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Synthesis of alkenyl succinic anhydrides from methyl esters of high oleic sunflower oil

Alkenyl succinic anhydrides (ASA) have been prepared by ene-reaction of high-oleic sunflower oil methyl esters with maleic anhydride in a 50% xylene medium. Response surface methodology (RSM) was used to investigate the influence of two factors: reaction temperature and molar ratio between maleic anhydride (MA) and methyl esters (SME). The studied parameters in 8-h reactions were the methyl oleate conversion, the distillation yield in ASA, and responses allowing the indirect estimation of side reaction products: clarity index and dynamic viscosity. The highest yield in ASA (>70%; clarity index ≈ 10) was reached for a temperature of 240–250 °C with a molar ratio of 1.5–1.7. But for an industrial application requiring minimized side products (clarity index >40), the optimal synthesis conditions were: temperature between 220 and 235 °C and molar ratio of 1.2–1.35 (yield $\approx 55\%$). Such conditions did not provide a medium free of side products, even if xylene decreased their formation. Compared to solvent-free synthesis, conversion was lower with xylene. With solvent, higher temperatures were needed to reach the same yields. Supplementary heating compensated the reagent dissolution effect that slows down the kinetics of the ene-reaction. The influence of reaction time at 220 °C with a MA/SME ratio of 1.2 in a 50% xylene medium was studied. A reaction time of 8–10 h provided a good compromise between ASA yield and side products.

Keywords: Alkenyl succinic anhydride, Doelhart uniform experimental design, response surface methodology, alkyl oleate, xylene, renewable resources.

1 Introduction

Alkenyl succinic anhydrides (ASA) are widely used in several fields, including additives for lubricants [1], intermediates in organic chemistry [2], wood preservation agents [3] or paper sizing agents [4]. They are obtained by ene-reaction [5] between maleic anhydride that plays the role of enophile and an alkene having an allylic hydrogen, *i.e.* the ene compound. During the reaction, a new bond is created between the two unsaturated termini, with an allylic shift of the ene double bond and transfer of the allylic hydrogen to the enophile. Usually, the alkene is a petrochemical olefin, but also triglycerides or vegetable oil derivatives such as fatty acids have been used, and in this case, the reaction is commonly named maleinization [6]. The ene-reaction requires a *Lewis* acid [7], metallic catalysts [8] and/or high temperatures (>200 °C) since its activation energy is high (>80 kJ/mol) [9]. Even though the conversion is improved at higher temperatures, various side reactions can take place: enophile polymerization,

alkene oligomerization, copolymerization between enophile and alkene, and thermal decomposition of ASA (retroene reaction) [10, 11]. Secondary products are usually black waxy solids that are not suitable for most uses of ASA.

Literature concerning the reaction between maleic anhydride and unsaturated molecules can be divided into three periods. First, during the forties and up to the early fifties, the studies of the reaction mechanism lead to ASA from fatty acids or fatty acid esters. The demonstration of the ene-reaction mechanism was debated and finally established during this period [12–14]. Second, the strong development of petrol resources in the early fifties favored the production of ASA from straight or branched olefins, or even from polyolefins [4, 15]. Since then, and up to the nineties, the studies aimed at limiting secondary products by adding reaction catalysts or polymerization inhibitors [9] or an aromatic solvent [16]. Third, with the rising interest for renewable resources neatly observed since the early nineties, new ASA have been synthesized from vegetable oils and their derivatives. They have been essentially used as monomers for the fabrication of thermosets [17], as the anhydride moiety can react with diamines, diols and polyols or epoxy resins to yield unsaturated polyester-like resins.

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We have limited our study to the optimization of the ene-reaction in the presence of an aromatic solvent (xylene) in order to limit side reaction products, color and viscosity of the reaction medium. Xylene has already demonstrated several advantages for the synthesis of ASA from petrochemical olefins [16, 18]. Our purpose was to study the advantages of the use of xylene for the synthesis of a vegetable ASA obtained from high oleic sunflower oil methyl esters, which is a renewable resource in huge development. The advantage of such products is that the formation of di- or tri-anhydride-substituted ASA formed from linoleic or linolenic molecules is limited. The latter are inconvenient for most applications. Another objective was to model the reaction and optimize the experimental conditions for the synthesis of this molecule. Aims were: maximum ASA yield with minimized side products, color and viscosity. By this study, we intend to favor the replacement of fossil resources by renewable resources in the different applications of ASA.

2 Materials and methods

2.1 Materials

High oleic (>80%) sunflower oil methyl esters (SME) were supplied by *Novance* (Compiègne, France). Maleic anhydride (MA) and xylene (all >99%) were purchased from *Sigma* (France). All reagents were used as received, without further purification. The composition of SME (wt-%), determined by GC, was: methyl oleate 81, methyl linoleate 10, methyl stearate 3.5, and methyl palmitate 4.

2.2 Experimental design

Preliminary works concerning the synthesis of ASA from rapeseed and sunflower oleic acid methyl esters, without solvent, demonstrated that an 8-h reaction time was optimal [10, 11]. We studied the combined influences on ASA synthesis of temperature ranging from 190 °C to 250 °C and of the molar ratio MA/SME from 0.7 to 1.7 in the presence of xylene. The MA/SME ratio corresponded to the ratio between the number of moles of maleic anhydride and the equivalent number of moles of double bonds present in methyl oleate and linoleate, which were the most abundant unsaturated esters in SME. This molar ratio was calculated by assuming that one molecule of methyl oleate consumes one molecule of enophile compound, whereas one molecule of linoleate consumes two molecules of enophile. This study was led using an experimental design based on a two-factors Doehlert's type uniform network as described elsewhere [19]. With this experimental design applied to two independent variables, seven experiments are required to fit a second-order polynomial model (Tab. 1).

SME (50 g), a given amount of maleic anhydride depending on the experiment (11.6–30.4 g) and xylene (amount calculated to have a final medium containing 50% xylene) were placed in a 250-mL pressure batch reactor. For a few minutes, a stream of N₂ was passed over the liquid medium to obtain an inert atmosphere. The mixture was heated at a variable temperature during 8 h and magnetically stirred at 300 rpm. At the end of the experiment, the sample remained for 12 h at room temperature without stirring, to favor the decantation of secondary products insoluble in xylene. The medium was then vacuum-filtrated over frittered glass. Xylene was distilled off in a rotative evaporator at 50 °C. A sample of the medium was analyzed by HPLC to determine the residual content of methyl oleate. The medium was then vacuum-distilled to remove residual maleic anhydride and SME. It was then analyzed by HPLC to check the removal of unreacted materials. Colorimetry and viscosity measurements were performed on the distilled medium.

Tab. 1. Experimental design conditions and responses for the preparation of ASA from high oleic sunflower oil methyl esters[†].

T [°C]	MA/SME	Responses				
		C [%]	M [kg/kg ester]	Cl	GC	V [Pa s]
190	1.2	20.4	0.39	17	18	4.34
205	0.7	24.5	0.37	17	18	2.71
205	1.7	43.4	0.60	3	18	0.65
220	1.2	54.9	0.60	46	18	0.40
235	0.7	51.2	0.52	35	18	0.64
235	1.7	79.3	0.87	21	18	0.52
250	1.2	74.8	0.90	12	18	0.54

[†] T – temperature; MA/SME – molar ratio maleic anhydride/methyl esters; C – conversion of methyl oleate; M – mass of ASA obtained from 1 kg methyl esters; Cl – clarity index; GC – Gardner color; V – viscosity.

2.3 Reaction time influence

Experiments were carried out during four different reaction times: 6, 8, 12 or 16 h. SME (50 g), maleic anhydride (19.9 g, for a MA/SME ratio of 1.2) and 69.9 g xylene (final medium containing 50% xylene) were placed in a 250-mL pressure batch reactor, through which a stream of N₂ was passed for a few minutes to obtain an inert atmosphere. The mixture was heated at 220 °C and magnetically stirred at 300 rpm. At the end of the experiment, the sample was treated and analyzed in the same way as for the experimental design.

2.4 Reference sample

A sample of ASA was prepared without solvent at 220 °C with a MA/SME of 1.2. SME (50 g) and maleic anhydride (19.9 g, for a MA/SME ratio of 1.2) were heated during 8 h under static nitrogen atmosphere in a three-neck reactor equipped with a magnetic stirrer (300 rpm) and a condenser heated at 60 °C to allow the reflux of liquid maleic anhydride (melting point: 53 °C). At the end of the reaction, the medium was vacuum-distilled (<1 mm Hg) in two steps. Unreacted maleic anhydride and oleic acid esters were distilled at 70 °C and between 160 °C and 190 °C, respectively. The sample obtained after this first distillation was named ASA1S. A part of ASA1S was then distilled. Pure ASA (ASA2S) was obtained between 240 °C and 250 °C under this pressure. ASA2S was used as standard for analytical methods. Its purity was assessed by HPLC, and its structure was confirmed by infrared and nuclear magnetic resonance spectroscopy.

2.5 Analytical methods

2.5.1 HPLC

The HPLC system was composed of a Spectra-Physics pump and a refractometer detector 350RI (*Varian*) at 35 °C. A Spherisorb ODS2 column (silica-grafted C₁₈) was operated at 25 °C, with a 1-mL/min acetonitrile (*Riedel de Haen*, France) flow as mobile phase.

2.5.2 GC

The fatty acid ester composition of SME was determined using a Varian 5800 gas chromatograph fitted with an FID and a CP-select CB FAME capillary column (50 m × 0.25 mm). The carrier gas was helium at 1.2 mL/min. The temperature program was 12 min at 185 °C, an increase of 15 °C/min up to 250 °C, and 5 min at 250 °C. The injector and detector temperatures were 250 °C.

2.5.3 Infrared spectroscopy

Transmission IR spectra of the liquid products were recorded on KBr windows, using a Perkin-Elmer 1600 FTIR in the 400–4000 cm⁻¹ region with a 4 cm⁻¹ resolution.

2.5.4 Nuclear magnetic resonance spectroscopy

¹H NMR spectra were obtained in a Bruker AC200 apparatus at 200 MHz. The samples were analyzed in CDCl₃ 99% (*Sigma*).

2.5.5 Thermo-gravimetric analysis

The degradation temperature of ASA corresponding to 5% mass loss was determined in a Setaram TG-DTG 92 apparatus. The sample was heated from 20 °C to 600 °C at 10 °C/min under air.

2.5.6 Spectrocolorimetry

Clarity index and Gardner color were determined by spectrocolorimetric methods. Gardner color was evaluated with a Minolta Mi 508 spectrocolorimeter equipped with Spectra Magic software. The method was based on the comparison between the color of the sample and that of a standard. A value of 1 corresponds to pale yellow, and 18 to dark brown. Clarity index was evaluated with the same material and software; the scale ranged from 0 for black to 100 for transparent.

2.5.7 Viscosity

Dynamic viscosities were measured with a Carrimed CSL100 viscometer. The operating conditions were: cone angle, 2°; cone diameter, 4 cm; truncation, 54 μm; strain, 50 N/m² during 1 min; temperature, 40 °C.

3 Results and discussion

3.1 Synthesis of standard ASA

A pure sample of ASA from methyl oleate (ASA2S) was needed as standard for analyses in the syntheses of the experimental design. The ene-reaction provides two regioisomers of ASA (Fig. 1), since the addition reaction of maleic anhydride on oleic acid esters can occur either on carbon 9 or carbon 10 (atoms concerned by the double bond) of the unsaturated chain. Each regioisomer is formed as a mixture of *erythro* and *threo* diastereoisomers, because in the ene-reaction, two stereogenic centers are formed [20]. Once the ene-reaction was completed, the two diastereoisomers of the two regioisomers could not be separated by vacuum distillation, and the HPLC analysis of the distillate showed a single peak for the four isomers. Besides, this analysis showed that the distilled ASA sample was free from the initial reagents.

Distilled ASA was a clear yellow oily liquid (Gardner color: 6). FTIR spectra of ASA2S presented the representative bands of the expected groups. The major infrared bands arising from anhydride carbonyl stretching were located at 1785 cm⁻¹ and 1863 cm⁻¹. Also, a stretch vibration band typical of five-membered cyclic anhy-

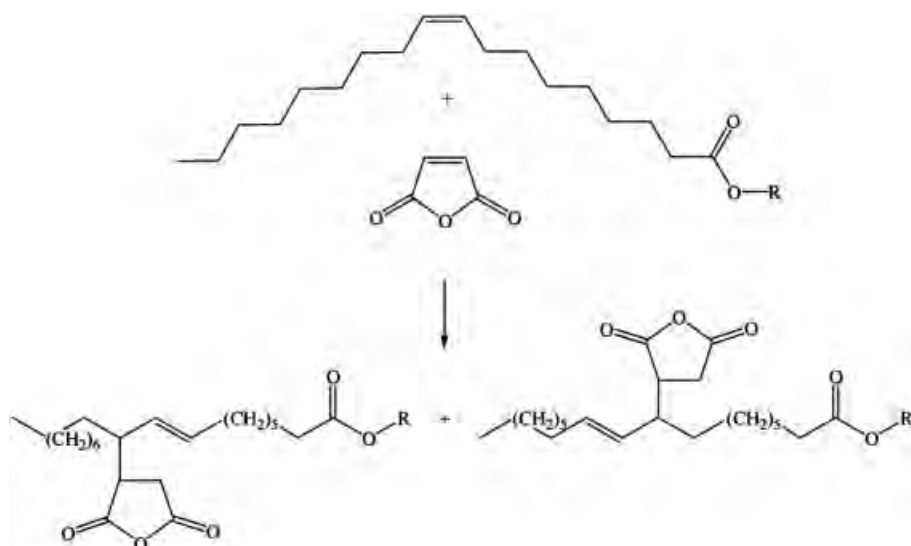


Fig. 1. ASA compounds (isomers) derived from methyl oleate ($R = \text{CH}_3$).

drides (succinic anhydride) was shown at 917 cm^{-1} . The carbonyl stretch band of the alkyl ester appeared at 1732 cm^{-1} . Finally, a stretch vibration band was presented at 970 cm^{-1} , typical of a *trans*-configured alkene double bond. This *trans* configuration confirmed that ASA was obtained by ene-reaction, as it is known that the ene-reaction of *cis* olefins yields only *trans*-configured adducts [20, 21].

^1H NMR spectra of the sample showed the expected characteristic peaks. ASA2S showed a peak at 5.5 ppm (m, 2H) belonging to the $-\text{CH}$ of the unsaturation. The peak at 3.6 ppm (s, 3H) belonged to the $-\text{CH}_3$ in the ester part. The peaks between 3.1 and 2.6 ppm (m, 3H) were assigned to $-\text{CH}$ belonging to the succinic link and to the anhydride moiety. The peaks at 2.2 ppm (t, 2H) and at 1.5 ppm (m, 2H) were identified as the $-\text{CH}_2$ in α and β positions, respectively, to the ester group and part of the unsaturated chain. The peak at 1.9 ppm (d, 2H) belonged to the $-\text{CH}_2$ in α position to the unsaturation. The peak at 1.2 ppm (m, 20H) represented the $-\text{CH}_2$ from the linear fatty chain. Finally, the peak at 0.80 ppm (t, 3H) can be assigned to the terminal $-\text{CH}_3$ moiety of the alkyl chain. This spectrum provided the confirmation of the chemical nature of our distilled sample.

3.2 Synthesis of ASA in solvent medium

The ene-reaction between SME and MA was characterized by the development of an autogene pressure in a closed vessel, because of high temperatures and the formation of gaseous products [11]. The reaction at 250°C with a MA/SME ratio of 1.2 showed a quick increase in pressure (from 0 to 7 bar in 0.5 h) corresponding to the

vapor pressure of xylene and maleic anhydride, followed by a slower increase (from 7 to 10.5 bar in 7.5 h) probably due to the formation gas by-products such as CO_2 [10].

The responses chosen for the experimental design were: the alkyl oleate conversion, the mass of ASA produced per kg of SME; and for the evaluation of side products: colorimetric and viscosimetric analysis. These answers recorded for the seven experiments (Tab. 1) of the Doehlert uniform network led to mathematical models. These equations allowed us to predict the values of the responses all over the experimental field. They consisted of second-order polynomials:

$$R = a_0 + a_1X_1 + a_2X_2 + a_{12}X_1X_2 + a_{11}X_1^2 + a_{22}X_2^2$$

where R represents the response, X_1 and X_2 the normalized independent variables (corresponding to the temperature and the ratio MA/SME, respectively), and a_0 , a_1 , a_2 , a_{12} , a_{11} and a_{22} the regression coefficients (Tab. 2), mathematically estimated from the experimental data in Tab. 1 and calculated by the formula:

$$\hat{a} = (X'X)^{-1}X'Y.$$

3.2.1 Conversion

Conversion was calculated as the ratio between the number of moles of methyl oleate that had reacted (evaluated by HPLC) and the initial number of moles of methyl oleate. Conversion represents the oleate consumption to yield not only ASA but also side products (Fig. 2).

Both temperature and molar ratio had an influence, as the values for a_1 and a_2 were significantly high. Besides, there was an appreciable interaction between these two

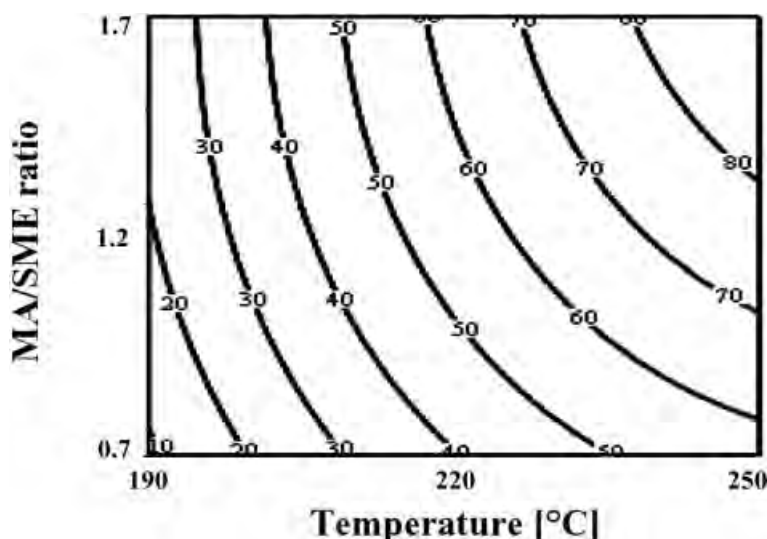


Fig. 2. Predicted contour levels for the conversion of methyl oleate as a function of temperature and MA/SME molar ratio.

Tab. 2. Regression coefficients (RC) of the model for ASA prepared from high oleic sunflower oil methyl esters (SME)[†].

RC	Responses			
	C	M	CI	V
a_0	54.9	0.596	45.9	0.404
a_1	28.6	0.242	4.1	-1.630
a_2	13.6	0.167	- 8.1	-0.627
a_{12}	5.3	0.070	- 0.23	1.120
a_{11}	-7.3	0.047	-31.2	2.040
a_{22}	-4.7	-0.028	-25.6	0.290

[†] C – conversion of methyl oleate; M – mass of ASA (kg) obtained from 1 kg methyl esters; CI – clarity index; V – viscosity.

Tab. 3. Comparison of conversion in methyl oleate for synthesis with and without xylene[†].

T [°C]	Conversion [%]		
	MA/SME	Solvent free [‡]	With xylene
190	0.7	35	8
220	1.2	75	55
250	1.5	88	87

[†] T – temperature; MA/SME – molar ratio maleic anhydride/methyl esters.

[‡] Data obtained from reference [10].

factors (a_{12}). Conversion increased with both temperature and molar ratio, to reach almost total conversion (90%) in the studied domain. However, an increase of temperature and molar ratio above the limits of the experimental domain would have resulted in enhanced polymerizations and retroene-reaction. The latter results in the cleavage of ASA into its initial reagents [11]. The starting degradation temperature of distilled ASA was evaluated by thermogravimetric analysis under air and defined as the temperature corresponding to a 5% weight loss. It corresponded to 260 °C. The ene-reaction should then be achieved at temperatures below 250 °C.

Compared to the results of solvent-free synthesis [11], our conversion was lower at the coldest temperatures (Tab. 3). The higher the temperatures and molar ratios, the shorter was the difference between the two synthesis methods. In solvent, higher energies were needed to achieve the same yields as obtained under solvent-free conditions. This contribution in heating should compensate the reagents dissolution effect in the medium that would have the tendency to slow down the kinetics of the reaction.

3.2.2 Yield of ASA

The yield of ASA was defined as the ratio between the mass of ASA obtained after removal of fatty esters and maleic anhydride and the initial mass of SME introduced (Fig. 3). It was evaluated by weighing the residue obtained after removal of the unreacted materials by one-step distillation. The aim of this study was to prevent heavy

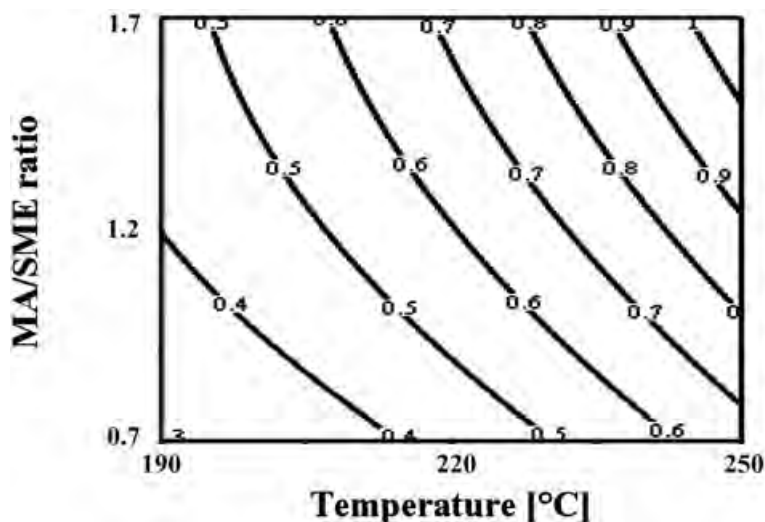


Fig. 3. Predicted contour levels for the distillation yield of ASA from oleic sunflower methyl esters as a function of temperature and MA/SME molar ratio.

purification steps by achieving the synthesis in xylene; that is why we assumed that these residues were essentially constituted by ASA, neglecting the amount of side products remaining. It can be observed that temperature and molar ratio both had an influence on the yield of ASA, as the values for a_1 and a_2 were high. Nevertheless, as a_1 was higher than a_2 , the higher influence of temperature was demonstrated. Besides, there was an appreciable interaction between the two factors (a_{12}). The available quantity of ASA increased with temperature and molar ratio. The contour plots of the mass indicated that the quantity of ASA passes through a maximum at 230–250 °C, depending on the molar ratio: the higher the molar ratio, the higher the maximum yield obtained. Optimal conditions would have allowed us to reach yields higher than 70%.

However, these samples were all dark brown liquids. This indicated the presence of residual side products in the sample. Use of xylene did not provide samples free from polymers under these conditions.

3.2.3 Colorimetric analysis

Direct quantification of side products was not possible. So we quantified them indirectly by colorimetric measurements. This study was carried out with the knowledge that ASA were yellow bright liquids and that the initial reagents were transparent or white, whereas the side products were dark brown solids or liquids. So, the more side products in the sample, the darker it was. For colorimetric measurements, the darkest samples provided the highest values of Gardner color, *i.e.* the lowest values of

clarity index. The Gardner color and clarity index were evaluated on residues containing ASA and side products. All these samples had a Gardner color of 18, assessing the polymers presence and revealing a lack of sensitivity in this scale. The curves obtained for the clarity index indicated that the sample's color also depended on temperature and molar ratio (Fig. 4). An optimal (lighter) color was observed for temperatures between 210 and 235 °C and for a MA/SME ratio between 0.8 and 1.35. Knowing that the clarity index for pure ASA (ASA2S) was 93, we concluded that the darkness of the samples was exclusively due to side products. Compared to ASA1S that went through the same distillation process, our samples were clearer. The ASA1S clarity index was 3, whereas the equivalent sample prepared with xylene presented a clarity index of 46. The use of xylene allowed the decrease in side products formation. Actually, the presence of xylene helped maleic anhydride solubilization. This might have prevented the development of local zones with high concentrations of anhydride. The presence of such zones would have favored the anhydride polymerization or anhydride-SME copolymerization. Besides, at the end of the reaction, xylene could have facilitated the polymers precipitation and the purification steps.

3.2.4 Viscosity

The viscosimetric study of the samples confirmed the previous tendencies (Fig. 5). Since side products were waxy solids, sample viscosity was increased with their presence. Knowing that distilled ASA viscosity was evaluated to 0.2 Pa s, optimal viscosities, corresponding to minimal presence of side products, were obtained at

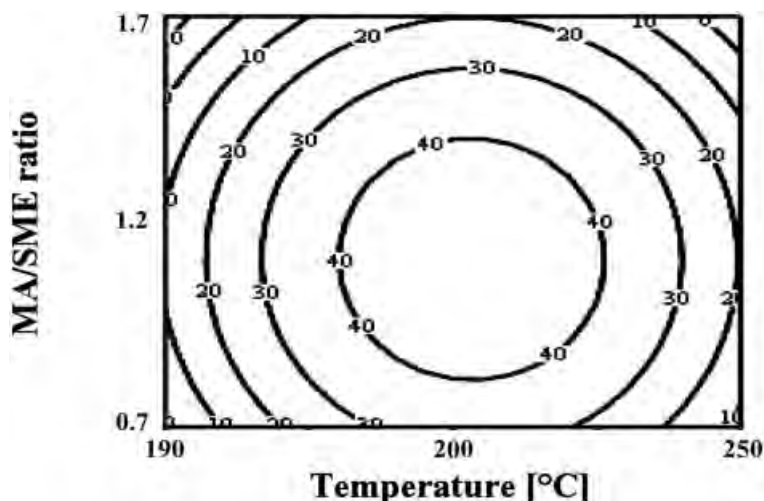


Fig. 4. Predicted contour levels for the clarity index of ASA from oleic sunflower methyl esters as a function of temperature and MA/SME molar ratio.

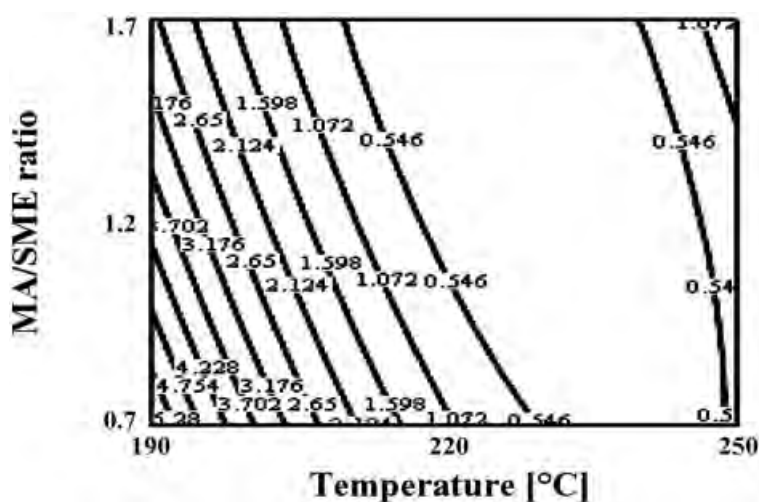


Fig. 5. Predicted contour levels for the viscosity of ASA from oleic sunflower methyl esters as a function of temperature and MA/SME molar ratio.

temperatures between 220 and 240 °C and ratios higher than 0.9. However, the sample viscosities were less than 0.4 Pa s, with or without the use of xylene.

3.2.5 Optimal experimental conditions

The experimental design using xylene allowed the determination of optimal (best compromise) experimental conditions: highest yield in ASA and minimized side products. These were a temperature of 220–235 °C and a MA/SME molar ratio of 1.2–1.35. They would provide a medium containing almost 55% ASA, with a clarity index of 40. These conditions were confirmed by the achievement of an experiment at 230 °C, with a MA/SME molar ratio of 1.3. This medium contained 67% of ASA with a

clarity index of 36, results in agreement with the values calculated with the experimental design equations (68.5% for yield in ASA and 38 for clarity index).

3.3 Reaction time influence

The optimized conditions did not provide a medium exempt of side products, even if the use of xylene decreased their formation. As the preceding results were evaluated for an 8-h reaction time, xylene could have reduced the ene-reaction kinetics. For this reason, we studied the influence of the reaction time at 220 °C with a MA/SME ratio of 1.2 (center of the experimental design) in a 50% xylene medium (Tab. 4).

Tab. 4. Reaction time influence at 220 °C with a MA/SME ratio of 1.2 in a 50% xylene medium[†].

Reaction time [h]	Responses		
	C	M	CI
6	45	0.60	60
8	55	0.60	46
12	60	0.71	23
16	68	0.83	6

[†] C – conversion of methyl ester; M – mass of ASA obtained from 1 kg methyl esters; CI – clarity index.

The longer the reaction time, the higher were the conversion and the distilled mass of ASA. Extending reaction time from 8 h to 16 h only allowed an increase from 55 to 68% in conversion, whereas it led to a 40% increase in distillation yield. Nevertheless, we supposed that longer reaction times provided media that were highly concentrated in ASA, but also in side products. Clarity index measurement confirmed this hypothesis, as it was noticed that it decreased with increasing reaction time. Knowing that the clarity index is equivalent to 90–100 before the synthesis, we noticed a linear decrease versus reaction time. Side product formation would be proportional to the time of exposure to high temperatures.

Achieving the synthesis in less than 8 h resulted in media with low ASA concentration. Increasing reaction times to 12 h or more provided higher yields in ASA, but also more side products. A reaction time of 8–10 h was a good compromise.

4 Conclusion

Alkenyl succinic anhydrides (ASA) have been prepared by ene-reaction of high oleic sunflower oil methyl esters with maleic anhydride in a 50% xylene medium. Thereby, we intended to facilitate the purification process. Besides, we discussed the solvent influence on the ene-reaction. Response surface methodology (RSM) was used to investigate the influence of two factors: reaction temperature and molar ratio between maleic anhydride (MA) and methyl esters (SME). For industrial application requiring minimal side products (clarity index >40), the optimal synthesis conditions were: temperature between 220 and 235 °C and molar ratio of 1.2–1.35 for an 8-h reaction (yield ≈55%). Such conditions did not provide a medium free of side products, although xylene decreased their formation by helping contact between reagents. Higher temperatures were needed to reach yields equal to the one obtained without xylene. Supplementary heating

compensated the reagent dissolution effect that slows down the kinetics of the ene-reaction. The observed influence of reaction time at 220 °C with a MA/SME ratio of 1.2 in a 50% xylene medium allowed us to conclude that 8–10 h of reaction time provided a good compromise between ASA yield and side product formation.

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