Synthesis of Bio-hexane and Bio-Hexene from Sorbitol Using Formic Acid as Reducing Agent

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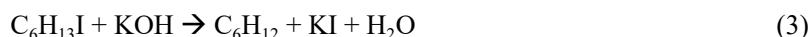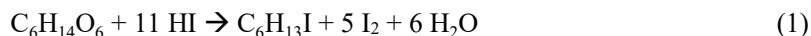*E-mail: t.hudaya@unpar.ac.id

Highlights:

- 2-iodohexane as precursor for bio-hydrocarbon synthesis was successfully synthesized from sorbitol by using formic acid as reductant and hydroiodic acid as intermediate reducing agent.
- In the 2-iodohexane synthesis, a higher molar ratio of HI/sorbitol resulted in a higher 2-iodohexane yield but slightly lower sorbitol conversion.
- In the 2-iodohexane synthesis, a longer reaction time resulted in a higher 2-iodohexane yield but no significant increase in sorbitol conversion.
- In the 2-iodohexane synthesis, the reactions carried out at 105 °C gave the highest 2-iodohexane yield, while the highest sorbitol conversion was achieved at 120 °C.
- Gas phase pyrolysis could effectively convert 2-iodohexane to bio-hydrocarbons consisting of alkanes and alkenes with optimum temperature at 285 °C for 45 min and with a bio-hydrocarbon yield of 77.52%.

Abstract. Sorbitol ($C_6H_{14}O_6$) is a sugar alcohol that can be synthesized from cellulose and has a similar skeletal structure as hexane (C_6H_{14}) so that it can straightforwardly be converted to hexane through deoxygenation. The bio-hydrocarbon synthesis from sorbitol in this investigation consisted of two main processes, namely synthesis of 2-iodohexane and deiodization of 2-iodohexane. The synthesis of 2-iodohexane from sorbitol and hydroiodic acid (HI) was conducted in a reflux system, to which formic acid as reducing agent was added gradually during the reaction to regenerate the iodine back to HI. The HI/sorbitol ratio (2:1 and 5:1), reaction temperature (90 °C, 105 °C, and 120 °C), and reaction time (between 2 and 6 hours) were varied throughout the experiment. Deiodization of 2-iodohexane was conducted via gas phase pyrolysis at various temperatures (265 °C to 285 °C) and reaction times (30 and 45 minutes). The sorbitol was effectively converted to a mixture of 2-iodohexane, hexane and other bio-hydrocarbons, with a 2-iodohexane yield of 23.15%. In the optimal reaction condition, pyrolysis of 2-iodohexane resulted in bio-hydrocarbon with a yield of 77.52%. The resulted hydrocarbon products were mixtures consisting of alkanes and alkenes.

1   Introduction

Fossil-based liquid fuels have been receiving increased attention in recent years because their consumption outpaces their production rate and because of the negative impact of greenhouse gas emissions. These problems encourage the interest in developing alternative fuels from renewable resources around the world. In Indonesia, one of the developments in looking for alternative fuels is the utilization of lignocellulosic biomass. Biomass-based bio-hydrocarbon is suitable to be utilized as fossil fuel replacement because it is carbon-neutral and biomass raw material is abundantly available [1]. Sorbitol ($C_6H_{14}O_6$) is a sugar alcohol that can be obtained by catalytic hydrogenation of D-glucose derived from starch and cellulose [2], and has a similar skeletal structure as hexane (C_6H_{14}). Bio-hexane therefore can be obtained through hydrodeoxygenation of sorbitol. Robinson [3,4] has executed this conversion through two main stages, namely 2-iodohexane synthesis and 2-iodohexane deiodization. In 2-iodohexane synthesis, sorbitol is reacted with hydroiodic acid at 117 °C for 2 hours resulting in 2-iodohexane ($C_6H_{13}I$) and iodine (I_2). Eq. (1) shows the reaction between sorbitol and hydroiodic acid. Red phosphorus as reducing agent is simultaneously fed with the sorbitol to regenerate the iodine produced from the previous reaction to form hydroiodic acid. The regeneration of hydroiodic acid shown in Eq. (2) occurs simultaneously with the 2-iodohexane synthesis. Subsequently, in the 2-iodohexane deiodization process, 2-iodohexane will be reacted with potassium hydroxide (KOH) at 136 °C for 30 minutes resulting in 1-hexene, as shown in Eq. (3).

$$C_6H_{14}O_6 + 11\ HI \rightarrow C_6H_{13}I + 5\ I_2 + 6\ H_2O \tag{1}$$

$$I_2 + H_2O + H_3PO_3 \rightarrow H_3PO_4 + 2\ HI \tag{2}$$

$$C_6H_{13}I + KOH \rightarrow C_6H_{12} + KI + H_2O \tag{3}$$

The above Robinson scheme for bio-hydrocarbon synthesis from sorbitol utilizes expensive chemicals such as red phosphorus and potassium hydroxide, which in the end will make the process economically unfeasible. In order to curtail the production cost, our investigation used much cheaper formic acid (HCOOH) as HI regenerating agent to replace red phosphorus. Also, during the HI regeneration, formic acid is oxidized to gaseous CO_2, thus simplifying the purification of the liquid reaction product. Gas phase pyrolysis of 2-iodohexane was also explored in this research, to eliminate the use of potassium hydroxide and also to design a zero-waste process, as will be described below.
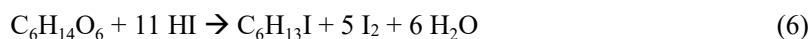
Eq. (4) shows the reaction between iodine and formic acid, forming carbon dioxide (CO_2) and hydroiodic acid [5-8].

$$I_2 + HCOOH \rightarrow CO_2 + 2\ HI \tag{4}$$

Studies on gas phase pyrolysis of iodoalkane have been published in [9-12]. The gas phase pyrolysis of 2-iodopropane and 2-iodobutane produces alkanes as well as alkenes. Eq. (5) shows the reaction that occurs during the gas phase pyrolysis of iodoalkanes, with n is the number of carbon atoms in the carbon chain.

$$2\ C_nH_{(2n+1)}I \rightarrow C_nH_{(2n)} + C_nH_{(2n+2)} + I_2 \tag{5}$$
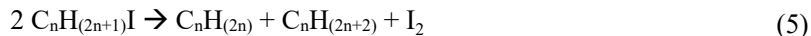
Therefore, all of the reactions that occurred in this research are shown by the equations below.

$$C_6H_{14}O_6 + 11\ HI \rightarrow C_6H_{13}I + 5\ I_2 + 6\ H_2O \tag{6}$$

$$I_2 + HCOOH \rightarrow CO_2 + 2\ HI \tag{7}$$

$$2\ C_6H_{13}I \rightarrow C_6H_{12} + C_6H_{14} + I_2 \tag{8}$$

With proper stoichiometric manipulation, Eq. (9) shows that an overall zero waste process will be obtained:

$$2\ C_6H_{14}O_6 + 11\ HCOOH \rightarrow C_6H_{12} + C_6H_{14} + 11\ CO_2 + 6\ H_2O \tag{9}$$
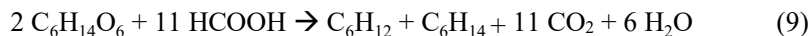
The objective of this study was the synthesis of an alternative fuel, i.e. hexane and hexene, from sorbitol by using formic acid as reducing agent and gas phase pyrolysis as an alternative deiodization method. This study particularly investigated the effect of reaction temperature, reaction time and HI/sorbitol molar ratio on the yield in the 2-iodohexane synthesis process. In addition, the effect of reaction temperature and reaction time on the yield of bio-hydrocarbon in the deiodization process was also investigated.

2   Experimental Setup

2.1   Materials and Methods

The sorbitol powder (Sigma Aldrich, US), hydroiodic acid solution (Merck, Germany), and formic acid solution (Merck, Germany) used in this study were analytical reagent (AR) grade with a purity of 99%, 57% and 98%, respectively. The methylene chloride (Brataco Chemicals, Indonesia) used was commercial-grade.

The synthesis of 2-iodohexane process was carried out in a 500-mL three-neck flask under nitrogen atmosphere. Sorbitol and hydroiodic acid at a specific molar ratio were added to a three-neck flask. The mixture was then heated and kept

boiling with a reflux system (Figure 1). Nitrogen as inert gas was injected continuously into the system during heating until the mixture temperature was about 40 °C. Formic acid was gradually fed in excess amount into the flask during the reaction through a dropping funnel (part A) to ensure that all of the iodine completely regenerated to hydroiodic acid. The HI/sorbitol molar ratio was varied from 2:1 to 5:1, the reaction temperature was varied at 90 °C, 105 °C and 120 °C. The reaction time was varied at 2 and 6 hours. The mixture was agitated using a magnetic stirrer for the purpose of homogenization.
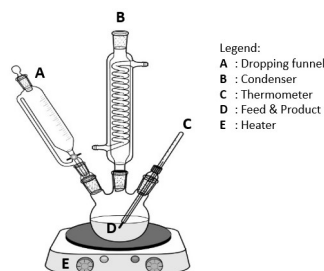

Legend:
A : Dropping funnel
B : Condenser
C : Thermometer
D : Feed & Product
E : Heater

Figure 1 Equipment setup for 2-iodohexane synthesis process.

After the reaction was finished, the mixture was cooled to ambient temperature and then transferred to a separatory funnel and extracted with methylene chloride (CH_2Cl_2). The upper layer (hydrocarbon layer) was isolated from the lower layer and transferred into the distillation system to isolate the 2-iodohexane from the methylene chloride. The 2-iodohexane deiodization process was carried out in a stainless-steel batch reactor (Figure 2).
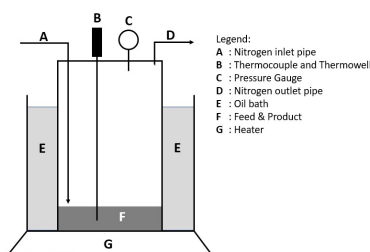

Legend:
A : Nitrogen inlet pipe
B : Thermocouple and Thermowell
C : Pressure Gauge
D : Nitrogen outlet pipe
E : Oil bath
F : Feed & Product
G : Heater

Figure 2 Equipment setup for the 2-iodohexane deiodization process.

The 2-iodohexane produced in an earlier stage was fed into the reactor and then the air in the reactor was purged using nitrogen gas through an inlet-outlet pipe (parts A and D). A leak test was performed to make sure that the reactor was completely airtight. The mixture was then heated up to the reaction temperature by using a heater and oil bath system (parts E and G) and then kept for a certain reaction time. To study the effect of the reaction conditions on the yield of bio-

hydrocarbon produced, the reaction temperature was varied at 265, 270, 275, 280 and 285 °C, while the reaction time was varied at 30 and 45 minutes.

After the reaction was finished, the mixtures were cooled to ambient temperature to condense all the bio-hydrocarbon produced. The iodine produced was separated from the bio-hydrocarbon product using filtration and then the product was analyzed to determine the bio-hydrocarbon yield. The overall process flow is shown in Figure 3.

2.2   Analysis Methods

The aqueous phase obtained from 2-iodohexane synthesis was analyzed quantitatively and qualitatively with a Hitachi (L-2000 type) High Performance Liquid Chromatograph (HPLC) equipped with an Aminex HPX-87H column with a sulfonate (hydrogen form) matrix. Sulfuric acid (H_2SO_4) solution 0.005 N was used as the mobile phase. The flow rate of the mobile phase was maintained at 0.6 mL/min by the column temperature at 65 °C [13]. A relative index detector was attached to measure what amount of each compound passed the detector during a certain retention time. The concentration of each compound is known by comparing its peak area with the standard. Each sample was analyzed 2 times and the average was taken as the final result.
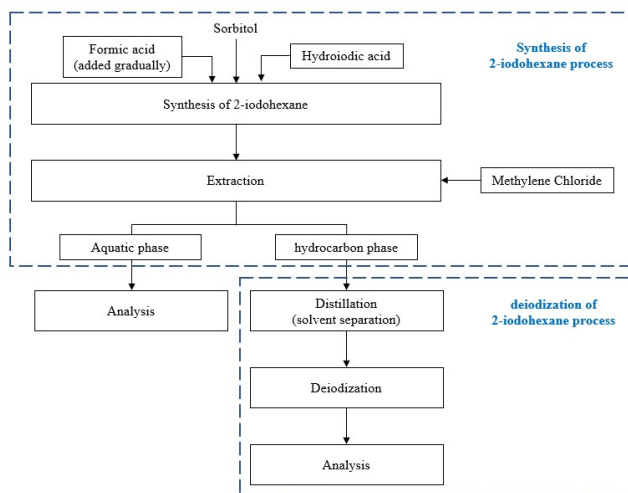
Figure 3   Overall process flow.

The bio-hydrocarbons produced from the 2-iodohexane de-iodization process were analyzed qualitatively by a Fourier transform infra-red spectroscope (FTIR) made by Shimadzu (IRAffinity-1S type) with a zinc selenide cuvette. The settings

for the number of scans and resolution used were 32 and 4, respectively. The bio-hydrocarbons produced were dissolved in methylene chloride of analytical reagent (AR) grade to ensure that the mixture covered the whole surface of the crystal in the cuvette. The spectra of the mixture were compared with the spectra of the solvent to eliminate peaks associated with the solvent.

3 Result and Discussion

3.1 2-Iodohexane Synthesis

Through some preliminary studies, the process variables to be studied were selected. The molar ratio between HI and sorbitol was varied to study the possibility of using less hydroiodic acid. The reduction of hydroiodic acid usage is highly favorable not only because it is costly but also because excess iodine ion (I^-) in the solution may react with iodine (I_2) resulting in triiodide ions (I_3^-), which hinder iodine (I_2) reduction by formic acid because the formate ions can only react with free-I_2 form [5]. The reaction temperature of the 2-iodohexane synthesis process was varied to find the optimum reaction temperature. A higher temperature can speed up the reaction but at the same time bring about a side reaction with sorbitol, which reduces the reaction's selectivity.

The experimental results of the 2-iodohexane synthesis process, i.e. sorbitol conversion, 2-iodohexane yield as well as 2-iodohexane selectivity, are shown in Table 1.

Table 1 Experimental result of 2-iodohexane synthesis.

Temperature (°C)	Molar Ratio (HI/sorbitol)	Reaction Time (hrs)	Conversion (%)	Yield (%)	Selectivity (%)
90	2	2	79.59	10.59	13.31
90	2	6	81.41	15.46	18.78
90	5	2	62.44	11.27	17.88
90	5	6	67.98	17.01	25.02
105	2	2	95.70	14.50	15.15
105	2	6	96.15	18.05	18.99
105	5	2	82.63	14.77	18.05
105	5	6	87.04	23.15	26.60
120	2	2	96.78	11.58	11.96
120	2	6	97.26	12.31	12.66
120	5	2	78.33	11.77	15.03
120	5	6	82.58	20.64	24.99

The experimental results in Figure 4 show that HI/sorbitol molar ratio, reaction temperature and reaction time affected the 2-iodohexane yield. The higher the HI/sorbitol molar ratio, the higher the yield of 2-iodohexane. This is because a higher concentration of reagent increases the 2-iodohexane synthesis reaction rate and more HI promotes the formation of halocarbons [14-17]. The reaction conducted for 2 hours did not give significant 2-iodohexane yield differences for a higher HI/sorbitol molar ratio at every reaction temperature. A similar increase in yield as due to an increased molar ratio of HI/sorbitol was also found in the research by Lv, *et al.* [14].

The reaction time significantly influenced the 2-iodohexane yield for every HI/sorbitol molar ratio and reaction temperature, except at 120 °C and a HI/sorbitol molar ratio of 2:1. The longer the reaction time, the more 2-iodohexane could be obtained. Increasing the reaction time from 2 to 6 hours resulted in an increase of the 2-iodohexane yield, i.e. from 11.27 to 17.01%; 14.77 to 23.15; and 11.17 to 20.64% for a HI/sorbitol molar ratio of 5:1 at a reaction temperature of 90, 105 and 120 °C, respectively. The effect of reaction time on yield is confirmed by the experiment conducted by Lv, *et al*. [14], which gave a significantly increased yield due to a longer reaction duration.
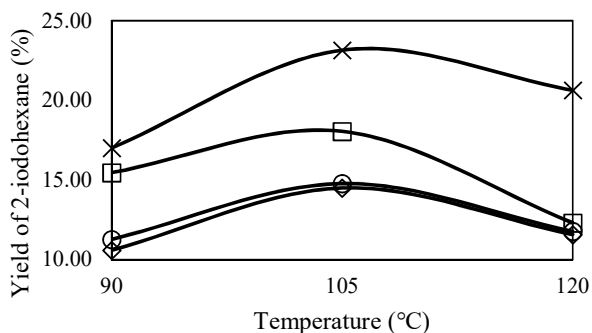

Figure 4 Yield of 2-iodohexane in various operating conditions.

Legend: ◊ = HI/sorbitol 2:1, 2 hrs; □ = HI/sorbitol 2:1, 6 hrs; o = HI/sorbitol 5:1, 2 hrs; ×= HI/sorbitol 5:1, 6 hrs

However, a higher temperature (120 °C) and a higher sorbitol concentration did not have a significant effect with a tripled reaction time. This result indicates the important influence of the side reactions mentioned earlier. Increasing the reaction time three-fold improved the yield only slightly due to selectivity. If no side reactions existed, a tripled reaction time would increase the reaction yield more significantly.

The reaction temperature gave the greatest 2-iodohexane yield at 105 °C and the lowest 2-iodohexane yield at 90 °C. The increase in temperature from 105 to 120 °C resulted in a deficiency in the yield of 2-iodohexane. This phenomenon may be explained by the fact that sorbitol can be dehydrated into 1,4-sorbitan and 3,6-sorbitan by the action of acid at high temperature [2], thus the amount of convertible sorbitol to form 2-iodohexane decreases. The optimum reaction condition was obtained with a HI/sorbitol molar ratio of 5:1 at 105 °C for 6 hours with a 23.15% yield of 2-iodohexane.

The 2-iodohexane yielded by these experiments was below the yield achieved by Robinson, *et al.* in [3,4], which was 99% of 2-iodohexane with an HI/sorbitol molar ratio of 5:1 and 20 hours of reaction time and temperature ranging between 110 °C and 127 °C. Robinson's optimum condition was different from this research's finding due to the different type of reductant involved. In this research, fomic acid was used instead of phosphoric acid. Phosphoric acid has stronger reducing capability compared to formic acid because phosphoric acid has a standard reduction potential of –0.276 V, whereas formic acid has a reduction potential of –0.199 V [18]. The weaker reduction capability of formic acid compared with phosphoric acid leads to a reduction of iodine (Eq. (4)) that is much slower than its production rate (Eq. (1)), which makes the overall process slower than Robinson's.

As presented in Figure 5, the HI/sorbitol molar ratio affected the sorbitol conversion significantly, i.e. a higher HI/sorbitol molar ratio resulted in a lower sorbitol conversion.
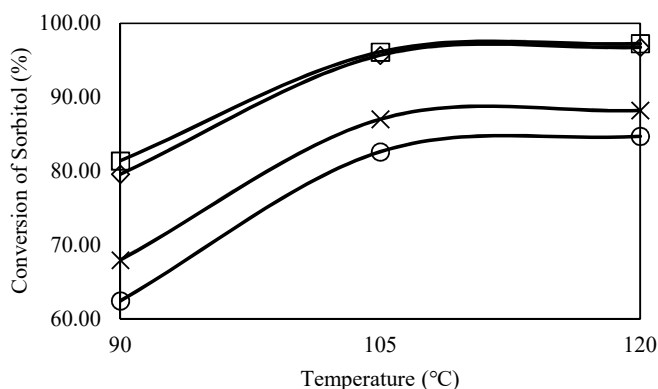

Figure 5 Conversion of sorbitol in various operating conditions.

Legend: ◊ = HI/Sorbitol 2:1, 2 hrs; □ = HI/Sorbitol 2:1, 6 hrs; o = HI/Sorbitol 5:1, 2 hrs; × = HI/Sorbitol 5:1, 6 hrs

A longer reaction time resulted in higher sorbitol conversion with a HI/sorbitol molar ratio of 5:1 but it did not do so at a 2:1 HI/sorbitol molar ratio. This phenomenon most likely occurs because the reaction equilibrium has been reached within 2 hours at a 2:1 HI/sorbitol molar ratio, so a longer reaction time no longer has an effect. At a 5:1 HI/sorbitol molar ratio, the reaction equilibrium is reached in more than 2 hours because the reaction rate is slower than at a 2:1 HI/sorbitol molar ratio.

During the reaction, the color of the reaction mixture became darker over time and after some time a small amount of I_2 crystal was formed in the reactor. This phenomenon may be caused by iodine (I_2) accumulation in the mixture. The brown color of the mixture indicates dissolved iodine in the water, thus the darker mixture indicates an increase of dissolved iodine. The dissolved iodine is accumulated because the rate of iodine reduction to hydroiodic acid (Eq. (4)) is not fast enough to equalize the rate of iodine production (Eq. (1)). According to Kimura [5], the rate of iodine reduction to hydroiodic acid is slow due to the very low pH of the mixture. Thus, pH adjustment by adding basic formate salt (e.g. potassium formate) or catalyst may be required to increase the rate of iodine reduction back to HI so it can catch up with the iodine production rate.

The experimental results in Figure 6 show that the HI/sorbitol molar ratio as well as the reaction temperature affected the selectivity of the 2-iodohexane significantly.
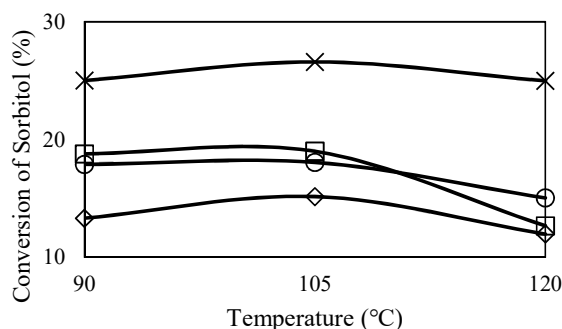

Figure 6 Selectivity of 2-iodohexane in various operating conditions.

Legend: ◊ = HI/Sorbitol 2:1, 2 hrs; □ = HI/Sorbitol 2:1, 6 hrs; o = HI/Sorbitol 5:1, 2 hrs; × = HI/Sorbitol 5:1, 6 hrs

The optimum temperature which gave the highest 2-iodohexane selectivity was 105 °C. The reaction conducted at 120 °C gave the lowest selectivity among all

temperatures. This phenomenon is caused by side reactions that occur more rapidly at higher temperatures. This observation was confirmed by the conversion of sorbitol, which increased at 120 °C but was not followed by a 2-iodohexane yield increase.

An increase of the HI/sorbitol molar ratio resulted in a higher 2-iodohexane selectivity. This is because the availability of HI in the mixture increases as result of the increasing HI/sorbitol molar ratio. The higher HI concentration in the mixture makes the rate of the sorbitol reduction reaction increase. This phenomenon occurs not only at a higher HI/sorbitol molar ratio but also at a longer reaction duration. A longer reaction duration also made the selectivity of 2-iodohexane higher.

3.2 2-Iodohexane De-Iodization

In general, a higher temperature and a longer pyrolysis time lead to a higher bio-hydrocarbon yield. As shown in Figure 7, the yield of bio-hydrocarbons varied from 41.34% (265 °C, 30 minutes) to 77.52% (285 °C, 45 minutes). The bio-hydrocarbon produced had a hydrocarbon-like odor and purple color, indicating the presence of dissolved iodine. The best operating condition was 285 °C with 45 minutes of reaction, yielding 77.52% of bio-hydrocarbon.
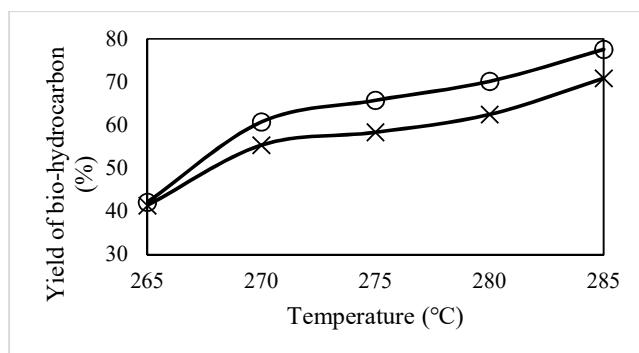

Figure 7   Yield of bio-hydrocarbon for various temperature and reaction time.

Legend: × = 30 minutes; O = 45 minutes.

In the FTIR spectra, peaks associated with C-H (in the range of 2850 to 3000), -C-H (in the range of 1350 to 1480), =C-H (in the range of 3010 to 3100 and 675 to 1000), in-plane -C-H (in the range of 1000 to 1300) and C=C (in the range of 1620 to 1680) were found in the hydrocarbon products. These peaks confirm the presence of alkenes with terminal and non-terminal double bonds as well as alkanes.

These results are basically consistent with the results reported by other researchers [10-13]. The FTIR spectrum of the bio-hydrocarbons produced by de-iodizing 2-iodohexane by gas phase pyrolysis at 260 °C for 45 minutes are shown in Figure 8.
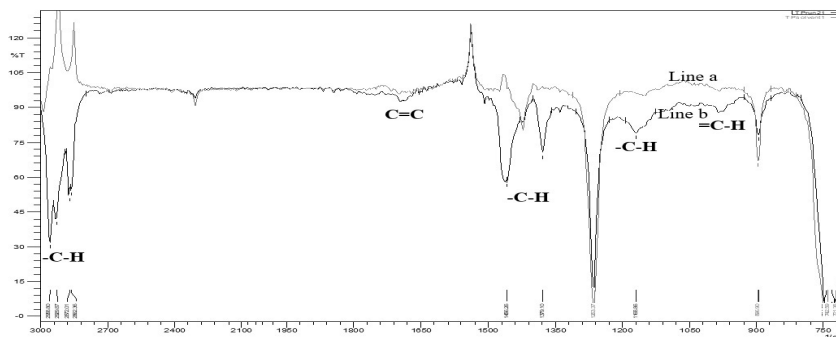

Figure 8 FTIR spectrum of bio-hydrocarbons (line b) produced by gas phase pyrolysis (T = 260 °C, reaction duration = 45 minutes) with dichloromethane as solvent (line a).

4   Conclusion

A bio-hydrocarbon mixture consisting of alkane and alkene was successfully synthesized from sorbitol using hydroiodic acid as intermediate reducing agent and formic acid as primary reducing agent, resulting in 2-iodohexane. Subsequent deiodization through gas phase pyrolysis produced hydrocarbons. The 2-iodohexane synthesis process conducted at 105 °C with a HI/sorbitol molar ratio of 5:1 for 6 hours effectively yielded 23.15% 2-iodohexane. Furthermore, deiodization of the 2-iodohexane process conducted at 285 °C for 45 minutes promisingly yielded 77.52% of bio-hydrocarbon mixture with alkane and alkene functional groups.

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