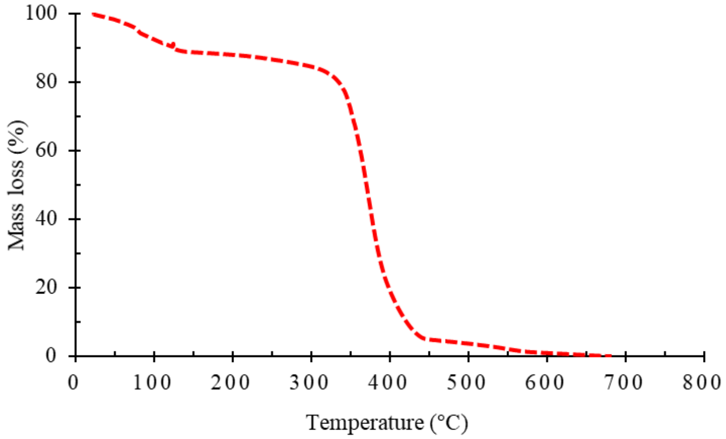

Fig. 4. Relationship between temperature and mass loss from the TGA analysis

3.3 Effect of Operating Parameters on Products

3.3.1 Effect of Temperature

In this study, the operating time and the mass ratio of H_2O/NR were fixed at 60 minutes and 1:1, 3:1 in order. Whereas, based on the TGA result, the temperature was varied at 325, 350, 375, and 400 °C to observe their effect on product yield. In Fig. 5, it can be observed that the yield of the liquid product increased from 20.65 to 67.59 wt% as the temperature was raised from 325 to 375 °C. However, higher temperature increments did not result in a notable increase in crude oil yield. As a result, the yield of the crude output from the soluble fraction exhibited an upward trend with the temperature increasing up to 375 °C, but thereafter, a decrease in crude yield was observed.

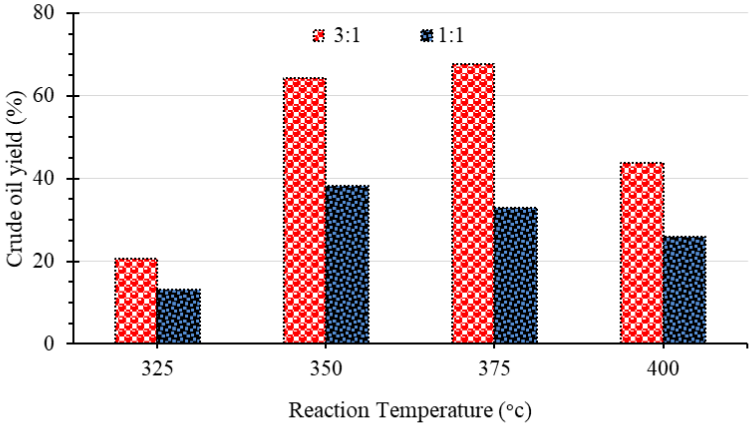

Fig. 5. Effect of temperature on crude oil yield.

3.3.2 Effect of Liquid to Natural Rubber Weight Ratios

Normally, in hydrothermal liquefaction, the introduction of water resulted in a milder conversion process compared to the direct pyrolysis of biomass. In this research, the impact of various H_2O/NR mass ratios was altered across ranges of 1:1, 2:1, 3:1, 4:1, and 5:1, accompanied by corresponding pressures of 7, 8, 9, and 10 MPa. The temperature were set at 350 and 375 °C, while the time was maintained at 60 minutes. It was observed that the enhancement in crude oil production displayed a linear trend when the water ratio was increased from 1:1 to 3:1 and subsequently to 4:1. Fig. 6 illustrates that the highest crude oil yield of 71.4 wt% was achieved when employing a mass ratio of H_2O/NR 4:1 and a reaction time of 60 minutes at 350 °C.

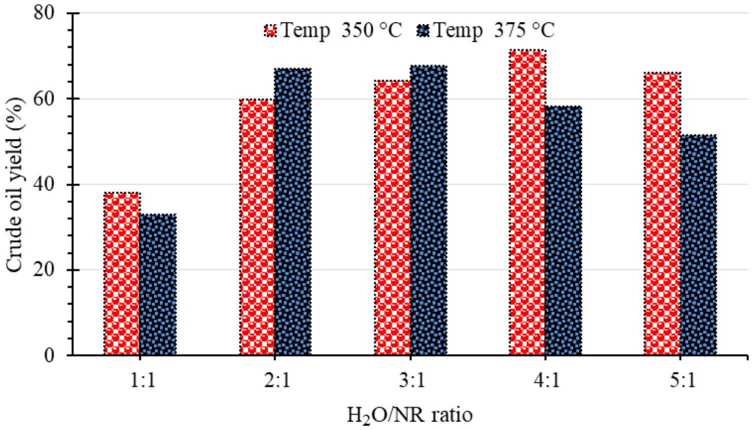

Fig. 6. Effect of water to natural rubber mass ratio on crude oil yield.

3.3.3 Effect of Reaction Time

To find out the optimum reaction time, the effect of reaction time on the product yield was carried out at 350 °C and with the H_2O/NR mass ratio of 4:1, while the reaction time varied from 30 to 75 min. From Fig. 7, it was observed that liquefaction continued to increase with the reaction time between 45 minutes and 60 minutes.The reaction time of 60 minutes at 350 °C was found to enable polymerization in NR for the liquid product at 71.4 wt%.

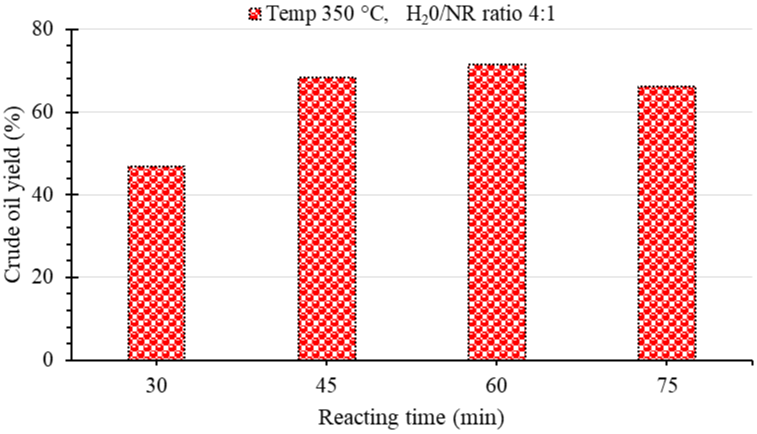

Fig. 7. The variation reacting time on crude oil yield.

3.3.4 Influence of Process on Relative Products

In the context of hydrothermal liquefaction, incorporating water resulted in a more gentle transformation compared to the direct pyrolysis of biomass. The products obtained from the liquefaction process can be divided into three main groups: bio-crude oil, residue, water-soluble, and gas. Throughout this investigation, explored the impact of varying H_2O/NR mass ratios, was varied at 1:1, 2:1, 3:1, 4:1, and 5:1. The phenomenon is attributed to the presence of water in the process, wherein water, acting as a nucleophile, contributes to an elevated concentration of nucleophiles as the H_2O ratio in NR increases [20]. In Fig. 8, as the H_2O/NR mass ratio moderately increased from 2:1 to 4:1, a decrease in both water-soluble and gas-soluble amounts was observed. However, a subsequent increase in the H_2O/NR mass ratio did not exhibit a notable impact on gas yield. Additionally, the variation in H_2O/NR mass ratio did not significantly affect the water-soluble fraction, with the highest yield of 71.4 wt% achieved at an H_2O/NR mass ratio of 4:1.

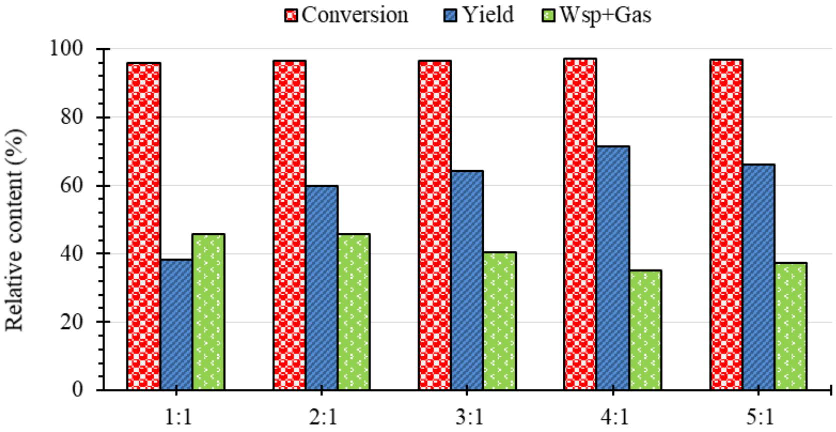

Fig. 8. Effect of H_2O/NR mass ratios on relative products.

3.4 Characterization of Liquid Products

3.4.1 Characterization of Bio-Crude Oil

The analytical results of bio-crude oil obtained by thermal liquefaction are shown in Table 2. The substantial quantities of hydrocarbons in natural rubber are crucial, as these serve as significant raw materials in the creation of liquid products rich in carbon and hydrogen content. Elemental analysis indicated that bio-crude oil has significant weight percentages of carbon and hydrogen, amounting to 85.10 wt% and 11.08 wt%, respectively.

Table 2: Ultimate analysis of bio-crude oil

Characteristic	**Raw sheet**	**SMR [17]**
Ultimate analysis (wt%)		
Carbon	85.10	84.62
Hydrogen	11.08	12.11
Nitrogen	0.30	0.41
Oxygen	3.47	2.67
Sulfur	0.06	0.19
HHV (MJ/kg)	43.78	43-45

* CHN: Application note No. 203-821-485 According to the LECO method.,
S: Application note No. 203-821-466 According to the LECO method.

3.4.2 Fourier Transform Infrared Spectroscopy (FTIR)

In this section, the FTIR analysis on the liquid product obtained under the optimal conditions of 350 °C, H_2O/NR mass ratio of 4:1 and 60 minutes is performed. As shown in Fig. 9, the FTIR result reveals distinct features in the fingerprint region of the bio crude oil sample, which indicates a range of approximately 814–885 cm^{-1}, indicative of C-H bending assignments. The detection of a peak around 1,374 cm^{-1} in an infrared (IR) spectrum typically suggests the presence of compounds that are commonly associated with the bending vibrations of methyl (CH_3) groups. In IR spectroscopy, a peak at 1,454 cm^{-1} signifies methylene (CH_2) group bending vibrations, known as the methylene scissoring peak, indicative of CH_2-containing compounds. The alkyl bond types, specifically the methyl and methylene groups, were discerned by observing peaks at 2,865 cm^{-1} and 2,921 cm^{-1}, respectively. This bio crude oil sample consists of an alkyl bond, specifically the methyl and methylene groups. The presence of this functional group indicates the presence of hydrocarbons in the bio-fuel. The same functional groups have also been reported by other studies [19, 21].

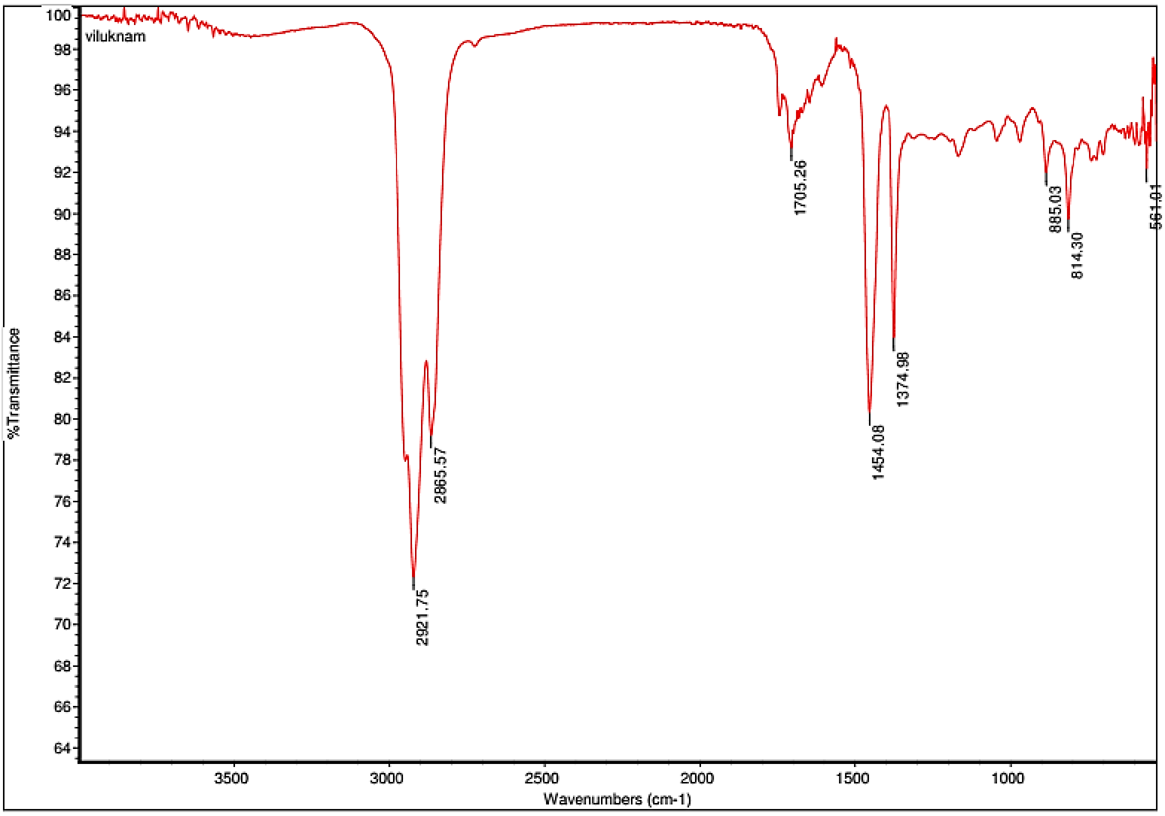

Fig. 9. FTIR spectrum crude oil.

3.5 Operating Costs of Bio-Crude Oil Production

The cost of producing bio-crude oil will be divided into the expenses incurred for energy and the chemicals utilized in the production process. The production cost was compared with the results of the experiment that yielded the highest amount of bio-crude oil. The highest product proportion was 71.4 wt%. The production costs shown in this study mainly arise from electrical energy and chemicals. The operation of heating the reactor, the cost was 6.27 baht and for chemicals it was 22.50 baht, as shown in Table 3. The total cost used to produce the highest product, 71.4 wt%, is 28.99 baht.

Table 3: Operating costs of bio-crude from natural rubber.

List	**Costs (Baht)**
Electricity of reactor (1.5 kW x 1 h)*	6.27
Chemical costs (DCM 150 mL)	22.50
Raw sheet costs (5 g.)**	0.22
Total bio-crude oil costs (yield at 71.4 wt%)	28.99
BCO/g.	8.12

*Electricity rates for 2023 are 4.18 baht per unit.

**Raw sheet rates for 2023 are 44.50 baht per kg.

4. Concluding Remark

The present study successfully investigates the yield and relative products from the hydrothermal liquefaction of natural rubber in Thailand. The experiment was performed in the laboratory scale batch reactor. The results of the TGA analysis showed that the temperature between 350–400 °C, was the optimum temperature for converting natural rubber to bio-crude oil. From various operation parameters, it was found that at reaction temperature 350 °C, the mass ratio of H_2O/NR at 4:1 the reaction time 60 minutes gave the highest bio-crude oil yield at 71.4 wt% which is considerably high. It was found that the cost used to produce bio-crude oil per gram was 8.12 baht.

The ultimate analysis of bio-crude oil has high carbon and hydrogen contents, while the FTIR showed good composition of various CH group. Therefore, this bio-crude oil has high potential in term of quality and energy content. It can be directly used as fuel in the burner or further refined to the higher-grade biofuel in the next process if required. Moreover, in the future, if the production process is further developed to be continuous and utilizes lower production costs, it could potentially increase the practical applicability of this technology.

Acknowledgments

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Nomenclature

NR	Natural rubber
$Yield_{oil}$	Bio-crude oil yield (%)
W_{oil}	Weight of bio crude oil (g).
W_{NR}	Weight of natural rubber feedstock (g)
W_{SR}	Weight of solid residue (g)
W_{sp}	Water-soluble product (g)
SMR	Malaysian Standard Rubber
DCM	Dichloromethane
TGA	Thermogravimetric analysis
FTIR	Fourier transform infrared spectroscopy

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