Brazilian Journal
of Chemical
Engineering

Vol. 35, No. 02, pp. 699 - 708, April - June, 2018
dx.doi.org/10.1590/0104-6632.20180352s20160125

ISSN 0104-6632
Printed in Brazil
www.scielo.br/bjce

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PRODUCTION OF CASTOR OIL MALEATE USING DI-TERT-BUTYL PEROXIDE AS FREE RADICAL CATALYST

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(Submitted: February 23, 2016; Revised: February 17, 2017; Accepted: April 16, 2017)

Abstract - Castor oil maleate is used in healthcare products, synthetic lubricants, drying oils, water-soluble paints and as a monomer in several polymers. This compound is formed by direct reaction between castor oil and maleic anhydride, which can be accelerated using free radical catalysts. In this work, the influence of processing temperature and the concentration of di-tert-butyl peroxide (DTBP) in the production of castor oil maleate was studied applying response surface methodology. The results showed that the use of the radical initiator increased the rate of reaction, leading to a shorter reaction time and higher productivity. The optimal operating condition was found at 120ºC, 1 mol of maleic anhydride/mol of castor oil and 0.005 mol of DTBP/mol of castor oil, yielding 90.2% of castor oil maleate in 90 min.

Keywords: Castor oil, maleic anhydride, free radical, DTBP.

INTRODUCTION

Castor oil maleate is a substance produced by the chemical reaction of castor oil and maleic anhydride. This maleinated oil is employed in healthcare products, synthetic lubricants, drying oils, water-soluble paints and as monomer in some biodegradable polymers (Candy et al., 2005; Hashem et al., 2013; Wang et al., 2008; Warth et al., 1997).

Vegetable oils can be chemically modified by anhydrides through esterification for oils containing an alcohol group, through the Diels-Alder reaction for oils containing conjugated dienes, through "ene-reactions" for oils containing allylic hydrogens and through esterification for oils containing a hydroxyl group (Candy et al., 2005; Mazo et al., 2011). Castor oil consists of 90-94% of 12-hydroxy-9-octadecenoic esters (esters from ricinoleic acid). This particular ester has three functional groups (carboxyl group, hydroxyl group and a C-C double bond) that can react producing several castor oil adducts (Mutlu and Meier, 2010; Ogunniyi, 2006). Its reaction with maleic anhydride occurs through the substitution of the hydroxyl group by maleic anhydride, forming castor oil maleate (Wang et al., 2008).

Tran et al. (2005) proposed the use of free radical catalysts in the reaction between oils and anhydrides and they studied the reaction between soybean oil and maleic anhydride using 2,5-bis (tert-butyl-peroxi)-2,5-dimethyl-hexane and di-tert-butyl peroxide as

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catalyst. The use of the free radical catalyst resulted in an improvement in yield compared to the reaction carried out without catalyst. The reaction of soybean oil and maleic anhydride differs from the reaction of castor oil and maleic anhydride because the first is a Diels-Alder reaction while the second one is an esterification reaction. Both reactions are autocatalyzed under temperatures above 80 ºC, but the reaction rate is low. Yields of 95% after 3-4 h are obtained only under temperatures above 140 ºC when higher reaction rates are attained.

The free radical formed by the decomposition of the peroxide reacts preferably with the anhydride rather than with the oil molecule (Eren et al., 2003). This anhydride radical may undergo homopolymerization or react with the oil molecule (Lang et al., 1963). Homopolymerization of maleic anhydride occurs only at very high concentrations of peroxides (5% w/v) and is a slow reaction (33% of conversion after 48 h at 70 ºC using benzoyl peroxide as catalyst) (Joshi, 1962; Lang et al., 1963); thus, homopolymerization of maleic anhydride can be ruled out under the operating conditions used to produce vegetable oil maleates. In the production of soybean oil maleate, the Diels-Alder reaction was favored and occurred more rapidly because of the presence of the more reactive anhydride radical (Tran et al., 2005).

In the esterification reaction of oils with anhydrides, the anhydride must undergo a ring opening reaction prior to the reaction with the oil (Figure 1). The ring opening reaction can occur through hydrolysis of the anhydride or by protonation of the molecule (West et al., 1998). In solvent-free esterification of oils and anhydrides, the reaction is faster when the anhydride is protonated rather than going through hydrolysis (Balland et al., 2002; Widell and Karlsson, 2006). In this work, we evaluate if a peroxide catalyst can improve the reaction rate by generating an anhydride radical that can go through ring opening in a way similar and as rapid as protonating the anhydride, thus resulting in a faster esterification reaction.

The chemical equilibrium between castor oil (and many other vegetable oils), maleic anhydride and the product (castor oil maleate) is inversely proportional to the temperature. Usually, the reaction is carried out at high temperatures (> 80 ºC) until yields of 90 to 95% are obtained, and then the reaction is cooled to room temperature and let reach equilibrium (98 to 99% of product), which is attained after 2 to 3 days. Due to the chemical equilibrium, it is not possible to attain a yield higher than 95% at temperatures above 80 ºC. If the reactants are fed at stoichiometric ratio, the amount of castor oil that remains in the castor oil maleate is insignificant and does not interfere with all known applications of castor oil maleate. Any catalyst added to the reaction mixture will remain with the product, thus it should be optimized to be kept at low levels (Bertz et al., 1999).

In this study, the influence of the concentration of di-tert-butyl peroxide and the temperature on the reaction dynamics of castor oil and maleic anhydride and on the yields of castor oil maleate were studied. The study of the influence of these variables was carried out applying response surface methodology. The increasing interest and demand for biodegradable polymers, and the potential application of castor oil maleate as monomer to produce these kinds of polymers justify this work, because an increase in productivity will be required. Thus, this work also aims at increasing the reaction rates to reduce production time and increase the productivity of castor oil maleate.

MATERIALS AND METHODS

Materials

Castor oil was supplied by OLVEQ Indústria e Comércio de Óleos Vegetais (Quixadá, Brazil). Maleic anhydride and di-tert-butyl peroxide (DTBP) were supplied by Vetec Química Fina and Sigma-Aldrich, respectively.

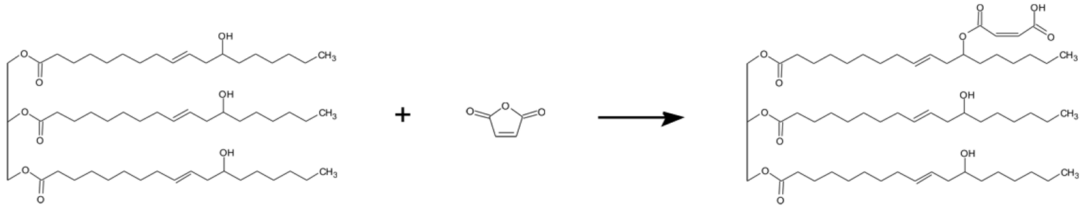

Figure 1. Reaction scheme between castor oil and maleic anhydride.

Synthesis of castor oil maleate

Castor oil (0.16 mol - 150 g) and maleic anhydride (0.16 mol - 15 g) were fed into a 400 mL stainless steel batch reactor. The molar ratio of 1:1 was used because the reaction occurs under stoichiometric ratio (Echeverri et al., 2013). Di-tert-butyl peroxide (DTBP) was fed to the reaction mixture before heating of the reactor started, following the mass ratios presented in Table 1, which were designed based on a 2^2 central composite experimental design. The -1 and +1 levels for the DTBP/oil molar ratio, in the experimental design, were set to 0.005 and 0.015, respectively.

The reactor was closed and the mixture was heated to its operating temperature, which was also set following a central composite experimental design (Table 1). The -1 and +1 levels for the temperature, in the experimental design, were set to 80 and 160 ºC, respectively. The reaction was carried out for 3 h and 2 mL samples were taken every 30 min to determine the yield of castor oil maleate. The reactor heater output a heating rate of 22 ºC/min, which allowed reaching 160 ºC in 6 min, minimizing the transient period of the reaction.

Reactions were also carried out without the addition of catalyst to allow comparing the reaction rate and dynamics with and without the addition of catalyst. The analysis of the data was carried out using surface response methodology and the software Statistica v.10 was used to handle the data.

Product characterization

The characterization of the product was done using NMR. An amount of 18.0 mg of the product was solubilized in 600 µL of DMSO (99.9%) and this solution was transferred to 5 mm NMR tubes. The NMR experiments were performed in an Agilent 600-MHz spectrometer equipped with a 5 mm (H-F/15N-31P) inverse detection One Probe™ with actively shielded Z-gradient. The ^{1}H NMR spectra were acquired with the RF pulse (p1) calibrated and 8 scans, 64k of time domain points for a spectral window of 12 ppm, acquisition time of 5.0 s and a relaxation delay of 10.0 s. The spectra were calibrated internally to the DMSO-d_6 resonance (δ 2.50 and JHD 1.9 Hz) and temperature controlled at 298 K. The ^{13}C NMR spectra were acquired with 5k scans, 32k of time domain points for the spectral window of 250 ppm, acquisition time of 0.87 s and a relaxation delay of 1.0 s.

Two-dimensional (2D) NMR experiments were acquired using the pulse sequences of the standard spectrometer library. One-bond ^{1}H-^{13}C HSQC experiments were acquired with an evolution delay of 1.7 ms for an average 1J(C,H) of 145 Hz; 1442 × 200 data matrix; 32 scans per t1 increment; spectral widths of 9615.4 Hz in f2 and 30165.9 Hz in f1 and relaxation delay of 1.0 s. The ^{1}H-^{1}H COSY experiments were carried out with a spectral width of 18028.1 Hz in both dimensions; 1442 × 200 data matrix; 16 scans per t_1 increment and relaxation delay of 1.0 s. Long-range ^{1}H-^{13}C HMBC experiments were recorded with an evolution delay of 50.0 ms for LRJ(C,H) of 10 Hz; 1442 × 200 data matrix; 64 scans per t1 increment; spectral widths of 9615.4 Hz in f2 and 30165.9 Hz in f1 and relaxation delay of 1.0 s.

Determination of the yield

The reaction yield was determined by FTIR spectroscopy in a FTIR model Cary 630. This was possible because it has been determined by NMR that the only reaction product was castor oil maleate and

Table 1. Yields of castor oil maleate using DTBP as free radical catalyst.

Temperature (ºC)	DTBP mass fraction (w/w %)	Yield (%)	
		1 h	3 h
80.0	0.005	13.3 ± 0.3	75.3 ± 0.3
80.0	0.015	8.4 ± 0.2	72.9 ± 0.3
160.0	0.005	87.3 ± 0.3	94.2 ± 0.3
160.0	0.015	88.0 ± 0.2	93.3 ± 0.2
63.4	0.010	0.0 ± 0.1	26.7 ± 0.5
176.6	0.010	88.2 ± 0.1	94.2 ± 0.2
120.0	0.003	74.4 ± 0.3	94.0 ± 0.2
120.0	0.017	84.7 ± 0.2	93.3 ± 0.1
120.0	0.010	85.8 ± 0.4	93.6 ± 0.3
120.0	0.010	85.8 ± 0.3	93.6 ± 0.2
120.0	0.010	84.2 ± 0.2	92.9 ± 0.3

no other by-product was produced. The FTIR spectra were collected at wavelengths from 900 to 4000 cm^{-1} at a spectral resolution of 1 cm^{-1}. All analyses were carried out in triplicate.

The yield was calculated based on the data regarding the absorbance at wavelength 1780 cm^{-1}, which corresponds to cyclic anhydride, using Equation 1. The absorbance at 1780 cm^{-1} has the tendency to decrease due to the consumption of maleic anhydride by the reaction. Total consumption of the maleic anhydride occurs when the absorbance at this band equals the absorbance of pure castor oil at this band (Mazo et al., 2012b).

$$Y = \frac{Abs^0 - Abs(t)}{Abs^0 - Abs^{oil}} \times 100 \qquad (1)$$

where Abs^0 is the absorbance at 1780 cm^{-1} of the initial reaction mixture, Abs^{oil} is the absorbance at 1780 cm^{-1} of the pure castor oil, and Abs(t) is the absorbance at 1780 cm^{-1} of the sample collected at time *t*.

RESULTS AND DISCUSSION

Product characterization

Samples of castor oil and of the product of the reactions were collected and analyzed by NMR following the procedure described previously. The HSQC and COSY spectra allowed assignment of the spin systems, while the connectivity was known from cross peaks in the HMBC spectrum. The complete hydrogen (^{1}H) and carbon (^{13}C) assignments were obtained by means of HMBC and ^{13}C NMR. Only multiplets were obtained due to overlapping signals of the spin systems. The NMR analysis of pure castor oil presented the signals regarding the olefin bond at^{1}H δ 5.36 (respective ^{13}C at 130.4) and ^{1}H δ 5.40 (^{13}C at 126.5), the ester signal at^{1}H δ 5.18 (^{13}C 68.7) and δ 4.26 (^{13}C 61.7), and the paraffin signals between δ 1.24 and 2.28 (^{13}C 13.8 and 30.1) (Table 2). The NMR analysis of the reaction product presented signals characteristic of the interaction between maleic anhydride and castor oil (Table 2) and a small shift in the olefin and paraffin signals in the castor oil unit. The connectivity between castor oil and the maleic unit was determined from the existence of the cross peak between the ^{1}H at δ 4.84 (^{13}C in 74.6) of the castor oil unit and the carbonyl carbon (δ 165.3) of the maleic unit in the HMBC spectrum (Figure 2).

Signals from the double bond of the maleic unit were recognized by their downfield positions at δ 128.9 and 131.4, which presented cross peaks in the HMBC spectrum with the castor oil unit (δ 32.3; 30.0; and 27.8), establishing the linkage between the two units. Thus, it was found that the carbonyl resonance belongs to the maleic unit interacting with the castor oil unit. Moreover, the comparison of the chemical shifts of ^{1}H and ^{13}C NMR spectra of castor oil and maleic anhydride in other works has reinforced this interpretation (Diehl, 2011; Husain et al., 1993; Knothe et al., 1996; Lan et al., 2014).

The HSQC, HMBC and ^{1}H NMR spectra were investigated to determine the detailed structural organization of the reaction product and to determine how the maleic units are interacting with the castor oil unit. The proton integrations of the H18 signals of the CO moiety at δ 0.87 in both spectra from the mix of maleate anhydride and castor oil in the proportion of 1:1 proved to be the same amount of castor oil in the samples. However, the integrations of the signal from the CO unit interacting with the MA unit (δ 4.84, and δ 6.32 and 6.34) confirmed that more MA units exist coupled to the CO unit. The integration values showed that mono-castor oil maleate is the main product of reaction and that it co-exists with a very small fraction of di-castor oil maleate (< 5%). The chemical shifts of the signals C10", C12’, and C12" were also indicative of the connection in only one other position (as illustrated in Figure 2), and that no tri-castor oil maleate was formed under the conditions applied in this study. The reactions of castor oil with anhydride maleate produced the same product when carried out with or without the reaction initiator.

Influence of the initiator concentration and temperature on the reaction

The conversion of castor oil into castor oil maleate is presented in Table 1. Yields above 88% could be obtained in one hour at high temperature (≥ 160 ºC) (Figure 3), while similar yields were also possible after one and a half hours of processing at a milder temperature (120 ºC) (Figure 4). At 80 ºC and below, it was not possible to achieve the same high yield (> 85%), even after 3 h of reaction (Figure 5). The highest yield found during the experiments was 94.2%, obtained using 0.005% w/w of DTBP and carrying out the reaction at 160ºC for 3 h. This condition was further confirmed by running three replicates of this condition, which outputted similar results (94.0 ± 0.5).

Considering the standard error of the experiments, the results obtained at 160 ºC were statistically similar to the results obtained at 120 ºC. As such, it would be preferred to run the reaction at 120 ºC to save on energy consumption.

Table 2. Chemical shifts (ppm) of ^1H and ^{13}C, and long range interactions (HMBC) between the castor oil (CO) and maleic unit (MA) presents in the samples.

Unit/Carbon	δ ^1H	δ ^{13}C	^1H-^{13}C HMBC
CO C1	-	173.4	
CO C1’	-	174.9	
CO C2	2.26	34.3	29.7; 24.6; 125.0; 133.1; 173.4; 174.9
CO C3	1.50	24.6	29.7; 34.3; 173.4; 174.9
CO C9	5.44	132.3	27.6; 31.9; 36.2; 124.5
CO C10	5.34	124.5	27.6; 31.9; 132.3
CO C10”	5.40	126.7	
CO C12	4.84	74.6	124.5; 165.8
CO C12’	4.91	74.6	
CO C12”	3.51	69.9	126.7
CO C13	2.09	36.2	
CO C18	0.87	14.4	23.3; 32.3
CO C19;21	4.27	62.0	69.0; 173.4
CO C20	5.19	69.0	124.5
MA C1	-	165.3	
MA C4	-	166.8	
MA C2	6.32	128.9	131.4, 165.3, 166.8
MA C3	6.34	131.4	128.9, 165.8

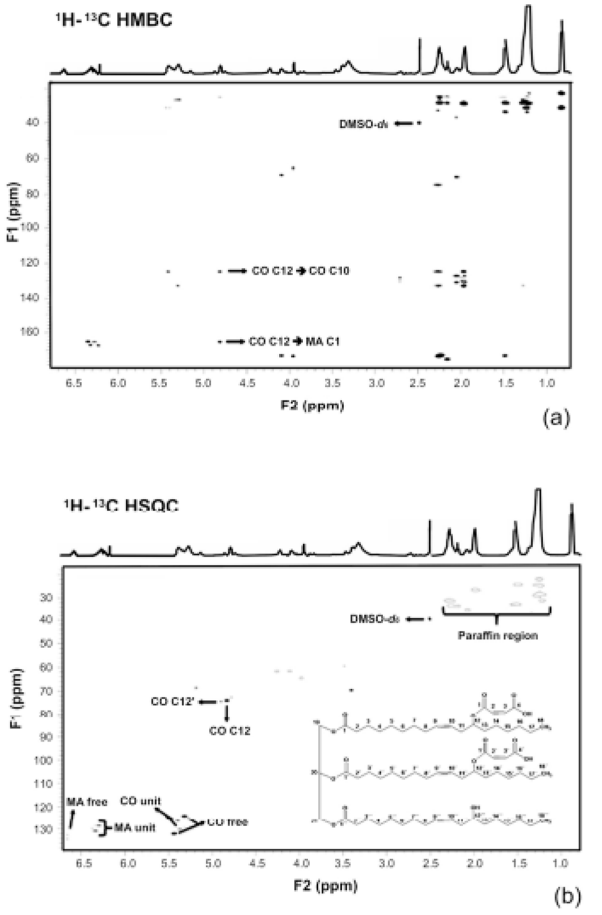

Figure 2. HSQC and HMBC NMR spectra of the reaction product and castor oil maleate structure illustrating the correlations and chemical shifts.

Table 3 presents the analysis of perturbation of the factors. The analysis showed that the yield was significantly influenced by the changes in temperature. The analysis also indicated that the significant effect of an increase in temperature had a lower influence at very high temperatures (> 120 ºC), denoted by the negative value of the quadratic effect of the temperature.

The analysis showed that the concentration of DTBP (free radical initiator) did not result in a significant effect on the process, but it showed that the initiator improves the rate of reaction. The positive effect shown by the analysis of perturbation of factor denotes that DTBP should be used, but the increase in its concentration does not increase significantly the yield, although it helps reaching this final yield at a much faster rate. Low amounts of DTBP (< 0.003%) did not improve the reaction and the results were like the results obtained without the reaction initiator.

We believe that the initiator acts in the reaction in a similar way as it acts in ring-opening copolymerization of anhydrides (Nejad et al., 2013, 2012; Pasquale et al., 2001). The free radical generated by the initiator reacts with maleic anhydride at the carbon double bond, opening the ring and producing an anhydride radical. This anhydride radical reacts with castor oil at the hydroxyl bond producing castor oil maleate and a hydrogen radical, which reacts with other free radicals terminating the reaction. Cyclic anhydrides

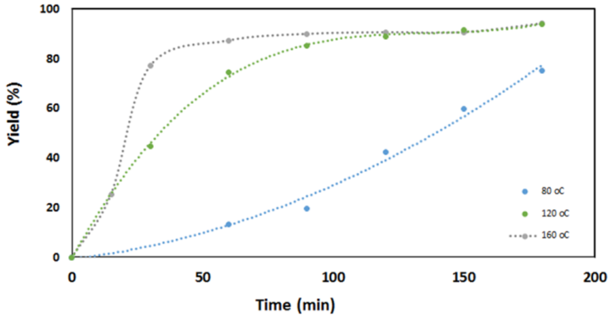

Figure 3. Yield in castor oil maleate as a function of temperature.

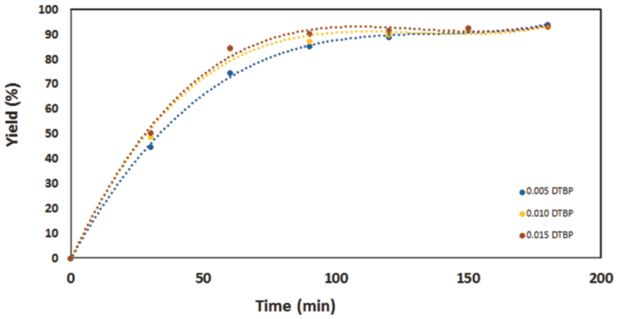

Figure 4. Yield in castor oil maleate as a function of DTBPmass fraction for the reaction carried out at 120 ºC.

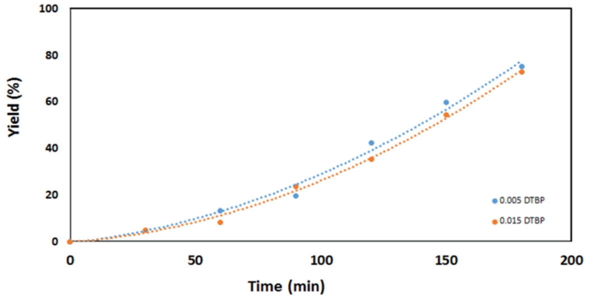

Figure 5. Yield in castor oil maleate as a function of DTBP mass fraction for the reaction carried out at 80 ºC.

homopolymerize poorly via free radical polymerization (Joshi, 1962; Pasquale et al., 2001). Thus, there is a higher preference for the anhydride radical to react with castor oil than to homopolymerize, a theory that corroborates with the results obtained by RMN, which indicates only the presence of castor oil maleate and no maleic anhydride homopolymer.

The yield of castor oil maleate could be correlated by Equation 2, which showed a correlation coefficient (r^2) of 0.997. The ANOVA presented an F-value for the regression 5 times greater than the listed F-value (5.0) at a level of confidence of 95%, indicating that the regression could be used to optimize the process.

$$Y = -250.7 + 4.36T - 0.01T^2 - 4215.11I - 239630.63I^2 + 6.94TI \tag{2}$$

where I is the initiator weight ratio (g initiator/g castor oil) and T is the temperature (ºC)

Reaction dynamics

Figures 3 to 5 show the dynamic behavior of the reaction between castor oil and maleic anhydride. The rate of reaction increased with increasing reaction temperature, as can be observed in Figure 3.The reaction dynamics showed little difference in the reaction carried out at 160 and 176 ºC. Yields near 90% were obtained under 1 h of reaction.

The reaction carried out at 120 ºC showed a lower rate of reaction and the yield reached 90% only after 90 min of reaction. The reaction rate was even slower when the reaction was carried out at 63 and at 80 ºC and a maximum of 75% of yield after 3 h was obtained under these conditions.

The concentration of initiator had a lower influence on the reaction yield. Overall, the increase in the initiator concentration increased slightly the

Table 3. Analysis of perturbation of factors on the yield of castor oil maleate.

Factor	Effect	Standard error	t	P
Mean	85.26	5.56	15.33	0.0000
T	69.58	6.81	10.21	0.0002
T^2	-47.43	8.11	-5.85	0.0021
I	2.56	1.81	-0.38	0.7227
I^2	-11.98	8.11	-1.48	0.1996
T × I	2.78	9.63	0.29	0.7847

I – DTBP mass fraction; T – temperature; Bold factors represent factors significant at a 95% level of confidence.

reaction rate (Figure 4), with exception at the lowest temperature that was studied (80 ºC) (Figure 5).

Comparison with the reaction carried out without DTBP

The reaction of castor oil and maleic anhydride can be carried out at temperatures above 80 ºC without the use of catalyst. The yield of castor oil maleate is presented in Table 4. The reaction presented a similar trend compared to the reaction that included the free radical initiator. A higher yield of castor oil maleate was found with increasing temperatures. Yields above 90% were obtained after 3 h of reaction applying temperatures of 120 ºC and above. Below this period, the yield was always lower than 90%. The results obtained herein were similar to the results reported by other authors for this reaction without the use of free radical initiator, showing that our results for this system are not under or overestimated (Mazo et al., 2012a, 2011).

The use of the catalyst improved the yield of castor oil maleate when operating at mild and low temperatures (up to 120 ºC) (Tables 1 and 5). Numerically, the reaction carried out without catalyst always resulted in lower yields. The yields were statistically different at a 95% confidence level for the reactions carried out up to 120 ºC, and were not statistically different for the reaction carried out above 120 ºC.

Figure 6 presents the kinetic behavior of the reaction carried out without the use of catalyst. Under this condition, the initial reaction rate was lower than when DTBP was used. The reactions carried out at 63 and 80 ºC presented a very low reaction rate and extremely low yields (< 40%) until 2 h of reaction.

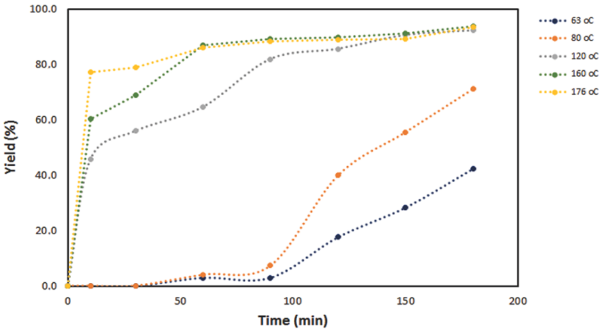

Figure 6. Yield in castor oil maleate as a function of temperature for the reaction carried out without free radical initiator.

The comparison of the reaction with and without the use of DTBP can be also evaluated by means of reactor productivity. In this case, the productivity can be compared with the productivities that would be obtained operating the reaction system aiming at yields of 90%, a value for which no separation process would be required for commercial purposes. Under this condition, the maximum productivity of the reaction running with DTBP would be 615 g/L.h (obtained when operating at 160ºC applying 0.005 % of DTBP).

The lower initial reaction rate of the system without catalyst was also reflected in the productivity of the reaction. Under no operating condition was the productivity of the non-catalytic system higher than the system carried out with DTBP as catalyst. The maximum productivity observed for the non-catalytic system was 553 g/L.h (operating at 176 ºC), representing a productivity 10% lower than the catalyzed reaction, but at a higher operating temperature. At the same temperature (160 ºC), the productivity of the autocatalyzed reaction would be 18% lower than the reaction running with DTBP.

The improvement in the reaction rate and productivity is more evident when the productivities are calculated at 120 ºC. In this case, the productivities that would be obtained with and without the use of

Table 4. ANOVA of the regression of the yield in castor oil maleate.

	Sum of squares	Degree of freedom	Mean squares	$F_{calc.}$
Regression	12884.9	5	2577.0	27.8
Error	464.1	5	92.8	
Total SS	13349.1	10		$F_{5,5}$=5.0

Table 5. Yield of castor oil maleate for the reaction of castor oil and maleic anhydride without using catalyst.

Temperature (°C)	Yield (%)	
	1 h	3 h
63.4	3.0 ± 0.3	42.3 ± 0.6
80.0	4.0 ± 0.8	71.3 ± 0.2
120.0	64.7 ± 0.2	92.3 ± 0.1
160.0	87.0 ± 0.1	94.0 ± 0.1
176.6	86.2 ± 0.2	93.6 ± 0.2

DTBP would be 560 and 336 g/L.h, respectively (a difference of 40%).

CONCLUSIONS

The use of di-tert-butyl peroxide (DTBP) increased the reaction rate and yield of the reaction when the reaction was carried out at mild and low temperatures (up to 120 ºC). At high temperatures (> 160 ºC), the thermal effect is higher than the chemical effect of the initiator and the use of the catalyst is not required. The study of the operating condition showed that low amounts of catalyst (0.005% w/w) can be used and that high yields (> 90%) can be obtained in 1 h at 160 ºC and in 1.5 h at 120 ºC.The productivity that could be obtained using the free radical catalyst DTBP increases by 10 to 40% depending of the reactor's operating temperature, which can be an improvement if this product is to be produced in larger scale following the increasing trend in demand for biodegradable plastic.

ACKNOWLEDGMENTS

The authors thank the Brazilian funding agency CAPES for the award of a scholarship; and Dr. E. Godoy for the NMR spectrum.

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