

Transesterification of Palm Stearin Methyl Ester and Triethanolamine: An Alternative Technology for Esterquats Production

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Abstract

Transesterification of methyl ester was found to be an alternative to the previously reported direct esterification from fatty acid, as it offers a milder and safer process. In this study, transesterification of palm stearin methyl ester and triethanolamine was performed for the production of palm-based esterquats cationic surfactant. Palm stearin methyl ester used as the raw material does not require any prior hydrogenation as compared to other vegetable oils because it has sufficient ratio of saturated to unsaturated fatty acid compositions suitable for fabric softener application. The study was successfully applied at a 25 L scale stirred tank reactor. The effect of process parameters on the rate of transesterification process were investigated in this study.

Keywords: esterquats, esteramine, transesterification, palm stearin methyl ester, triethanolamine

1. Introduction

Esterquats are classified as cationic surfactants and increasingly used as an active ingredient in fabric softeners and hair conditioners (Friedli *et al.*, 2001). Although the conventional distearyl dimethyl ammonium compounds possess excellent softening performance, their poor biodegradability limits their commercial usefulness. Thus, esterquats are becoming the surfactants of choice for environmental reasons. Most European producers of fabric softeners have converted to esterquats because of the environmental concern in using dialkyl quats (Tyagi *et al.*, 2006). Esterquats are unique in such that they have at least one ester group between the long hydrocarbon chain and triethanolamine hydroxyl group. This ester linkage provides site for easy hydrolysis to fatty acids and short chain quats, where subsequently microorganism will be able to digest the fatty acid to give carbon dioxide and water (Puchta *et al.*, 1993; Levinson, 1999; Waters *et al.*, 1991).

Typically, esterquats are produced by direct esterification of fatty acid and alkanolamine in the presence of acid catalyst to produce esteramine and the esteramine is subsequently quaternized with dimethyl sulfate or methyl chloride to form esterquats. Literatures had reported that the production of esteramine, an intermediate for the production of esterquats was performed via direct esterification of fatty acids and triethanolamine in the presence of acidic catalyst (Trius *et al.*, 1991; Idris *et al.*, 2003). The direct esterification normally requires high temperatures and vacuum as well as corrosion-resistant equipment, which often result in undesired by-products. The preparation of the fatty acid substrates, for example, produces many impurities giving a dark-coloured product. Subsequent downstream processes such as bleaching and distillation are needed to obtain purer and lighter-coloured products (Narula, 1995)]. In addition, this process employs toxic organic solvents as the reaction media due to their high capability of solvating the raw materials. Those toxic solvents are potentially harmful to the workers in chemical plants. The product esters containing toxic solvent residue are not permitted in the food and pharmaceutical industries. A complete removal of the solvents from products is costly and not economically feasible for industry (Cao *et al.*, 1997). Extra costs are incurred for the high consumption of energy, special vessels suitable for high temperature and vacuum, plant infrastructure in terms of establishment of a power-supply plant and facility maintenance.

Due to the problem from direct esterification derived from fatty acid as discussed above, an alternative process for the production of esterquats had been explored. These extreme conditions of direct esterification can be replaced with a milder process conditions from transesterification of methyl ester and triethanolamine. Moreover, reactor design is relatively simple and also meet the industries desire to reduce the operation cost and equipment expenses and to improve safety in the workplace. The current study involves the process, in which the fatty acid is replaced by methyl ester derived from palm oil, which are transesterified with triethanolamine to produce esteramine (Figure 1) and subsequently quaternized with dimethyl sulfate to introduce the positive charge onto the esterquats molecule (Figure 2).

Selection of raw material for esterquats production is very crucial for providing an excellent performance of the fabric softeners. Palm stearin methyl ester is the suitable raw material for esterquats particularly for fabric softeners application. This raw material does not requires any prior hydrogenation compared to other vegetable oils, as this feedstock has sufficient ratio of saturated to unsaturated fatty acid compositions, which can offers optimum rewetting characteristics, providing some water repellency and at the same time exhibit good softening power for the esterquats. Palm stearin methyl ester offers good alternative feedstock for the production of environmentally friendly surfactant as it derived from renewable vegetable feedstock. In addition, the abundance supply of palm-based methyl ester from large oleochemical complex nowadays, ensures their availabilities at competitive prices.

In the production of esterquats cationic surfactant via transesterification of palm stearin methyl ester, several process parameters such as temperature, vacuum, catalyst amount, agitation speed and mole ratio of palm stearin methyl ester to triethanolamine are regarded as the important factors. To the best of our knowledge, there is no study was reported on the transesterification of palm stearin methyl ester and triethanolamine for esterquats production. This study will highlights the effect of process parameters on transesterification process of palm stearin methyl ester and triethanolamine in the presence of sodium methoxide as catalyst.

2. Materials and Methods

Palm stearin methyl ester (99 %), triethanolamine (99.5%), sodium methoxide (1 % solution) were obtained from commercial suppliers.

2.1 Esterquats Production

Esterquats production is a two-stage process, which involves transesterification of fatty acid methyl ester and triethanolamine and the quaternization of the esteramine with dimethyl sulfate to introduce the positive charge to the molecule. Transesterification and quaternization were carried out in a 25 L stirred tank reactor equipped with a heating jacket. The catalytic transesterification between fatty acid methyl ester and triethanolamine produces three major products of mono-esteramine, di-esteramine and tri-esteramine. Methanol was generated as the by-product. The reactants were mixed and heated to the desired reaction temperature and vacuum. The reaction was completed when constant / plateau amine value of product was achieved. The esteramine formed was expressed as equivalent to the amine value of the product. A rotary vane vacuum pump was used to remove methanol formed by the reaction. Removal of methanol is important, as its removal promoted the forward reaction. Mixing in the reactor was by a pitched-blade impeller, a flat angled blade suitable for moderate and intense mixing. The esteramine produced was then quaternized with dimethyl sulfate in the presence of isopropanol. The vaporized isopropanol was condensed and returned to the reactor. Slow addition was preferred over all-at-once addition of the dimethyl sulfate in order to moderate the heat evolved from the exothermic reaction. The temperature in the reactor was kept at 45 to 50 °C throughout the addition of the alkylating agent. Upon completion of the addition, the mixture was maintained at the reaction temperature and atmospheric pressure until ≤ 5 mg KOH /g sample amine value in esterquats was achieved.

2.2 Amine Value Analysis

A total of 1.5 g sample was dissolved in 50 ml acetic acid glacial. The sample was titrated potentiometrically with 0.1 N perchloric acid in acetic acid. Two inflection points were observed in the potentiometric titration curve.

3. Results and Discussion

3.1 Effect of Temperature

Study on the effect of temperature on transesterification of palm stearin methyl ester and triethanolamine were conducted at temperatures of 80, 100, 130 and 150 °C. Vacuum, catalyst amount, agitator speed and mole ratio of palm stearin methyl ester to triethanolamine were held constant at 200 mbar, 5%, 540 rpm and 2:1 respectively. However, when the reactions were conducted at high temperature of 130 and 150 °C, palm stearin methyl ester was vaporized and pulled away via vacuum. Therefore, the production was only conducted at 80 and 100 °C. Figure 3 shows the transesterification conducted at 80 °C achieved only up to amine value of 88 mg KOH/g sample within 255 minutes of reaction time. When the reaction was conducted at 100 °C, maximum amine value of 92 mg KOH/g sample was achieved within 135 minutes reaction times.

3.2 Effect of Vacuum

Methanol removal drives the esterification to completion. This can be done by applying a vacuum to the system. Several batches were made in pilot plant trials with different vacuum levels to study the effect of vacuum on the transesterification process as monitored by the amine value of the esteramine produced. Figure 4 shows the amine values of esteramine at vacuum of 500, 400, 300, 200 and 160 mbars at 100 °C with catalyst amount of 5%, agitator speed of 540 rpm and mole ratio palm stearin methyl ester to triethanolamine of 2:1. When the transesterification was conducted at 500 and 400 mbars, the amine values were only achieved up to 55 mg KOH/g sample and 66 mg KOH/g sample, respectively. As vacuum of 300 mbar was applied, the reaction reached maximum amine value of 95 mg KOH/g sample within 135 minutes. Reaction conducted at vacuum of 200 mbar led to the formation of esteramine with maximum amine value of 95 mg KOH/g sample in shorter duration (75 minutes). No further improvement on the reaction time was observed at 160 mbar, as the maximum amine value of 95 mg KOH/g sample were also achieved within 75 minutes.

3.3 Effect of Catalyst

Generally, sodium or potassium alkoxides (e.g methoxides) are used in transesterification process. Besides that, the use of divalent zinc as homogenous catalyst in transesterification process had been reported (Marshall *et al.*, 2012). Enzymatic synthesis of esteramine using lipase as an alternative to chemical catalyst was also reported (Masoumi *et al.*, 2011; Masoumi *et al.*, 2013; Masoumi *et al.*, 2014). In this study, the influence of sodium methoxide amount ranging from 1% to 10% on the reaction was examined (Figure 5). Other process parameters were held constant at 100 °C, 200 mbar, agitator speed of 540 rpm and mole ratio palm stearin methyl ester to triethanolamine of 2:1. With the incorporation of 1% sodium methoxide, only up to amine values of 32.05 mg KOH/g sample was achieved within 150 minutes reaction period. As catalyst amount were increased to 3%, maximum amine value of 93 mg KOH/g sample was achieved within 150 minutes. Duration to obtain maximum amine value of 93 mg KOH/g sample was reduced from 150 minutes to 90 minutes when the catalyst amount was increased from 3% to 4%. As higher catalyst amount of 5% was incorporated in the system, the maximum amine values of 93 mg KOH/g sample were achieved at shorter transesterification duration of 30 minutes. No further improvement on the reaction time was observed when more than 5% catalyst amount was incorporated.

3.4 Effect of Agitator Speed

In order to ensure homogenous condition of reaction mixtures, an adequate agitation is required to create circulatory flow induced by agitator (Sulaiman *et al.*, 2007). Agitation is not a significant concern in small scale experiment, nevertheless, as the scale increase and the reaction vessel gets larger, agitation may become crucial in a chemical process. Theoretically, the greater the agitation, the more the reacting molecules come into contact with each other to facilitate the chemical reaction. The influence of the pilot plant agitator speed of pitched-blade type impeller was studied at temperature of 100 °C, vacuum of 200 mbar, 5 % catalyst amount and mole ratio palm stearin methyl ester to triethanolamine of 2:1. The investigation was only performed at minimum and maximum speed of 77 and 540 rpm respectively as the pilot plant mechanical agitator was only limited to these two speeds. In Figure 6, it was observed that when the reaction was conducted at agitator speed of 77 rpm, only amine value up to 68 mg KOH/g sample was obtained within 135 minutes reaction time. At higher agitator speed of 540 rpm, maximum amine value of 93 mg KOH/ g sample was achieved within 75 minutes reaction time.

3.5 Effect of Reactants Mole Ratio

Mole ratio of palm stearin methyl ester to triethanolamine had an influence on the cationic content of esterquats. Table 1 shows the effect of reactants mole ratio on cationic content. The study was performed by varying the palm stearin methyl ester to triethanolamine ratio between 1:1 to 2.5:1 with other process parameters constant at temperature of 100 °C, vacuum of 200 mbar, 5% catalyst amount and agitator speed of 540 rpm. When the ratio was increased from 1:1 to 1.8:1, the cationic content of esterquats was increased from 42 to 51.6%. Maximum amount of cationic content of esterquats was found to be at 60% when the mole ratio was increased to 2:1. Nevertheless, no further increment on the cationic content was experienced when the mole ratio was further increased to 2.5:1.

3.6 Process Comparison between Direct Esterification and Transesterification of Palm Stearin Methyl Ester

The process conditions of esterquats via transesterification were compared with the reported direct esterification process as shown in Table 2. Apparently, the transesterification of palm stearin methyl ester are more preferred as the process conditions was found to be milder since lower vacuum and temperature were applied in the system. Unlike the transesterification process, preparation of esterquats via direct esterification utilized considerable amount of energy as high vacuum was applied in order to acquire light-colour esteramine. Moreover, the batch processing time for transesterification of palm stearin methyl ester was only 2.25 hours compared to that of direct esterification, which requires longer time to complete the process.

4. Conclusion

Transesterification of palm stearin methyl ester and triethanolamine was successfully performed for the production of esterquats cationic surfactant, replacing the typical direct esterification from fatty acids. The effects of temperature, vacuum, catalyst amount and mole ratio of palm stearin methyl ester to triethanolamine on transesterification process were profoundly observed. The studied transesterification process derived from palm stearin methyl ester was established at 100 °C, 200 mbar, 5 % catalyst, 540 rpm and mole ratio (palm stearin methyl ester : triethanolamine) of 2:1. Extreme conditions involves in reported direct esterification from fatty acids have made way to the less energy consumption and safer transesterification process from palm stearin methyl ester for the production of esterquats.

5. Acknowledgement

This work was carried out in Advanced Oleochemical Technology Division of Malaysian Palm Oil Board (MPOB). This study was financially supported by MPOB.

6. References

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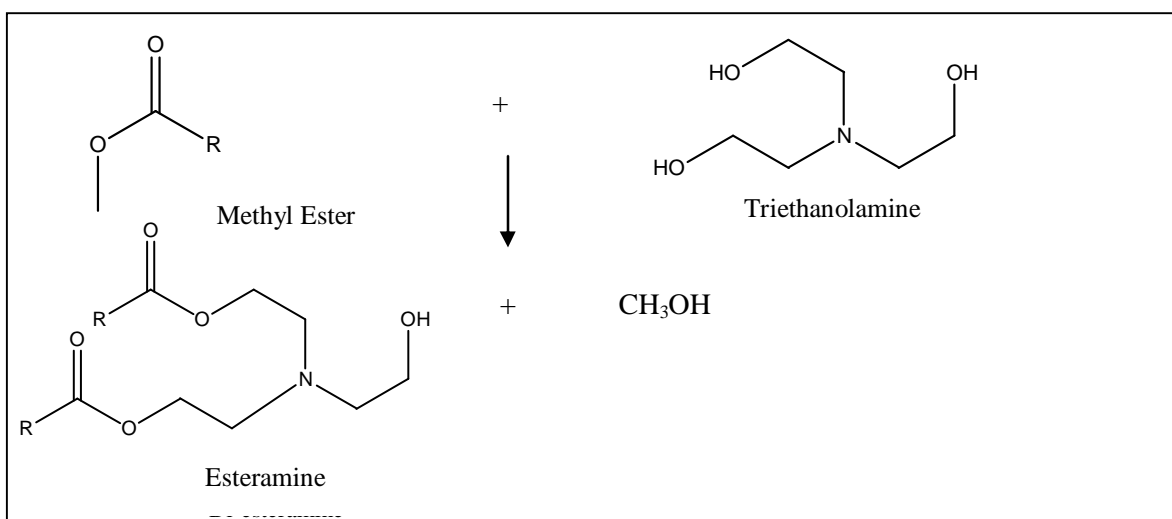


Figure 1: Transesterification of Methyl Ester and Triethanolamine

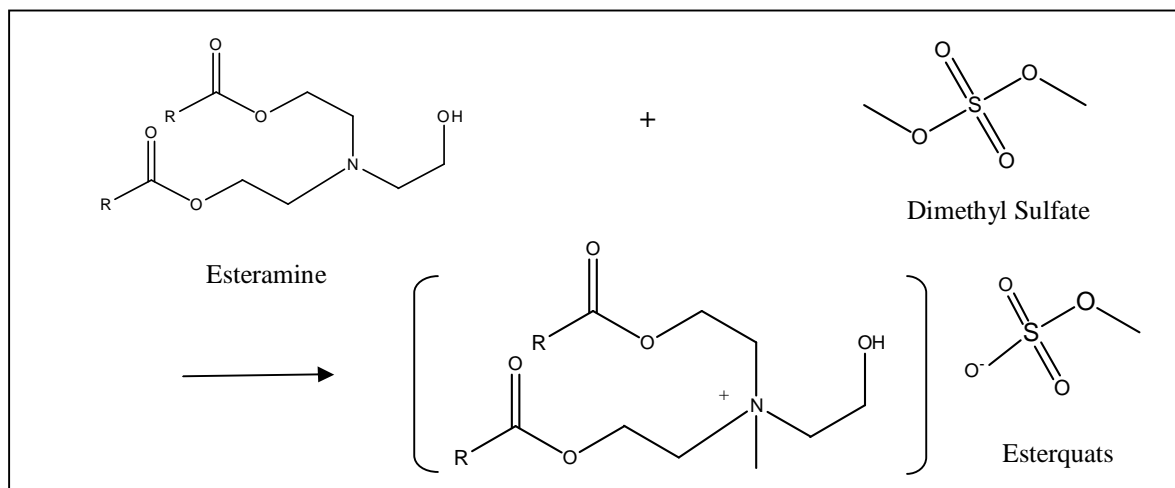


Figure 2: Quaternization of Esteramine with Dimethyl Sulfate

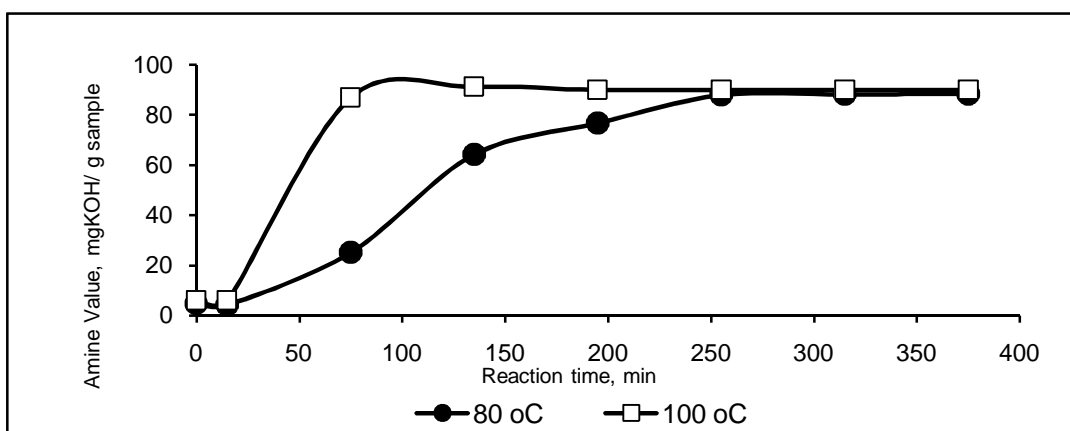


Figure 3: Effect of Temperature on Transesterification at 200 mbar, 5% catalyst amount, 540 rpm, mole ratio ME:TEA of 2:1

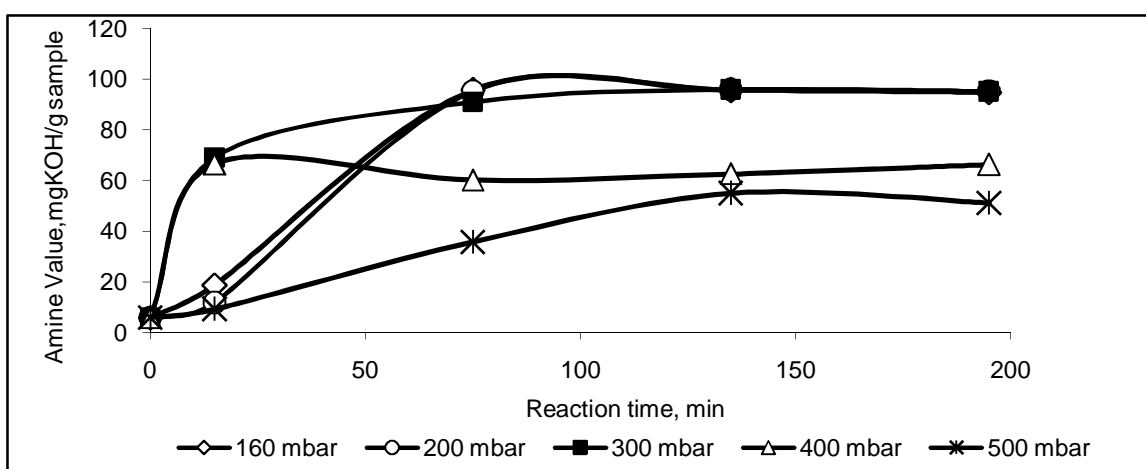


Figure 4: Effect of Vacuum on Transesterification at 100 °C, 5% catalyst amount, 540 rpm and mole ratio ME:TEA of 2:1

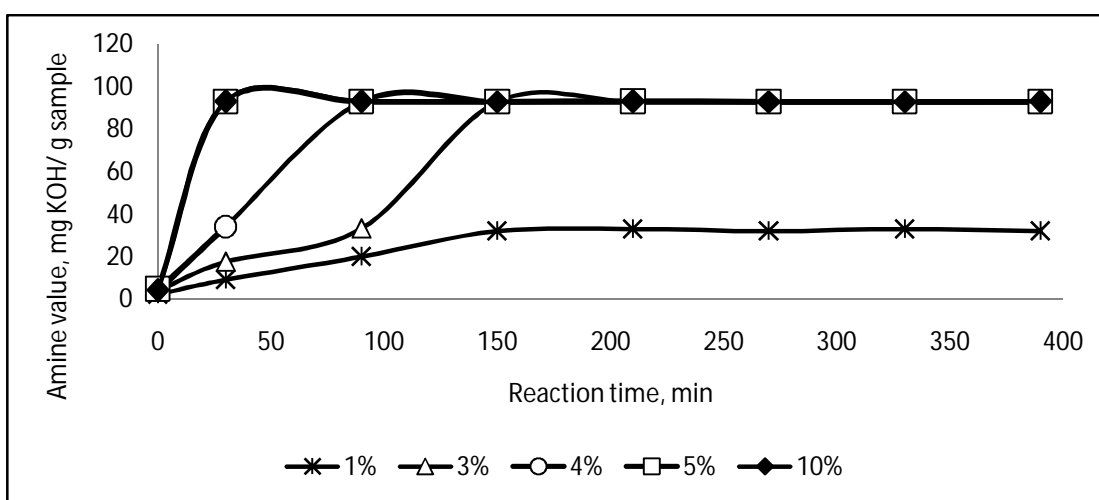


Figure 5: Effect of Catalyst Amount on Transesterification at 100 °C, 200 mbar, 540 rpm, mole ratio ME:TEA of 2:1

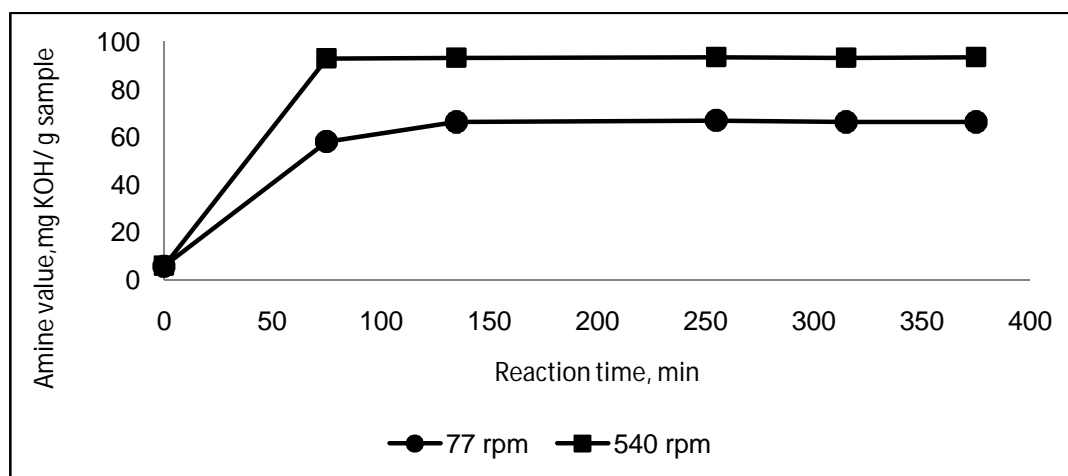


Figure 6: Effect of Agitator Speed on Transesterification at 100 °C, 200 mbar, 5% catalyst amount and mole ratio ME:TEA of 2:1

Table 1: Effect of Mole Ratio of Palm Stearin Methyl Ester to Triethanolamine on Cationic Content of Esterquats

Mole ratio of palm stearin methyl ester to triethanolamine	Cationic content (%)
1:1	42.0
1.5:1	42.0
1.8:1	51.6
2:1	60.1
2.2:1	60.0
2.5:1	59.9

Table 2: Process Comparison between the Reported Direct Esterification of Fatty Acid and Transesterification of Palm Stearin Methyl Ester

Process Parameters	Esterification of fatty acid and triethanolamine (Trius <i>et al.</i> , 1991)	Transesterification of palm stearin methyl ester and triethanolamine
Vacuum (mbar)	1.3 – 6.7	200
Temperature (°C)	160 - 180	100
Reaction Time (hour)	4	2.25