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# Synthesis of neopentyl glycol and ethylene glycol esters by fatty acids in the presence of acidic ion exchange resin catalyst

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## Abstract

In this study, one of the most effective and less energy demanding method of producing fatty esters, diol esters, by esterifying fatty acids, with neopentyl glycol and ethylene glycol alcohols in the presence of an acidic ion exchange resin catalyst(polyestyrendivinylbenzensulfated) was investigated at elevated temperature. In this process an azeotroping agent, toluene, was used to facilitate continuous removal of water by distillation, formed as a by-product during the esterification reaction.The esterification reaction is completed within 4-5 hours and neopentyl glycol and ethylene glycol esters were produced with properties of lubricity and biodegradability.

**Keywords:** Ethylenglycol esters; neopenthylglycol estesr; fatty esters; synthetic lubricant ester; resin catalyst.

## Introduction

One of the most important modifications of the carboxyl group of the fatty acid chain is the esterification of the fatty acids obtained by cleavage of such esters. Those processes are performed on large scale .Esterification reactions of neopentyl polyols are normally catalysed by acidic or basic catalysts.Typical homogeneous catalysts are *p*-toluene sulphonic acid, phosphoric acid, sulphuric acid, sodium hydroxide, sodium ethoxide and sodium methoxide[1-5]. In some cases, heterogeneous catalysts such as Sn-oxalate or cation exchange resins are used .Enzyme

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catalysed reactions which are known[6,7] as Aliphatic polyols may also be employed .In general, the polyols contain from about 2 to about 10 hydroxyl groups per molecule and up to about 36 carbon atoms, preferably about 2 to 5 hydroxyl groups and up to about 18 carbon atoms .Examples of such polyols include the glycols including ethylene glycol, propylene glycol, hexanediol and the like; the triols such as glycerine, trimethylolpropane, trimethylolethane and the tetraols, such as pentaerythritol .Useful polyols may also be formed by etherifying the above-mentioned polyols .Examples of these materials include the polyglycols such as diethylene and triethylene glycols and also the polypentaethritols such as di and tri pentaerythritol[8,9].The esters of this polyhydroxy alcohols have applications as high performance lubricant because of their high stability to thermo-oxidation, high flash point, and low volatility[10] .The esters of these polyhydroxy alcohols have low volatility, and their bulky structure confers excellent resistance to hydrolysis[11,12]. viewing these properties, the lubricant which has been based on these esters are more economical in use and have shown considerable development as synthetic lubricant in automotive applications, marine diesel engines, transmission system and the aerospace industry[13-15].However we report the synthesis of neopentylglycol and ethylenglycol esters by fatty acids in the presence of acidic ion exchange resin catalyst.

## Experimental

All materials were purchased from Merck Company.IR spectra were recorded with a Shimadzu FTIR-408 spectrophotometer as KBr pells. HNMR and CNMR spectra were recorded on a Brucker 400 AC spectrometer in $CDCl_3$ as a solvent at room temperature.

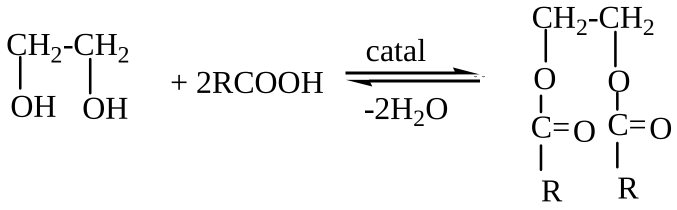
### Typical procedure for preparation of diol esters

3 moles of fatty acid for 1mole of ethylenglycol) was transferred into a reaction flask. The reaction flask was equipped with a modified Dean - Stark distillation set-up, magnetic stirrer, condenser, dropping funnel and heating plate. 150 mL of toluene is added to the reaction mixture. Forty weight percent of acidic ion exchange resin (based on weight of acidic ion exchange resin/weight of fatty acid used) was added to the reaction mixture when the temperature has reached to $120^{0C.}$ That amount of water formed as by-product of the esterification reaction was removed continuously by means of distillation with the aid of toluene while toluene was recycled continuously back to the reaction mixture. After the reaction was completed,

the crude product was cooled to ambient temperature. Then, heterogeneous acid catalyst (polyestyrendivinylbenzensulfated) can be removed by simple filtration and excess solvent was removed from the crude product by means of rotary evaporation. The product was dried with anhydrous sodium sulphate and then the hydrated sodium sulphate was removed from the dried product. The dried product was further purified by using a column packed with silica gel in toluene solvent. Trace solvent was further removed by a vacuum pump and finally unreacted fatty acid was also removed by means of vacuum distillation. Moreover, Unreacted fatty acid would remain as residue while diol esters would be collected as distillates.

## Results and discussion

The preparation of carboxylic acid esters has been carried out employing a wide variety of chemical reaction processes. The process of synthetic fatty esters preparation comprises the following steps: (a) esterifying fatty acids thereof with an ethylenglycol or neopentylglycol in the presence of acidic ion exchange resin catalyst at elevated temperature. (b) Continuously removing water formed as a by-product during the reaction in (a) by distillation, (c) removing the impurities from the resultant product of steps (a) and (b) characterized by adding an azeotroping agent to facilitate continuous removal of water in step (b). Reaction pathways were shown in Figure (1).



R= $CH_2(CH_2)_2$-$CH_3$ 1a
ethylenglycoldipentanoate este
R= $CH_2(CH_2)_3$-$CH_3$ 1b
ethylenglycoldicaproate este
R= $CH_2(CH_2)_4$-$CH_3$ 1c
ethylenglycoldiheptanoate estes

**Figure1.** Reaction synthesis of ethylenglycol esters

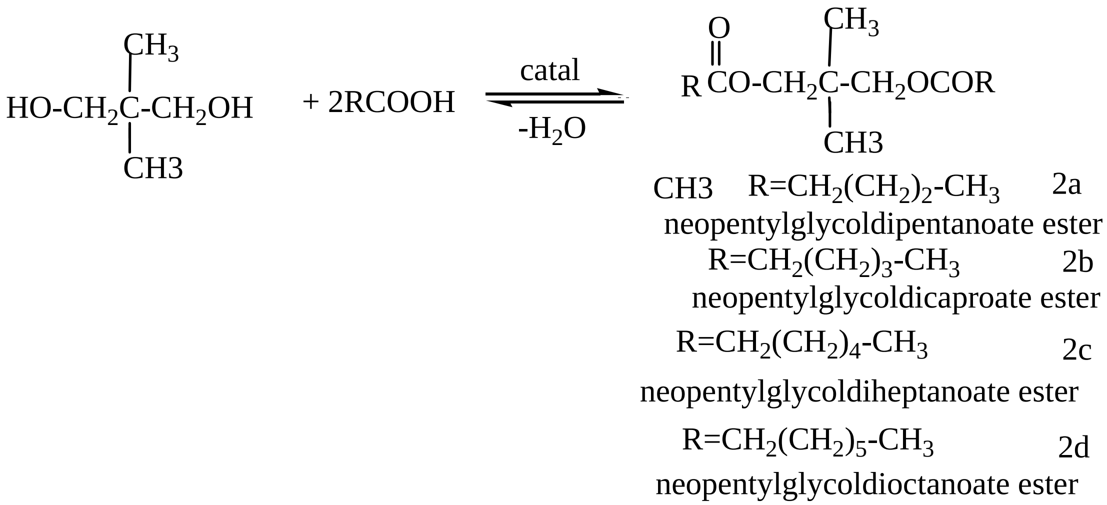


**Figure 2.** Synthesis of neopenthylglycol esters

The structure of catalyst (ion exchange resin) is shown in Figure 3.

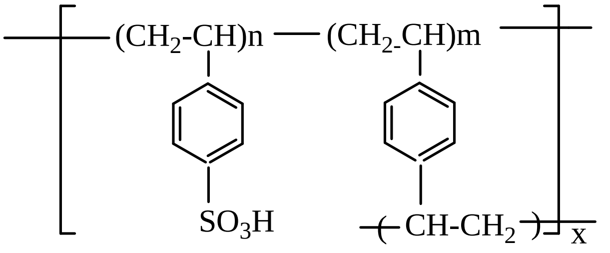


**Figure 3.** The structure of polyestyrendivinylbenzensulfated

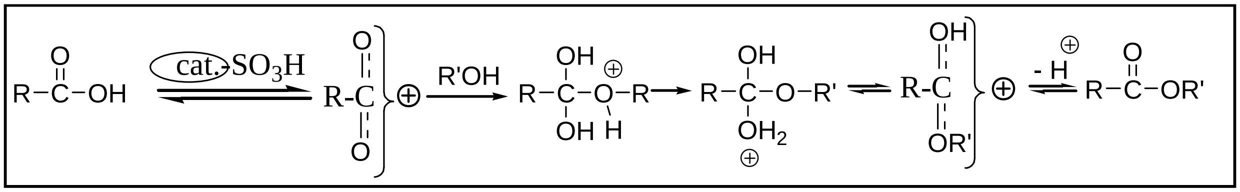


**Figure 4.** Total mechanism of esterification

**Table1.** The reaction conditions and yields of different esters are summarized

| Product | Temperature | Time reaction | Toluene (mL) | Catalyst(mass%)[a] | Yield(%) |
|---|---|---|---|---|---|
| **1a** | 120-200$^{0C}$ | 4h | 150 | 2.2 | 90 |
| **1b** | 110-190$^{0C}$ | 4.5h | 150 | 2.2 | 87 |
| **1c** | 110-195$^{0C}$ | 5h | 150 | 2.2 | 90 |
| **2a** | 100-200$^{0C}$ | 4.5 | 150 | 2.2 | 88 |
| **2b** | 120-210$^{0C}$ | 5 | 150 | 2.2 | 90 |
| **2c** | 120-220$^{0C}$ | 5 | 150 | 2.2 | 87 |
| **2d** | 110-205$^{0C}$ | 5 | 150 | 2.2 | 82 |

[a] Based on acid oralcohol

The esterification reaction was conducted at a relatively moderate temperature and yet achieved high conversion rates over a short reaction time. Moreover we reached that status by the use of an azeotroping agent to assist the removal of water formed as reaction by-product, thus resulted in driving the reaction to complection. The esterification reaction was completed utilizing an acidic ion exchange resin acid catalyst at temperatures in the range of 80 to 210$^{0C}$ and in the vicinity of 120 to 210$^{0C}$ for production of diol esters. Suitably, the esterification reaction was complete in4-5 hours. Addition of a forementioned azeotroping agent helps to facilitate the removal of water from the reaction mixture by distillation. Preferably, the water was removed in the form of a binary mixture (water and toluene). Suitably, the azeotrope mixture condenses, for example in a separating funnel, and separates into two layers wherein the bottom layer is water and the top layer would be an organic phase. The bottom layer of water collected in the separating funnel was drained from time to time. At a time during the reaction, the organic phase overflow and recycle back to the reaction mixture. Advantageously, this typically ensures a substantial amount of toluene was present in the reaction mixture in order to form an azeotrope mixture with water .Excess solvent was removed from the fatty esters by means of rotary evaporation and then heterogeneous acid catalyst was removed by filtration method., afterwards, the fatty ester was dried using a drying agent and then purified to remove excess fatty acid, impurities and trace of solvent. However the ester was synthesised in this paper and identified by H-NMR, $^{13}$C-NMR and FT-IR spectra.

**Ethyleneglycoldipentanoate ester,** this ester was prepared according to the general procedure by using ethylenglycol (1 mol) and pentanoeic acid (3moles) to give desired ester in 90% yield Oil, (Yield 90%). $^{1}$H NMR (400MHz, $CDCl_3$) $\delta$(ppm); 0.91 (t, 6H,J=7.5Hz, $2CH_3$), 1.33 (quin, J=7.2Hz, 4H, $2CH_2$), 1.60 (quin, J=7.5 Hz ,4H, $2CH_2$ ), 2.32 ( t, J= 7.5, 4H, $2CH_2CO$), 4.26 (s, 4H, $2CH_2O$); FT-IR(KBr): $\overline{3}$ ($cm^{-1}$) 2955, 2867, 1741, 1459, 1378, 1241, 1167, 1105 $cm^{-1}$.

Its structure was identified by H-NMR, $^{13}C$ NMR and FT-IR spectra. Its $^{1}H$ NMR spectrum in d-chloroform showed a triplet at $\delta$ 0.91 ppm with J=7.5Hz for two methyl groups, a quintet at $\delta$ 1.33 ppm with J=7.2Hz for two methylene groups, a quintet at $\delta$ 1.60 ppm with J=7.5Hz for two methylene groups, a triplet at $\delta$ 2.32 ppm with J=7.5 Hz for two methylene carbonyl groups and singlet at $\delta$ 4.26 ppm for two methylene related to oxygene. Its FT-IR showed a strong absorption at 1741$cm^{-1}$ due to carbonyl ester group.

**Ethyleneglycoldicaproate ester** was prepared according to the general procedure by using ethylenglycol (1 mol) and caproeic acid (3 mol) to give desired ester in 87% yield; Oil, (Yield 87%).$^{1}$H-NMR(FT-400MHz, $CDCl_3$): $\delta$ (ppm); 0.86 ( t ,J=6.3Hz, 6H ,2 $CH_3$),1.29 (bs , 8H, $4CH_2$), 1.61 (quin, J=6.3 Hz, 4H, $2CH_2$ ), 2.31 ( t, J= 7.5, 4H, $2CH_2CO$), 4.26 (s, 4H, $2CH_2O$). $^{13}C$ NMR(FT-400MHz, $CDCl_3$) $\delta$ (ppm);13.82, 22.24, 24.52, 31.21, 34.04, 61.93, 173.50.

FT-IR(KBr): $\overline{3}$ ($cm^{-1}$) ; 2956, 2868, 1742, 1450, 1379, 1347, 1277, 1242, 1167, 1105,1060.

Its structure was identified by $^{1}$HNMR, $^{13}$CNMR and FT-IR spectra. Its $^{1}$HNMR spectrum in d- chloroform showed a triplet at $\delta$ 0.86 ppm with j=6.3Hz for two methyl groups, a broad singlet at $\delta$ 1.29 ppm for four methylene groups, a quintet at 1.61 ppm with J=6.3 Hz for two methylene groups, a triplet at $\delta$ 2.31ppm with J=7.5 Hz for two methylene groups related to carbonyl, and a singletat $\delta$ 4.26 ppm for two methylene groups related to oxygene. Its $^{13}C$ NMR showed seven peaks for seven different carbons of which the peak at $\delta$ 173.50 ppm was due to carbonyl groups. The peak at $\delta$ 61.93 ppm was due to methylene carbon group related to oxygene .and other five peaks are due to aliphatic alkyle chain.

**Ethylenglycoldiheptanoate ester** was prepared according to the general procedure by using ethylenglycol (1 mol) and heptanoeic acid (3 mol) to give desired ester in 90% yield; Oil, (Yield 90%),$^{1}$H-NMR(FT-400MHz, $CDCl_3$): $\delta$ (ppm); 0.86 (t, J=7.5Hz, 6H, 2 $CH_3$),1.27 (m,12H, 7.2Hz, $6CH_2$), 1.58 (quin, J=7.2 Hz ,4H, $2CH_2CO$ ), 2.30 ( t, J= 7.5Hz, 4H, $2CH_2$ ), 4.25 (s, 4H ,$2CH_2O$) $^{13}C$ NMR (FT-400MHz, $CDCl_3$): $\delta$ (ppm);13.93, 22.42, 24.81, 28.72, 31.39, 34.10, 61.95, 173.54; FT-IR(KBr): $\overline{3}$ ( $cm^{-1}$); 2955, 2867, 1741, 1459,1378, 1241, 1167, 1105, 1061. Its structure was identified by HNMR, $^{13}$C NMR and FT-IR spectra. Its $^{1}$HNMR spectrum in d-chloroform showed a triplet at δ 0.86 ppm with J=7.5Hz for two methyl groups, a multiplate δ 1.27 ppm with J=7,2Hz for six methylene groups,and a quintet at δ 1.58 ppm with J=7.2 Hz for two methylene related to carbonyl, triplet at δ 2.30 ppm with J=7.5Hz for two methylene groups and a singlet at δ 4.25 ppm for two methylene related to oxygene. Its $^{13}$CNMR showed eight peaks for eight different carbons of which the peak at δ 173.54 ppm was due to carbonyl groups. The peak at δ 61.95 ppm was due to carbon of methylene related to oxygene and other six peaks are due to aliphatic alkyl chain.

**Neopenthylglycoldipentanoate ester** was prepared according to the general procedure by using neopenthylglycol (1 mol) and pentanoeic acid (3moles) to give desired ester in 88% yield; Oil, (Yield 90%),$^{1}$H-NMR(FT-400MHz, $CDCl_3$): δ (ppm); 0.89 ( t, J=7.5Hz, 6H, 2 $CH_3$), 0.94 (s, 6H, 2$CH_3$), 1.30 (quin, J=7.2 Hz ,4H, 2$CH_2$ ), 1.58 ( quin , J= 7.2Hz, 4H, 2$CH_2$), 1.58 (quin, J=7.5Hz, 4H, 2$CH_2$), 2.29 (t, J=7.5Hz, 4H, 2$CH_2$CO), 3.85 (s, 4H, 2$CH_2$O); $^{13}$CNMR(FT-400MHz, $CDCl_3$): δ (ppm) ;13.64, 21.73, 22.22, 27.02, 33.99, 34.59, 68.97, 173. Its H-NMR spectrum in d-chloroform showed a triplet at δ 0.89 ppm with J=7.5Hz for two methyl groups, a singlet at δ 0.94 ppm for two methyl groups, a quintet at δ 1.30 ppm with J=7.2 Hz for two methylene, a quintet at δ 1.58 with J=7.2Hz for two methylene, a quintet at δ 1.58 with J=7.5Hz for two methylene groups,a triplet at δ 2.29 ppm with J=7.5Hz for two, methylene related to carbonyl groups and a singlet δ 3.85 ppm for two methylene related to oxygene. Its $^{13}$CNMR showed eight peaks for eight different carbons of which the peak at δ 173.70 ppm was due to carbonyl groups. The peak at δ 68.97 ppm was due to carbon of methylene related to oxygene and other peaks are due to aliphatic alkyl chain.

**Neopenthylglycoldicaproate ester** was prepared according to the general procedure by using neopenthylglycol (1 mol) and caproeic acid (3 mol) to give desired ester in 90% yield; Oil, (Yield 90%). $^{1}$H NMR: (FT-400MHz, $CDCl_3$): δ (ppm) ; 0.89 (t, J=7.5Hz, 6H ,2 $CH_3$), 0.96 (s, 6H 2$CH_3$), 1.30 (m,8 H, 4$CH_2$ ), 1.62 ( quin, J= 7.2Hz, 4H, 2$CH_2$), 2.30 (t, J=7.5Hz, 4H, 2$CH_2$CO), 3.87(s, 4H , 2$CH_2$O), 3.87 (s , 4H, 2$CH_2$O). $^{13}$C

NMR(FT-400MHz, $CDCl_3$): δ (ppm); 13.77, 21.67, 22.20, 24.58, 31.22, 34.15, 34.56, 68.90, 173.58; FT-IR(KBr) $\bar{3}$ ( $cm^{-1}$); 2958, 2869, 1739, 1466, 1378, 1244, 1168, 1104, 1006($cm^{-1}$). Its $^1H$ NMR spectrum in d-chloroform showed a triplet at δ 0.89 ppm with J=7.5Hz for two methyl groups, a singlet at δ 0.96 ppm for two methylene groups, a multiplate at δ 1.30 ppm for four methylene groups ,a quintet at δ 1.62 ppm with J=7.2Hz for two methylene groups, and triplet at δ 2.30 ppm for two methylene related to carbonyl groups and a singlet at δ 3.85-3.87 for four methylene groups related to oxygene. Its $^{13}C$ NMR showed nine peaks for nine different carbons of which the peak at δ 173.58 ppm was due to carbonyl groups. The peak at δ 68.97 ppm was due to carbon of methylene related to oxygene and other peaks are due to aliphatic alkyl chain.

**Neopenthylglycoldiheptanoate ester** was prepared according to the general procedure by using neopenthylglycol (1 mol) and heptanoeic acid (3 mol) to give desired ester in 87% yield; Oil, (Yield 87%),$^1H$-NMR(FT-400MHz, $CDCl_3$): δ (ppm); 0.90 (t, J=7.5Hz, 6H, 2 $CH_3$),0.97 (s , 6H, $2CH_3$), 1.30(m,12H, $6CH_2$), 1.63 (quin, J= 7.2Hz, 4H, $2CH_2$ ), 2.32 (t, J=7.5Hz, 4H, $2CH_2CO$), 3.89 (s, 4H, $2CH_2O$). $^{13}C$ NMR(FT-400MHz, $CDCl_3$): δ (ppm); 13.93, 21.70, 22.42, 24.89, 28.77 , 31.39, 34.24, 34.58, 68.93, 173.62; FT-IR(KBr): $\bar{3}$ ($cm^{-1}$) 2932, 2864, 1740, 1465, 1378, 1234, 1165, 1106, 1024. Its $^1H$ NMR spectrum in d-chloroform showed a triplet at δ 0 .9 ppm with J=7.5 Hz for methyl group, a singlet at δ 0.97 ppm for two methyl groups, a multiplate at δ 1.30 ppm for six methylene groups, a quintet at δ 1.63 ppm with J=7.2Hz for two methylene groups, and triplet at δ 2.32 ppm with J=7.5Hz for two methylene groups related to carbonyl and a singlet at δ 3.89 ppm for two methylene groups related to oxygene. Its $^{13}C$-NMR showed ten peaks for ten different carbons of which the peak at δ 173.62 ppm was due to carbonyl groups .The peak at δ 68.93 ppm was due to carbon of methylene related to oxygene and other peaks are due to aliphatic alkyl chain. Its FT-IR showed strong absorption at 1740 $cm^{-1}$ due to carbonyl groups.

**Neopenthylglycoldioctanoate ester** was prepared according to the general procedure by using neopenthylglycol (1 mol) and octanoeic acid (3 mol) to give desired ester in 82% yield; Oil, (Yield 82%),$^1H$-NMR(FT-400MHz, $CDCl_3$): δ (ppm); 0.88 ( t ,J=7.2Hz, 6H, 2 $CH_3$), 0.97 (s, 6H, $2CH_3$), 1.28

(bm,16H , $8CH_2$ ), 1.62(quin, J= 7.5Hz, 4H, $2CH_2$), 2.31( t, J=7.5Hz, 4H, $2CH_2CO$), 3.88(s, 4H, $2CH_2O$); $^{13}C$ NMR : δ (ppm) 13.94 , 21.670 , 22.51, 24.91 , 28.84 , 26.04 , 31.59, 34.19, 34.56, 68.88, 173.53; FT-IR(KBr): $\bar{3}$ ($cm^{-1}$); 2929, 2861, 1741, 1465, 1378, 1163, 1108, 1006. Its $^1H$ NMR spectrum in d-chloroform showed a triplet at δ 0 .88 ppm with J=7.2Hz for methyl groups, a singlet at δ 0.97 ppm for two methylene groups, a broad multiplate at δ1.28 ppm for eight methylene groups, a quintet at δ 1.62 ppm with J=7.5Hz for two methylene groups, a triplet at δ 2.31 ppm with J=7.5Hz for two methylene groups related to carbonyl and a singlet at δ 3.88 ppm for two methylene groups related to oxygene. Its $^{13}$CNMR, showed 11 peaks for 11 different carbons of which the peak at δ 173.53 ppm was due to carbonyl groups. The peak at δ 68.88 ppm was due to carbon of methylene groups related to oxygene and other peaks are due to aliphatic alkyl chain.

## Conclusion

In this study, the synthesis of diol esters by fatty acids in the presence of acidic ion exchange resin catalyst has been investigated. Thus, in order to get diol esters with good quality, we tried to facilitate the production technology by finding a desirable method and accompanied awoiding the waste of energy and materials' as a result, the overall price which can be reduced has no bio-environmental pollution.

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