SCALED-UP PRODUCTION AND OPTIMIZATION STUDY ON THE ESTERIFICATION OF PALM-BASED FATTY ACID AND TRIETHANOLAMINE

HALIZA ABDUL AZIZ*; PARTHIBAN SIWAYANAN* and SALMIAH AHMAD*

ABSTRACT

Esterquats or cationic surfactants are increasingly used because of their fabric softening effect and excellent biodegradability. Esterquats production is a two-stage process involving esterification and quaternization. Esteramines, an intermediate for the production of esterquats is produced by esterifying of palm-based fatty acid and triethanolamine in the presence of hypophosphorous acid of 50% purity. The esterification variables, namely, pressure, temperature and mixing intensity were investigated for their effect on the rate of esterification and colour of esteramines produced. Vacuum and temperature had a profound impact on the esterification process. A vacuum of at least 40 mbar was required for the formation of a light-colour esteramines. The reaction time was shortened from 9 hr to approximately 4 hr when the reactor temperature was increased from 160°C to 180°C. Improved colour of the esteramine was also observed with the higher temperature effect. However, mixing intensity only had minimal effect on both the esterification rate and colour of the esteramines.

Keywords: biodegradable esterquats, esteramines, esterification, fabric softener, quaternization.

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INTRODUCTION

Quaternized fatty acid triethanolamine esters or esterquats are cationic surfactants and increasingly used as fabric softeners and hair conditioners. Although the conventional distearyl dimethyl ammonium compounds possess excellent softening performance, their poor biodegradability limit 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. North America conversion has plateaued with half the market now using esterquats (Dan Scheraga, 1998). The uniqueness of the esterquats molecule is due to the presence of at least one ester group between the long hydrocarbon chain and triethanolamine hydroxyl group. This ester link provides for easy hydrolysis to fatty acids and short chain quats (Puchta *et al.,* 1993). Generally, esterquats are produced via a two-stage process in which triethanolamine is first esterified with a fatty acid in the presence of a catalyst, with formation of three major products monoester, diester and triester as illustrated in *Figure 1*. The reaction mixture is then quaternized with an alkylating agent in monohydric solution to introduce the positive charge to the esterquats molecule as shown in *Figure 2* (Zainab Idris, 2000).

The importance of producing esterquats from plant raw materials has many aspects. Due to the ample and continuous supply of palm oil in Malaysia, palm-based esterquats are expected to replace the animal-based raw material. Malaysia, being the largest producer of palm oil products, should exploit this advantage to produce palm-based esterquats. Moreover, based on a previous study by MPOB, the performance of palm-based esterquats is comparable to that of tallow-based esterquats (Zainab Idris and Salmiah Ahmad, 2001).

In MPOB, the production of palm-based esterquats has been scaled-up from laboratory

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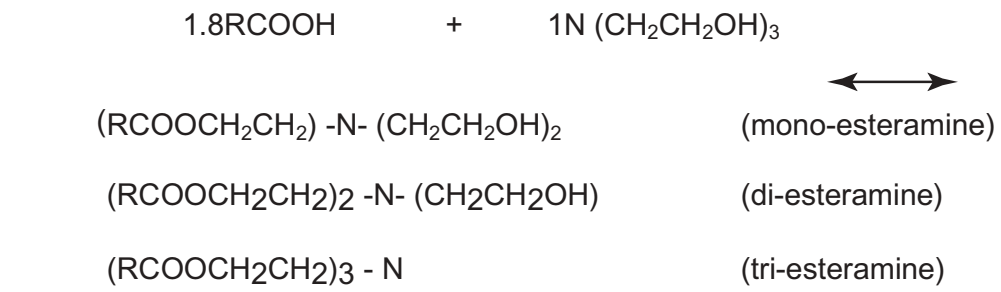

Figure 1. Esterification of palm-based fatty acid and triethanolamine.

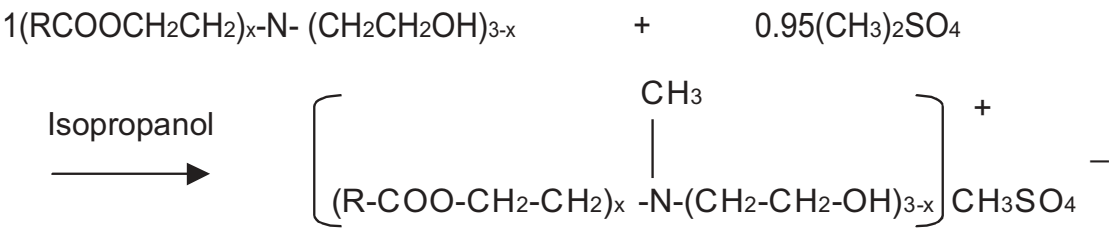

Figure 2. Quaternization of esteramines with dimethyl sulphate.

operation to a 25 kg/batch pilot plant is shown in *Figure 3*. Based on the figures in *Table 1*, the palm-based esterquats specifications are comparable to those of commercial esterquats from tallow. Earlier, the synthesis of palm-based esterquats had been optimized in the laboratory. The optimized conditions were initially used to operate the pilot plant and then the parameters including pressure, mixing intensity and temperature tweaked to improve the efficiency and esterquats quality, particularly the colour. An earlier study (Haliza and Zainab Idris, 2003) in MPOB had indicated that incorporation of hypophosphorous acid in the esterification improved the colour of the esteramines produced. Coloured esterquats used in fabric softeners will taint the fabrics, limiting their commercial usefulness. Therefore, light-coloured esterquats are preferred to minimize tainting.

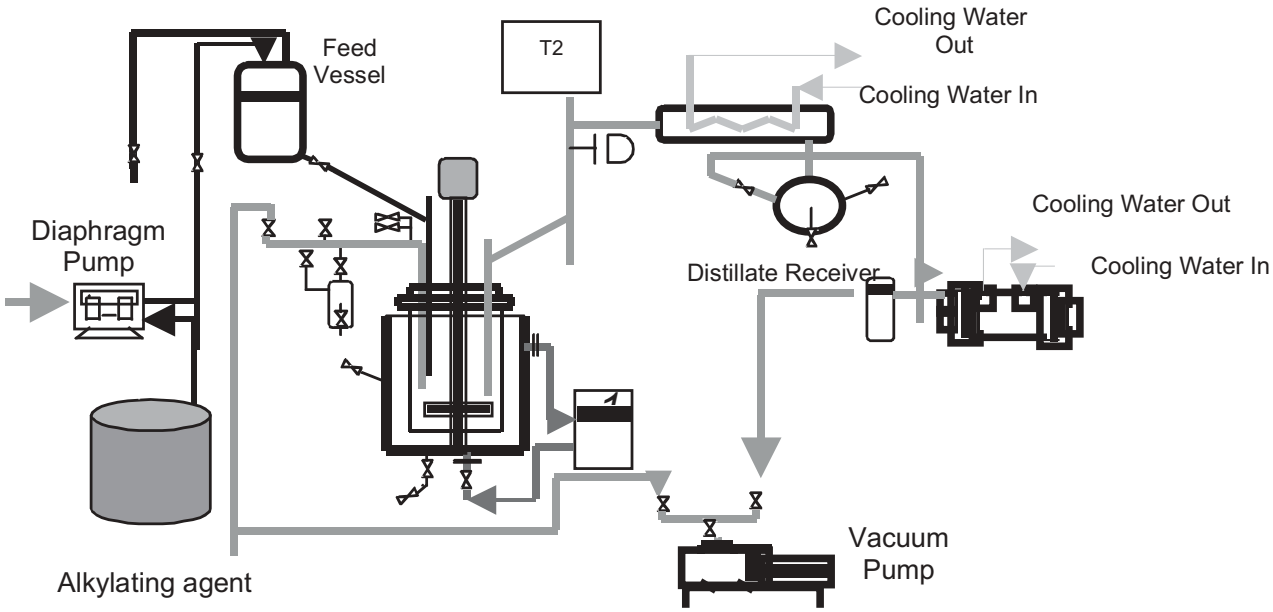

Figure 3. Schematic diagram of 25 kg/batch esterquats pilot plant.

TABLE 1. PALM-BASED ESTERQUATS SPECIFICATIONS

Specification	Palm-based esterquats	Commercial esterquats
Form	Paste	Paste
Active matter (meq g^{-1} sample)	0.91	0.95 - 1.05
Amine value (mg KOH g^{-1} sample)	5.23	< 5.00
Total solid content	89.2%	85.0%
pH	2.74	2.5 - 3.5
Colour Lovibond (red scale)	3.0 R	2.9 R

METHODS

Materials

Distilled palm stearin fatty acid was obtained from Palm Oleo (M) Sdn Bhd. Triethanolamine (99.5%) was purchased from Euro Chemo-Pharma Sdn Bhd. Hypophosphorous acid (50%) was obtained from Fluka Chemical Switzerland.

Palm-Based Esterquats Production

Esterquats production is a two-stage process, which involves esterification of palm-based fatty acid and triethanolamine and the quaternization of the esteramines with an alkylation agent to introduce the positive charge to the molecule. Esterification and quaternization were carried out in a 25-litre stirred tank reactor equipped with a heating jacket. The catalytic esterification between palm-based fatty acid and triethanolamine produces three major products mono-esteramine, di-esteramine and tri-esteramine. Water is generated as a by-product. The reactants were mixed and heated to the reaction temperature in a vacuum of 1 mbar. The vacuum was reduced to 40 mbar by allowing in nitrogen gas once the reaction temperature was reached. The reaction temperature and vacuum were maintained until the acid value of fatty esteramine reached ≤ 5 mg KOH g^{-1} sample. A rotary vane vacuum pump was used to remove the water formed by the reaction. Removal of the water is important, as its presence will favour the forward reaction. Mixing in the reactor was by a pitched-blade impeller, a flat angled blade suitable for moderate and intense mixing (Rose, 1981).

The fatty esteramines produced were then quaternized with dimethyl sulphate in the presence of isopropanol. The vaporized isopropanol was condensed and returned to the reactor. Slow addition is preferred over all-at-once addition of the dimethyl sulphate in order to moderate the heat evolved from the exothermic reaction. The temperature in the reactor was kept at 45°C 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^{-1} sample amine content in esterquats was achieved.

RESULTS

Effect of Pressure

Water 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 rate of esterification as monitored by the acid value of the esteramines produced. *Figure 4* shows the acid value of esteramines at vacuum of 450 mbar, 40 mbar and 1 mbar at 160°C with stirring rate of 77 rpm. There were no marked differences in the acid value profile as the vacuum increased. The influence of vacuum on the rate of esterification was therefore to be marginal.

However, the vacuum affected the colour of the esteramines, which improved with higher vacuum. *Table 2* shows that as the vacuum increased, the red scale Lovibond colour-colour difference of the esteramines decreased. Light-coloured esteramine are favoured in fabric softeners to minimize tainting of the fabrics. Although a lighter colour esteramines were produced at a very high vacuum of 1 mbar at the reaction temperature of 160°C, considerable energy was required to generate and maintain the vacuum. Also, as the saturation temperature at 1 mbar is extremely low; an expensive coolant was required to condense the superheated vapour at 160°C. Thus, esterification at 40 mbar is more cost effective as the superheated vapour can be condensed at ambient temperature using only tap water instead of expensive coolant. Therefore, 40 mbar is the optimum vacuum at 160°C.

TABLE 2. RED SCALE LOVIBOND COLOUR-COLOUR DIFFERENCE OF ESTERAMINE AT VARIOUS VACUUMS

Trial	Vacuum (mbar)	Colour Lovibond (Red scale)
1	600	Cannot be detected (dark)
2	450	Cannot be detected (dark)
3	100	Cannot be detected (dark)
4	40	4.9
5	1	4.0

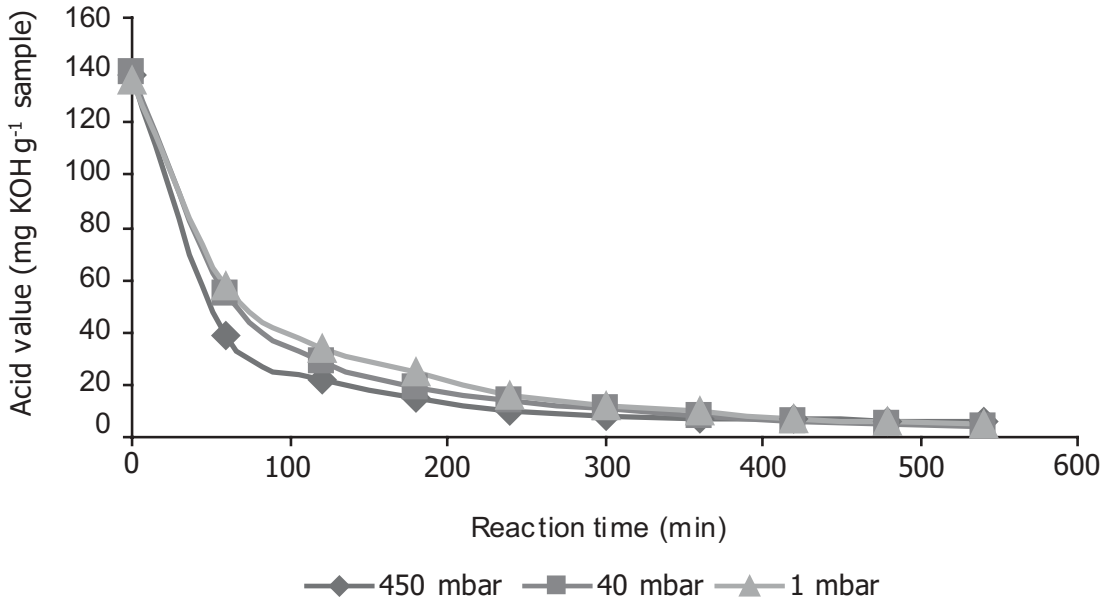

Figure 4. Effect of vacuum pressure on rate of esterification @ 160°C, 77 rpm.

Effect of Mixing Intensity

Mixing is very important in the design of chemical reactor with the reagents used, especially to veer the competing reactions, to the products/by-products desired. Mixing is not a great concern in a small experiment; but gives a greater importance in the chemical process (Erik Kataisto, 2001). Theoretically, the greater the agitation, the more the reacting molecules come into contact with each other to facilitate the chemical reaction. The rate of esterification was observed in the stirred tank reactor to be related to the degree of agitation. The stirring rate of the pitched-blade type impeller was set at 77 rpm and 540 rpm at reaction temperatures of 160°C and 180°C as shown in *Figures 5* and *6*. In *Figure 5*, no significant changes on the acid value profile of the esteramines at 160°C were observed by increasing the stirring speed. A similar response was observed with the reactor temperature at 180°C as shown in *Figure 6*. These Figures show that the best stirring rate to use is 77 rpm.

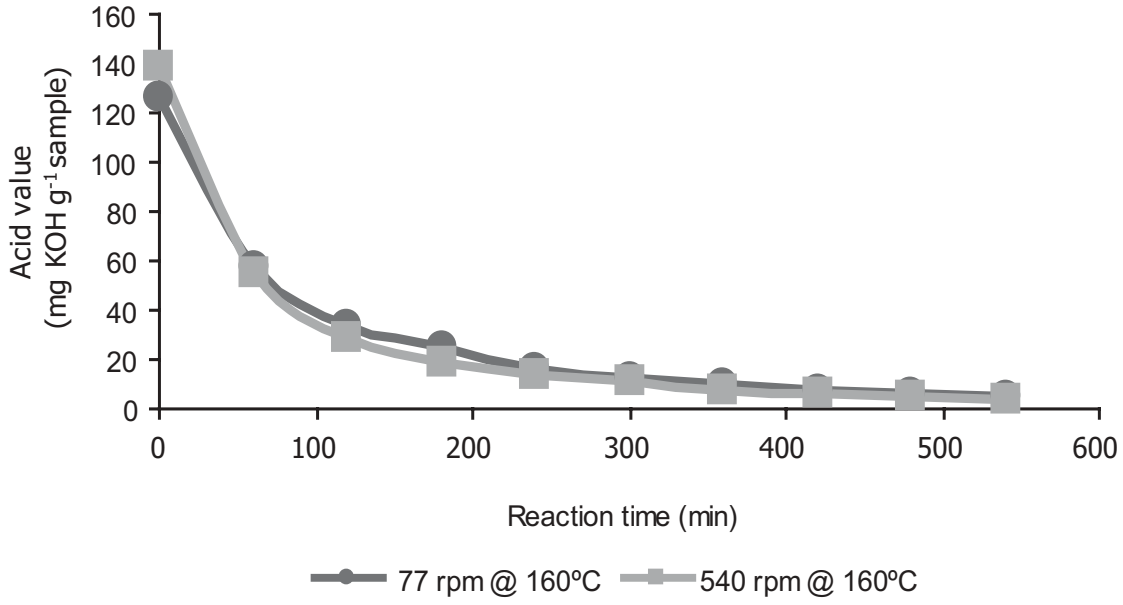

Figure 5. Effect of mixing intensity rate of esterification @160°C, 1 mbar.

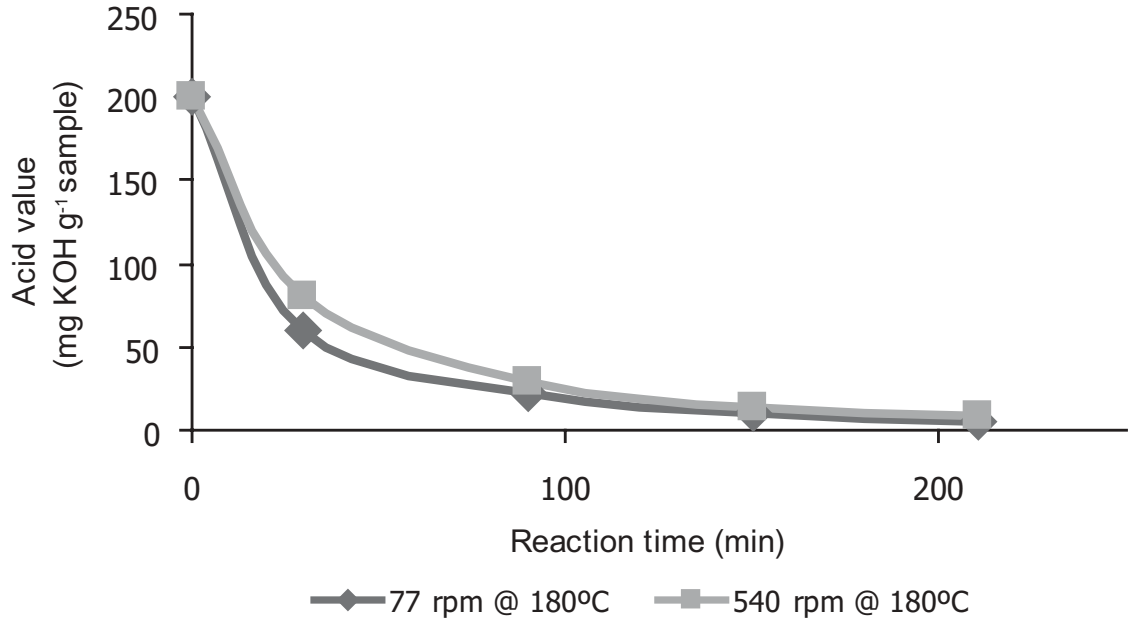

Figure 6. Effect of mixing intensity on the rate of esterification @180°C, 1 mbar.

Effect of Temperature

An earlier study indicated that the optimum temperature for esterification in the laboratory is 160°C (Zainab Idris, 2002). However, a long reaction time was required at pilot scale at the same temperature. Several pilot trials were carried out at higher temperatures in an attempt to expedite the reaction. Effect of temperature on the rate of esterification was found to be important for both stirring rates of 77 rpm and 540 rpm. A shorter reaction time was achieved 180°C for both stirring rates. Based on *Figures 7* and *8*, the reaction was completed in 4 hr instead of approximately 9 hr at 160°C.

Besides reducing the reaction time, the higher temperature also produced a lower colour esteramines. The esteramines were coloured in the first 30 min of the reaction, but then became discoloured at the mixing intensity of 540 rpm (*Figure 9*). Thus, the optimum temperature for esterification of palm stearin fatty acid and triethanolamine is 180°C.

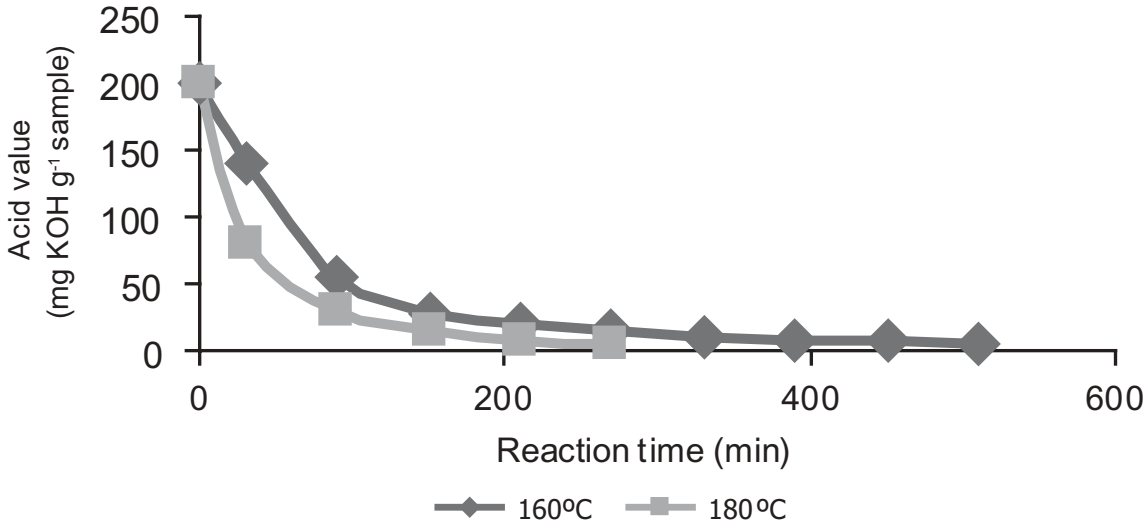

Figure 7. Effect of reaction temperature on the rate of esterification @ 77 rpm.

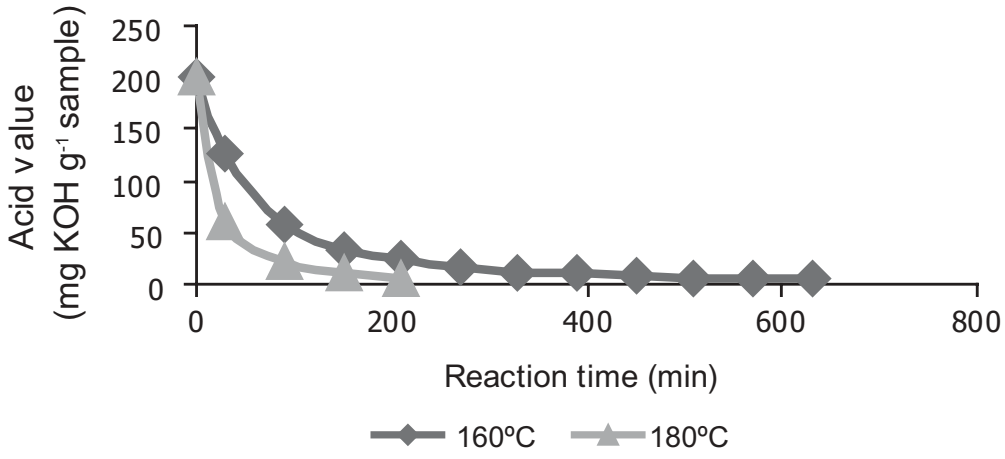

Figure 8. Effect of reaction temperature on the rate of esterification @ 540 rpm.

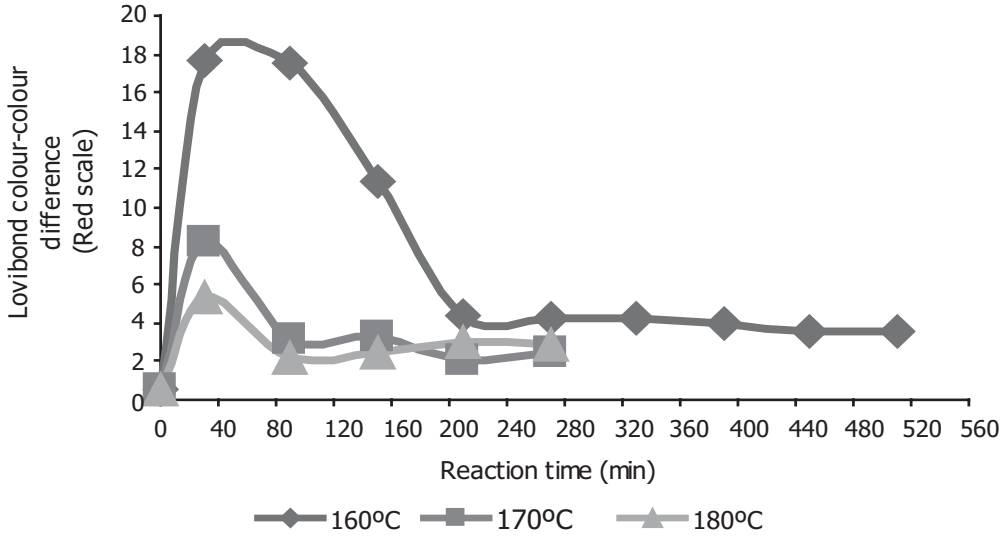

Figure 9. Effect of reaction temperature on the Lovibond colour-colour difference @ 540 rpm.

CONCLUSION

The effect of vacuum on the colour of esteramines were profound in which the colour improved with the vacuum to as high as 1 mbar. However, generating this high vacuum is extremely energy intensive and would not be viable for commercial production. Using a lower vacuum of 40 mbar had only a marginal effect on the rate of esterification. Temperature had an importance effect on both the rate of esterification and colour of the esteramines. A shorter reaction time was needed at 180°C than 160°C. In addition, the colour of esteramine improved with the higher temperature. The mixing intensity had only a minimal effect on both the esterification rate and colour of the esteramines. In conclusion, the optimal reaction conditions are at temperature of 180°C,vacuum of 40 mbar and mixing intensity of 77 rpm.

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