Directed Study of Abietic Acid Reaction in Pine Rosin under Non-Precious-Metal Catalyst

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Abstract

Pine rosin of *Pinus merkusii* Jung at de Vriese is produced industrially from a distillation process of pine sap. The high total Indonesian production leads the primary derivatization strategy into several derivates to fulfill the market demand. Abietic acid (AA) is a major compound in pine rosin, used as the object of observation in this study. The general methodology for transformation reported involves using palladium (Pd) and platinum (Pt)-based catalysts. Both are precious metal catalysts to proceed with oxidative dehydrogenative-aromatization of the rosin. The synthesized product provides dehydroabietic acid (DHA) derivatives in high yield. This paper reports that non-precious metal-based catalysts such as iron (Fe), zinc (Zn), or copper (Cu) with iodine (I_2) were applied to deliver the reaction by steam cracking without nitrogen (N_2) and oxygen (O_2) for economical, efficient, and greenway's catalyst. It was found that a similar product was isolated, including several by-products. Under high temperatures with a various metal transitions and halogen by $FeCl_3$-I_2 and $Cu(NO_3)_2.3H_2O$ and $ZnCl_2$ catalyst, four compounds were identified employing spectroscopic methods in the reaction product: 7-hydroxy-dehydroabietic acid (5), 1,7-dihydroxy-dehydroabietic acid (6), 7-isopropyl-1-methylphenanthren-9-ol (7) and polymer (8). This modified pine rosin was mainly used as an emulsifier for the synthetic rubber industry, varnish, ink, paper sizing, etc. The products are determined based on LC-MS/MS, UV-Vis, and ATR-FTIR spectroscopy.

Keywords: Abietic acid (AA), dehydrogenative-aromatization, dehydroabietic acid (DHA), oxidative-dehydrogenation, pine rosin.

1. INTRODUCTION

Pine forest is one of the natural resources in Indonesia. Pine resin is commonly exported from Indonesia, known as the third largest resin producer in the world (Kugler et al., 2019). It has been used for reforestation in East Java, including Malang, Jombang, Kediri, Pasuruan, Blitar, Probolinggo, Jember, Trenggalek, Banyuwangi, etc. (Corryanti & Rahmawati, 2015). Gum oleoresin is pain rosin of *Pinus Merkusii* Jung at De Vriese's tree, and pine rosin distillation was produced by gum rosin and tall oil rosin (Kuspradini et al., 2016), which contains 80-90% abietane skeletone and 10-20% terpene skeletone (Y. Li et al., 2019) The compound of abietane skeletone 80-90% is isomers of rosin acid and abietic acid (AA) compound is 40-60% (Brocas et al., 2014). However, abietic acid's

pure compound was not readily for sale in the chemical market. Therefore, the scientist of pine rosin used gum rosin as a starting material or sample for their experience because the major compound in the gum rosin is abietic acid that can occur in the reaction in the pine rosin.

An abietic acid (AA) with the typical formula $C_{19}H_{29}COOH$ has two conjugated double bonds but not good physical and chemical properties because it is unstable, resistant to color, easily oxidized, and cheaply for industry (Frances et al., 2020). Dehydroabietic acid (DHA) is a high modified product of abietic acid (AA) from dehydrogenation reaction by Palladium (Pd) or Platinum (Pt) (Abdel-raouf & Abdul, 2018) and a significantly modified product of rosin acid compound for the anti-microbial agent,

anti-fungal, anti-cancer, anti-inflammatory, the ingredient in synthetic rubber, chewing gum, adhesives, paints, glues, tires, hair removal wax, detergents, soaps, etc. (Gonçalves & Al., 2018).

In recent years, the dehydrogenation of abietic acid's compound has become exciting research for the pine rosin industry. However, the process of modifying pine rosin was constrained by the high production cost and environmental pollution effects of the chemical reaction process (Primaningtyas & Widyorini, 2020). Transition metals have provided halogens such as Br_2, I_2, and Cl_2 the electrons they need to fill their d-type vacant orbitals (Upham et al., 2016) for C-C bonds and C-H heteroatoms in abietic acid compounds by oxidative and aromatize dehydrogenation of C-H bonds (Y. Li et al., 2019). Mostafalu et al. (2017) reported that the addition of Iodine (I_2) or sulfur (S) in various $FeCl_3$ catalysts had given the dehydroabietic acid (DHA) product 72% and 51% (Mostafalu et al., 2017). $ZnCl_2$ and $FeCl_3$ are various metal chlorides with base activators (Setianingsih, 2017). Zn^{2+} and Cu^{2+} are divalent cations, and Fe^{3+} is trivalent metal cations by octahedral's structures (Hongo, 2008). Bromine is another halogen compound that can be combined with a non-precious metal catalyst such as $CaCO_3$ to support a high yield percentage value in the modification reaction of abietic acid to dehydroabietic acid and their derivates (Alvarez, 2007). As a versatile and environmentally benign reagent, iodine compounds in higher oxidation states have become popular organic chemistry. Recently, Iodine has been discovered to be a catalytic agent in numerous oxidative transformations for new C-O, C-N, C-C, C=C, and C-H bonds in organic compounds.

These catalytic transformations are often similar to non-precious metal-catalyzed reactions, with the advantage of being environmentally sustainable and efficiently utilizing natural resources. In current industrial applications, Iodine is underutilized because it is relatively cheap and environmental friendly (Yusubov & Zhdankin, 2015). Nowadays, oxidative dehydrogenative aromatization has high energy efficiency because it occurs at a low exothermic reaction temperature, and the energy required is not high. Industry can process reactions at low cost and temperature because it decreases greenhouse gas emissions

(Lemonidou, 2010). The method of steam cracking in industrial oxidative dehydrogenation can decrease economic and environmental restrictions (Skoufa Z, 2015). This work aims to investigate the effect of a non-precious metal-based catalyst such as an Iron (Fe), Copper (Cu), and Zinc (Zn) performance for halogen (Iodine or I_2) in oxidative and aromatize dehydrogenation's reaction of abietic acid by steam cracking (Gu & Al., 2020).
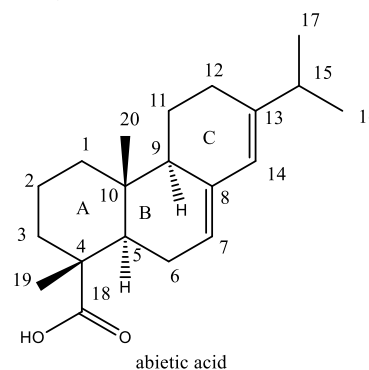

Figure 1. Chemical structures of abietic acid

2. MATERIALS AND METHODS
Materials

Abietic acid is a major compound in Gondorukem's rosin was commercially available from PT. Perhutani Anugerah Kimia (PAK) in Trenggalek, East Java, Indonesia. The reagents used in this study were *pro analyst* (p.a) grade produced by Merck i.e. NaOH (s), $ZnCl_2$ (s), $Cu(NO_3)_2.3H_2O$ (s), n-Hexane (aq), TLC plates, hydrochloric acid (aq), chloroform (aq) and Ferrum chloride (s) and iodine by SmartLab.

Modification's Reaction of Abietic acid's in Pine's Rosin by High Temperature

The gondorukem's sample is prepared by mashed with mortar. Ten grams of gum rosin (contain an abietic acid 60% or 6 gram) turned into weighed in three neck round backside flask equipped with a mechanical stirrer, temperature sensor, and condenser (Mostafalu *et al.*, 2017). The one pot reaction became run at 280 ^{0}C without N_2 atmosphere to get an oxidation. The first temperature was found of the rosin started to melt. While the reaction of temperature was reached, the $FeCl_3$-I_2, Cu-addition and Zn-Addition at dosages 1 wt% (see **Table 1**) was added to the reaction. More samples were taken during for each hour to monitoring by TLC (Thin Layer Chromatography) by eluen's ratio n-

hexane:ethyl acetate = 8:2, UV VIS (Ultra Violet Visible) Spectroscopy and FT-IR (Fourrier Transform Infra-Red) analysis in a bottle sample and the reaction was continued for 6 hours.

Neutralization of Product's Reaction

After the reaction, 25 mL of ethyl acetate was added to solubilize the product's reaction. Liquid extraction was carried out to extract a rosin acid compound by adding 12.5 mL NaOH 1.5 M to form a dissolved salt. Then a dissolved salt was extracted again by adding 12.5 mL 1.5 HCl 1.5 M to form organic's an aqueous's layer phases. The organic phase layer will be analyzed as a synthesized product of dehydroabietic acid's derivate. This extraction was repeated three times. The organic phase was subsequently separated. After the separation, the organic phase in ethyl acetate was evaporated using a rotary evaporator then the product reaction was analyzed by LCMS/MS (Liquid Chromatography-Mass Spectrophotometry/Mass Spectrophotometry). The functional group of rosin acid was generated and analyzed from the oxidative dehydrogenation-aromatization's reaction of ATR-FTIR (Attenuated Total Reflection-Fourier Transform Infra-Red) by the instrument of SHIMADZU Single Reflection ATR. Accessory (QATR-S) IR Spirit (Fourier Transform Infrared Spectrometer) Serial No. A224158. The UV-VIS spectrophotometer was used to calculate an abietic acid and the dehydroabietic acid derivate level by the following equation:

$$Abietic\ acid\ content : W\% = \frac{[E_{241} - E_{250}]}{ckl} \times 100\% \quad (1)$$

$$Dehydroabietic\ acid\ content : W\% = \frac{[E_{276} - E_{273}]}{cfl} \times 100\% \quad (2)$$

According to Yongwan Gu (2020), E_{241}, E_{250}, E_{273}, and E_{276} can be defined by the absorption at the wavelength (241 nm, 250 nm, 273 nm, and 276 nm), c for sample concentration (g/L), l for cuvette thickness (cm), k for coefficient specific absorption of pure abietic acid can be equated to 28, f for coefficient specific absorption of pure dehydroabietic acid can be equated to 1,06 (Meesupthong et al., 2020) by using GENESYS 10S UV VIS spectrometer with dual beam-interface reference and the maximum absorption of samples was used by SHIMADZU UV-1601 with UV PROBE's software.

Attenuated Total Reflection-Fourier Transform Infra-Red (ATR-FTIR) spectroscopy of natural material is needed to generate of functional group in rosin acid by giving overlapping spectral bands in a mixture plot for identifying a material (Martín-ramos, 2018). Smeds et al. (2017) reported that a High-Performance Liquid Chromatography (HPLC) Quadrupole Time of Flight Mass Spectrometry (QTOF-MS/MS) was identified the molar mass (MM) and fragmentation of major and minor organic compounds in pine-sap (Smeds et al., 2017) those abietic acid (AA), hydroxylated rosin acid (OH-RA), dehydroabietic acid (DHA)'s derivatives, and another resin acid (RA). The starting gum rosin was company available from PT. Perhutani Anugerah Kimia (PAK) and the product reactions were analyzed by UPLC-QTOFMS/MS (Waters) with ACQUITY UPLC®H-Class System (Waters) equipped with ACQUITY UPLC®HSS C18 (1.8 μm 2.1 x 150 mm) capillary column, with flow rate 0.2 ml/minutes for 23 minutes. Collision energy is 4 Volt and 25-70 Volt.

The experiment was repeated for other various catalysts and reagents by $FeCl_3$, I_2, $Cu(NO_3)_2.3H_2O$, and $ZnCl_2$ in table 1.

Table 1. Experimental design of dehydrogenation-aromatization reaction for 6 h and temperature 280 ^{0}C

Variation	Gum Rosin	FeCl$_3$	Iodine (I$_2$)	Cu(NO$_3$)$_2$.3H$_2$O	ZnCl$_2$
Various 1 (FeCl$_3$-I$_2$)	10 g	0.1 g	0.1 g	0 g	0 g
Various 2 (Cu-add)	10 g	0.1 g	0.1 g	0.1 g	0 g
Various 3 (Zn-add)	10 g	0.1 g	0.1 g	0 g	0.1 g

3. RESULTS AND DISCUSSION
Effect of Variation Non-Metal Precious on the Oxidative-Dehydrogenative-Aromatization's Product of Reaction

The compound of abietic acid (AA) was detected in starting material of pine rosin, which is shown in Fig. 2. Fig. 2 presented the abietic acid peak in pine of rosin chromatogram by retention time (12.42 min), and the isomer compound of abietic acid (iso-AA) those a levopimaric acid and Neoabietic acid were presented by retention time (14.28 min). An effect of promoting non-precious-metal catalyst was given the differences in product reaction in LCMS/MS chromatogram. A various of $FeCl_3$-I_2 1% (w%) was expressed product reaction for dehydrogenation and oxidation 2 step's reaction was 1,7-dihydroxy dehydroabietic acid about 33.46% by retention's time in 15.17 minutes. The product of dehydrogenation and oxidation 1 step's reaction was 7-hydroxy dehydroabietic acid, about 20.71% by the time of retention in 12.66 minutes. However, the product's oxidation 1 step and stepwise dehydrogenation reaction was 7-isopropyl-1-methylphenantrene-9-ol only 1.31% at 11.64 minutes.

An effect of promoted Cu-addition in the various catalyst by $FeCl_3$-I_2-$Cu(NO_3)2.3H_2O$ 1% (w%) was given some product's reaction for dehydrogenation and oxidation 1 step's reaction was 7-hydroxy dehydroabietic acid about 49.15% by retention's time in 12.81 minutes. Nevertheless, the dehydrogenation and oxidation 2-step reaction product was 1,7-dihydroxy-dehydroabietic acid, only 2.79% by the time of retention in 10.02 minutes. However, the product's oxidation 1 step and stepwise dehydrogenation reaction was 7-isopropyl-1-methylphenantrene-9-ol only 0.76% at 10,81 minutes. The Cu-addition in the various catalyst of $FeCl_3$-I_2-$Cu(NO_3)2.3H_2O$ 1% (w%) was given the polymer's product at 18.04 minutes, about 17.94%.

An effect of promoted Zn-addition in the various catalyst by $FeCl_3$-I_2-$ZnCl_2$ 1% (w%) was given some product's reaction for dehydrogenation and oxidation 1 step's reaction was 7-hydroxy dehydroabietic acid about 43.06% by retention's time in 12.81 minutes. Nevertheless, the dehydrogenation and oxidation 2-step reaction product was 1,7-dihydroxy-dehydroabietic acid, only 4.25% by the time of retention in 10.02 minutes. However, the product's oxidation 1 step and stepwise dehydrogenation reaction were 7-isopropyl-1-methylphenantrene-9-ol of about 10,9% at 14.37 minutes. The Zn-addition in various catalysts of $FeCl_3$-I_2- $ZnCl_2$ 1% (w%) was given the polymer's product at 18.02 minutes, only about 4.99%.

In previous work by this experiment, the synthesis of intermediate compound of dehydroabietic acid (DHA) at m/z 300.21 and their derivatives by various non-precious metal catalysts has been described in Fig.3. An abietic acid (AA) at m/z 302.22 has isomerized with levopimaric acid at m/z 302.22 and neoabietic acid at m/z 302.22. However, that compound was not stable and changed an Abietic Acid (AA) for a better compound. Abietic acid (AA) has been dehydrogenated to dehydroabietic acid (DHA) and has been hydroxylated to 7-hydroxy abietic acid (7-OH-DHA) at m/z 318.22, then has detilated and removed an etil to m/z 290,19; had dehydrogenated to 7-hydroxydehydrodehydroabietic acid (7-OH-DHA) at m/z 316.20 and then has etilated to m/z 288.17 for the time leading from 1 hour to 6 hours reaction (Berg & Boon 2000). The dehydroabietic acid (DHA) at m/z 300.21 has transformed to 7-Hydroxydehydroabietic acid (7-OH-DHA) at m/z 316.20 through hydroxylation in dehydrogenation and oxidation 1 step's reaction. The product's reaction of 1,7-dihydroxydehydroabietic acid (1,7-di-OH-DHA) at m/z 332.20 has been transformed from dehydrogenation and oxidation 2-step reaction of abietic acid (AA) or derived from some compound of 7-hydroxy-dehydroabietic acid (7-OH-DHA) that oxidized again after oxidized 1-step. Dehydroabietic acid (di-DHA) compound at m/z 298.19 derived from the intermediate's compound of dehydroabietic acid (DHA) that dehydrogenized again for 2 step dehydrogenation. An oxidative dehydrogenative-aromatization reaction was identified, which found a phenanthrene's derivatives derived from some 7-hydroxy-dehydroabietic acid's (7-OH-DHA) compound at m/z 266.17. Then, this compound was transformed into the polymer of dehydroabietic acid (Poly-DHA) because of the high-temperature reaction at 280 °C. Chlorine (Cl) is a very efficient halogen promoter, while Iodine (I_2) is the least efficient, but iodine (I_2)

is the best effective halogen promoter because of the ease with which HI is oxidized for oxidative dehydrogenation (Pasternak & Vadekar, 1970).

The mechanism reaction of oxidative dehydrogenation's reaction, aromatization dehydrogenation's reaction, and polymerization's reaction has been explained in Figure 4. First, the unstable abietic acid's (AA) isomer was, namely neoabietic acid (Iso-AA) and levopimaric acid (Iso-AA), will undergo isomerization to form an abietic's acid (AA), which was more stable due to the influence of high temperature. Second, abietic's acid (AA) will be dehydrogenated into an intermediate compound, dehydroabietic acid (DHA). Third, dehydroabietic acid (DHA) will be directly oxidized in stage 1 to form 7-hydroxy dehydroabietic acid (7-OH-DHA), and this compound will be directly oxidized

again (step 2) to form 1,7-dihydroxy dehydroabietic acid (1,7-di-OH-DHA). Fourth, some of the compounds (5) will undergo dehydrogenation reactions to produce phenanthrene derivatives (7), and further, under the influence of high temperature, will undergo polymerization reactions to form a polymer product. The selectivity of this reaction cannot be calculated quantitatively because the compound of this product was formed through 1 original abietic acid compound and isomer of abietic acid, which directly undergoes various reactions. The level of the product's reaction was also determined by lewis acid present in the non-precious metal's transition catalyst. The stronger lewis's acid increased the oxidation's reaction or product, but the weaker lewis's acid decreased the oxidation's reaction of product.
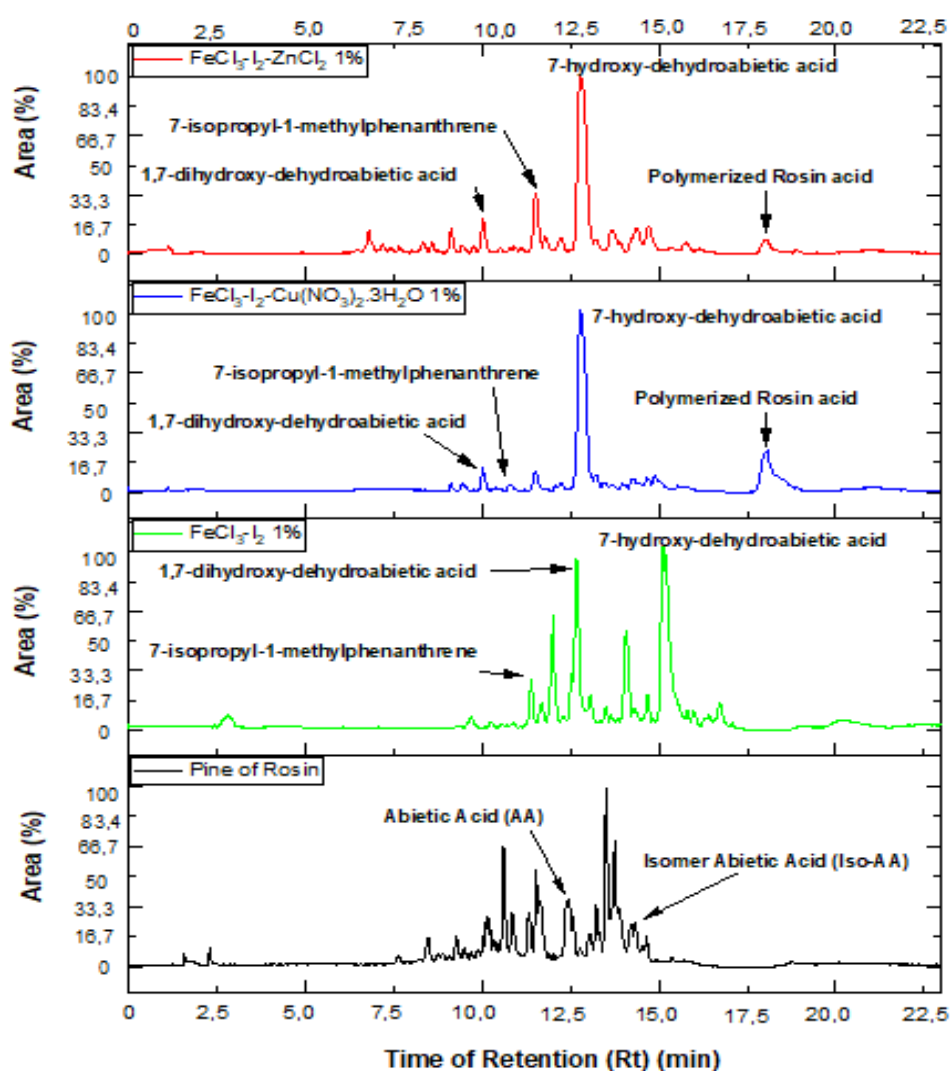

Figure 2. Total ion LCMS/MS chromatogram the pine rosin with various of non-precious metal's catalyst and product's reaction
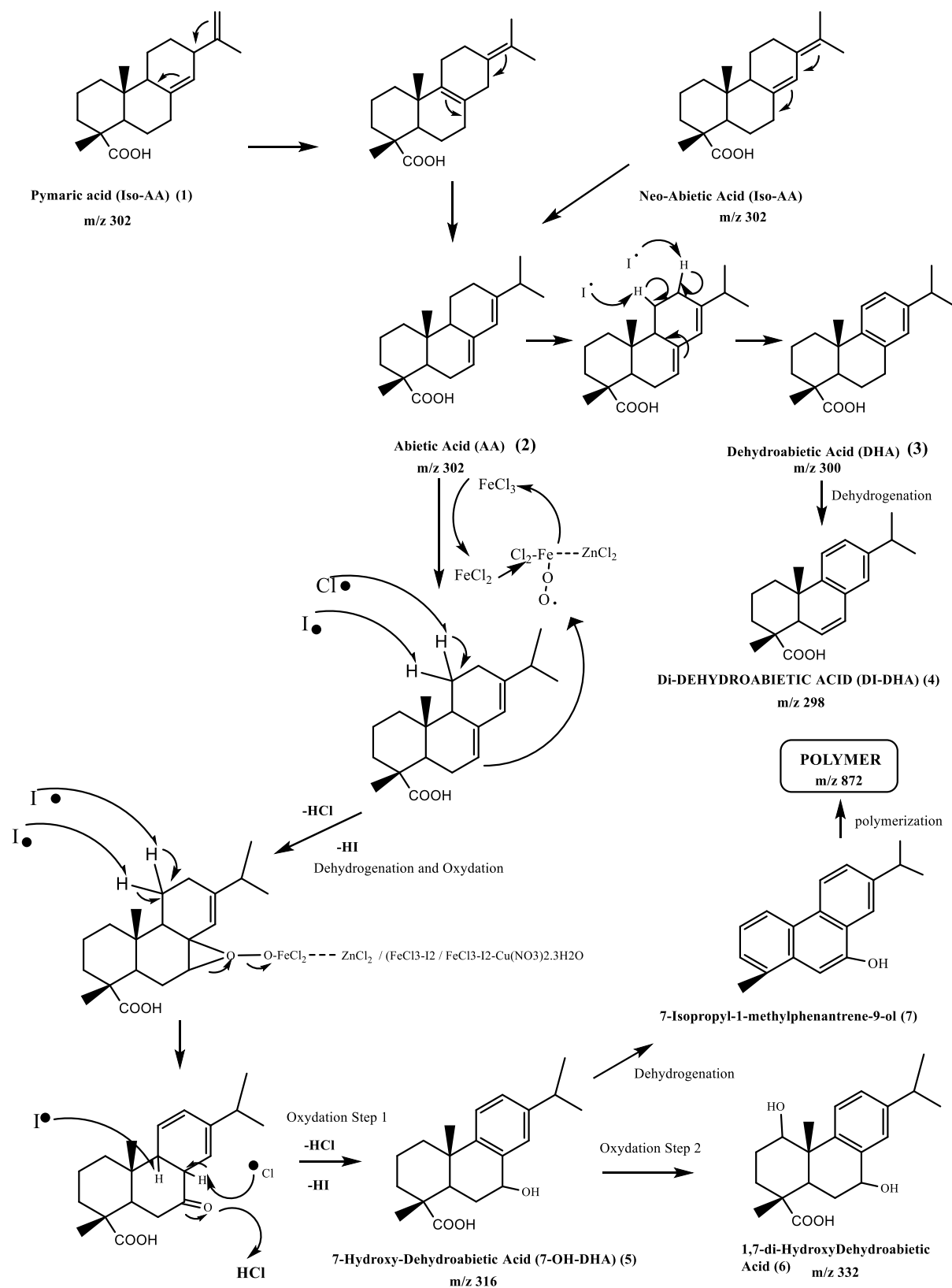
Figure 3. Oxidative-dehydrogenative–aromatization reaction paths of diterpenoid compounds (abietic acid) in pine of rosin with the relative suggested of oxidative-dehydrogenation and aromatization (Smeds *et al*., 2017; Adilbekov, 2016)

Figure 4. The mechanism's process reaction of oxydative-dehydrogenation and aromatization-dehydrogenation by various catalyst of $FeCl_3$-I_2-$ZnCl_2$ / $FeCl_3$-I_2-$Cu(NO_3)_2.3H_2O$ / $FeCl_3$-I_2 (1%)

Table 2. ESI-QtoF-LC/MS Fragmentation of Abietic Acid (AA), Dehydroabietic Acid (DHA) and their derivates

Compound	Molecular Formula, $[M-H]^-$	Mono-Isotopic Mass, $[M-H]^-$	MS^2 and MS^3 Fragmentations, m/z (Relative Abundance)[a]
Abietic Acid (AA)	$C_{20}H_{29}O_2$	301.2170	MS^2: 299,2011 (100); MS^3:297,6426 (100)
Levopimaric Acid (Iso-AA)	$C_{20}H_{29}O_2$	301.2193	MS^2: 299,2010 (100); MS^3:299,2010 (100)
Neoabietic Acid (Iso-AA)	$C_{20}H_{29}O_2$	301.2193	MS^2: 299,2010 (100); MS^3:299,2010 (100)
Dehydroabietic Acid (DHA)	$C_{20}H_{27}O_2$	299.2020	MS^2: 297,1856 (100); MS^3:287,2013 (100)
7-Hydroxyabietic Acid (7-OH-AA)	$C_{20}H_{29}O_3$	317.2115	MS^2: 293,1752 (100); MS^3:285,1850 (100)
7-Hydroxy-Dehydroabietic Acid (7-OH-DHA)	$C_{20}H_{27}O_3$	315.1954	MS^2: 269,1896 (100); MS^3:187,1118 (100)
1,7-Dihydroxydehydroabietic Acid (1,7-di-OH-DHA)	$C_{20}H_{27}O_4$	331.1901	MS^2: 313,1791(98), 329 (100); MS^3: 301,1791 (100)
Didehydroabietic Acid (Di-DHA)	$C_{20}H_{25}O_2$	297.1850	MS^2: 277,1797 (100); MS^3: 251,1792 (100)
7-isopropyl-1-methylphenanthren-9-ol	$C_{19}H_{21}O$	265.1601	MS^2:250,1362(100); MS^3:222,1051 (100)
7-Hydroxy-De-RA (7-OH-de-RA)	$C_{18}H_{23}O_3$	287.1647	MS^2:285,1846(100); MS^3:159,0805 (100)
7-Hydroxy-RA (7-OH-RA)	$C_{18}H_{25}O_3$	289.1437	MS^2:240,1745(100); MS^3:212,1434(100)
Polymer	$C_{20}H_{29}O_2$	871.5733	MS^2:821,5660(100); MS^3:705,4750 (100)

Thirteen resin acid compounds can be classified by ESI-QtoF-LC/MS investigation from Table 2. Based on the fragmentation table of abietic acid (AA), dehydroabietic acid (DHA) and its derivatives can be seen in the deprotonated molecular ions ($[M-H]^-$) in MS^1, MS^2, and MS^3. Abietic acid (AA) and its isomers of abietic's acid (neoabietic acid and levopimaric acid) were detected in m/z 301. The first product of dehydrogenation is Dehydroabietic Acid (DHA), which was detected at m/z 299, and this product of dehydroabietic acid (DHA) is only intermediate. This intermediate compound of dehydroabietic acid would immediately undergo an oxidation reaction in stage 1 and stage 2. The oxidation product from abietic acid (AA) and dehydroabietic acid (DHA) was detected at m/z 317 for 7-Hydroxyabietic acid (7-OH-AA) and 315 for 7-Hydroxy-Dehydroabietic acid (7-OH-DHA). The reaction of the second dehydrogenation detected a fragment in m/z 297. The other product also detected a fragment at m/z 287 for 7-Hydroxy-Dehydro-Rosin Acid (7-OH-De-RA) and fragment m/z 289 for 7-Hydroxy-Rosin Acid (7-OH-RA). The compound of 7-hydroxy-dehydroabietic acid (7-OH-DHA) was to get an oxidation reaction in step 2 to form 1,7-dihydroxy-dehydroabietic acid (1,7-OH-DHA). The ESI-QtoF-LC/MS results can be investigated that 7-isopropyl-1-methylphenanthren-9-ol (7) and polymer's product of modification an abietic acid (AA) by the ion m/z 265 (100) and 871 (100). The abietic acid (AA) and dehydroabietic acid (DHA) can be continuously extracted and analyzed by LC/MS without any other pretreatments because a sample can easily be analyzed as it is easy to implement simple, fast, selective, and sensitive (Mitani, 2007).

The compound of abietic acid was detected in starting material of pine rosin, as shown in Fig. 5. Fig. 5 presents the abietic acid peak absorption in wavelength 241 nm until 250 nm by UV VIS spectrometer of SHIMADZU UV-1601 with UV PROBE's software. The pine rosin was weighed at 0,1 gr by analytical scale in a 10 ml volumetric flask. The ethyl acetate solvent was added and homogenized to wholly dissolved. After the solvent was dissolved, the solution was quickly qualitatively analyzed by UV VIS spectrometer of SHIMADZU UV-1601 with UV PROBE's software (Li, 2014).

The quantitative analysis of abietic acid (AA) and dehydroabietic acid (DHA) levels was represented by Yongwan Gu (2019). An abietic acid (AA) and dehydroabietic acid (DHA) levels were calculated by the equation of (i) in multiwavelength absorption for abietic acid (AA) in wavelengths of 241 nm and 250

nm, then dehydroabietic acid (DHA) in wavelength of 273 nm and 276 nm. The content compound of abietic acid (AA) and dehydroabietic acid (DHA) has reacted with various catalysts in the non-precious metal catalyst.

Fig. 6 compares the intercorrelations among the % content compound, various catalyzed, and reaction times. A weak positive correlation was found between % content compound, various catalyzed, and reaction time. A correlation was also present between the optimum time of reaction and % content compound of dehydroabietic acid (DHA) in product reaction and excellent variation of catalyzed in this reaction. Xuan Dai et al. (2018) explained that non-precious metals (Ni, Fe, Co, and Cu) are efficient's catalysts for oxidative dehydrogenation aromatization reaction in hydrocarbon compounds using molecular oxygen as the ultimate oxidant (Meesupthong et al., 2018). Huahua Fan et al. (2020) said the presence of Zn and Fe can increase selectivity and % yield of aromatic products in ethane oxidative dehydrogenation by DFT study (Fan. Huahua, 2020). The results indicated that relatively optimum of reaction time by promoted a non-precious metal catalyst in $FeCl_3$-I_2 1% (b/b) is 5'th hours, $FeCl_3$-I_2-$Cu(NO_3)_2.3H_2O$ 1% (b/b) is only 2 hours, and for various catalysts of $FeCl_3$-I_2-$ZnCl_2$ 1% (b/b) is 4 hours. The effect of various catalysts in the oxidative dehydrogenation and aromatization of abietic acid (AA) to dehydroabietic acid's (DHA) derivatives were investigated in Fig. 6.
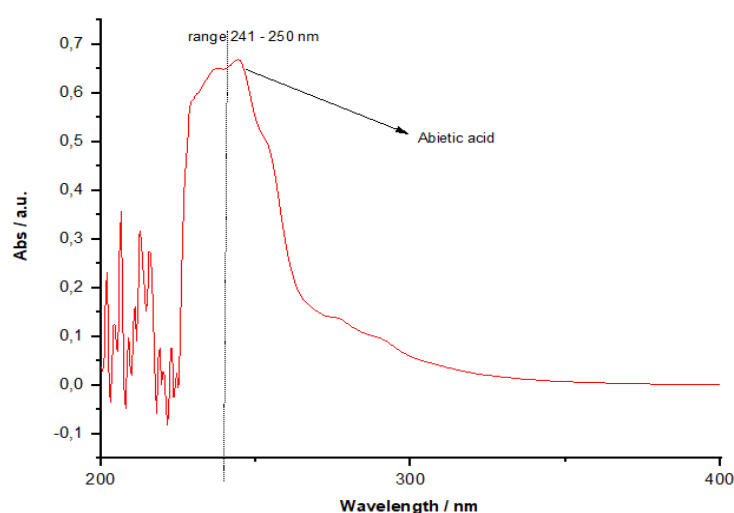

Figure 5. UV spectra of abietic acid in starting material of pine rosin. The scan range of the UV spectra
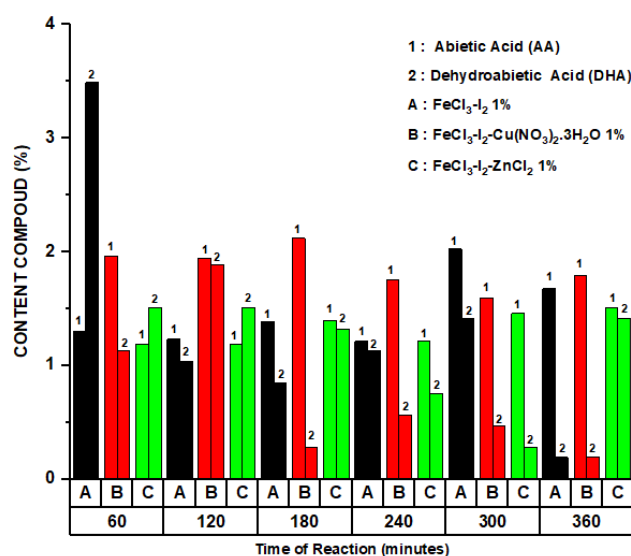

Figure 6. The quantitave analysis of abietic acid's (1) content to dehydroabietic acid's derivatives (2) content by variuos catalyst with $FeCl_3$-I_2 1% (w%) (A), $FeCl_3$-I_2-$Cu(NO_3)_2.3H_2O$ 1% (w%) (B), and $FeCl_3$-I_2-$ZnCl_2$ 1% (w%) (C) for 6 hours

Table 3. Main band observed on FTIR spectra of reaction resin with variuos catalyst under inverstigation and their assignment based on the literature data of table 1 (in supplementary's data)

Bond No.	Pine of Rosin	Various 1 (FeCl$_3$-I$_2$)	Various 2 (Cu-add)	Various 3 (Zn-add)
1	3424.33	3293.12 sh	3441.45	3437.17 s
2	3077.76 w	3060.65 sh	Nd	3063.50 vw
3	2938.00	2957.96 s	2956.54 s	2957.96 s
		2928.01 s	2926.59 s	2928.01 s
4	2870.96	2868.11 w	2866.69	2868.11
6	-	1741.40 vw	1798.45	1741.40
9	1697.19 s	1694.34 w	1652.98	1688.63
10	nd	1600.21 w	1601.64	1601.64
11	nd	1496.10	-	1496.10
12	1463.29	1459.01 w	1456.16	1457.59

*nd is not detection, vw is very weak, s is strong, and sh is shoulder, Various 1 (FeCl$_3$-I$_2$ (1%)), Various 2 (FeCl$_3$-I$_2$-Cu Add (1%)), and Various 3 (FeCl$_3$-I$_2$-Zn Add (1%)).

Table 4. FT-IR band positions and intensities prior to normalization of the C=C and =C-H exocylic methylene groups, alkene (phenolic resin), benzene (aromatic's ring) and hydroxil region of the spectra, and their relevant assignment (Pagacz, 2019)

Band/cm-1	Sample and Intensity				Assignment
	Pine of Rosin	FeCl$_3$-I$_2$ (1%)	FeCl$_3$-I$_2$-Cu Add (1%)	FeCl$_3$-I$_2$-Zn Add (1%)	
1630–1650 cm^{-1}	17.48	47.64	59.60	44.90	C=C (exocyclic methylene groups, typical of Resins)
1590-1615 cm^{-1}	-	54.02	56.94	50.14	C=C aromatic ring
1490-1515 cm^{-1}	50.74	62.33	45.51	66.59	C=C typical of phenolic resins
2845-2865 cm^{-1}	22.09	23.42	31.72	23.01	Sym. Stretc. =CH$_2$
3000-3100 cm^{-1}	36.63	55.36	12.63	63.85	=C-H aromatic ring
3230-3550 cm^{-1}	39.60	66.61	25.85	45.26	-O-H hydroxil

Table 5. FT-IR band positions and intensities after normalization of the C=C and =C-H exocylic methylene groups, alkene (phenolic resin), benzene (aromatic's ring) and hydroxil region of the spectra, and their relevant assignment (Pagacz, 2019)

Band/cm-1	Sample and Intensity				Assignment
	Pine of Rosin	FeCl$_3$-I$_2$ (1%)	FeCl$_3$-I$_2$-Cu Add (1%)	FeCl$_3$-I$_2$-Zn Add (1%)	
1630–1650 cm^{-1}	0	0.62246	1	0.50229	C=C (exocyclic methylene groups, typical of resins)
1590-1615 cm^{-1}	0	0.78643	0.94337	0.62253	C=C aromatic ring
1490-1515 cm^{-1}	1	1	0.70002	1	C=C typical of phenolic resins
2845-2865 cm^{-1}	0.1386	0	0.40643	0	sym. stretc. =CH$_2$
3000-3100 cm^{-1}	0.57577	0.82087	0	0.93713	=C-H aromatic ring
3230-3550 cm^{-1}	0.66506	1	0.28146	0.51056	-O-H hydroxil

The ATR-FTIR spectra of Pine rosin and three product reaction with various non-precious metal catalysts are shown in TABLE 3. Their bands have been correlated with those of other rosin acids (RA) reported in the literature (see TABLE 1 in supplementary's data). Band assignments are summarized in TABLE 1. Then the analysis of Peak Intensity

and FT-IR band position before normalization are shown in TABLE 4. After normalizing the intensity of several peaks, it can be seen that the dominant chemical reaction occurred from the chemical group functional to be identified by the high value in TABLE 5. The intensity of a band 1490-1515 cm^{-1} matching the C=C vibration of phenolic resin groups is high, then the dominant vibration of OH (Hydroxyl) in band 3230-3550 cm^{-1} for the dominant's reaction of dehydrogenation and oxidation 1-2 step's reaction, the next a vibration of C=C typical aromatic ring for a band 1590-1615 cm^{-1} and the last vibration is C=C of exocyclic methylene groups for a band 1630-1650 cm^{-1} for all the reaction of dehydrogenation's reaction. Another interesting observation is a band about 3000-3100 cm^{-1} related to =C-H aromatic ring vibration, and the last is symmetry stretching of =CH$_2$ vibration in a band 2845-2865 cm^{-1} for the non-dominant dehydrogenation and aromatization reaction (Pagacz, 2019). The dominant vibration is C=C phenolic resin, aromatic's ring, =C-H aromatic's ring is higher these experiments are dehydrogenation and aromatization reaction (Ramos, Martin. Fernandez, 2018).

Fig. 7 shows spectra of pine rosin as starting material and their's product reaction by non-precious metal catalysts promoted with FeCl$_3$-I$_2$ 1%; FeCl$_3$-I$_2$-Cu(NO$_3$)2.3H$_2$O 1%, and FeCl$_3$-I$_2$-ZnCl$_2$. Changing the C=C and =C-H functional group and -OH functional group can be identified by FT-IR spectrophotometry. The hydroxyl group (-OH) vibration is usually the most intense signal on the FT-IR spectra. The complex compound of gum rosin and its modification product by high thermal can be noticeable by the side of the FT-IR spectra, mainly in the hydroxyl area. In order to succeed in the signals in the hydroxyl area (3230-3550 cm^{-1}), we follow a correct approach. This reaction of modification of abietic acid (AA) can be distinguished from three types of vibration, the first is due to (C=C) vibrations, the second is related to =C-H vibration, and the last –O-H (hydroxyl) vibration. One more unique band from all peaks is a strong C=C of phenolic resin at 1490-1515 cm^{-1}, the other is a C=C aromatic ring at 1590-1615 cm^{-1}, the other between the weak vibration is C=C exocyclic methylene groups. Another vibration is =C-H alkene is less visible than =C-H aromatic's ring vibration and the stretching vibration of hydroxyl (-O-H) on the spectra of FT-IR (Y, 2014). It indicates that pine of rosin was dehydrogenated, oxidized, and aromatized well in gum rosin's modified product.
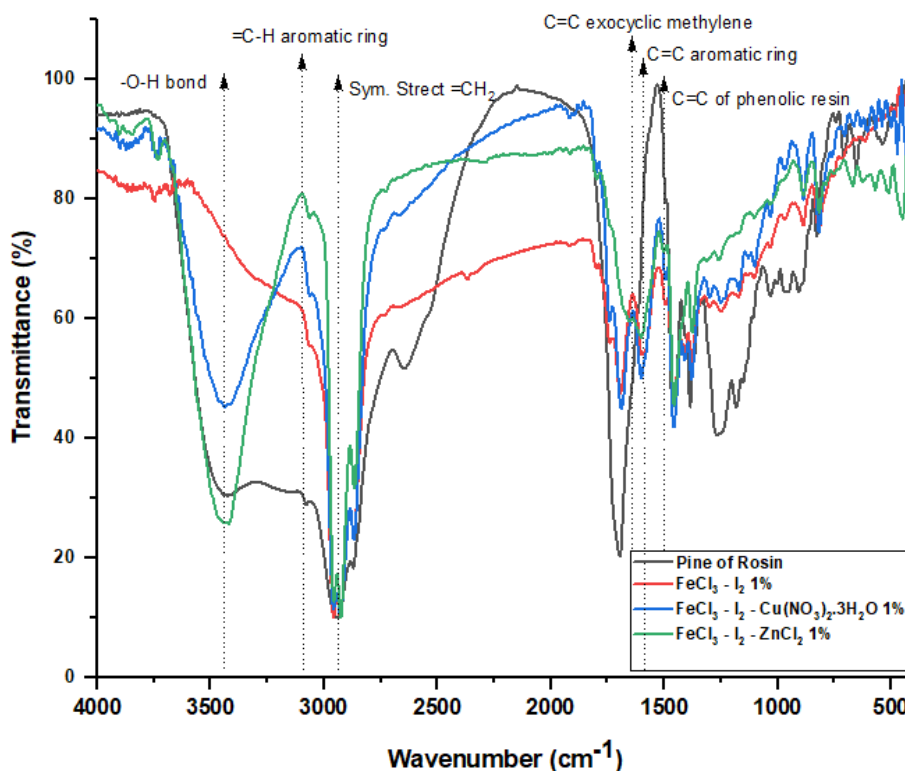

Figure 7. FTIR spectra of pine of rosin and three samples with various non-precious metal's catalyst

4. CONCLUSION

In this study, we examine the effectiveness of variation non-precious metal catalysts (as Fe, Cu, and Zn) and halogen (I_2 – Iodine) as an oxidant for modification's reaction in pine rosin. This research used an ESI-Quadrupole Time of Flight-Liquid Chromatography-Mass Spectrometry (QtoF-LC/MS) and successfully obtained thirteen derived rosin acid (RA) compounds to investigate a chemical reaction with various non-precious-metal catalysts (Fe, Cu, Zn) and halogen oxidant (I_2) in high temperature. The product reactions were derived from the intermediate compound of dehydroabietic acid (DHA) that 7-hydroxyabietic acid (7-OH-AA); 7-hydroxydehydroabietic acid (7-OH-DHA); 1,7-dihydroxydehydroabietic acid (1,7-Di-OH-DHA); dehydroabietic acid (Di-DHA); 7-hydroxy-dehydro-rosin acid (7-OH-De-RA); 7-hydroxy-rosin acid (7-OH-RA); 7-Isopropyl-1-methylphenantrene-9-ol; and polymer's product. Nevertheless, the object's compounds of product reaction in this study were only four, 7-hydroxy-dehydroabietic acid (7-OH-DHA), 1,7-dihydroxydehydroabietic acid (1,7-di-OH-DHA), 7-Isopropyl-1-methylphenantrene-9-ol, and polymer's compound. The qualitative UV spectra suggest that abietic acid (AA) has a similar absorption peak from 241 nm to 250 nm and the dehydroabietic acid (DHA) in 273 nm to 276 nm. It was chosen as the wavelength test for quantitative analysis by multiwavelength. The ATR-FTIR method was proper to identify the chemical reaction process of pine rosin based on a set of band positions. The vibrational functional group between C=C of phenolic resin, aromatic ring, and exocyclic methylene group; =C-H of aromatic's ring and alkene, and –OH hydroxyl's vibration is clearly explained the chemical reaction of oxidative dehydrogenation and aromatization of an abietic acid (AA) to form derivatives of dehydroabietic acid (DHA) as an intermediate's product.

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