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Article

Kinetic of Hydroxyl Growth on Natural Rubber Depolymerization with H_2O_2 /Fenton Using Infrared Spectroscopy

Heri Budi Wibowo ^{1,2,*}, Sutrisno Sutrisno ¹, Hamonangan Rekso Diputro Sitompul ¹, Retno Ardianingsih ¹, Luthfia Hajar Abdilah ¹, Kendra Hartaya ¹ and Ario Witjakso ¹

¹ Rocket Technology Center, National Research and Innovation Agency

² Indonesia Defence University

* Correspondence: heri012@brin.go.id

Abstract: The kinetic of NR depolymerization to HTNR using H_2O_2 under the presence of Fenton catalyst in acidic environment and ultraviolet radiation has been studied using Infrared Spectroscopy to inspect the changes of molecular weight and functionality of HTNR product. The kinetic model is studied follow reaction mechanism: 1) hydroxyl radical and NR produce radical NR and hydroxylated NR, 2) radical NR and hydroxyl radical produce hydroxylated NR, 3) hydroxylated NR is reacted with hydroxyl radical produce lower radical NR, hydroxylated terminated NR, radical NR, and hydroxylated NR. The NR polymer conversion and total hydroxyl was observed at absorption band of $\text{CH}_2\text{-CH}_2$ and OH group at 850 cm^{-1} and $3,400\text{ cm}^{-1}$. Absorption of CH_3 at 1850 cm^{-1} was used as reference group. The average molecular weight is calculated using Stockmayer equation. The hydroxylated NR production follow 2th order, the hydroxylated terminated NR production was conformed to be 1st order. The average molecular weight and functionality of HTNR is well estimated. The temperature effect on depolymerization followed Arrhenius reaction with activation energy E_{a1}/R and E_{a34}/R are 750 K and 1200 K. The effect of H_2O_2 /Fenton ratio on the depolymerization followed power equation with power coefficient are 1.97 and 1.82 for k_1 and k_{34} .

Keywords: hydroxylated natural rubber; Photo-Fenton; photo chemical depolymerization; depolymerization kinetics; natural rubber;

1. Introduction

Natural rubber widely had been used for many purposes due to their environmentally friendly dan renewable properties. The new elastomers material can be obtained by modifying natural rubber structures. Natural Rubber can undergo depolymerization into smaller natural rubber structures with hydroxyl or carboxyl functional group at their terminal chain position. The new materials derived from natural rubber were synthesized by polymer chain scission (depolymerization) from liquid natural rubber (LNR) into lower molecular weight rubber structures with the addition of the reactive terminal groups to form telechelic natural rubber (TLNR) [1]. One of derived materials from the natural rubber is Hydroxyl Terminated Natural Rubber (HTNR) with -OH groups at the terminal polymer have been used for grafting [2,3], chain extension [4,5], adhesive [3,6,7, 36], chain modifier [8–10] and propellant binder [11–15].

LNR depolymerization into HTNR had been carried out by various depolymerization reaction's routes [30,31,32]. The HTNR can be synthesized by photochemical [16,17,18,19], metal catalyst [30,31,32, 33,34, 39], redox [35,36], thermal degradation [37,40], and selected chemical oxidation [38].

Ravindran [16,17]; Pham [18] had explored the usage of radical from H_2O_2 in depolymerization reaction assisted by UV light from a mercury vapor lamp. Ravindran attempted to use a 125 W of UV mercury vapor lamp with 30% of H_2O_2 to undergoes 30 hours depolymerization reaction of LNR [16]

and used a 400 W of mercury vapor lamp for 52 hours of depolymerization reaction in his second attempt [17]. Ravindran's first depolymerization experiment resulting a 90% HTNR product with Mn 5,000; Mw 8,100; PDI of 1.61 with hydroxyl functionality of 1.91 compared to his second attempt of 90% HTNR product with Mn 4,100; Mw 8,300; PDI of 2.02 with slightly better -OH functionality of 1.97. Pham [18] introduced the usage of FeSO_4 as Photo-Fenton catalyst to assist the production of hydroxyl radicals from H_2O_2 decomposition. By using a Photo-Fenton catalyst enabled Pham to use a lower specification of UV mercury vapor lamp compared to that of Ravindran. Pham used a 160 W of mercury vapor lamp with 32 hours radiation time in depolymerization of LNR to HTNR, with reported of 92-93% yield of HTNR products with 1.97-1.98 of -OH functionality and Mn of 3,060. Depolymerization reaction from Ravindran and Pham's works follow a radical depolymerization mechanism by OH radical attack on $\text{CH}_2\text{-CH}_2$ bond ($\text{C}\alpha$) with site of lower steric hindrance is preferred.

Baharulrazi [11] and Giang [19] had carried out the depolymerization of LNR by a controlled reduction-oxidation process. Baharulrazi [11] used Co-bis-acetylacetonate with ethanol and NaBH_4 to produce an oxidant specimen of NaBO_2 which would oxide the $\text{CH}_2\text{-CH}_2$ bond ($\text{C}\alpha$) continued by a reduction by NaBH_4 resulted a HTNR product with Mn 6,691 and Mw of 27,560 with PDI score of 4.12 from 1 hour reaction time. Giang [19] took a different approach by using a pH 9 borate buffer solution ($\text{H}_2\text{B}_4\text{O}_7$, NaCl , $\text{Na}_2\text{H}_{20}\text{B}_4\text{O}_{17}$), THF and 0.1 g of $(\text{NH}_4)_2\text{S}_2\text{O}_7$ to produce OH radical specimen from Redox Reaction between OH^- ion and borate buffer solution. HTNR product was separated with properties of Mn 4,334; Mw 11,702 and PDI score of 2.7.

Azhar [20] employed a combined photosensitizer of methylene blue and rose Bengal in degradation reaction of LNR under visible light during 14 days radiation time. Oxidation occurred in two steps by using H_2O_2 and acetic acid with Na_2WO_4 catalyst. First oxidation reaction was the conversion of LNR structures to their epoxidized counterpart, the LENR, which undergo further oxidation to hydroxylated LNR of LNR-OH. The hydroxyl functional groups of LNR-OH from Azhar's experiment are present not only at terminal, the OH groups were bonded to another C atoms ($\text{C}\beta$). A 55.4% yield of LNR-OH products was recovered with properties of Mn 1,800; Mw 3,200; and PDI score of 1.78.

The kinetic of photochemical depolymerization of natural rubber or polyisoprene with catalyst H_2O_2 /Fenton/Acid was studied based on the radical reaction mechanism proposed by Pham and Ravindran [17,18]. Hydroxyl radicals are generated by redox reaction of H_2O_2 /Fenton/Acid in the presence of UV radiation. The rubber depolymerization is initiated by hydroxyl radical attacked to $\alpha\text{-CH}_2\text{-CH}_2$ bond of natural rubber. The depolymerizations were terminated by radical-radical interaction. The final product is hydroxyl terminated natural rubber with by-product of lightly crosslinked with carbonyl, carboxyl, and hydroxyl functional groups. The molecular weight and functionality are characterized and affected by acidity, composition, UV radiation, and catalyst.

Changes on functional groups could be used as base for kinetic study of natural rubber depolymerization. Reaction rate was controlled by reaction between polymer and radicals. The initiation and termination stages are very fast. The reaction is assumed to be simple and following the second order reaction [17,21]. This kinetic model could not be used to describe the changes of molecular weight and functionality of HTNR. Nevertheless, the kinetic model based on molecular approach is well equipped to describe the molecular weight and functionality on the hydroxyl terminated polybutadiene [22] and polycondensation of hydroxylated polybutadiene [23]. This kinetic model would be applied to natural rubber depolymerization to explain the functionality and crosslinked. The radical polymer is classified in the mono hydroxylated rubber (R-OH) and di-hydroxylated rubber (OH-R-OH). These functional groups were added to describe the functionality and crosslinked of HTNR.

Their kinetics have been studied by gravimetric [17], viscometry [17,18], and thermal [24,25]. The infrared spectroscopy is simplest and fast methods to study kinetic of polymerization and depolymerization [23]. In this paper, the kinetic model was studied by infrared spectroscopy. The

hydroxyl, carbonyl, carboxyl, and methyl groups are measured by their infrared absorption. The reference spectra used is methyl (CH_3) absorption.

2. Materials and Methods

2.1. Materials

Acetone, toluene, methanol, and tetrahydrofuran (THF), sodium ascorbate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, H_2O_2 (50%w/w), H_2SO_4 and NaOH were supplied by BRIN. Deproteinized Natural Rubber liquid (DPNR) was supplied by Indonesian Rubber Institute. Natural Crumb Rubber was obtained by coagulating DPNR with acetone.

2.2. Methods

2.2.1. Synthesis of HTNR

Natural Crumb Rubber (NCR) was masticated at temperature 30°C in 60 minutes. 15 gram of masticated NCR was dissolved in 150 ml toluene and charged into 1000 ml glass reactor. The reactor was equipped with magnetic stirrer, water heater, water condenser and mercury vapor UV lamp 320 W. Precise amounts of Fenton reagent (H_2O_2 and Fe (II)) were added dropwise and continuously stirred with a magnetic bar. The mixture was homogenized with 50 ml THF. The reaction of the mixture was conducted at 60°C and pH about 2.5-3.0 by addition of H_2SO_4 in THF solution and the molar ratio of $\text{H}_2\text{O}_2/\text{Fe}$ (II) was set at 1.5 [18]. The UV radiation was exposed to the reactor after 50 hours reaction. The distance between reactor wall and the UV beam source was 3 cm. A 0.06 g hydroquinone (about 0.02% w/v of the sample mixture) was dispersed to the solution and allowed for certain time. The water layer at the bottom was separated and remove while the liquid rubber recovered from the toluene layer by distilling off the solvent at low pressure. The rubber product was washed using aquades and methanol respectively and added with antioxidant sodium ascorbate 0.04 gram (0.6 w/w). The HTNR layer was separated and washed with toluene and methanol. The sample for the test and analysis was purified by repeated precipitation of methanol from the toluene solution and dried in vacuum oven.

2.2.2. Analysis

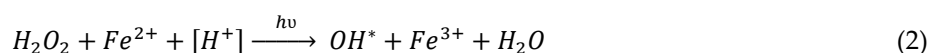
FTIR (*Fourier Transform InfraRed*) spectra of HTNR samples were tested using FT-IR Spectrometer BRUKER Model: Alpha II for analysis and scanned from $400\text{--}4000\text{ cm}^{-1}$. The infrared spectra of HTNR were analyzed with 20 hours interval during a period of 80 hours UV radiation exposure. H-NMR and C-NMR were used to measure the chemical shift such as the H-shift and C-shift of NR Crumb(t_0) and HTNR samples (t_{20} , t_{40} , t_{60} , t_{80}). H-NMR and C-NMR analysis were carried out by using NMR (*Nuclear Magnetic Resonance*) BRUKER ASCEND 700 MHz with 54 mm ASCEND Magnet, and was operated at 28°C . The solvent used for H-NMR and C-NMR analysis was CDCl_3 (Deuterated Chloroform).

The molecular weight of NR and HTNR were determined by GPC (Gel Permeating Chromatography) Shimadzu LC-20AD, with DGU-20ASR degassing unit, and RID-10A Detector [47]. The operation of GPC measurement with the usage of PEEK Columns of $8\mu\text{m}$, $50 \times 7.5\text{ mm}$ and maintained at 30°C , with THF as mobile phase flowing at 1.0 mL/min .

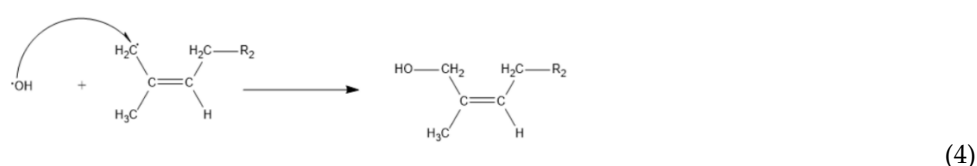
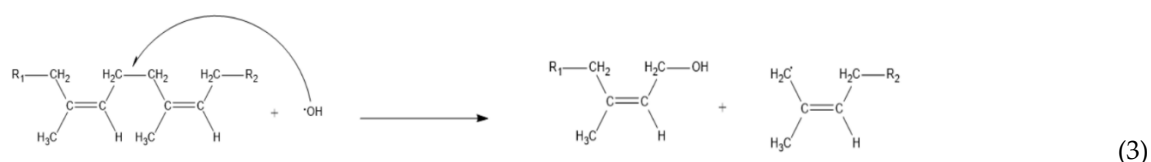
Hydroxyl, Hydroperoxide, Carbonyl and Carboxyl groups concentration were estimated using ATR methods [26, 41, 42, 43, 44, 45, 46]. Hydroxyl broad absorption band (O-H Stretching, b, $3600\text{--}3400\text{ cm}^{-1}$) and C-O stretching of primary alcohol absorption band (m, 1310 cm^{-1}) could be used to confirm the presence of primary hydroxyl groups in HTNR. The addition of TMS (Tetramethyl Silane) was used as reference compound in NMR measurement. ^1H and ^{13}C shielding shift and new peaks could be used to differentiate between NR and its depolymerized counterpart HTNR [26].

2.2.3. Kinetic Model

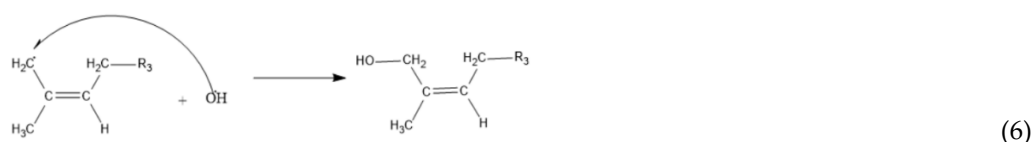
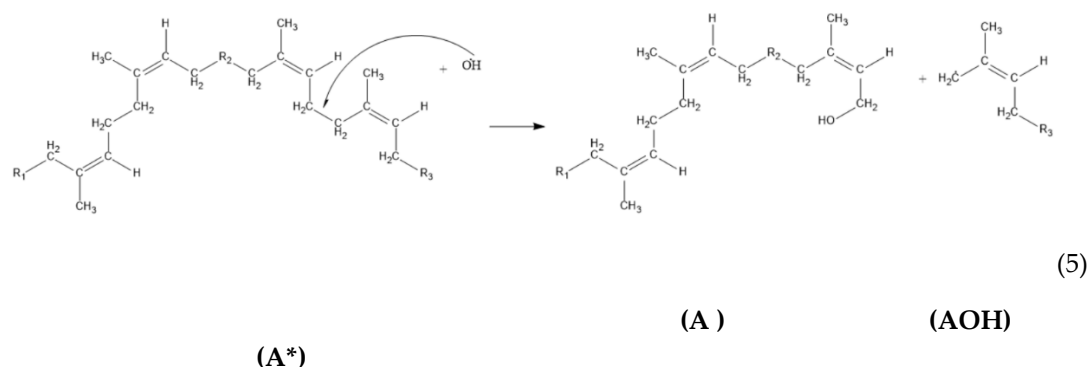
Ravindran (1988) and Pham (2015) proposed a mechanism of HTNR production from LNR depolymerization was initiated by hydroxyl radical production from H₂O₂ decomposition under the radiation of UV light, with the presence of Fenton catalyst or other catalyst in acidic solution which undergo a redox reaction [17,18].

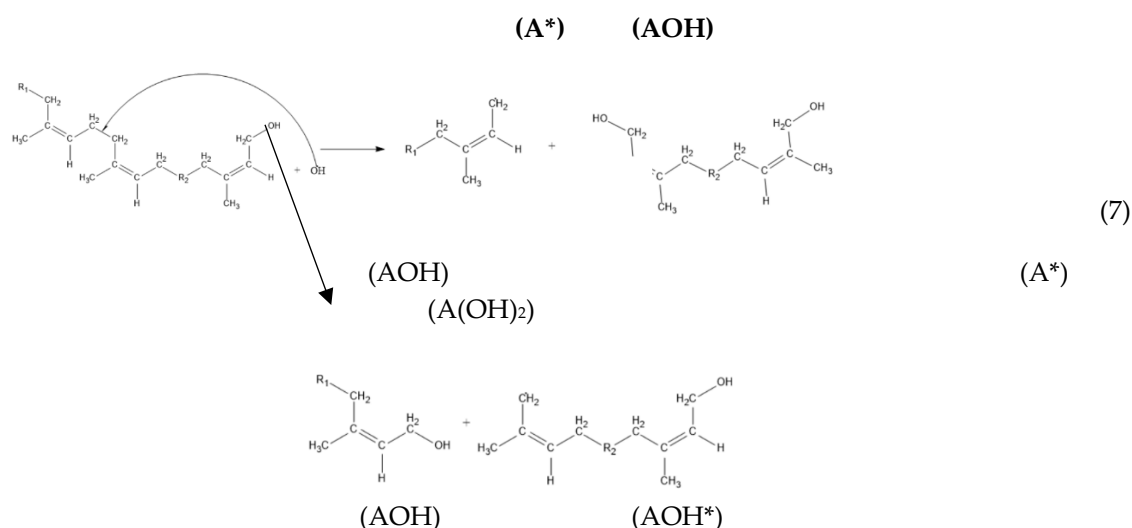


Hydroxyl radical will carried out an attack on CH₂-CH₂ bond with C α site that had a lower steric hindrance is the preferred attack point to produce a pair of hydroxylated natural rubber structure (AOH) and radical natural rubber structure (A*) as depicted in equation (3). Radical structure of natural rubber (A*) will reacted with another hydroxyl radical (OH*) to produce another hydroxylated natural rubber which would have a lower molecular weight as depicted in equation 4. These reactions will occur steadily, resulting much smaller hydroxylated rubber structure's size until depolymerization reaction was terminated.

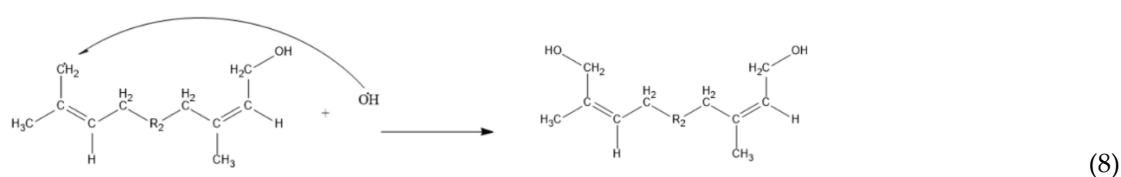


The reaction mechanism was not developed enough to illustrate the production of HTNR, which can be developed further by introducing the HTNR production reaction. Model of Liquid Deproteinized Natural Rubber (DPLNR) [A] reacted with OH radicals generated from Fenton Reaction. The hydroxyl radicals attack the C α site (-CH₂-CH₂-), with the site of lower steric hindrance is preferred to produce one sided hydroxyl terminated natural rubber structure [AOH], and CH₂ radical structure [A*] which will be terminated with OH radicals resulting another one-sided hydroxyl terminated natural rubber structure [AOH].





Structure [AOH] which has one sided hydroxyl group in termination reacted further with hydroxyl radicals. We proposed two reaction pathways, which resulting a one-sided hydroxyl terminated natural rubber structure [F] similar from previous reaction and a two-sided hydroxyl terminated natural rubber structure [H]. The difference of reaction pathways is the radical formation [AOH*] and [A(OH)₂] which may influence the characteristic of the two-sided hydroxyl terminated natural rubber structure.



Hydroxyl radical (OH*) was produced by decomposition of H₂O₂ under radiation of ultraviolet from mercury lamp [16], sunlight [17] and catalyzation by Fenton agent under ultraviolet radiation in acidic solution [18]. The rate constant of hydroxyl radical production was growing to 1,000-10,000 times in the presence of Fenton catalyst [18]. Hydroxyl radical attack on natural rubber (A) resulting to a radical polymer structure (A*) and hydroxylated polymer (AOH) with rate reaction constant of k_p . Radicalized polymer will react with hydroxyl radicals to produce a hydroxylated polymer with rate of reaction of k_t . Depolymerization reaction will occur continuously until the hydroxyl radical was depleted or a termination process occurred. The depolymerization equation of natural rubber followed equation (9) and (10). Rate equation of depletion of reacting polymer (A) will follow a second order reaction and presented in equation (11), which the concentration of hydroxyl radical is excessive. [27].



$$-\frac{d[A]}{dt} = k_p[A]^2 \quad (11)$$

Formation rate of polymer radicals [A*] is steady against time which could be assumed the concentration is constant ($d[A^*]/dt = 0$). The rate of radical polymer [A*] formation is presented with equation (12), while the rate of hydroxylated natural rubber [AOH] was depicted in equation (13).

$$\frac{d[A^*]}{dt} = k_p[A]^2 - k_t[A^*] = 0 \quad (12)$$

$$\frac{d[AOH]}{dt} = k_p[A]^2 + k_t[A^*] = k_p[A]^2 + k_t[A]^2 = 2k_p[A]^2 \quad (13)$$

Referring to equation (13), the kinetics of depolymerization reaction of natural rubber is sufficiently represented by equation (11). Differential equation (11) with natural rubber's initial concentration of $[A]_0$ with time from 0 to t could be solved as equation (14). The value of reaction rate k_p could be obtained by using the data of concentration of natural rubber $[A]$ against time.

$$-\frac{1}{[A]_0} + \frac{1}{[A]} = k_p t \quad (14)$$

The equation reaction (14) could not properly explain the changes in hydroxyl functionality during the depolymerization of NR polymer to HTNR. The equation of reaction could be solved by presenting the formation phase of Hydroxylated Terminated Natural Rubber from NR polymer, which will be written as equation (15) to equation (19). At the initial phase, natural rubber is reacting with hydroxyl radical to form polymer radical $[A^*]$ and a hydroxylated polymer $[AOH]$ with reaction rate constant of k_1 . The polymer radical will react further with another hydroxyl radical to form a new hydroxylated polymer $[AOH]$ with rate constant of k_2 . The hydroxylated polymer will react with hydroxyl radical to form a hydroxylated terminated natural rubber $[A(OH)_2]$ and another polymer radical with reaction rate constant of k_3 . The hydroxylated polymer could also react with a hydroxyl radical to form a hydroxylated polymer radical $[AOH^*]$ and hydroxylated polymer of $[AOH]$ with the rate constant of k_4 . The radical of hydroxylated polymer $[AOH]$ will undergoes a termination reaction with a hydroxyl radical to form a hydroxylated terminated natural rubber $[A(OH)_2]$ with rate constant of k_5 .



Reaction of hydroxyl radical with reactant $[A]$ is second order reaction with the rate equation is similar to equation (13)-(14) with rate constant of reaction is k_1 . The equation of reactant depletion rate is depicted with equation (21).

$$-\frac{d[A]}{dt} = k_1[A]^2 \quad (20)$$

$$-\frac{1}{[A]_0} + \frac{1}{[A]} = k_1 t \quad (21)$$

Polymer radical $[A^*]$ concentration is relatively constant during the depolymerization, thus the change in rate of polymer radical formation is equal to zero. Concentration of polymer radical is

derived in equation (22). The concentration of hydroxylated polymer radical [*AOH] is also relatively constant, with the change in the rate of hydroxylated polymer radical formation is zero as presented in equation (24).

$$+ \frac{d[A^*]}{dt} = k_1[A]^2 + k_3[AOH] - k_2[A^*] = 0 \quad (22)$$

$$[A^*] = \frac{k_1[A]^2 + k_3[AOH]}{k_2} \quad (23)$$

$$\frac{d[^*AOH]}{dt} = k_4[^*AOH] - k_5[AOH] = 0 \quad (24)$$

$$[^*AOH] = \frac{k_5}{k_4} [AOH] \quad (25)$$

The change in growth of concentration of the hydroxylated polymer (AOH) was represented in equation (26). Substituting equation (26) into equation (25) and (24) resulting equation (27). The value of [AOH] concentration is a function of concentration of [A] with rate constant of k_1 .

$$\frac{d[AOH]}{dt} = k_1[A]^2 + (k_3 + k_4)[AOH] - k_4[AOH] + k_2[A^*] \quad (26)$$

$$\frac{d[AOH]}{dt} = 2k_1[A]^2 \quad (27)$$

By combining equation (27) with equation (21) resulting equation (28), with the solvation of differential equation (28) under the initial condition as boundary $[A]_0$, $[AOH]_0$, and reaction time of 0 to t resulting equation (29).

$$\frac{d[AOH]}{d[A]} = 2 \quad (28)$$

$$[AOH] - [AOH]_0 = 2[A] - 2[A]_0 \quad (29)$$

The change in rate of formation of hydroxylated terminated polymer was presented in equation (30). The incorporation of equation (25) and (26) into equation (30) resulted in equation (31) with $k_{34} = k_3 + k_4$. Substitution of equation (25) into equation (30) resulting in equation of $[A(OH)_2]$ as function of [A]. The solution to differential equation of (31) by initial condition as boundary $[A]_0$, $[AOH]_0$ and $[A(OH)_2]_0$ from time 0 to t resulted in equation (33).

$$\frac{d[A(OH)_2]}{dt} = k_3[AOH] + (k_5)[^*AOH] = k_3[AOH] + k_4[AOH] = k_{34}[AOH] \quad (30)$$

$$\frac{d[A(OH)_2]}{d[A]} = \left(\frac{k_{34}}{k_1} \right) \frac{[AOH]_0 + 2[A]}{[A]} \quad (31)$$

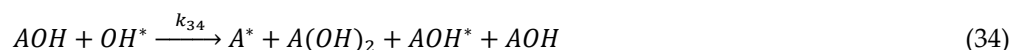
$$[A(OH)_2] - [A(OH)_2]_0 = \left(\frac{k_{34}}{k_1} \right) \left([AOH]_0 \ln \frac{[A]}{[A]_0} + 2([A] - [A]_0) \right) \quad (32)$$

$$[AOH] + [A(OH)_2] = [A(OH)_2]_0 + [AOH]_0 + 2[A] + \left(\frac{k_{34}}{k_1} \right) \left([AOH]_0 \ln \frac{[A]}{[A]_0} + 2([A] - [A]_0) \right) \quad (33)$$

According to equation (25), the value of reaction rate k_1 is obtained from the slope of $1/[A]$ - $1/[A]_0$ plotted against reaction time (t). If the concentration of hydroxylated polymer of [AOH] and $[A(OH)_2]$ was measured in any given time, then the value of (k_{34}/k_1) was obtained from the

relationship of $[AOH] + [A(OH)_2]$ plotted against $[AOH]_0 \ln \frac{[A]}{[A]_0} + 2([A] - [A]_0)$. The value of k_{34} could be determined from the calculated value of k_1 and (k_{34}/k_1) .

The equation of reaction could be simplified into equation (13), (15) and equation (34) to be solve the reaction kinetics.



Hydroxyl functionality value could be determined by using the value of hydroxylated polymer $[AOH]$ which had functionality of 1 and $[A(OH)_2]$ with functionality score of 2 as depicted in equation (35).

$$f_{OH} = \frac{[AOH] + 2[A(OH)_2]}{[AOH] + [A(OH)_2]} \quad (35)$$

The average of molecule weight of polyurethane could be calculated by using a Stockmayer equation [22,28]. The molecular weight average of number of polymer depolymerisation could be calculated using equation (36), which the mole fraction of initial polymer n_A , the weight average of polymer M_A , functionality f_A , and the converted fraction p_A .

$$\overline{M}_n = \frac{n_A M_A}{(n_A) - (n_A f_A p_A)} \quad (36)$$

$$\overline{M}_w = \frac{n_A^2 M_A}{(n_A^2) - (n_A^2 f_A^2 p_A^2)} \quad (37)$$

The influence of reaction temperature against reaction rate constant was studied by observing reaction temperature variation toward changes in reaction rates [48, 49,50]. The relationship of reaction temperature with reaction rates of k_1 and k_{34} followed Arrhenius equation (38) and (39) with A_1 and A_{34} are frequency factor, E_{a1} and E_{a34} are activation energies, with R is ideal gas constant and T is reaction temperature. By plotting the value of $\ln(k)$ against $(-1/T)$ the activation energy values of E_{a1}/R and E_{a34}/R could be derived.

$$k_1 = A_1 \exp \left(\frac{-E_{a1}}{RT} \right) \quad (38)$$

$$k_{34} = A_{34} \exp \left(\frac{-E_{a34}}{RT} \right) \quad (39)$$

3. Results and Discussion

3.1. HTNR Characterization

Infrared spectra of HTNR product and NR under reaction temperature of 30°C, pH system of 2, concentration of $[H_2O_2]$ was 2M, ratio of $[H_2O_2]/[Fe^{2+}]$ was set at 1.5, while the ratio of $[A]/[H_2O_2]$ is equal to 5 and irradiated under UV lights of 320 Watt for 80 hours radiation time $\{t_{80}\}$ was presented by Figure 3.1.

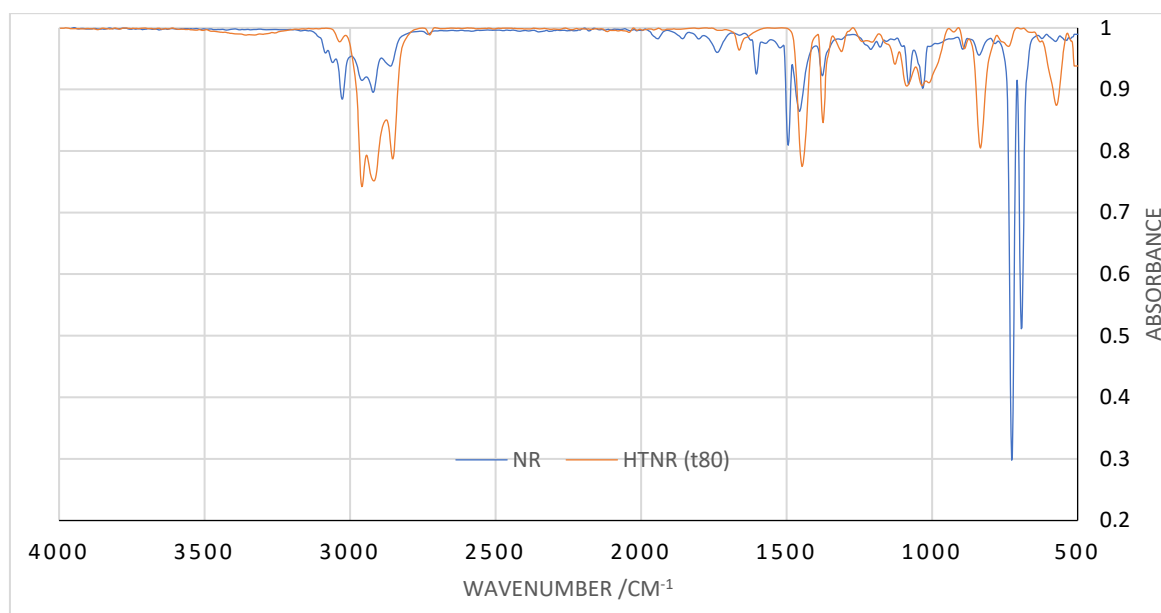


Figure 3.1. NR and HTNR infrared spectra under specific reaction conditions.

The following absorption on IR spectra, both HTNR and NR show the absorption in 3040-3032 cm^{-1} (m), 2980-2958 cm^{-1} (s), 2862 cm^{-1} (s), 2726 cm^{-1} (s) (C-H str.); 1661 cm^{-1} (m, C=C, cis-vinylene); 1446 cm^{-1} (s), 1377 cm^{-1} (s) (C-H def.); 891 cm^{-1} (m, -CH₃ def.); 830 cm^{-1} (s, C-H out of plane def. in -CHR=CCR1) as major IR absorption band characteristics for cis-1,4-polyisoprene (cis-1,4-PIP) [12,16,18]. The HTNR product is characterized by a broad absorption band at 3600 - 3400 cm^{-1} , characteristic of OH stretching vibration; an absorption band at 1310 cm^{-1} (m, C-O str., aliphatic primary alcohol). Meanwhile, the presence of other groups on the LNR chains prepared in neutral and alkaline media can be attributed to the appearance of carbonyl peaks (C=O) at 1720 cm^{-1} for ketone and 1739 cm^{-1} for aldehyde, respectively. The chain breaking of NR at the carbon-carbon single bond is usually due to an attack of radicals and leaving a hydroxyl end group. In contrast, an oxidizing agent can oxidize the broken carbon-carbon double bond in the NR chains to leave a carbonyl end group [27,29].

Spektra 1H-NMR dan 13C-NMR dalam CDCl₃ pada 30°C HTNR yang diperoleh dengan waktu reaksi 20 jam dengan [H₂O₂]=2M, rasio [H₂O₂]/[Fe²⁺]=1.5, dan rasio [A]/[H₂O₂]=5, pH=2, radiasi UV 320 Watt ditunjukkan pada gambar 2 dan 3. Hasil spektra 1HNMR: d = 1.679 p.p.m. [s; -CH₃ (5), 3H]; d = 2.042 p.p.m. [brs; -CH₂-(1) and -CH₂-(4), 4H]; d = 5.125 p.p.m. [m; CH (3), 1H]. Minor peak muncul pada d = 1.254-1.611 ppm menunjukkan adanya produk samping. Peak minor juga ditunjukkan pada d = 2.69 ppm menunjukkan terjadinya epoxy group (Pham, Ravindran). Sinyal proton hydroxyl dalam gugus hydroxymethyl tidak muncul pada d = 4.0 ppm sampai 4.2 ppm.

Spektrum 13C-NMR menunjukkan adanya cis-1,4-PIP at the following positions: C1: d = 32.23 p.p.m.; C2: d = 135.16 p.p.m.; C3: d = 125.03 p.p.m.; C4: d = 26.38 p.p.m.; C5: d = 23.4 p.p.m. Peak minor muncul pada d = 78.39, 76.98 and 75.57 p.p.m. due to CDCl₃ dan d = 60.847 and 64.540 p.p.m. could be due to α -carbons attached to the hydroxyl groups in structures like (I) and (II) (Ravindran, Pham). The allylic hydroxyl protons in the 1H-NMR spectra were masked by the multiples at d = 5.125 p.p.m. of the >C=C-H protons (Equation 9). Several minor peaks could also be observed at d from 2.00 to 3.53 p.p.m. in the 13C-NMR spectrum of HTNR (Figure 3b), indicating the probable side products due to the formation of epoxy group. Adanya gugus hidroksil dari CH₂-OH ditunjukkan adanya the peaks at d = 60.847 p.p.m. and 64.540 p.p.m. yang merupakan characteristic of the α -carbons of allyl alcohol in the 13C-NMR spectrum of HTNR suggest the terminal hydroxyl groups in the product. The allylic hydroxyl protons in the 1H-NMR spectra were masked by the multiples at d = 5.125 p.p.m. of the >C=C-H protons. All the other signal characteristics for both NR and HTNR were observed in the 1H-NMR spectrum (Figures 2a, b): d = 5.08 p.p.m., (=CH); d = 2.00 p.p.m., (-CH₂-); d = 1.67 p.p.m., (-CH₃), as well as in the 13C-NMR spectrum (Figure 3): d = 135.012 p.p.m., (C2 atom); d = 124.900

p.p.m., (C3 atom); d = 32.216 p.p.m., (C1 atom); d = 26.409 p.p.m., (C4 atom); and d = 23.433 p.p.m., (C5 atom). Further evidence was the fact that there was no observed change in the absorption band of the isoprene unit, i.e. at 836 cm⁻¹ in the FTIR spectrum.

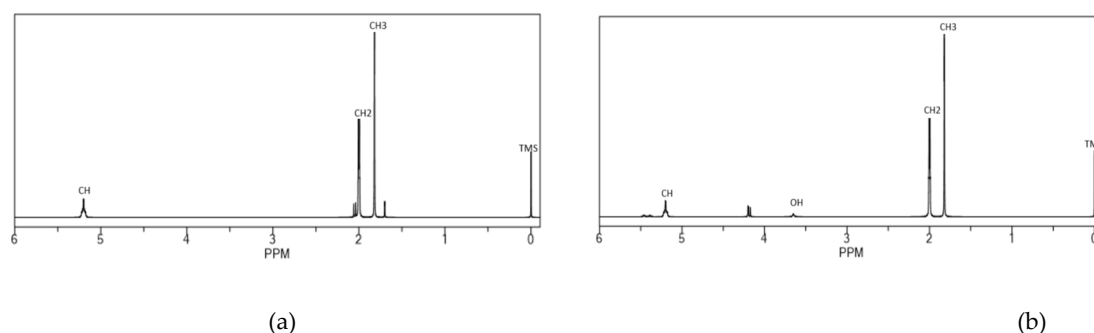


Figure 3.1. H-NMR Spectra of (a) NR and (b) HTNR, prepared by photo-Fenton process.

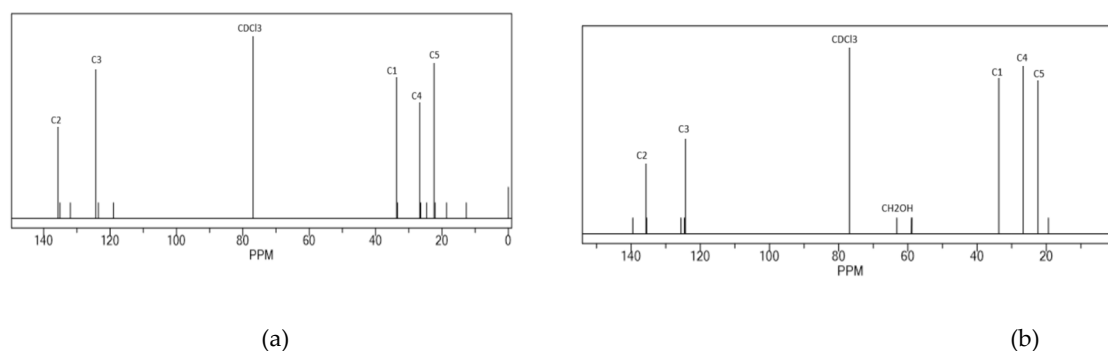


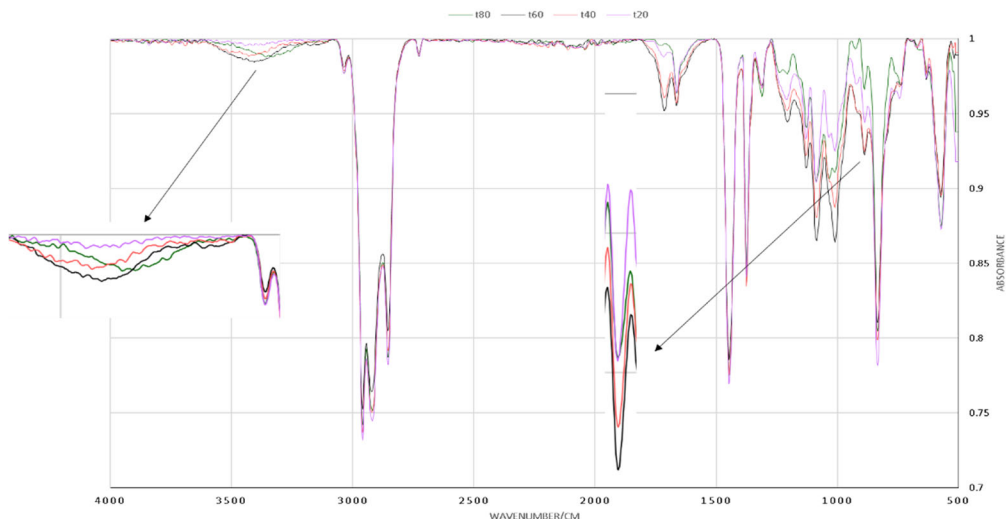
Figure 3.2. C-NMR Spectra of (a) NR and (b) HTNR, prepared by photo-Fenton process.

3.2. Penggunaan Serapan Infra Merah Untuk Analisis Depolimerisasi

Kinetika reaksi depolimerisasi dipelajari dengan melihat absorpsi spesifik dari HTNR dan NR. Pembentukan gugus hidroksil dapat dikarakterisasi dengan absorpsi O-H pada panjang gelombang 3400cm⁻¹. Pengurangan polimer yang terjadi melalui pemecahan ikatan CH₂-CH₂ yang ditunjukkan dengan pengurangan serapan tajam pada panjang gelombang 830cm⁻¹. Peak pada panjang gelombang 1610 terlalu banyak interferensinya. Sebagai referensi, maka dapat digunakan ikatan methyl CH₃ pada panjang gelombang 2980 cm⁻¹ yang relatif tetap (tidak berubah). Untuk kepentingan kinetika reaksi, maka digunakan perubahan absorpsi pada panjang gelombang 830cm⁻¹ untuk pengurangan reaktan, panjang gelombang 3400cm⁻¹ untuk jumlah gugus hidroksil total setiap waktu. Konversi reaktan yang berkurang dihitung dengan persamaan (1).

$$x[A] = \frac{A_{830} - A_{2980}}{A_{2980}} \quad (1)$$

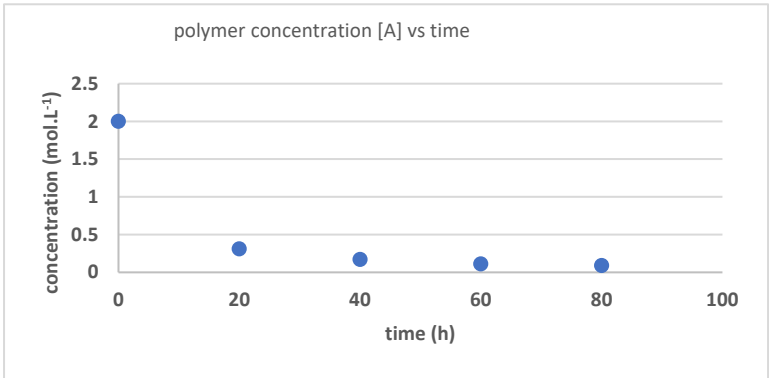
Hasil pengamatan perubahan spektra pada Panjang gelombang 830cm⁻¹, 2980cm⁻¹, dan 3400cm⁻¹ setiap 20 jam untuk reaksi depolimerisasi NR dengan hidrogen peroksida dengan [H₂O₂]=2M, rasio [H₂O₂]/[Fe²⁺]=1.5, dan rasio [A]/[H₂O₂]=5, pH=2, radiasi UV 320 Watt selama 80 jam (t₈₀) ditampilkan pada gambar 2. Terdapat perubahan peningkatan konsentrasi gugus hidroksil [OH] pada panjang gelombang 2400cm⁻¹ secara signifikan, dan penurunan konsentrasi reaktan [A] dengan penurunan absorpsi gugus methylen pada panjang gelombang 830cm⁻¹ secara signifikan. Jumlah gugus methyl pada panjang gelombang 2980cm⁻¹ terlihat konstan, sehingga bisa digunakan sebagai absorpsi referensi.



Gambar 2. Penurunan konsentrasi CH₂-CH₂ dan kenaikan konsentrasi CH₂-OH pada panjang gelombang 830cm⁻¹ dan 3400cm⁻¹ reaksi depolimerisasi NR dengan H₂O₂/Fenton.

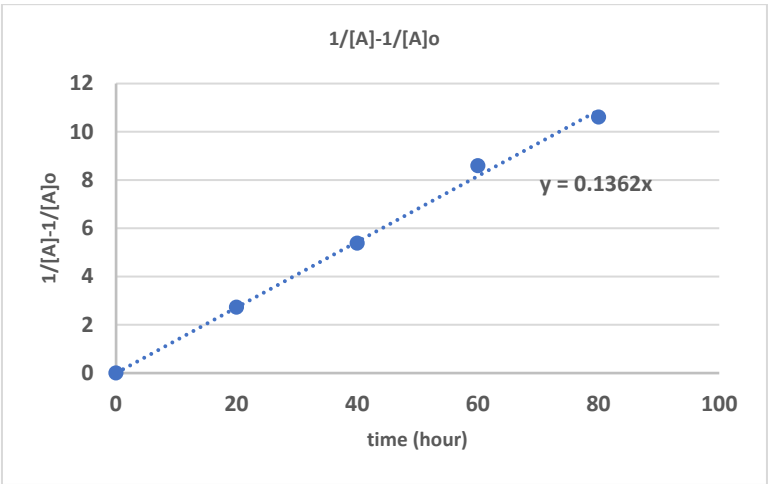
3.3. Kinetika reaksi pembentukan HTNR

Perubahan konsentrasi polimer [A] terhadap waktu ditampilkan pada gambar 4-1. Konsentrasi polimer turun seiring waktu, kemudian penurunan menjadi relatif kecil setelah 60 jam reaksi depolimerisasi dengan konversi di atas 90%. Reaksi dikondisikan dengan gugus hidroksil berlebihan, sehingga tetapan reaksi pembentukan gugus hidroksil tidak dipelajari.



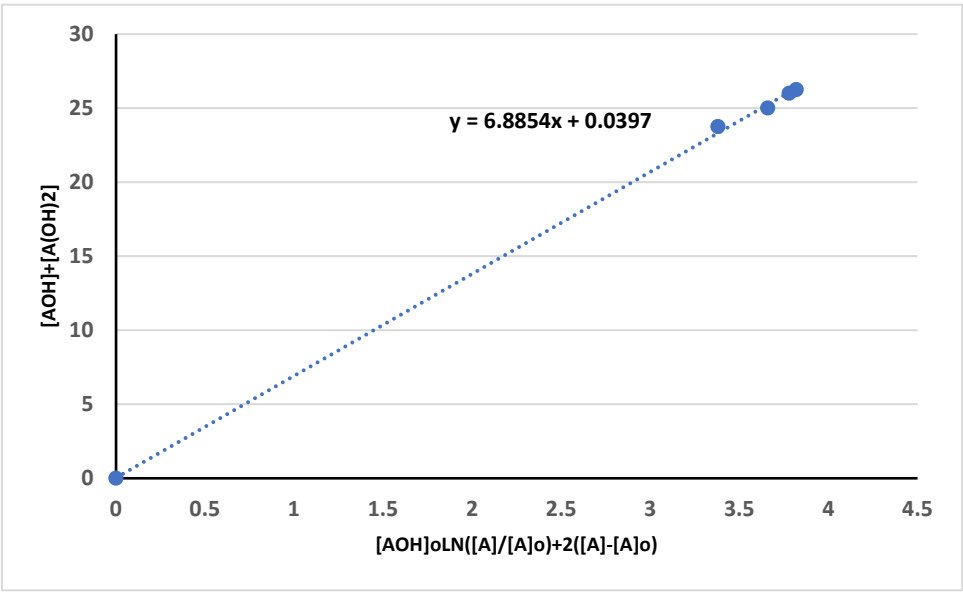
Gambar 4.1. Perubahan konsentrasi [A] terhadap waktu pembuatan HNR.

Reaksi penurunan konsentrasi polimer [A] mengikuti reaksi order 2 ditunjukkan dengan grafik $1/[A]-1/[A]_0$ terhadap waktu dalam bentuk garis lurus. Reaksi depolimerisasi polimer dengan radikal hidroksil merupakan reaksi order 2 seperti hasil serupa dari reaksi depolimerisasi natural rubber dengan hydrogen peroksida pada suhu tinggi (Grishchenko, 1992)), radiasi UV (Ravindran 1986), dan penambahan katalis NaNO₂ (Arayaprane, 2023). Grafik hubungan $1/[A]-1/[A]_0$ terhadap waktu sesuai persamaan (3-13) ditunjukkan pada gambar 4.2. Nilai k_1 diperoleh dari slope grafik tersebut. Nilai k_1 terhitung adalah 0.01356 L.mol⁻¹.s⁻¹.



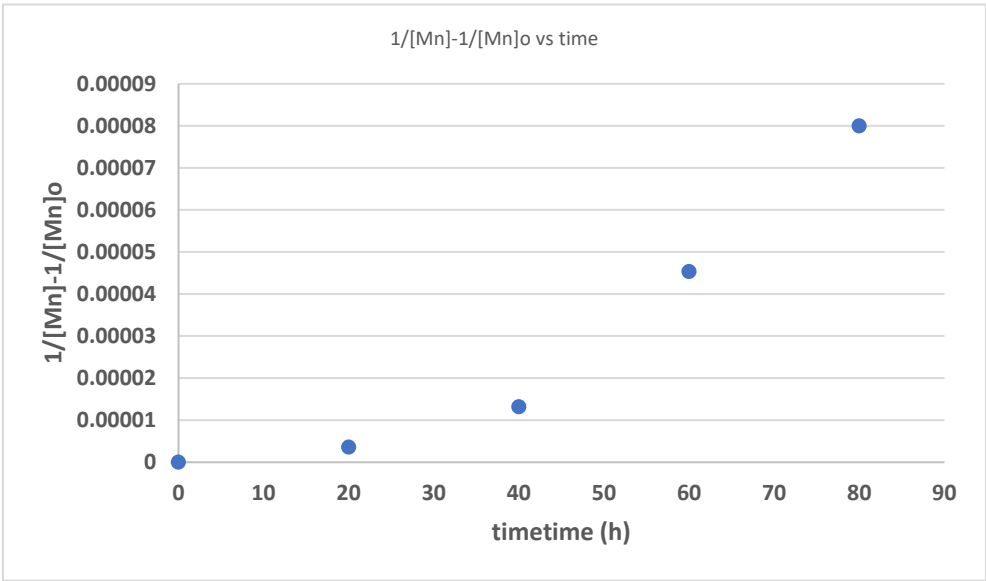
Gambar 4.2. grafik hubungan $1/[A]-1/[A]_0$ terhadap waktu.

Rasio tetapan kecepatan reaksi degradasi AOH terhadap A (k_{34}/k_1) diperoleh dari slope grafik hubungan konsentrasi gugus hidroksil terukur $[AOH]+[A(OH)_2]$ terhadap $[AOH]_0$. $\ln([A]/[A]_0)+2([A]-[A]_0)$ seperti ditunjukkan pada gambar 4.3 mengikuti persamaan (3-24). Berdasarkan nilai (k_{34}/k_1) terhitung, maka nilai k_{34} terhitung adalah $0.9337 \text{ mol.L}^{-1}.\text{s}^{-1}$. Nilai $k_{34}>k_1$ menunjukkan bahwa sebagian besar AOH bereaksi dengan hidroksil membentuk hydroxylated terminated natural rubber (HTNR). Dengan demikian, maka produk dominan adalah HTNR.



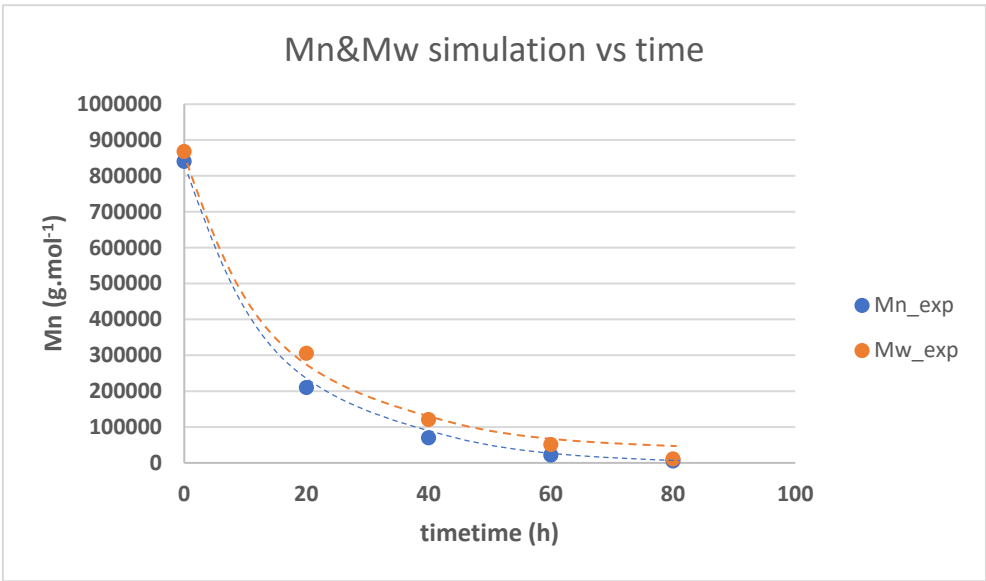
Gambar 4.3. Grafik hubungan $[AOH]+[A(OH)_2]$ terhadap $[AOH]_0 \ln([A]/[A]_0)+2([A]-[A]_0)$.

Perubahan berat molekul rata-rata jumlah (M_n) dan berat molekul rata-rata berat (M_w) hasil pengukuran dan simulasi persamaan (3-27) ditampilkan pada gambar 4.4. Hasil pengukuran dan simulasi memiliki kecenderungan yang sama. Kesalahan estimasi sebesar 2,7%. Hasil tersebut memiliki kemiripan tren dengan percobaan Ravindran, Parmenant (2023), dan Pham (2015) dimana nilai penurunan berat molekul tidak linier. Hasil penurunan dengan basis reaksi order 2, menunjukkan penurunan $1/[Mn]-1/[Mn]_0$ terhadap waktu tidak memberikan garis linier juga (nilai kelurusan 0.820). Hasil tersebut semakin menguatkan hipotesis bahwa terbentuk reaksi pembentukan hydroxylated terminated natural rubber.



Gambar 4.4. Grafik hubungan 1/[Mn]-1/[Mn]o vs time.

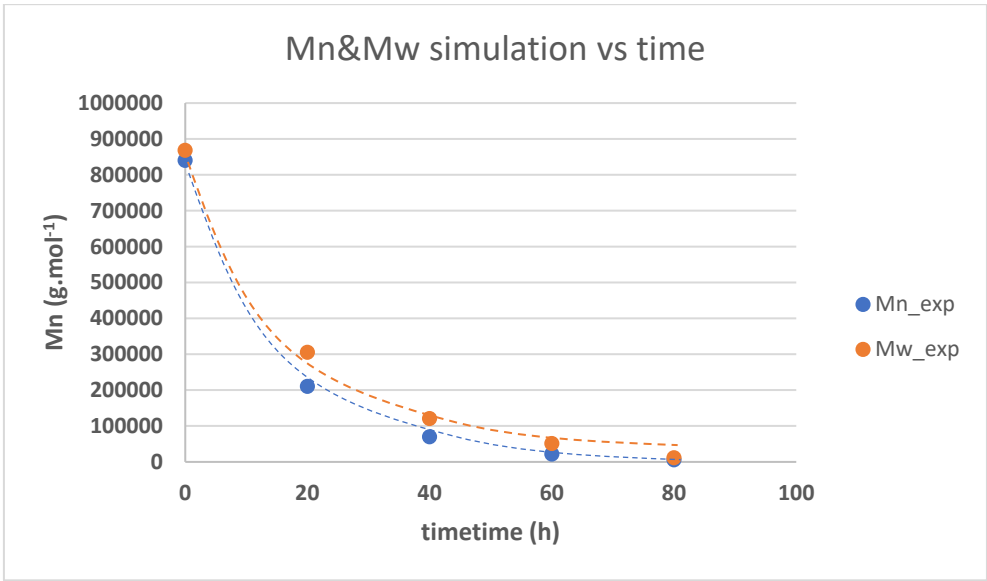
Hasil simulasi berat molekul rata-rata berat dan berat molekul rata-rata jumlah setiap waktu dan hasil pengukuran ditunjukkan pada gambar 4.5. Hasil simulasi menunjukkan nilai yang selalu sedikit di bawah dari nilai hasil eksperimen. Tren tersebut mendekati hasil percobaan dari Ravindran maupun Pham. Nilai PDI (polymerization degree index) menunjukkan nilai sekitar 2, seperti ditunjukkan pada table 4.1. Nilai PDI semakin meningkat seiring dengan waktu.



Gambar 4.5. Grafik hubungan Mn dan Mw terhadap waktu dan hasil simulasinya.

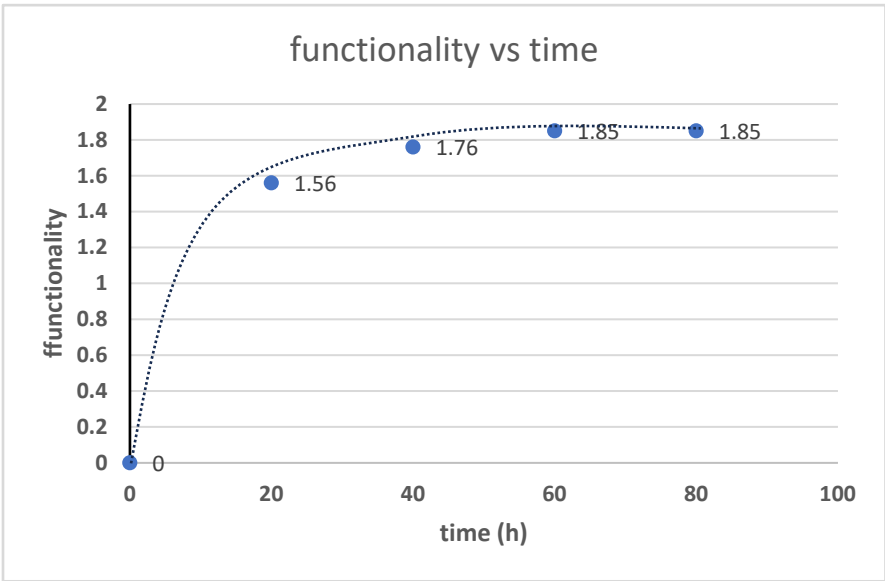
Table 4.1. PDI of HTNR.

Time (hours)	Mn_exp	Mw_exp	1/[Mn]-1/[Mn]o	PDI
0	840000	868000	0	1.033333
20	210000	305100	3.57E-06	1.452857
40	69700	120500	1.32E-05	1.728838
60	21500	51000	4.53E-05	2.372093
80	5300	11100	0.00008	2.09434



Gambar 4.5. Profile berat molekul rata-rata hasil pengukuran dan simulasi terhadap waktu.

Fungsionalitas HTNR dihitung menggunakan persamaan (3-27), grafik hubungan fungsionalitas simulasi dan hasil pengukuran ditampilkan pada gambar 4.6. Nilai hasil pengukuran lebih rendah daripada hasil simulasi dengan tingkat kesalahan 2%. Nilai fungsionalitas dapat didekati dengan model kinetika tersebut sangat baik.

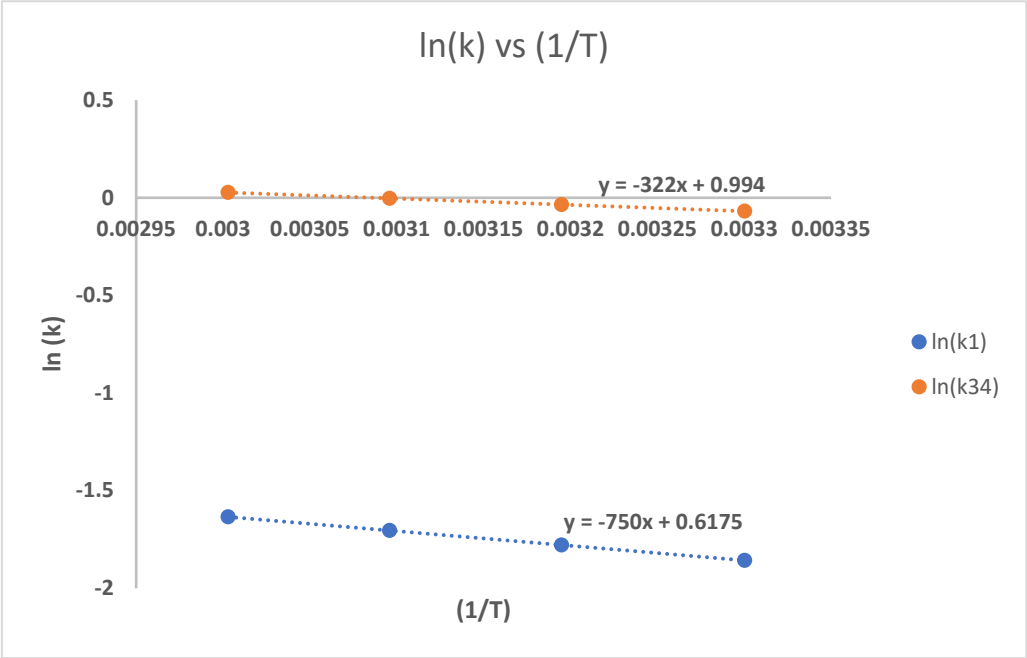


Gambar 4.6. fungsionalitas hidroksil terhadap waktu.

3.4. Pengaruh Suhu Reaksi

Pengaruh suhu reaksi terhadap tetapan kecepatan reaksi pembentukan HTNR dipelajari dengan menggunakan variasi suhu reaksi 30, 40, 50, dan 60oC dengan parameter lain tetap [H₂O₂]=0.2M, [H₂O₂]/[Fe(II)⁺⁺]=1.5, pH=2.5, and [H₂O₂]/[A]=1.5. Nilai k₁ dan k₃₄ diperoleh dari grafik 1/[Mn]-1/[Mn]_o terhadap waktu dan [AOH]+[A(OH)₂] terhadap [AOH]_o Ln([A]/[A]_o)+2([A]-[A]_o). Hasil perhitungan nilai k₁ dan k₃₄ digunakan untuk membuat grafik hubungan ln k terhadap (-1/T) seperti ditunjukkan pada gambar 4.7. Nilai Energi aktivasi (Ea₁/R dan Ea₃₄/R) diperoleh sebagai slope dari grafik tersebut mengikuti persamaan Arrhenius (3-28) dan (3-29). Nilai koefisien tumbukan A₁ dan A₃₄ merupakan intersep dari grafik tersebut. Nilai Ea₁/R, Ea₃₄/R, A₁, dan A₃₄ terhitung adalah 750 K dan 1200 K, 1.854, and 2.72. Nilai Ea/R positive menunjukkan bahwa reaksi bersifat eksotermis. Nilai Ea₁/R<Ea₃₄/R menunjukkan bahwa reaksi pembentukan radikal lebih cepat daripada reaksi pemecahan AOH.

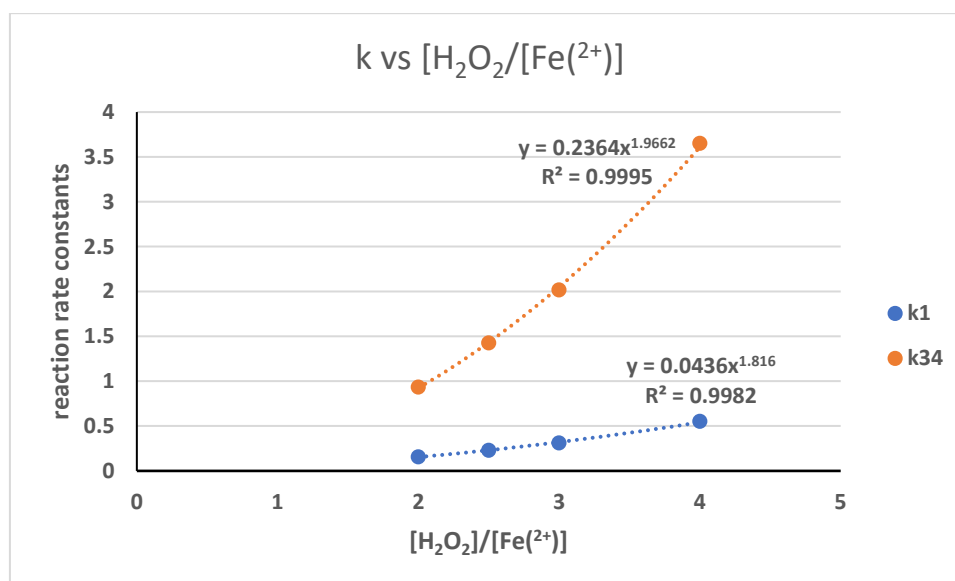
Menurut Pham (2015), reaktivitas radikal hidroksil untuk menyerang ikatan CH₂-CH₂ lebih besar daripada ikatan CH₂-CH₂ yang terdapat gugus hidroksil, karena elektronegativitasnya lebih bermuatan positive. Bla-bla-bla. Kenaikan k₁ dan k₃₄ untuk setiap kenaikan suhu 10 derajat menunjukkan kurang dari dua kali dari nilai k₁ dan k₃₄ semula, menunjukkan bahwa reaksi depolimerisasi merupakan reaksi rezim difusi. Difusifitas merupakan tahapan yang menentukan reaksi dan areaksi dianggap reaksi yang cukup cepat.



Gambar 4.7. grafik hubungan ln (k) terhadap (1/T).

3.5. Pengaruh Rasio Reaktan Dengan Katalis

The optimal ratio of [A]/[H₂O₂] optimal was 1.5 which indicate the excessive presence of hydroxyl radicals (Pham, 2015). Meanwhile the influence of [H₂O₂]/[Fe(II)] ratio against reaction rate was studied using ratio variation of 1, 1.5, 2.0, and 2.5. The ratio influence of [A]/[H₂O₂] toward the calculated reaction rate constant was depicted by gambar 4.8. The graph illustrated the relationship of k₁ and k₃₄ against [A]/[H₂O₂] as power equation with the power value of 1.97 against k₁ and 1.82 toward k₃₄. This result is in accordance with Arayaprane works (2023) of similar depolymerization reaction using NaNO₂ catalyst, which depict the influence of concentration of H₂O₂ and NaNO₂ against radical production as power equation.



Gambar

4. Conclusions

In general, the depolymerization reaction kinetics of NR conversion to HTNR using H₂O₂ under the presence of Fenton catalyst in acidic environment and ultraviolet radiation can be studied using Infrared Spectroscopy to inspect the changes of molecular weight and functionality of HTNR product. HTNR synthesis follow reaction mechanism of: a) hydrogen peroxide react with Fenton in the acid condition produce hydroxyl radical, b) hydroxyl radical is reacted with NR produce radical NR and hydroxylated NR, c) radical NR is reacted with hydroxyl radical produce hydroxylated NR, and d) hydroxylated NR is reacted with hydroxyl radical produce lower radical NR, hydroxylated terminated NR, radical NR, and hydroxylated NR.

Elucidation of product revealing the presence of HTNR with hydroxyl group absorption at wavenumber of 3,400 cm⁻¹. Depolymerization also occurred with the decline of average molecular weight for each period of sample measurement. The NR polymer decline due to conversion to HTNR was observed at absorption band of CH₂-CH₂ group at 850 cm⁻¹, the value of total hydroxyl produced at 3,400 cm⁻¹ and absorption of CH₃ reference group which remain unchanged at 1850 cm⁻¹.

Reaction kinetics was studied by employing an assumption of the excessive hydroxyl concentration. The NR polymer degradation reaction is following reaction order of 2 with rate constant k_1 . Hydroxylated natural rubber production reaction was conformed to be first order reaction with rate constant of k_{34} . The number average of molecular weight (M_n), and weight average of molecular weight (M_w), and OH functionality was matched in satisfactory condition. Reaction rate data of $k_{34} > k_1$ described the conversion reaction of HTNR occurred quickly. The average of functionality is between 1.8 to 1.9 revealed a dominant HTNR production. Reaction reached an optimum rate at 60 hours period which the OH functionality at the maximum value.

The influence of reaction's temperature against reaction rate followed Arrhenius reaction with activation energy values of E_{a1}/R and E_{a34}/R are 750 K and 1200 K. Meanwhile the effect of concentration of H₂O₂/Fenton is following Fenton reaction with power coefficient of 1.97 against k_1 and 1.82 toward k_{34} .

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