



# Effects of Production Parameters on the Development of Polymer-Based Biodiesel Heterogeneous Catalyst I

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## Abstract

*Polymer catalyst for biodiesel production was developed and the catalytic activity dependence on preparation condition, ranging from adsorbed radiation dose, reaction temperature and retention time were investigated in this study. The catalyst was synthesized by radiation-induced graft polymerization of 4-chloromethylstyrene onto a polyethylene substrate followed by amination with trimethylamine and was further treated with sodium hydroxide solution. Gamma radiation was directed at a constant rate of 20kGy/hr on four different samples of polyethylene substrates at different exposure times ranging from 60 to 150 minutes to attain the required dose, a zero rate order was established for the grafting stage. X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) were employed to characterize the catalyst, the results indicate that polymer catalyst is a potential heterogeneous catalyst for biodiesel production.*

**Keywords:** Polymer catalyst, polyethylene, 4-chloromethylstyrene, gamma radiation.

## 1. Introduction

Over the years, efforts have been directed towards salvaging our world through provision of environment friendly alternative energy sources. Biodiesel is a clean burning fuel derived from a renewable feedstock such as vegetable oil or animal fat (Daniel, 2010). It is biodegradable, non-inflammable and non-toxic and produces lesser carbon IV oxide than petroleum based fuel (Dhanasekaran *et al*, 2012). Currently, biofuels development focuses more on boosting feedstock production and development of novel heterogeneous catalyst (Yuji *et al*, 2011). Conventional biodiesel production is currently based on transesterification of vegetable oil or animal fats (Gerpen *et al*, 2004; Gelbard, 2005 and Daniel, 2010) using homogeneous alkaline catalyst (Encinar *et al*, 2005 and Felizardo *et al*, 2006). The major setback of the method is complexity on catalyst separation from the product after production (Ueki *et al*, 2010). So efforts are being made by scientists globally to develop novel catalysts that will offer best environmental practices at relatively good cost for the production of biodiesel (Ejikeme *et al*, 2009).

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Daniel Bowen (2010): Effect of Fatty Acid Structure on Biodiesel (<http://biodieselisgood.Com/Chemistry/Effect-Of-Fatty-Acid-Structure-On-Biodiesel>) Pp 1-4

Dhanasekaran, K. and Dharmendirakumar, M.D. (2012): A Kinetics Study of Biodiesel in Waste Cooking Oil. African Journal of Biotechnology, 11(41): 9797-9804

Ejikeme P. M., Anyaogu I. D., Ejikeme C. L., Nwafor N.P., Egbuonu, C. A. C., Ukogu K and Ibemesi J. A. (2009): Catalysis in Biodiesel Production by Transesterification Processes- An Insight. E-Journal of Chemistry, 7(4), 1120 – 1132.

Ejikeme P. M., Egbuonu C. A. C. and Anyaogu I. D. (2008): Fatty Acid Methyl Esters on Melon Seed Oil, Characterization for Potential Fuel Applications Book of Proceedings, Coalcity Chem. Enugu Nigeria.

Encinar J M., Gonzalez J. F., Rodriguez-Reinares A, (2005): Biodiesel from used frying oil. Variables affecting the yields and characteristics of the biodiesel. Ind. Eng. Chem. Res. 44, 5491-449.

Felizardo, P., Correia, M.J., Raposo, I., Mendes, J.F., Berkemeier, R., Bordado, J.M. (2006): Production of biodiesel from waste frying oils. Waste Manager., 26(5), 487-494.

Gelbard, G. (2005): "Organic Synthesis by Catalysis with Ion-Exchange Resins", Industrial and Engineering Chemistry Research 44, 8468-8498.

Gerpen Van J., Shanks B., Pruszko R., Clements D., and Knothe G, (2004): Biodiesel Analytical Methods. National Renewable Energy Lab. 1617 Cole Boulevard, Golden, Colorado 80401-3393, 303-275-3000

Ueki Yuji and Masao Tanada (2010): Catalyst for Production of Biodiesel and its Production Method, and Method for Producing Biodiesel. Patent Application Publication US2010/0170145A1

The economy of transesterification process depends primarily on the type and quantity of the catalyst used among other factors. An insight into some of the various types of catalysts that have been used to effect the transesterification of vegetable oil in the production of biodiesel (Ejikeme *et al*, 2009) reveals the urgent need for further research for a more effective catalyst for biodiesel production (Yuji *et al*, 2011).

Several investigators (Knothe *et al*, 1997 and 2005; Graille *et al*, 1986; Ejikeme *et al*, 2009; Freedman *et al*, 1984; Nouredдини *et al*, 1997) explored the use of base catalyzed process in the production of biodiesel. Knothe *et al*, investigated the use of boiler ashes, potassium hydroxide and sodium hydroxide in the transesterification of palm and coconut oils. It was reported by Freedman *et al*, and Ejikeme *et al*, that the yield was as high as 90%. An identical trend was observed by other investigators (Nouredдини *et al*, 1997; Karaosmanoglu *et al*, 1996 and Jeromin *et al*, 1987). Base catalyzed method has some short coming in that it requires a step of separating and removing the alkali catalyst dissolved in the resulting mixture from transesterification (Ueki *et al*, 2010) in the purification stage. Other obvious setbacks encountered by their uses are high energy demand interference occasioned by the presence of free fatty acid and water vapor during the reaction (Ejikeme *et al*, 2009). The catalyst is also difficult to recycle.

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Freedman, B., Pryde E.H. and Mounts T.L. (1984): "Variables Affecting the Yields of Fatty Esters from Transesterified Vegetable Oils", *Journal of the American Oil Chemists' Society* 61:1638-1643.

Graille J., Lazano P., Pioch D. and Geneste P. (1986): *Oleagineux*, 41, 457-464.

Ejikeme P. M., Anyaogu I. D., Ejikeme C. L., Nwafor N.P., Egbuonu, C. A. C., Ukogu K and Ibemesi J. A. (2009): Catalysis in Biodiesel Production by Transesterification Processes- An Insight. *E-Journal of Chemistry*, 7(4), 1120 – 1132.

Jeromin, L., Peukert, E., Wollman, G., (1987): Process for the Pre-Esterification of Free Fatty Acids in Fats and Oils. US Patent 4698186.

Karaosmanoglu, F., Cigizoghi, K.B., Tuter M., and Ertekin, S., (1996): Investigation of the Refining Step of Biodiesel Production. *Energy Fuels* 10 890 895.

Knothe G, (2005): Dependence of Biodiesel Fuel Properties on the Structure of Fatty Acid Alkyl Esters. *Fuel Processing Technology*, 86(10) 1059-70.

Knothe G., Dunn R. O. and Bagby M. O. (1997): "Biodiesel: the Use of Vegetable Oils and their Derivations as Alternative Diesel Fuels" In *Fuels and Chemicals from Biomass*, ACS, Washington, DC, USA, 172 – 208.

Ueki Yuji and Masao Tanada (2010): Catalyst for Production of Biodiesel and its Production Method, and Method for Producing Biodiesel. Patent Application Publication US2010/0170145A1

Yuji Ueki, Nor Hasimah, Noriaki Seko, and Masao Tamada (2011): Rapid Biodiesel Fuel Production Using Novel Fibrous Catalyst Synthesized by Radiation-Induced Graft Polymerization: *International Journal of Organic Chemistry*, 1, 20-25.

Yonemoto T., N. Kitakawa and T. Toda (2006), "Method for Producing Fatty Acid Ester," Japan Kokai Tokyo Koho, Article ID: 2006-104316, Pp. 1-14.

Zheng S., Kates M., Bube M. A, and Mclean D. D. (2006): *Biomass; Bioenergy*, 30 (3) Pp 267-272.

Most recently, great effort has been contributed by numerous researchers (Zheng *et al*, 2006; Siakpas *et al*, 2006; Shimada *et al*, 2001; Watanabe *et al*, 2005; Nadir *et al*, 2008; Freedman *et al*, 1984; Lotero *et al*, 2005; Wang *et al*, 2006; Crabba *et al*, 2001; Mittelbach *et al*, 1990; Bajaj *et al*, 2010; Stamenkovic *et al*, 2010 and Chiang, 2007)

to develop a biodiesel production method not requiring a complicated catalyst separating step and not producing side products; for example an acid catalyst method, a lipase enzyme method, a solid catalyst etc.

However, these methods still have some problems in that high temperature/high pressure is needed, catalyst regeneration is difficult, catalyst is expensive, catalyst activity is low, reaction speed is slow and the alcohol additional amount control is indispensable; therefore, it is said that these methods are unfavorable for industrial use (Ueki *et al*, 2010).

Recently, the use of porous anion exchange resins was investigated by Shibasaki-kitakawa *et al*, as a modification technique over the traditional alkaline catalyst method (Yonemoto *et al*, 2006 and Shibasaki-kitakawa *et al*, 2007). According to the method of using such a porous anion exchange resin, the catalyst does not dissolve in the reaction system, and therefore a step of separating the catalyst is omitted. However, sample diffusion into the pores of the catalyst has been found to be rate-limiting since the catalyst has a reaction site inside the pores (Yuji *et al*, 2011), thus limiting its use in the mass-scale industrial production of biodiesel fuel. Thus this study is aimed at the development of a polymer catalyst through radiation-induced graft polymerization of polyethylene substrate, investigating its catalytic activity dependence on preparatory condition

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Bajaj. A, P. Lohan, P. N. Jha and R. Mehrotra, (2010): Biodiesel Production through Lipase Catalyzed Transesterification: An Overview, *Journal of Molecular Catalysis B: Enzymatic*, Vol. 62, No. 1, Pp. 9-14.

Crabba E., Nolasco-Hipolito C, Kobayashi G., Sonomoto K., and Ishizaki A., (2001): Biodiesel Production from Crude Palm Oil and Evaluation of Butanol Extraction and Fuel Properties, *Process Biochemistry*, 37 (1), 67-71.

Chiang Mai J. (2007): Biodiesel Synthesis from Transesterification by Clay-Based Catalyst. [www.Science.Cmu.Ac.Th/Journal-Science/Josci.Html](http://www.Science.Cmu.Ac.Th/Journal-Science/Josci.Html) 34(2): 201 - 207.

Lotero E, Liu Y, Lopez D E, Suwannakarn K, Bruce D A, and Goodwin Jr J. G., (2005): Synthesis of Biodiesel Via Acid Catalysis. *Ind Eng Chem Research*, 44(14)5353-5363.

Mittelbach. M, (1990): Lipase Catalyzed Alcoholysis of Sunflower Oil, *Journal of American Oil Chemists' Society*, Vol. 67, No. 3, Pp. 168-170.

Nadir D and Bulent K. (2008): *Biomass. Bioenergy*, 32(12), 1274 – 1278 DOI: 10.1016/J. Biombioe 005.

Noureddini H., Zhu D, (1997): Kinetics of Transesterification of Soybean Oil. *J Am Chem Soc* 74(11)1457-1463. Shimada V. Watanabe Y, Sugighara A, Baba T, Ooguri T, Moriyana S, Tarai T and Tominaga Y. (2001): *J. Biosci; Bioeng*, 92(1), 19 – 23.

Siakpas P., Karagiannidis A. and Theodoseli M. (2006): Biodiesel Feedstock, Production and Uses in World Sustainable Energy Days, 1-3 March, Wels/Austria, *Electronic Proceedings in CD-ROM*, Editor: O Oe Energies-Parverband.

Stamenković. O. S , V. B. Veljkovic, Z. B. Todorovic, M. L. Lazić, I. B. Banković-Ilić and D. U. Skala, (2010): Modeling the Kinetics of Calcium Hydroxide Catalyzed Methanolysis of Sunflower Oil,” *Bioresource Technology*, Vol. 101, No. 12, Pp. 4423-4430.

Shibasaki-Kitakawa N, H. Honda, H. Kuribayashi, T. Toda, T. Fukumura and T. Yonemoto, (2007): Biodiesel Production Using Anionic Ion Exchange Resin as Heterogeneous Catalyst, *Bioresource Technology*, Vol. 98, No. 2, Pp. 416-421.

Ueki Yuji and Masao Tanada (2010): Catalyst for Production of Biodiesel and its Production Method, and Method for Producing Biodiesel. Patent Application Publication US2010/0170145A1

Wang Y, Ou S., Liu P, Xue F, and Tang S. (2006): Comparison of Two Different Processes to Synthesize Biodiesel by Waste Cooking Oil. *Journal Molecule Catalysis A: Chemical* 252(1-2), pp. 107-112.

Watanabe Y., Pinsirodom P., Nagao T., Kobayashi T., Nishida Y., Takagi Y and Shimada Y. (2005): *J. Am. Oil Chem. Soc.*, 82 (11) 825-831.

Yuji Ueki, Nor Hasimah, Noriaki Seko, and Masao Tamada (2011): Rapid Biodiesel Fuel Production Using Novel Fibrous Catalyst Synthesized by Radiation-Induced Graft Polymerization: *International Journal of Organic Chemistry*, 1, 20-25.

## 2. Materials and Methods

### 2.1 Materials

The reagents used in this study include analytical grade polyethylene substrate, 4-chloromethylstyrene, polysorbate20 or tween20 concentration, trimethylamine solution; methanol obtained from SIGMA-ALDRICH Chemicals and Co, USA and distilled water.

### 2.2 Methods

#### 2.2.1 Polymer Catalyst Preparation

##### 1. Polyethylene Substrate Activation Step (Pre-irradiation/irradiation)

Scout Pro SPU 401 weighing scale was used to weigh 240g of polyethylene sample. The sample was then divided into four (4) equal parts of 60g each and then packaged. The samples labeled A, B, C, and D respectively were irradiated using the radiation facilities at the VINCA Institute of Nuclear Sciences (laboratory for radiation chemistry and physics) Belgrade Serbia. The irradiation was conducted at a dose rate of 20kGy/h for 20, 30, 40 and 50kGy with polyethylene samples A, B, C and D respectively (Cleland, 1992 and Ueki *et al*, 2010). Thereafter, the dose rate, absorbed dose and exposure times were measured and recorded.

##### 2. Graft Polymerization of Irradiated Polyethylene Substrates

(a.) The Monomer Emulsion Solution (MES) was obtained by using equation 2 as follows: 50ml of 4-Chloromethylstyrene solution was measured into a beaker using a measuring cylinder. 10% of its equivalent volume amounting to 5ml of Polysorbate 20 (tween20 concentration) was measured and added to the content inside the beaker. 50ml of distilled water was also measured and added to the mixture and then stirred vigorously (Bhattacharya *et al*, 2004 and Ueki *et al*, 2010). The beaker labeled Sample E was carefully observed and the findings were recorded accordingly.

$$\left( \begin{array}{c} \text{Monomer} \\ \text{Emulsion} \\ \text{Solution} \\ \text{[MES]} \end{array} \right) = \left( \begin{array}{c} \text{Functional} \\ \text{Monomer} \end{array} \right) + (\text{Surfactant}) + (\text{Solvent}) \dots \dots \dots 1$$

$$\left( \begin{array}{c} \text{Monomer} \\ \text{Emulsion} \\ \text{Solution} \end{array} \right) = \left( \begin{array}{c} 50\text{ml} \\ \text{of} \\ 4\text{-Chloromethylstyrene} \end{array} \right) + \left( \begin{array}{c} 5\text{ml} \\ \text{of} \\ \text{Polysorbate} \\ 20 \end{array} \right) + \left( \begin{array}{c} 50\text{ml} \\ \text{of} \\ \text{Distilled} \\ \text{Water} \end{array} \right) \dots \dots 2$$

Sources: Ueki *et al*, (2010) and Yuji *et al*, (2011)

(b.) Irradiated samples A, B, C, and D, each weighing 5.1g were measured and packaged in sacks made from open mesh fabrics. The sacks with their respective contents were each dipped into beakers containing sample E in them and then placed inside an electrical thermostatic water bath boiler model DK-420. The temperature of the system was regulated and maintained at 40°C for a period of 4hours. At every interval of 60minutes (1hour) sample E was withdrawn and analyzed for a change in concentration from the initial concentration at time  $t = 0$  using the Jenway Model 6800 Double-beam spectrometer.

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Bhattacharya A. and Misra B. N (2004): Grafting a Versatile means of Modify Polymers Techniques, Factors and Applications; Progress in Polymer Science Journal. Prog. Polym. Sci 29 767 – 814.  
Cleland M. R. (1992). High Power Electron Accelerators for Industrial Radiation Processing of Polymers, Chapter 3 in Radiation Processing of Polymers, A. Singl and J. Silverman (Eds), Hanser, Munich. 23 – 49.  
Ueki Yuji and Masao Tanada (2010): Catalyst for Production of Biodiesel and its Production Method, and Method for Producing Biodiesel. Patent Application Publication US2010/0170145A1

The weights of samples A, B, C, and D were also measured and recorded using Scout Pro SPU 401 weighing scale having been dried in an oven after grafting (Ueki *et al*, 2010). The procedure was repeated at reaction temperatures of 50°C and 60°C. The temperatures were maintained throughout the specified reaction time by regulating the thermostat of the water bath to the required reaction temperature. The concentration of the monomer emulsion solution for each substrate was recorded accordingly.

### 3. Functional Groups Introduction Step (Amination)

100ml of 0.25mol/L aqueous trimethylamine solution was measured into a beaker. Three different beakers of the same amount were obtained also making a total of four set-ups. The substrate from experiment 2b was then transferred into these beakers by dipping them into the solution contained in them and kept inside the water bath. The temperature of the apparatus was maintained at a constant temperature of 50°C for a retention time of two hours (Ueki *et al*, 2010 and Yuji *et al*, 2011)

### 4. Hydroxyl group substitution step

The resulting substrate from experiment 3 above was transferred into a beaker containing 100ml of 0.1M solution of sodium hydroxide. The reaction condition was maintained at atmospheric temperature and pressure for a retention time of 6hours (Ueki *et al*, 2010 and Yuji *et al*, 2011). After that, the sample was withdrawn and set for the washing operation.

### 5. Washing step

The products from the experimental step above were washed in distilled water and then dried in a laboratory oven Model DHG-9101 at a controlled temperature of 105± 5°C for a period of 1hour (Ueki *et al*, 2010 and Yuji *et al*, 2011). The final products were analyzed and used as biodiesel catalysts.

## 2.2.2 Kinetic study of the polymer catalyst graft polymerization production stage.

The reaction kinetic for the production of the catalyst was explored in order to determine the order of the reaction and rate constant for the graft reaction during catalyst synthesis. Three tests were performed for the order of reaction: zero order, first order, and second order. All kinetics calculations assumed a constant density system (Octave, 2003).

The rate equation for the zero order reaction is shown below in equation 3

$$-r_{MES} = \frac{-dC_{MES}}{dt} = k \dots \dots \dots 3$$

Where,  $-r_{MES}$  is the reaction rate of the monomer emulsion solution,  $C_{MES}$  is the concentration of monomer emulsion solution and k is the rate constant.

The conversion of MES is shown in equation 4 below

$$X_{MES} = \frac{C_{MES,0} - C_{MES}}{C_{MES,0}} \dots \dots \dots 4$$

Where,  $C_{MES,0}$  is the initial concentration of the monomer emulsion solution at time t=0

Separating variables and integrating equation 4, and also putting in terms of conversion, yields equation 5 below

$$\frac{C_{MES,0} - C_{MES}}{C_{MES,0}} = X_{MES} = \left( \frac{k}{C_{MES,0}} \right) t \dots \dots \dots 5$$

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Plotting  $X_{MES}$  versus time will yield a linear pattern with a slope of  $\frac{k}{C_{MES,0}}$  if the reaction is zero order.

The rate equation for a first order reaction is shown in equation 6 below

$$-r_{MES} = \frac{dC_{MES}}{dt} = kC_{MES} \dots \dots \dots 6$$

Separation of variables and integrating of equation 6 and also putting in terms of conversion yields equation 7

$$-\ln\left(\frac{C_{MES}}{C_{MES0}}\right) = -\ln(1 - X_{MES}) = kt \dots \dots \dots 7$$

Plotting  $-\ln\left(\frac{C_{MES}}{C_{MES0}}\right)$  or  $-\ln(1 - X_{MES})$  versus time will yield a linear pattern with a slope equal to k if the reaction is first order

3. The rate equation for a second order reaction is given by equation 8

$$-r_{MES} = \frac{dC_{MES}}{dt} = kC_{MES}^2 \dots \dots \dots 8$$

Separation of variables and integration of equation 8 and also putting in terms of conversion yield equation 9

$$\frac{1}{C_{MES}} - \frac{1}{C_{MES0}} = \frac{1}{C_{MES0}} \left(\frac{X_{MES}}{1 - X_{MES}}\right) = kt \dots \dots \dots 9$$

A Plot of  $\frac{1}{C_{MES}} - \frac{1}{C_{MES0}}$  versus time, t from equation 9 will show a linear graph with slope equal to k when the reaction is of a second order.

### 2.2.3 Polymer Catalyst Characterization

The physicochemical properties of the synthesized polymer catalysts were studied by X-ray diffraction and Fourier transform infrared characterization techniques. The powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max-3B diffractometer with filtered Cu/K $\alpha$  radiation ( $\lambda = 0.154\text{nm}$ ) of the Advance Physics laboratory at SHESTCO, Abuja, operating at 40kV and 50mA over a  $2\Theta$  range of 0–100° at a scanning speed of 5°min<sup>-1</sup>. Diffraction peaks of crystalline phases present in the samples were compared with those of standard compounds reported in the JCPDS (Joint Committee of the Powder Diffraction Standards) database. A Fourier transform infrared (FT-IR) spectrophotometer was used to identify the functional group of the polymer catalyst. The FT-IR spectra of the polymer catalyst was recorded as KBr disks in the wave number region of 350–4000cm<sup>-1</sup> on Shimadzu IR-Prestige-21 spectrometer with 4cm<sup>-1</sup> resolution. Chemical elemental analyses of the polymer catalysts were carried out by Multi Environmental Management Consultants Limited, Lagos

## 3. Results and Discussion

### 3.1 Catalyst Preparation result

The gamma irradiation was carried out on the substrates to activate the substrates by creating active surface areas in them (Ueki *et al*, 2010 and Bhattacharya *et al*, 2004).

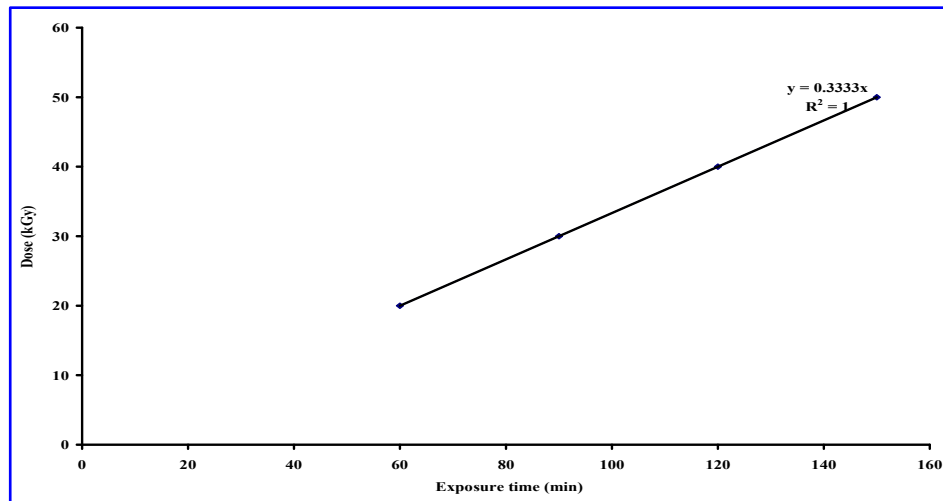
Bhattacharya A. and Misra B. N (2004): Grafting a Versatile means of Modify Polymers Techniques, Factors and Applications; Progress in Polymer Science Journal. Prog. Polym. Sci 29 767 – 814.

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**Table 1: Results of the Irradiation of Polyethylene Substrates.**

Sample	Dose (kGy)	Time of Exposure (min)
A	20	60
B	30	90
C	40	120
D	50	150

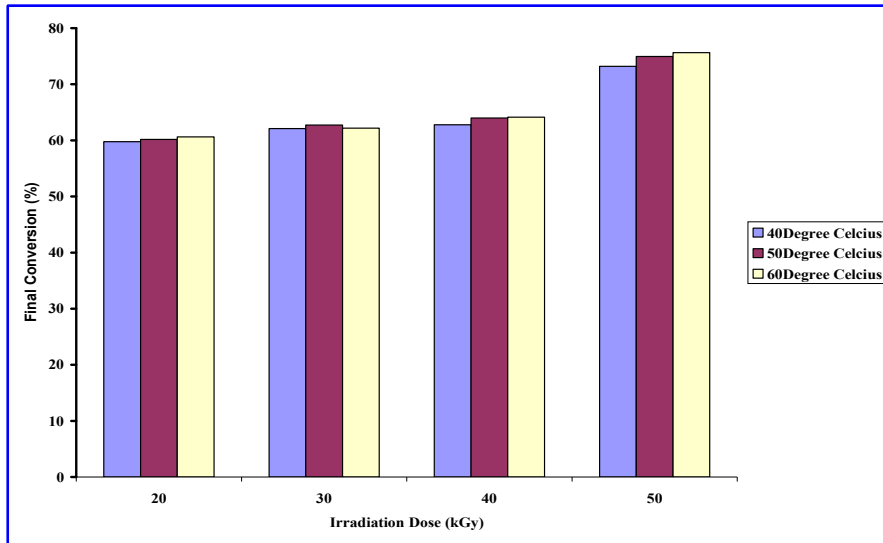
Table 1 shows the gamma irradiation result of the polyethylene substrates. The absorbed doses were found to increase simultaneously as the retention time increases, in line with the reports on the irradiation of non woven polyethylene substrate to 100kGy at a constant dose rate of 20kGy in five hours (Ueki *et al*, 2010 and Yuji *et al*, 2011), while that of this study showed that the substrates that were irradiated at a constant dose rate of 20kGy/hr were found to have adsorbed 20, 30, 40 and 50kGy at exposure times of 60, 90, 120 and 150minutes respectively. This range of irradiation dosage was adopted in line with 20-50kGy reported as adsorbed dose requirement for grafting monomers or Polymerization process (Cleland *et al*, 1993).



**Figure 1: Effect of Exposure time on the Irradiation Dose of Polyethylene Substrates**

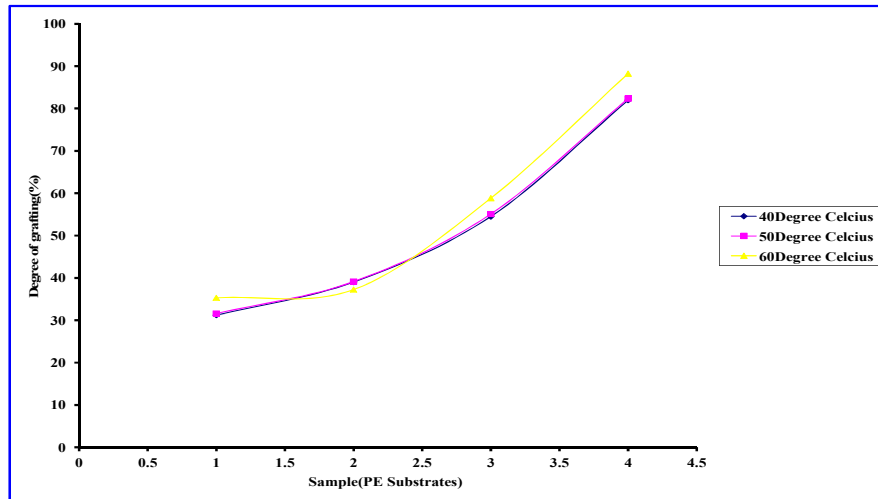
Figure 1 shows the effect of exposure time on the amount of dosage each of the substrates absorbed during the cause of irradiation. Accordingly, Irradiation Dose in kGy was plotted against Exposure Time in minutes. The correlation coefficient  $R^2$  was 1.0 and rate constant 'k' was 0.3333. A correlation coefficient greater than 0.9 ( $R^2 > 0.9$ ) (Anthon *et al*, 2002 and Oderinde *et al*, 2009) in this case confirmed a linear relationship between adsorbed irradiation dose in kGy and exposure time in minutes.

- Anthon, G.E and Barrett, D.M. (2002): Kinetic parameter for the thermal inactivation of quality related enzymes in carrots and potatoes. *Journal of Agriculture and Food Chemistry*, 50, 4119-4125.
- Cleland M. R., O' Neil, M. T. and Thompson C. C. (1993): Sterilization with Accelerated Electrons, Chapter 9 in *Sterilization Technology, a Practical Guide for Manufacturers and Users of Health Care Products*, R. F. Morrissey and G. B Phillips (Eds), Van Nostrand Reinhold, New York 218-253.
- Oderinde, R.A., Ajayi, I.A. and Dewuyi, A.A (2009): Characterization of Seed and Seed Oil of *Huracrepitans* and the Kinetics of Degradation of the Oil during Heating, *electronic journal of environment, agriculture and food chemistry*. ISSN: 1579-4377, 8 (3),
- Ueki Yuji and Masao Tanada (2010): Catalyst for Production of Biodiesel and its Production Method, and Method for Producing Biodiesel. Patent Application Publication US2010/0170145A1
- Yuji Ueki, Nor Hasimah, Noriaki Seko, and Masao Tamada (2011): Rapid Biodiesel Fuel Production Using Novel Fibrous Catalyst Synthesized by Radiation-Induced Graft Polymerization: *International Journal of Organic Chemistry*, 1, 20-25.



**Figure 2: Effect of Irradiation Dose at various temperatures on Substrates Conversion during Grafting.**

Figure 2 shows the effects of reaction temperature and the amount of irradiation doses on the rate of grafting or modification of the substrates. The result reveals that reaction temperature has no significant effect on the rate of modification of the substrate whilst irradiation dose absorbed affect significantly the grafting/modification rate of the substrates. This arises from the fact that the irradiation creates significant or larger surface area on the surface of the substrate and as well as produces unique effects that cannot be duplicated by other means (Ueki *et al*, 2010 and Cleland *et al*, 2002). From the results sample D varies in conversion from 60.62 to 75.64% at the same reaction temperature. This shows a significant increase of 24.78% due to varied irradiation dose as compared to 59.78 to 60.62% amounting to 1.41% insignificant increase arising from varied reaction temperatures.



**Figure 3: Effect of Temperature on the Degree of Grafting of Polyethylene Samples**

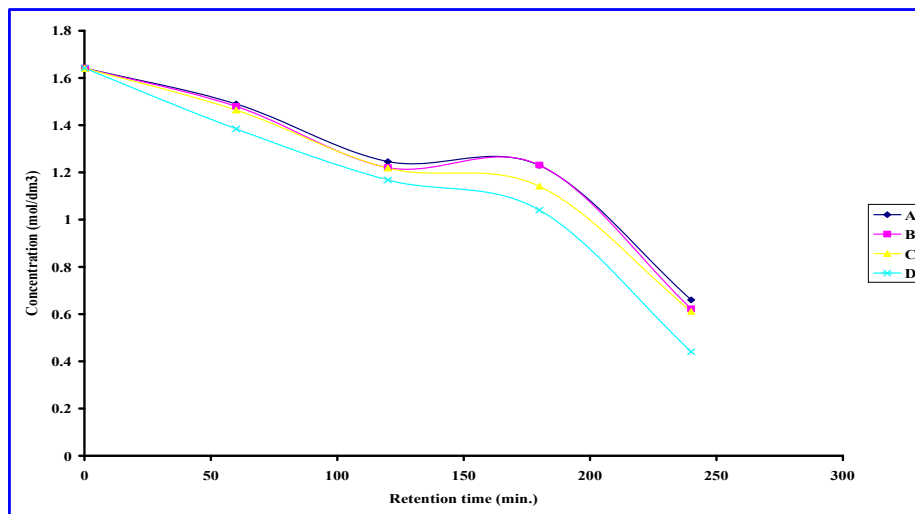
Figure 3 reveals the effect of temperature on the degree of grafting in the grafting of irradiated polyethylene substrates. Temperature effect is minimal when compared to the effect of pre-irradiation on this same variable.

Cleland M. R, (2002): The Use of Dose and Charge Distributions in Electron Beam Processing Radiat. Phys. Chem. Vol. 63, Nos. 3-6: 729-733

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For polyethylene substrate irradiated at 20kGy, 60°C reaction temperature gave the highest percentage of degree of grafting but yielded the lowest on polyethylene substrate irradiated at 30kGy. At the same reaction temperature of 60°C the substrates irradiated at 40 and 50kGy respectively produced the high degree of grafting when compared to reaction temperatures of 40 and 50°C respectively. Higher temperatures were being avoided during the cause of carrying out the experiment based on the observation and strengthened by the fact that heating a catalyst above a certain critical temperature may cause it to lose its activity, often permanently (Octave, 2003).



**Figure 4: Concentration Profile of Sample E at 40°C on the Grafting of polyethylene**

Figure 4 shows concentration profile of sample E (Monomer Emulsion Solution) during grafting, at 40°C the concentrations of sample E on reacting with samples A, B, C and D show a rapid decline in their respective curves as the retention times increase. This shows that the monomer is being grafted to the PE substrate main chain. Variations in the curves as observed from these results reveal the effects of irradiation on the rate at which the monomer is being grafted to the parent chain of the substrate (Yamaki *et al*, 2003 and Bhattacharya *et al*, 2004). Samples A, B, C and D were irradiated at 20, 30, 40 and 50kGy respectively; thus reacted differently with sample E. Radiation changes the physical and chemical or biological characteristics of a material (Cleland *et al*, 1992). Sample D with an irradiation dose of 50kGy has the lowest curve which reveals the highest uptake of monomer from the monomer emulsion solution all through the retention time, followed by samples C, B and A in that order respectively. These trends of curves were expected arising from the surface area created on the substrates by the irradiation carried out on the substrates at different irradiation doses during the substrate activation step (Ueki *et al*, 2010).

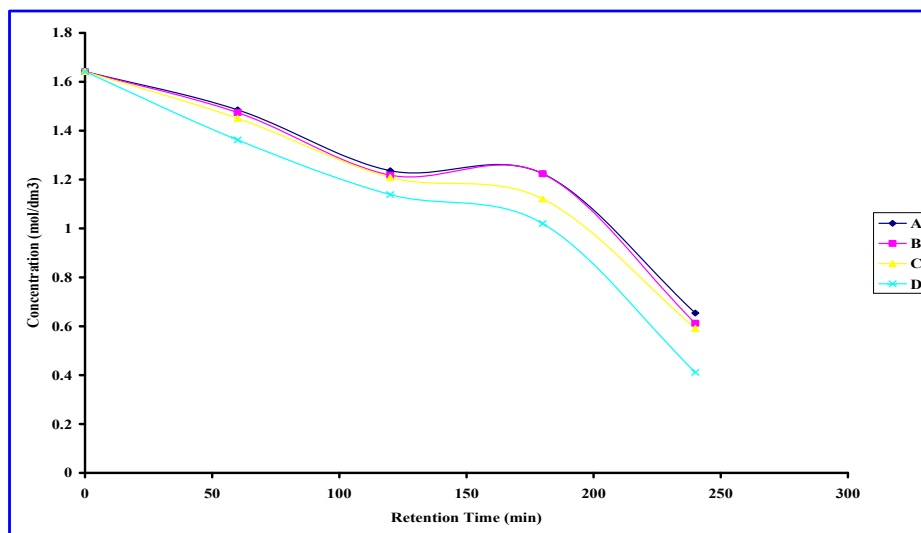
Bhattacharya A. and Misra B. N (2004): Grafting a Versatile means of Modify Polymers Techniques, Factors and Applications; Progress in Polymer Science Journal. Prog. Polym. Sci 29 767 – 814.

Cleland M. R. (1992). High Power Electron Accelerators for Industrial Radiation Processing of Polymers, Chapter 3 in Radiation Processing of Polymers, A. Singl and J. Silverman (Eds), Hanser, Munich. 23 – 49.

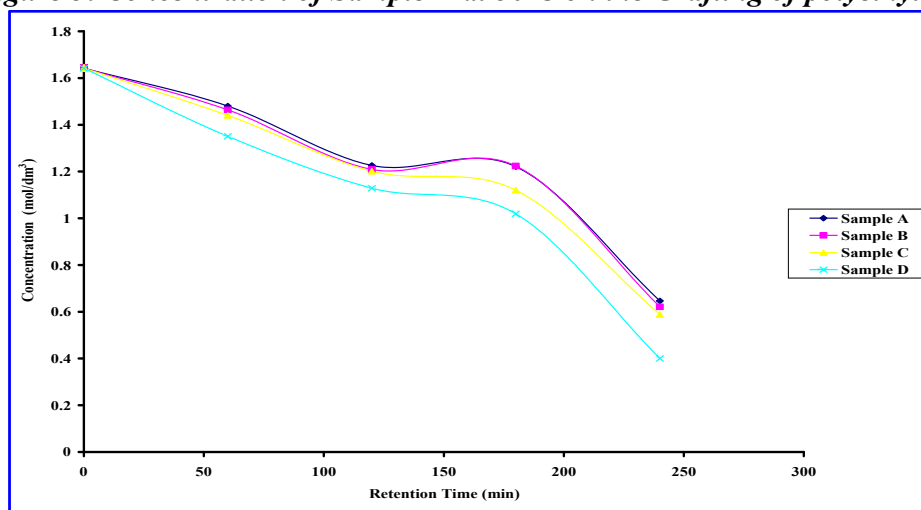
Ueki Yuji and Masao Tanada (2010): Catalyst for Production of Biodiesel and its Production Method, and Method for Producing Biodiesel. Patent Application Publication US2010/0170145A1

Octave Levenspiel, (2003): Chemical Reaction Engineering. Third Edition; John Wiley and Sons: New York, Chichester, Weinheim, Brisbane, Singapore, Toronto.

Yamaki T., Asano M., Maekawa Y., Morita Y, Suwa T, Chen J., Tsubokawa N., Kobayashi K., Kubota H. and Yoshida M. (2003): Radiation Grafting of Styrene into Cross Linked PTFE Films and Subsequent Sulfonation for Fuel Cell Applications. Radiation Physics Chemistry 67: 403-7.



**Figure 5: Concentration of Sample E at 50°C on the Grafting of polyethylene**

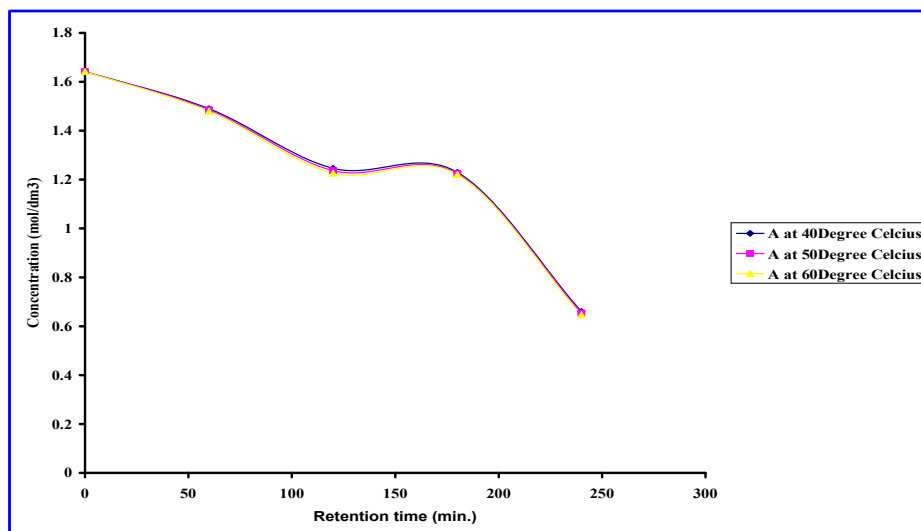


**Figure 6: Concentration of Sample E at 60°C on the Grafting of polyethylene**

Figures 5 and 6 above show the concentration profiles of sample E on the grafting of polyethylene substrates conducted at 50 and 60°C reaction temperatures respectively. The results are similar to that of Figure 4 and follow the same curve trends. The irradiation doses were suitably determined under the condition that the doses are enough to form the reaction active points required on the substrates (Bhattacharya *et al*, 2004). These results show that the higher the dose the larger the reaction active points and a better uptake of the monomer by substrate.

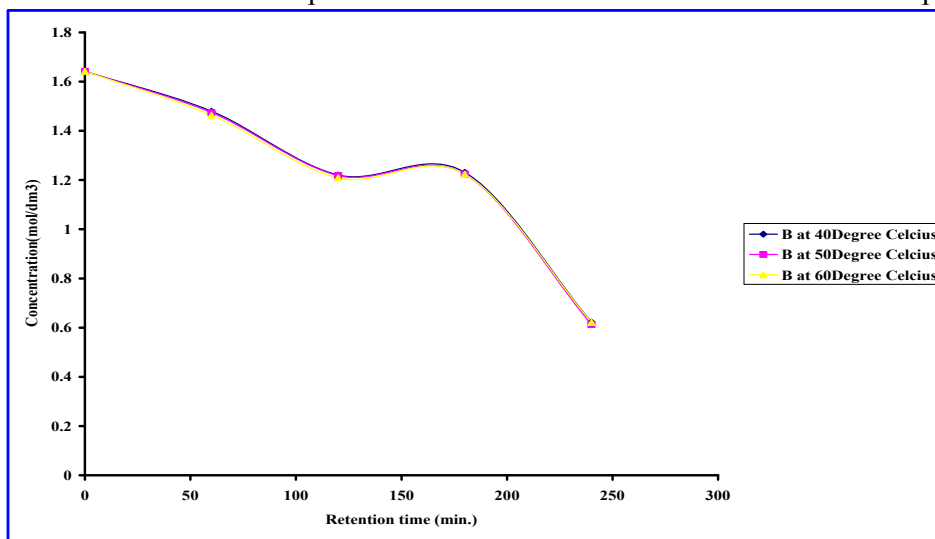
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Bhattacharya A. and Misra B. N (2004): Grafting a Versatile means of Modify Polymers Techniques, Factors and Applications; Progress in Polymer Science Journal. Prog. Polym. Sci 29 767 – 814.



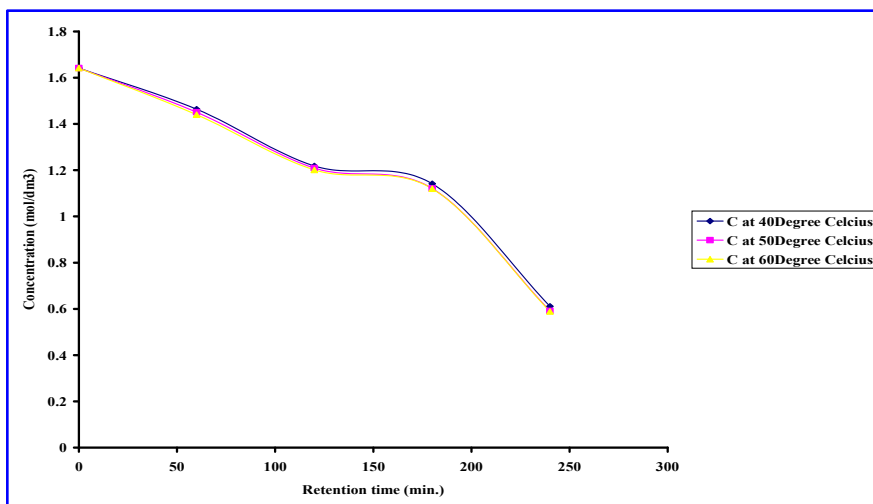
**Figure 7: Effect of Temperature on the Concentration of Sample E on the Grafting of polyethylene substrate A Sample**

Figure 7 shows the effect of temperature on the uptake of monomer from sample E onto the main chain of the substrate. This result reveals that reaction temperature variation on the grafting of monomer onto polyethylene substrate A remains significantly unchanged for reaction temperatures of 40, 50 and 60°C respectively. The concentration profile at these reaction temperatures follows the same trend and same curve patterns.



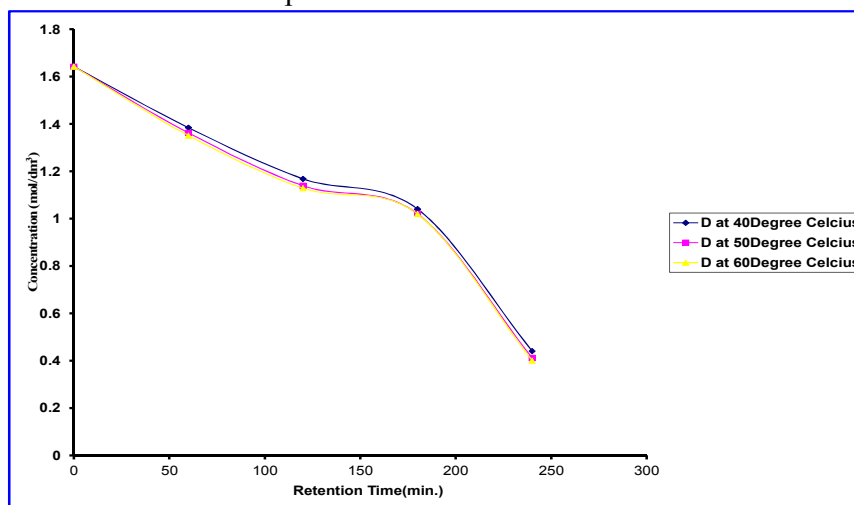
**Figure 8: Effect of Temperature on the Concentration of Sample E on the Grafting of polyethylene substrate B sample**

Figure 8 shows the effect of temperature on the uptake of monomer from sample E onto the main chain of the substrate. This result reveals that reaction temperature variation on the grafting of monomer onto polyethylene substrate B remains significantly unchanged for reaction temperatures of 40, 50 and 60°C respectively. The concentration profile, like that of Figure 7, for same reaction temperature also follows the same trends and same curve patterns, hence the rate at which the monomer in the monomer emulsion solution was taken up by substrates A and B are the same, from the nature and trend of their concentration versus retention time profile.



**Figure 9: Effect of Temperature on the Concentration of Sample E on the Grafting of polyethylene substrate C Sample**

Figure 9 shows the effect of temperature on the uptake of monomer from sample E onto the main chain of the substrate. This result reveals that reaction temperature variation on the grafting of monomer onto polyethylene substrate C remains significantly unchanged for reaction temperatures of 40, 50 and 60°C respectively. The concentration profile at these reaction temperatures also follows the same trends and same curve patterns.



**Figure 10: Effect of Temperature on the Concentration of Sample E on the Grafting of polyethylene substrate D Sample**

Figure 10 shows the effect of temperature on the uptake of monomer from sample E onto the main chain of the substrate D irradiated initially at 50kGy during the activation step. This result reveals that reaction temperature change on the grafting of monomer onto polyethylene substrate D remain significantly unchanged for reaction temperatures 50 and 60°C respectively; except at a reaction temperature of 40°C where the concentration curves show a slower decline within 25-175 minutes retention time range of the reaction. But the concentration profile at these reaction temperatures does follows the same trends and same curve patterns with those of Figures 7-9.

**Table 2: Comparison of Overall Rate Constants and Correlation Coefficients of the Catalyst Production**

Substrates	Temperature (°C)	Zero Order		First Order		Second Order	
		k(mol min <sup>-1</sup> dm <sup>-3</sup> )	R <sup>2</sup>	k(min <sup>-1</sup> )	R <sup>2</sup>	k(dm <sup>3</sup> mol <sup>-1</sup> min <sup>-1</sup> )	R <sup>2</sup>
A (kGy)	40	0.003394	0.8747	0.002867	0.7792	0.002601	0.6762
	50	0.003428	0.8766	0.002906	0.7811	0.002649	0.6772
	60	0.003466	0.8776	0.002947	0.7820	0.002700	0.6771
B (kGy)	40	0.003509	0.8625	0.003024	0.7627	0.002828	0.6568
	50	0.003548	0.8649	0.003074	0.7630	0.002898	0.6550
	60	0.003545	0.8681	0.003054	0.7698	0.002854	0.6630
C (kGy)	40	0.003696	0.9186	0.003198	0.8184	0.003005	0.7020
	50	0.003790	0.9248	0.003315	0.8222	0.003163	0.7014
	60	0.003813	0.9255	0.003336	0.8236	0.003189	0.7023
D (kGy)	40	0.004343	0.9260	0.004159	0.7910	0.004619	0.6414
	50	0.004486	0.9294	0.004380	0.7909	0.005038	0.6344
	60	0.004530	0.9269	0.004457	0.7866	0.002981	0.8574

In order to obtain the reaction order of the catalyst production as a tool in the design of a process plant for the process, rate orders were assumed and test on data obtained in the graft polymerization step of the catalyst production process; plots from the relations 5, 7 and 9 (Octave, 2003) respectively were tested or linearity. The best-fitted reaction order was determined by comparing the coefficient of determination ( $R^2$ ) for all the reaction temperatures and for the samples of polyethylene substrates used in this study. Table 2 shows the comparison of correlation coefficients  $R^2$  and rate constants 'k' that were determined from the slopes of the lines of the assumed zero, first and second order rate that were tested in this study. Correlation coefficients greater than 0.9 ( $R^2 > 0.9$ ) (Anthon *et al*, 2002 and Oderinde *et al*, 2009)

Anthon, G.E and Barrett, D.M. (2002): Kinetic parameter for the thermal inactivation of quality related enzymes in carrots and potatoes. *Journal of Agriculture and Food Chemistry*, 50, 4119-4125.

. Octave Levenspiel, (2003): *Chemical Reaction Engineering*. Third Edition; John Wiley and Sons: New York, Chichester, Weinheim, Brisbane, Singapore, Toronto

Oderinde, R.A., Ajayi, I.A. and Dewuyi, A.A (2009): Characterization of Seed and Seed Oil of *Huracrepitans* and the Kinetics of Degradation of the Oil during Heating, *electronic journal of environment, agriculture and food chemistry*. ISSN: 1579-4377, 8 (3),

in this case confirmed a linear relationship for the established correlation coefficients greater than 0.9 and hence a zero rate law with respect to the monomer emulsion solution (MES) is confirmed based on report given by Octave, (2003).

### 3.2 Polymer catalysts characterization result

**Table 3: Pattern of Product q-type Catalyst (Product from Substrate Irradiated at 50kGy)**

Visible Reference Code	Score	Compound Name	Scale Factor	Chemical Formula
00-053-1772	39	(4-Methyl-1,3-phenyl)(2-methyl-1,3-phenyl)-bis-dihexadecyl carbamate	0.552	$C_{41}H_{74}N_2O_4$
00-048-2333	26	N-Amylenyl-p-nitroaniline nano(p-nitroaniline)	0.277	$C_{11}H_{14}N_2O_2 \cdot 9(C_6H_6N_2O_2)$

Table 3: shows the X-ray diffraction patterns determined for the q-type polymer catalyst developed in this study. The X-ray diffraction result indicates that the polyethylene-base carbamate contained only the tetragonal phase of polyethylene with carbamate oxide or p-nitroaniline species existing only as amorphous species or small crystallites  $\leq 5$ nm in diameter. The diffraction pattern of q-type polymer catalyst was compared with literature powder x-ray diffraction standard reference data and confirmed the correct structure and level of crystallinity.

**Table 4: Pattern List of r-type Catalyst (Product from Substrate Irradiated at 40kGy)**

Visible Reference Code	Score	Compound Name	Scale Factor	Chemical Formula
00-053-1772	42	(4-Methyl-1,3-phenyl)(2-methyl-1,3-phenyl)-bis-dihexadecyl carbamate	0.549	$C_{41}H_{74}N_2O_4$
00-048-2332	24	N-2-Butenyl-p-nitroaniline nano(p-nitroaniline)	0.298	$C_{10}H_{12}N_2O_2 \cdot 9(C_6H_6N_2O_2)$

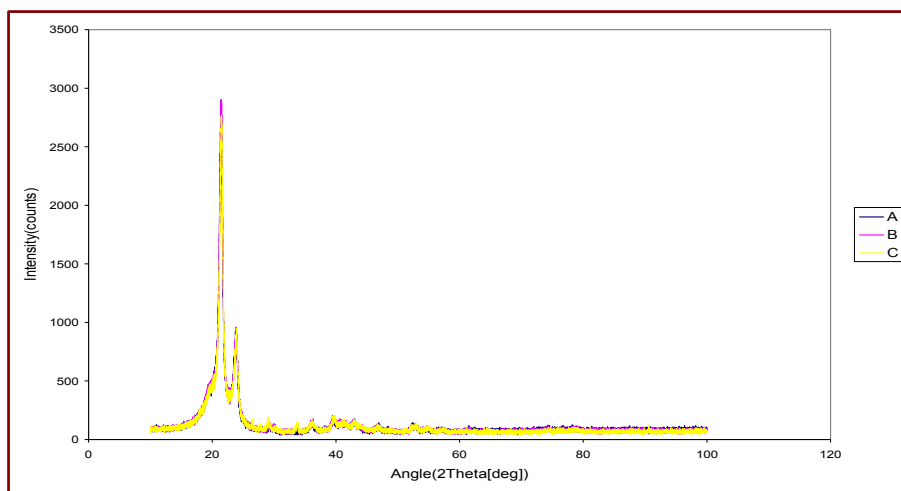
Table 4: showed the x-ray diffraction patterns determined for the r-type polymer catalyst developed in this study. The x-ray diffraction result indicated that the polyethylene- based carbamate contained only the tetragonal phase of polyethylene with carbamate oxide or P-nitroaniline species existing only as amorphous species or small crystallites  $\leq 5$ nm in diameter. The diffraction pattern of r-type polymer catalyst was also compared with literature powder x-ray diffraction standard reference data and confirmed the correct structure and level of crytallinity.

Octave Levenspiel, (2003): Chemical Reaction Engineering. Third Edition; John Wiley and Sons: New York, Chichester, Weinheim, Brisbane, Singapore, Toronto.

**Table 5: Pattern of s-type Catalyst (Product from Substrate Irradiated at 30kGy)**

Visible Reference Code	Score	Compound Name	Scale Factor	Chemical Formula
00-053-1772	30	(4-Methyl-1,3-phenyl)(2-methyl-1,3-phenyl)-bis-dihexadecyl carbamate	0.582	$C_{41}H_{74}N_2O_4$
00-058-1018	20	Methyl-3,1((2R,4S,5R)-4-hydroxy-5-(hydroxymethyl)tetrahydro-2-furanyl)-2,4-dioxo-1,2,3,4-tetrahydro-5-pyrimidinylpropanone	0.162	$C_{13}H_{18}N_2O_7$

Table 5: shows the x-ray diffraction patterns determined for the s-type polymer catalyst developed in this study. The x-ray diffraction result showed that the polyethylene–base carbamate contained only the tetragonal phase of polyethylene with carbamate oxide or 2,4-dioxo-1,2,3,4 tetrahydro-5-pyrimidinylpropane species existing only as amorphous species or small crystallites  $\leq 5\text{nm}$  in diameter. The diffraction pattern of the s-type polymer catalysts was compared with literature powder x-ray diffraction standard reference data, confirming the correct structure and level of Crystallinity.



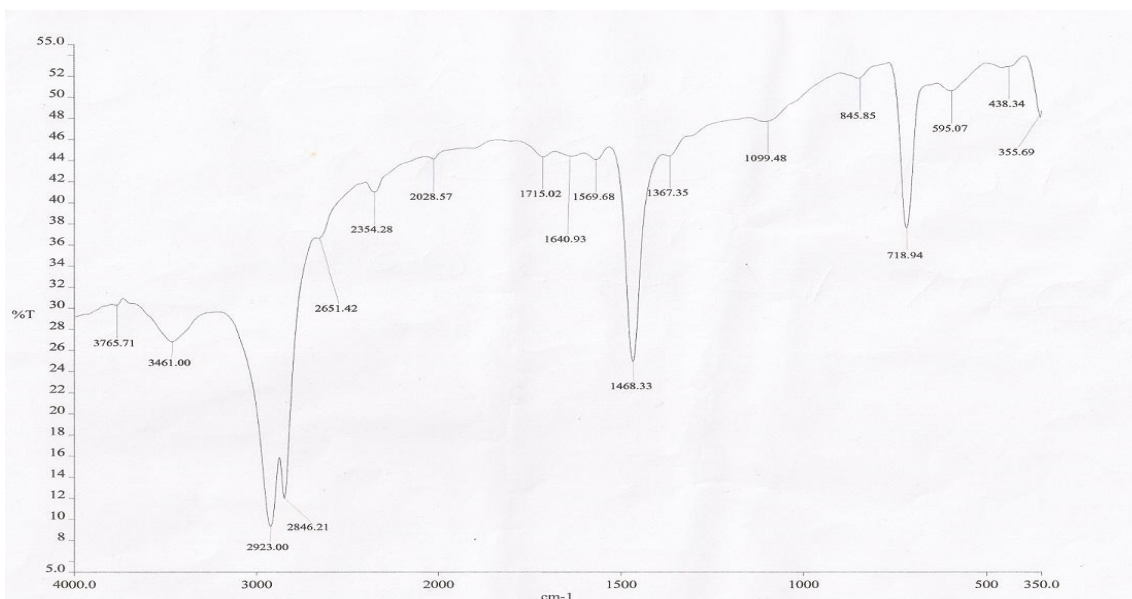
**Figure 11: Showing Comparisons of the graphics for q, r and s Catalysts**

Figure 11, compares the three catalysts products x-ray diffraction patterns compared in a single graphics; q-type shows higher range of intensity at Angle 20deg than the s and r-types. The peaks when carefully observed show dominance of the q-type catalyst intensity mostly all through the graphics angle as it progresses.

Elemental Analysis: The concentration of basic sites for the polymer catalyst was estimated from its carbamate content, assuming that every tetrahedral carbamate atom, in the framework accounted for a basic site and that all these sites were accessible. Camiloti *et al*, (1999) employed 12-tungstophosphoric acid of ammonia to determine the acidity of zeolite H $\beta$  and found the NH<sub>3</sub>/Al ratio were equal to one, suggesting that every aluminum atom provides an accessible potential site. The basic site concentrations of q, r and s polymer catalysts measured by carbamate 12-tungstophosphoric acid (2.8wt%, 2.1wt% and 1.6wt% carbamate respectively) are in agreement with those reported by (Yuji *et al*, 2011) (3.5mmol-TMA/g-catalysts) for a fibrous polymer catalyst.

Camilot A.M., Jahn, S.L., Velasco N.D., Moura, L.F. and Cardoso, D. (1999): "Acidity of Beta zeolite Determined by TPD of Ammonia and Ethylbenzene Disproportionation" Appl. Catal. A 182,107.

Yuji Ueki, Nor Hasimah, Noriaki Seko, and Masao Tamada (2011): Rapid Biodiesel Fuel Production Using Novel Fibrous Catalyst Synthesized by Radiation-Induced Graft Polymerization: International Journal of Organic Chemistry, 1, 20-25.



**Figure 12: FT-IR spectra of synthesized polymer catalyst**

The functional groups of the developed polymer catalyst were investigated via FT-IR spectra. The chemical structure of the polymer catalyst is shown in Figure 12. The FT-IR spectra of the polymer catalyst show a strong characteristic carbon-carbon double bond and carbon-nitrogen double (Boyer *et al*, 1998) absorption peak at  $1468.33\text{cm}^{-1}$  stretching vibration. This could be attributed to the aromatic compound of the 4-chloromethylstyrene functional monomer grafted to the main chain of the polyethylene substrate forming the base of the polymer catalyst. The peaks at  $2923$  and  $2846.23\text{cm}^{-1}$  show the characteristic carbon-hydrogen stretching vibration indicating the nature of the C-H linkage of the grafted substrate and quaternary ammonium cation (Hippis *et al*, 1987 and Portehault *et al*, 2010) of the Trimethylamine solution treatment. The medium broad spectra peak at  $3461\text{cm}^{-1}$  shows the presence of the amine functional group, an indication of the presence of the influence of the Trimethylamine in the synthesized polymer catalyst. The strong peak at  $718\text{cm}^{-1}$  shows the presence of the aliphatic chloromethyl (C-Cl) compounds (Jang *et al*, 1998 and Jenkins *et al* 2002) in the polymer based catalyst and hence the modification of polyethylene substrate with biodiesel catalytic functional groups. The vanishing peaks at  $1099.48$ ,  $845.85$ ,  $595.07$  and  $355.69\text{cm}^{-1}$  show the presence of the out-of-plane -OH stretching due to the treatment of the substrate with sodium hydroxide solution. The weak peaks at  $1715$ ,  $1640$ ,  $1569$  and  $1367.35\text{cm}^{-1}$  are an indication of the presence of methyl (C-H) bond of the aromatic ring in the polymer catalyst. The vanishing peaks at  $2651$ ,  $2354$  and  $2028\text{cm}^{-1}$  indicate the presence of the O-CH<sub>3</sub> stretch (<http://science-and-fun.de/tools>).

Boyer M.I., Quillard S., Rebourt E., Louarn G., Buisson J. P, Monkman A. and Lefrant S. (1998): "Vibrational Analysis of Polyaniline: A Model Compound Approach," The Journal of Physical Chemistry B, Vol. 102, No. 38, pp. 7382-7392.

Hippis K. W. and Mazur U. (1987): "Vibrational and Low-Lying Electronic Transitions in Tetraalkylammonium Salts of  $\text{CoBr}_4^{2-}$ ,  $\text{CoCl}_4^{2-}$  and  $\text{Co}(\text{CNS})_4^{2-}$  as observed by Raman, Infrared, and Tunneling Spectroscopies," The Journal of Physical Chemistry, Vol. 91, No. 20, pp. 5218-5224

Infrared (IR) Spectra-Wizard Results: <http://science-and-fun.de/tools/> 3/7/2014 7:04PM

Jang B. B., Lee K. P., Min D. H and Suh J. (19998): "Immobile Artificial Metalloproteinase Containing both Catalytic and Binding Groups," Journal of American Oil Chemists' Society, Vol. 120, No. 46, pp. 12008-12016

Jenkins D. W and Hudson S. M. (2002): "Heterogeneous Graft Copolymerization of Chitosan Powder with Methyl Acrylate Using Trichloroacetyl-Manganese Carbonyl Co-Initiation," Macromolecules, Vol. 35, No. 9, pp. 3413-3419

Portehault D., Giordano C., Sanchez C. and Antonietti M. (2010): "Nonaqueous Route toward a Nanostructured Hybrid Titanate," Chemistry of Materials, Vol. 22, No. 6, pp. 2125-2131



#### 4. Conclusion

This work has shown that, the absorbed dose and retention time are the fundamental parameters (dependent variables) affecting the polymer catalyst production process and it was established that reaction temperature variation has no significant effect on the production process. Furthermore a zero order rate constant was established for the grafting stage, while the x-ray diffraction result and that of the Fourier transform infrared spectra show the successful modification of polyethylene substrate with biodiesel catalytic functional groups.

