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# Preparation of Alkenyl Succinic Anhydrides from Vegetable Oil FAME

Joaquín Quesada<sup>a,\*</sup>, Marie Morard<sup>b</sup>, Carlos Vaca-García<sup>b</sup>, and Elisabeth Borredon<sup>b</sup>

<sup>a</sup>Departamento de Ingeniería Química, Facultad de Química, Universidad de Murcia, Campus de Espinardo, 30071 Murcia, Spain, and <sup>b</sup>Laboratoire de Chimie Agro-Industrielle—UMR 1010, INRA/INP—Ecole Nationale Supérieure des Ingénieurs en Arts Chimiques et Technologiques de Toulouse, 31077 Toulouse Cedex 4, France

**ABSTRACT:** Sunflower oil and oleic motif-enriched sunflower oil methyl esters were used to prepare alkenyl succinic anhydrides. A classic batch reactor was selected to carry out the synthesis. The range in which the temperature, reaction time, and molar ratio between the number of moles of maleic anhydride and the equivalent number of double bonds present in the unsaturated vegetable oil methyl esters (the most influential factors in the process) varied was determined in a preliminary study. A second-order Doehlert uniform network design was used to investigate the influence of the temperature and molar ratio for all the methyl esters on the yield of alkenyl succinic anhydride from methyl oleate, the conversion of methyl oleate, the formation of side reaction products, the Gardner color of the product, and viscosity. The optimal reaction conditions for obtaining the maximal yield (around 95%) of alkenyl succinic anhydride from methyl oleate were 235°C, a molar ratio of 1.5, and a reaction lasting 8 h. However, the products synthesized under these conditions showed high viscosity (215 cP), a very dark color (18+ Gardner color), and a high content of undesirable side products (4%), which hindered their direct industrial use. The increase in the product viscosity was probably due to the formation of side reaction products. A molar ratio of less than 1.5 led to a less viscous product, although with a lower alkenyl succinic anhydride content.

**KEY WORDS:** Alkenyl succinic anhydride preparation, Doehlert uniform network experimental design, Gardner color, HPLC and GLC analysis, oleic motif-enriched sunflower oil methyl ester, side reaction products, sunflower oil methyl ester, viscosity.

Almost all alkenyl succinic anhydrides (ASA) are reaction products of olefinically unsaturated hydrocarbons (olefins) and maleic anhydride (MA). They are produced by the ene-reaction (1) [or Diels–Alder reaction when conjugated double bonds exist (2)], an indirect substituting addition from a compound with an electron-poor double bond (enophil) to a compound that contains an allylic hydrogen (ene). In this work the enophil component was MA and the ene-component was a C<sub>18</sub> unsaturated FAME.

The olefins used in the preparation of ASA are generally derived from petroleum hydrocarbons by a cracking process. They are of widely varying lengths, ranging from propylene to polymers with hundreds of carbon atoms. The structure and molar mass of the olefin used depend on the intended end use of the ASA. In this way, ASA prepared from C<sub>10</sub>–C<sub>35</sub> olefins

are used in the hydrophobic sizing of paper and as epoxy resin setting agents, corrosion inhibitors, leather-finishing agents, and additives in fuels, lubricants, and paints, whereas those prepared from lighter-weight olefins (<C<sub>10</sub>) are used as thickeners in foods, juices, and puddings (3–5).

Vegetable oils or their derivatives are an attractive renewable resource, rich in C<sub>18</sub> unsaturated FA chains with oleic (18:1, one double bond), linoleic (18:2, two double bonds), and linolenic (18:3, three double bonds) motifs, which can also be used in the preparation of ASA as an alternative to using petrochemical olefins. Interest in the use of these unsaturated vegetable oils for ASA preparation was expressed in the 1990s (6) because of environmental concerns and the quest for sustainable development. ASA molecules from vegetal sources are obtained basically from unsaturated FA and FAME (7), and are used in varnishes, paints, and as corrosion inhibitors (8,9). Maleinated oils (reaction products between vegetable oils and MA) are used as anhydride-functional curing agents for the manufacture of thermosetting unsaturated polyester resins (4). ASA also can be used in the field of wood protection (10) as a substitute for the widely used and highly polluting chromated copper arsenate (CCA) wood preservative treatment, thus reducing the environmental impact of treated wood.

Of all the unsaturated molecules of a vegetable origin that can be used to produce ASA on an industrial scale, FAME are one of the best options because of their availability (there is an active market for this product principally for use as biodiesel) and because the ASA synthesized from them are less viscous than those obtained from TG, thus facilitating their industrial application.

Our aim was to prepare ASA from the methyl esters obtained from sunflower oil (SO) and oleic motif-enriched sunflower oil (OMSO) (chosen by varietal selection). The necessary reactions were carried out under conditions that respect the environment (no solvents) and with no added catalysts or inhibitors of secondary reactions that might make production more expensive.

## EXPERIMENTAL PROCEDURES

**Materials.** Methyl esters of SO and OMSO were supplied by Novance (Compiègne, France), and MA by Sigma-Aldrich (St. Quentin Fallavier, France). These compounds were used as received. The composition of SO and OMSO methyl esters (% weight) was the following: methyl oleate, 24.0 and 82.6; methyl linoleate, 56.0 and 8.4; methyl palmitate, 5.0 and 4.0; methyl stearate, 5.0 and 2.0; FFA, 4.0 and 3.0; and nonanalyzed compounds, 6.0 and 0.0, respectively. ASA from

\*To whom correspondence should be addressed at Departamento de Ingeniería Química, Facultad de Química, Universidad de Murcia, Campus de Espinardo, Apartado de Correos 4021, 30071 Murcia, Spain.  
E-mail: quesamed@um.es

methyl oleate was synthesized from OMSO methyl ester (at 230°C for 8 h and a MA/OMSO methyl ester molar ratio of 1), purified by preparative column chromatography using C<sub>18</sub>-bonded silica gel as sorbent and acetonitrile as eluent, and used for quantitative HPLC analysis.

*Preliminary experiments: Principal reaction variables and their range of variation.* With the aim of selecting the main variables that influence the development of the reaction, a bibliographical search revealed that the most influential factors in ASA production, the formation of side products, and viscosity are the temperature and duration of the reaction, and the molar ratio between MA and the ene-compound. The range of variation of these variables depends on the type of ene-compound being used; the temperature, ranging from 160 to 280°C; the time, from 1 to 17 h; and the MA/ene-compound molar ratio, between 0.5 and 2.

A series of preliminary experiments was carried out using OMSO methyl ester in order to determine the type of reactor (pressure batch or open batch) to be used and the most suitable values for the process variables based on those mentioned in the literature. The first parameter investigated was the temperature (160, 170, 180, 190, 200, 210, 220, and 230°C) with the reaction time fixed at 8 h and with a MA/vegetable oil methyl ester molar ratio (MA/VOME) of 1. The second parameter studied was the reaction time (between 1 and 17 h, with 1-h increments) using the best temperature obtained and the same MA/VOME ratio as above. Finally, the MA/VOME was varied between 1 and 2 (1, 1.25, 1.50, 1.75, and 2) for the best temperature and time selected in the first two series of experiments. MA/VOME corresponds to the ratio between the number of moles of MA and the equivalent number of double bonds present in methyl oleate and linoleate, which were the main unsaturated esters present.

*Experimental design.* The effect of temperature and MA/VOME ratio on ASA production and the formation of side reaction products was investigated using an experimental design based on a two-factor Doehlert uniform network. This experimental design was applied to the SO and OMSO methyl esters. The reaction time was fixed at a value obtained from the preliminary experiments, in which the type of reactor was also selected. This design meets the general requirements that every parameter in a polynomial model should be estimated from a reduced number of observations and that observations should be spread as evenly as possible over the experimental region of interest. With two independent variables, seven distinct experiments were sufficient to fit a second-order polynomial model. The central combination for the experimental design was a temperature of 220°C and a MA/VOME of 1, and was repeated twice to estimate the experimental error. These two variables were varied over the ranges obtained in the preliminary phase (160–280°C and 0.5–1.5, respectively). The results were subjected to multiple linear regression in the Microsoft Excel 97 spreadsheet program.

*Synthesis in a pressure batch reactor.* OMSO methyl ester (100 g) together with a molar equivalent amount of MA were placed in a 300-mL Parr pressure reactor, through which a stream of N<sub>2</sub> was passed for a few minutes to obtain an inert atmosphere. The mixture was heated to the desired tempera-

ture (190, 210, 230, and 270°C) and maintained there for 8 h while being continuously stirred (8 s<sup>-1</sup>). A series of experiments was carried out in an open batch reactor (see below) with the same reaction conditions for comparison purposes.

*Synthesis in an open batch reactor.* One hundred grams of each of the different VOME was continuously stirred (8 s<sup>-1</sup>) under a slight stream of N<sub>2</sub> in a three-necked flask reactor equipped with a reflux condenser at 65°C. After immersing the reactor in an oil bath and when its content had reached the desired reaction temperature, a given amount of MA, depending on the experiment, was added. The mixture was maintained at that temperature throughout the experiment. The values for temperature, time, and MA/VOME are indicated in the preliminary experiment section.

After reaction, one aliquot was taken from each of the reactors and analyzed by HPLC and for side reaction products, Gardner color, and viscosity.

*HPLC.* Before injection into the chromatograph, samples were taken from the reactor and dissolved in an acetonitrile solution containing methyl margarate as internal standard. The liquid chromatograph was a Thermo Separation Product P2000 Spectro System coupled to two detectors connected in series, a Milton Roy 3100 UV detector (UVD) and an ELSD. A wavelength of 245 nm was used for UVD analysis. The apparatus was equipped with a C<sub>18</sub> reversed-phase SGE Wakosil column (Melbourne, Australia; 150 × 4.6 mm, 5 μm particle size). Maleic anhydride was analyzed with the UVD, and the rest of compounds with the ELSD. The analysis was carried out in isocratic conditions using acetonitrile as the mobile phase. ASA from methyl oleate always appears as two isomers (11), whereas that from methyl linoleate is composed of at least 12 isomers. The isomers from individual methyl esters have never been separated (7). In our study, the isomers from methyl oleate were present under only one peak and those from methyl linoleate under two overlapping peaks, which were analyzed by MS, in the HPLC conditions used.

*GLC.* Methyl palmitate and methyl oleate have the same retention time in HPLC. These two compounds were separated in a 5890 Hewlett-Packard gas chromatograph fitted with an FID and an SGE OV-101 capillary column (30 m × 0.25 mm i.d.). Helium was used as carrier gas (1.5 bar). The temperature programming was 15 min at 230°C. The injector and detector temperatures were 250°C. Since the quantity of methyl palmitate (saturated and inert for the reaction) was supposed to be the same before and after the reaction, the corresponding value was subtracted for each analysis.

The gas generated during ASA preparation in the pressure batch reactor was analyzed by a Hewlett-Packard 5890 gas chromatograph coupled to a Hewlett-Packard 5971 mass spectrometer (Melbourne, Australia). The apparatus was equipped with a BPX-5 capillary column (SGE). Helium was used as carrier gas at a constant flow rate of 1.5 mL/min. The temperature programming was as follows: 5 min at 40°C, 3°C/min to 200°C, and 5 min at 200°C. The injector temperature was 220°C and that of the detector 240°C.

*Side reaction products.* Side reaction products were partially determined by a gravimetric method. For this, 135 mL

of xylene was added to 7.5 g of sample, some of the side reaction products being precipitated in the solvent. The mixture was stirred for 30 min, after which it was filtered to recover the solid. This was then washed with 50 mL of xylene, dried, and weighed. The side reaction products were calculated as the ratio between the weight of the solid recovered and the total weight (7.5 g), expressed as a percentage.

**Gardner color.** Gardner color was determined by a colorimetric method based on a comparison between the color of the sample and that of a standard from a Gardner color scale. The Gardner color number corresponds to the number of a standard color closest to that of the sample, a value of 1 corresponding to pale yellow liquids, and 18 to dark brown liquids. The apparatus used was a Minolta Mi 508 spectrophotometer equipped with Spectra Magic software.

**Viscosity.** The viscosity of the samples was measured at 23°C in a Brookfield rheoviscometer. In most cases, a no. 4 rotor and a rotation rate of 1.67 s<sup>-1</sup> were used. The samples were placed in a 250-mL Erlenmeyer flask to prevent border effects.

## RESULTS AND DISCUSSION

**Election of a reactor.** To assess the two types of reactors used (pressure batch and open batch), we studied the behavior of the main reagents (methyl oleate and MA) and the ASA production. The conversion (calculated as the ratio between the amount of reagent reacted and its initial amount in the reactor, expressed as percentage by weight) of methyl oleate and MA is shown in Table 1, in which it is observed that the two reagents behaved similarly in both reactors. Above 230°C the conversion of the reagents increased by only 5%, possibly because part of the ASA generated broke down into its initial reagents (retro-ene-reaction) (3).

As can also be seen in Table 1, the yield of ASA (calculated as the ratio between the number of moles of ASA generated from methyl oleate and the number of moles of methyl oleate initially present in the reactor, expressed as mole percentage) from methyl oleate was higher in the pressure reactor at temperatures lower than 230°C. An autogenous pressure (pressure difference between the pressure at the end of the reaction when the reactor was at ambient temperature and the pressure at the beginning, i.e., atmospheric pressure) was observed to be generated while operating in the pressure batch reactor, which reached the following values: 0, 0.4, 1.1, and 1.8 MPa at 190, 210, 230, and 270°C, respectively. Therefore, the autogenerated pressure seems to favor the synthesis of ASA at temperatures lower than 230°C. However, between 230 and 270°C the yield was practically the same in both reactors and ASA production decreased, the retro-ene-reaction being more important than the ene-reaction. Moreover, above 230°C the conversion of methyl oleate (around 75%) and MA (around 85%) was higher than the yield of ASA (around 65%), indicating that methyl oleate and MA were probably consumed during side reactions such as the polymerization of MA, the copolymerization of methyl oleate and MA, the oligomerization of methyl oleate and the further reaction of ASA with MA. In addition to these undesired reactions, thermal decomposition of

**TABLE 1**  
Conversion of the Reagents and Yield of ASA<sup>a</sup> from Methyl Oleate in Pressure and Open Batch Reactors

Temperature (°C)	Pressure reactor	Open reactor
Conversion of methyl oleate (wt%)		
190	34.6	39.6
210	53.1	54.9
230	70.3	74.5
270	75.5	80.5
Conversion of maleic anhydride (wt%)		
190	34.0	25.7
210	58.8	51.9
230	79.2	77.7
270	84.3	89.5
Yield of ASA from methyl oleate (molar%)		
190	42.9	25.4
210	64.7	49.4
230	71.4	72.0
270	63.2	59.0

<sup>a</sup>ASA, alkenyl succinic anhydrides.

methyl oleate, MA, and ASA may have occurred. Hence, the application of moderately high temperatures (250–270°C) hinders the formation of ASA molecules.

The occurrence of thermal decomposition reactions was confirmed by measuring the autogenous pressure in the reactor: the higher the autogenerated pressure, the greater the thermal degradation of the compounds. GC–MS analysis of the gas generated during the reaction showed that it basically was composed of CO<sub>2</sub> (the main degradation product) and, to a much lesser extent, of alkanes such as butane, pentane, and heptane. The presence of CO<sub>2</sub> was also proved by the formation of a white BaCO<sub>3</sub> precipitate after bubbling the gas through a Ba(OH)<sub>2</sub> solution. CO<sub>2</sub> probably arose mainly from the degradation of MA, which was more prone to disappear than methyl esters during the reaction, while alkanes were probably generated from the thermal cracking of methyl ester chains. Although we have not been able to carry out a similar analysis for the open batch reactor, the same degradation reactions probably took place as a result of the high temperature used.

The combination of all these results led us to a compromise between the pressure and open batch reactors: the semiclosed batch reactor. This reactor is the same as the open batch, the only exception being that the reflux condenser is closed by means of a balloon, which ensures a static inert atmosphere of N<sub>2</sub> and completely prevents MA being carried away by the stream of N<sub>2</sub>. In addition, the use of this balloon means it is possible to maintain a practically constant low pressure (around 0.18 MPa) in the reactor during the experiments, which, as we have seen, seems to favor the synthesis reaction. Hence, all the experiments described in the experimental design were carried out using the semiclosed batch reactor.

**Determination of the range of variation of the main process variables.** (i) *Effect of temperature.* As shown in Figure 1A, the conversion of methyl oleate and MA, and the yield of ASA from methyl oleate steadily increased with the temperature.

Methyl linoleate reacted poorly below 190°C but completely at around 200°C. The reaction proceeding quickly in a very narrow range of temperature. Above 200°C methyl linoleate reacted more rapidly than methyl oleate (12). The fact that the conversion of MA was greater than that of methyl oleate above 210°C could be due to the methyl linoleate (8.4% of OMSO methyl ester) reacting completely with MA. ASA production seemed to reach a plateau at 230°C.

The temperature chosen for observing the effect of the reaction time and the MA/OMSO molar ratio was 230°C. However, because there was no apparent maximum to ASA production, we extended the range of temperature to be used in the experimental design up to 280°C.

(ii) *Effect of the reaction time.* The results for the conversion of reagents and for the yield of ASA from methyl oleate are presented in Figure 1B. As above, we see that methyl oleate reacted more slowly than methyl linoleate, the latter being completely and rapidly consumed after 1–2 h. Methyl oleate and MA conversion, on the one hand, and ASA production on the other reached plateaus of around 75 and 65%, respectively, after 8 h, suggesting that a chemical equilibrium was reached. The fact that at equilibrium the conversion of the main reagents was higher than the yield of ASA could be due to the polymerization and/or thermal cracking of MA and methyl oleate. However, the remaining MA was completely consumed after 15 h of treatment. A reaction time of 8 h was chosen to study the effect of the molar ratio on the behavior of the reaction.

(iii) *Effect of the molar ratio between MA and OMSO.* This molar ratio was calculated by assuming that methyl oleate consumes one molecule of MA whereas methyl linoleate may consume two. As observed in Figure 1C, the conversion of methyl oleate can be improved by up to 95% by increasing the amount of MA introduced into the reactor. Methyl linoleate reacted readily even for an MA/OMSO molar ratio of 1. The yield of ASA from methyl oleate increased with the MA/OMSO molar ratio, reaching a value of around 90% for a molar ratio of 2.

Based on the results of this preliminary study, we fixed an optimal reaction time of 8 h. Next, we investigated the synergy between the temperature and the MA/VOME according to the experimental design for that optimal reaction time. The temperature was varied in the range 160–280°C, the value of 280°C being selected according to the literature (13). A range of 0.5–1.5 was fixed for MA/VOME because a higher value than 1.5 would involve considerable excess of MA in the medium, which would have to be removed by distillation, thus increasing the cost of the ASA production process.

*Experimental design.* Application of the Doehlert uniform network led to mathematical models capable of predicting the yield of ASA from methyl oleate, the conversion of methyl oleate, the side reaction products, the Gardner color, and the viscosity in the experimental domain. When the central operating conditions (220°C and a molar ratio of 1) were used in three experiments, the results obtained in each experiment for the responses studied differed by less than 5% of the average values in the case of ASA preparation from OMSO methyl ester, with the only exception of viscosity, which differed by less than 10%.

The proposed experimental design was used to obtain the results given in Table 2. Experimental data were modeled using the second-order polynomial  $Z = a_0 + a_1 X_1 + a_2 X_2 + a_{12} X_1 X_2 + a_{11} X_1^2 + a_{22} X_2^2$ , where  $Z$  represents the response studied,  $X_1$  and  $X_2$  the normalized independent variables (corresponding to the reaction temperature and MA/VOME, respectively), and  $a_1, a_2, a_{12}, a_{11},$  and  $a_{22}$  the regression coefficients, which must be estimated from the experimental data in Table 2. The estimated regression coefficients together with the  $r^2$  values and Snedecor's  $F$ -values for the fitted models from OMSO methyl ester are shown in Table 3. The excessively high  $F$  value calculated for the side reaction products is due to the very low mean square of the pure error obtained (0.003) in relation to that of the lack of fit (5.0416).

(i) *ASA preparation from OMSO methyl ester.* In the coefficients calculated for the yield, it can be observed that the most

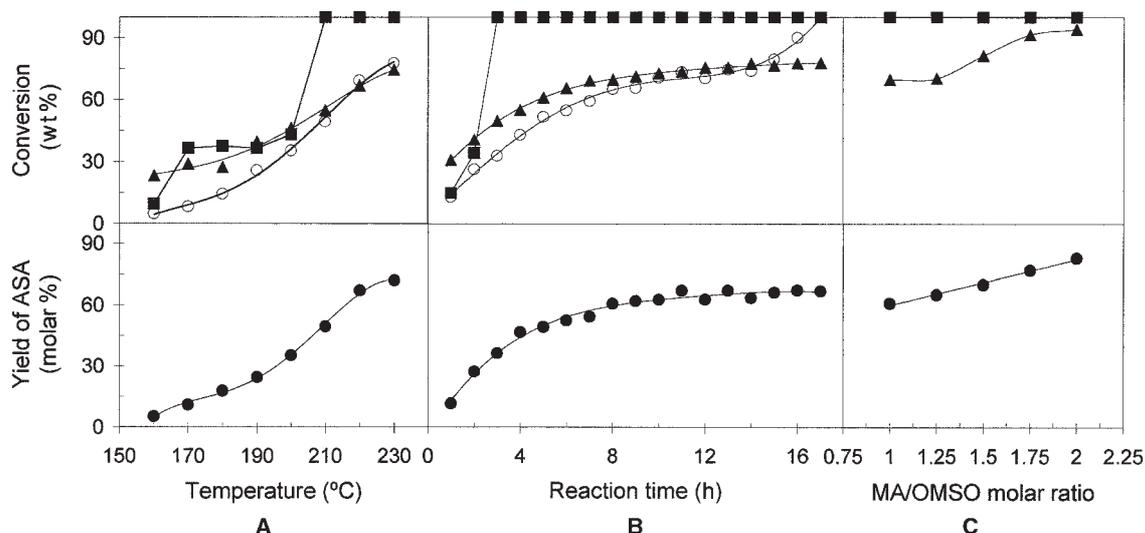


FIG. 1. Evolution of the conversion of various reagents and the yield of alkenyl succinic anhydrides (ASA) from methyl oleate as a function of temperature, reaction time, and maleic anhydride/oleic motif-enriched sunflower oil methyl ester (MA/OMSO) molar ratio (■: methyl linoleate, ▲: methyl oleate, ○: maleic anhydride, ●: ASA from methyl oleate).

influential factor was the molar ratio ( $a_2 > a_1$ ), there being an appreciable interaction between temperature and molar ratio ( $a_{12}$ ). The contour plots for the yield of ASA obtained from methyl oleate are shown in Figure 2A, in which it can be seen that the yield passes through a maximum at temperatures of 220–240°C, depending on the molar ratio: the higher the molar ratio, the greater the maximum yield obtained. These results were similar to those obtained in the preliminary study, the ASA production decreasing at high temperatures as a result of the retro-ene and ASA degradation and/or polymerization reactions. The optimal yield (>90%) was reached at 235°C and a molar ratio higher than 1.5. In the case of the conversion of methyl oleate (Fig. 2B), the two variables have similar ( $a_1 \approx a_2$ ) and important influences, and there is no interaction between them ( $a_{12} \approx 0$ ). A comparison of Figures 2A and 2B indicates that methyl oleate was also consumed by side reactions, which were favored at high temperatures. Thus, 80% of methyl oleate was transformed at 280°C and a molar ratio of 1, while the yield of ASA from methyl oleate was only of 45%.

The coefficient values for the side reaction products show that their formation was, once again, more sensitive to molar ratio changes than to temperature, the quantity of these undesirable products increasing with both and being in all cases lower than 5% (Fig. 3A). In this case, there was a very significant interaction between temperature and molar ratio. Regarding the viscosity of the medium, this parameter behaved similarly to the side reaction products (Fig. 3B), indicating that these were probably responsible for the increase in viscosity. As regards the Gardner color of the reaction medium, the most important main effect was the reaction temperature, there being no interaction among variables. The fact that the Gardner color was maximal for a molar ratio near 1 and tem-

**TABLE 2**  
Experimental Design Conditions and Results for ASA Preparation from OMSO and SO Methyl Esters<sup>a</sup>

T (°C)	MA/VOME	Y (molar%)	Co (wt%)	SRP (wt%)	GC	V (cP)
OMSO methyl ester						
160	1	9.1	23.8	1.0	8	9
190	0.5	18.0	18.4	0.1	5	21
190	1.5	62.2	61.5	0.2	8	22
220	1	71.9	69.8	2.4	19	80
250	0.5	34.1	46.4	0.2	18	112
250	1.5	100.0	98.5	5.2	19	233
280	1	35.2	79.8	0.6	19	102
220	1	72.1	66.9	2.4	18	85
220	1	74.8	68.5	2.5	17	70
SO methyl ester						
160	1	7.2	7.5	0.2	7	40
190	0.5	24.4	18.2	0.7	14	50
190	1.5	68.4	66.7	4.4	19	430
220	1	39.8	46.8	1.9	17	2210
250	0.5	32.8	51.2	0.1	15	110
250	1.5	100.0	97.4	1.7	19	8260
280	1	44.1	74.0	0.7	17	2720

<sup>a</sup>T = temperature; MA/VOME = molar ratio between maleic anhydride and vegetable oil methyl ester; Y = yield of ASA from methyl oleate; Co = conversion of methyl oleate; SRP = side reaction products; GC = Gardner color; V = viscosity; SO = sunflower oil; OMSO = oleic motif-enriched sunflower oil; for other abbreviation see Table 1.

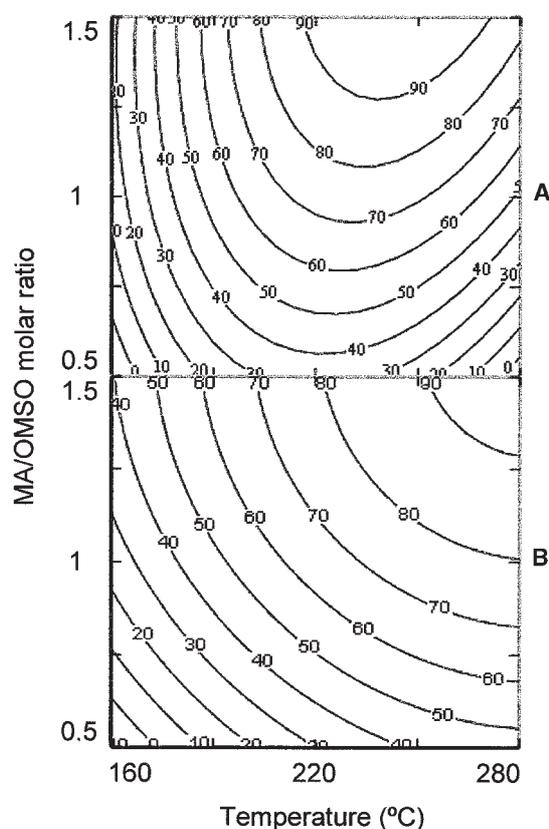
**TABLE 3**  
Regression Coefficients of the Model,  $r^2$  Values, and Snedecor's F-Values for ASA Preparation from OMSO Methyl Ester<sup>a</sup>

	Y	Co	SRP	GC	V
$a_0$	73.00	64.48	2.33	16.67	78.33
$a_1$	17.38	27.79	0.67	7.50	51.33
$a_2$	29.36	24.65	1.46	1.44	87.18
$a_{11}$	15.99	-0.69	2.77	-0.58	69.28
$a_{12}$	-42.50	-12.70	-1.58	-3.17	-22.83
$a_{22}$	-9.73	-10.08	-0.68	-4.83	32.50
$r^2$	0.9817	0.9967	0.7764	0.8867	0.7996
F	49.100	6.398	1512.5	28.167	124.803

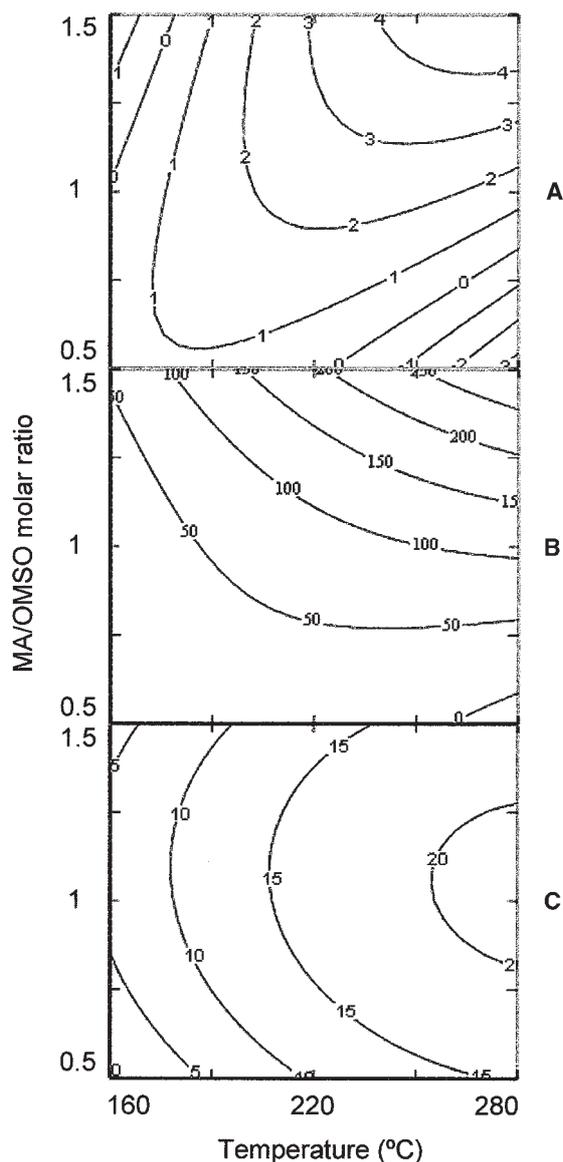
<sup>a</sup>For abbreviations see Tables 1 and 2.

peratures higher than 250°C (Fig. 3C), whereas the quantity of side reaction products increased with the amount of MA introduced into the reactor, indicated that the side products were not the only compounds that contributed to the color of the medium. The Gardner color and viscosity were dependent not only on polymer formation but also on the decomposition of heat-sensitive molecules of a vegetal origin. In fact, the thermogravimetric analysis of OMSO methyl ester showed that 3% was degraded at 220°C and 10% at 280°C. The same occurred with the ASA from methyl oleate.

Therefore, to obtain maximal ASA yield (around 95%) in the experimental domain from OMSO methyl ester, it was nec-



**FIG. 2.** Predicted contour levels for (A) the yield (molar%) of ASA from methyl oleate and (B) the conversion (wt%) of methyl oleate as a function of temperature and MA/OMSO molar ratio. For abbreviations see Figure 1.



**FIG. 3.** Predicted contour levels for (A) the formation of side products (wt%), (B) the viscosity (cP), and (C) the Gardner color as a function of temperature and MA/OMSO molar ratio. For abbreviations see Figure 1.

essary for synthesis to be carried out at 235°C for 8 h and with a MA/OMSO molar ratio of 1.5. However, the main disadvantage in the application of these conditions was the quality of the final product, which was viscous (215 cP) and dark (15 Gardner color) and presented a high content of undesirable side products (4%). Hence, if a low content of side reaction products (<1.5%) together with a low level of viscosity (<50 cP) are considered desirable characteristics for ASA produced, a molar ratio lower than 0.8 and a temperature of 220–230°C should be used. These conditions lead to a clearer product (<15 Gardner color) with an acceptable ASA content (between 35 and 60% yield), which can be directly used on an industrial scale.

(ii) *ASA preparation from SO methyl ester.* The yield of ASA from methyl oleate, the conversion of methyl oleate, the side reaction products, the Gardner color, and the viscosity

were similar to those observed with the OMSO methyl ester. Optimal ASA production (95% yield) in the experimental domain was also reached in the same reaction conditions as above, i.e., at 235°C for 8 h of reaction and a molar ratio of 1.5. However, in this case the Gardner color and viscosity were in general higher, perhaps because methyl linoleate (present in much greater quantities than in OMSO methyl ester) reacted with one or two molecules of MA, leading to the possible generation of colored conjugated double bonds (11) and larger ASA molecules. Moreover, the presence of two double bonds in methyl linoleate would favor the formation of side products.

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