

Synthesis and characterization of ASA samples

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Abstract

Alkenyl succinic anhydride (ASA) are widely used as paper sizing agents providing more resistance and hydrophobic character to the paper, overcoming the inherent wettability of cellulose by avoiding that a polar liquid spreads on his surface and penetration in the paper web. The main goals of this work was to do a chemical characterization of comercial samples of ASA by gas chromatography-mass spectrometry (GC-MS) and optimization of the reaction conditions on the synthesis of ASA, as an initial contribution to a better understanding of the performance on the papermaking systems. Results obtained by GC-MS, allowed to see the differences of chemical composition between the commercial samples of ASA. Analysis of the GC-MS data showed that octadecenyl succinic anhydride (18-ASA) is the main component of the commercial samples of ASA. Alkenyl succinic anhydrides are prepared by ene-reaction between maleic anhydride and an alkene with an allylic hydrogen and after optimization of the reaction conditions, it was possible to obtain a product with a rather high yield and low side products content at a temperature of 210 °C, reaction time between 6 and 8 hours, molar ratio alkene : maleic anhydride between 1.0 and 1.5 and 2.5% weight of hydroquinone calculated on maleic anhydride. In these optimized synthesis conditions it was obtained rather pure products with a yield between 74.2% and 77.6% for the 16-ASA synthesis and 74.0% and 78.4% for the 18-ASA synthesis.

Keywords: Alkenyl succinic anhydride, ene reaction, GC-MS.

1 Introduction

Alkenyl succinic anhydrides (ASA) are widely used in different areas, including additives for lubricants [1], intermediates in organic chemistry [2], corrosion inhibitors [3], wood preservation [4] and paper sizing agents. The use of alkenyl succinic anhydride as an internal paper sizing agent has grown rapidly since its introduction on the early 1960s by Wurzburg and Mazzarella. [5]. They are obtained by a ene reaction between unsaturated hydrocarbons (olefins) that plays the role of ene compound and maleic

anhydride (enophile). The ene reaction is defined as a six-electron pericyclic process between an alkene bearing an allylic hydrogen and an electron deficient multiple bond to form two σ -bonds with migration of the π -bond. Due to a high activation energy the ene reaction requires a Lewis acid [6-7], metallic catalysts [8] and/or high temperatures (higher than 200 °C). The reaction speed increases strongly as a function of the temperature, and thus it is preferable to use a relatively high reaction temperature in order for the product to form at a satisfactory reaction speed. At a high temperature the

probability of the formation of side products like enophile polymerization, alkene and enophile oxidation, alkene oligomerization, copolymerization between enophile and alkene and thermal decomposition of ASA (retroene reaction) ^[9]. The side products are usually black solids and are not suitable for most uses of ASA ^[10], and this products are responsible for the decreases in the yield and quality of the product. To reduce the side reactions occurring in the synthesis, different additives are used with the purpose of obtaining a product more pure, higher yield, less color and more monomeric product. Since the ASA have a high molecular weight and in practice it is

almost impossible to purify by distillation, the use of additives is highly recommended. The additives may work through various mechanisms, for example through the catalysis of the principal reaction or the inhibition of the side reactions, but with respect to many of the additives used in the synthesis of ASA, the way in which the additive works is not known with full certainty. The additives used in the preparation of ASA include aromatic compounds with sulfur and/or nitrogen atoms, phenolic antioxidants and metallic compounds ^[11]. The ene reactions between α -olefins and maleic anhydride result in the synthesis of isomers cis and trans (Figure 1).

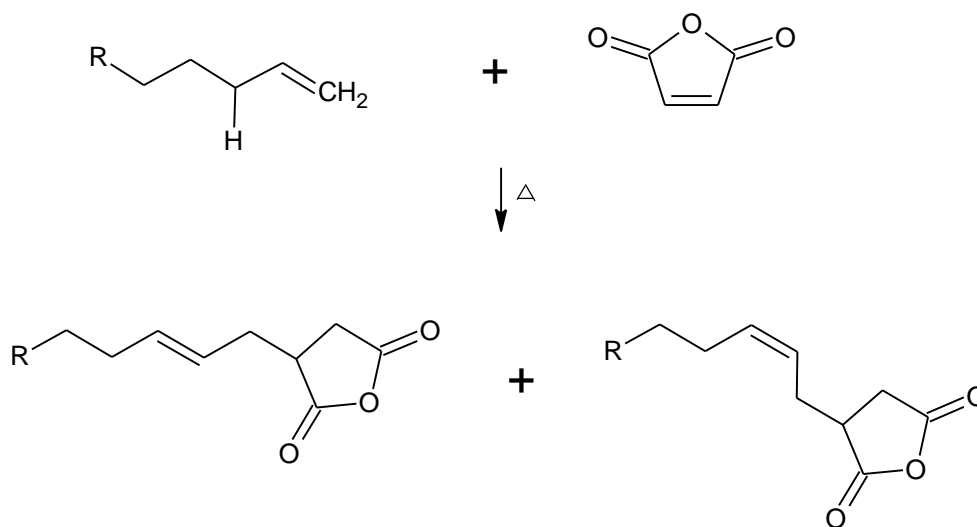


Figure 1. Ene reaction between α -olefin and maleic anhydride.

The ene reaction with internal olefins and maleic anhydride reveals regioselectivity, corresponding to the transfer of the allylic hydrogen of each side of the double bond (Figure 2). For thermal ene reactions, the primary hydrogen is abstracted more readily than a secondary and much faster than a tertiary one, irrespective of the

thermodynamic stability of the internal olefin product.

2 Materials and methods

2.1 Materials

All solvents were used as received, without further purification. Maleic anhydride was purchased from Merck (99%), 1-hexadecene (92%) and

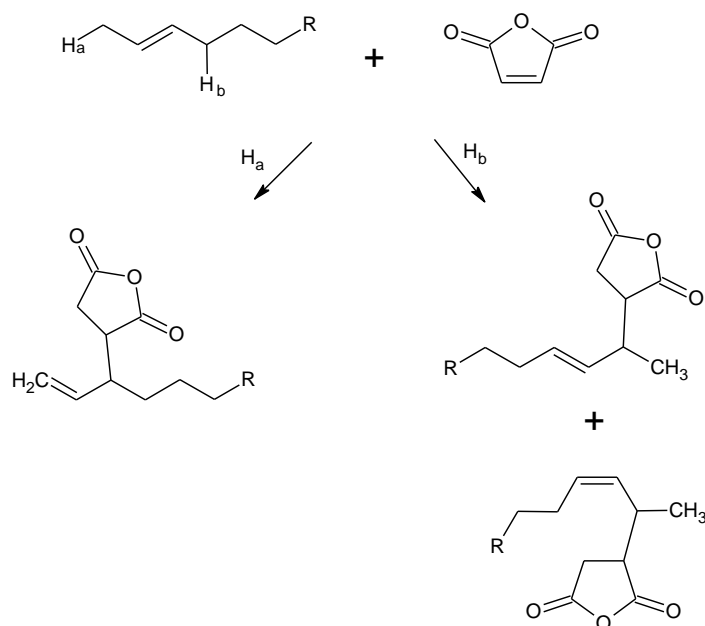


Figure 2. Ene reaction between an internal olefin and maleic anhydride.

1-octadecene (94%) were purchased from Aldrich, phenothiazine was acquired from Fluka (> 98%), hydroquinone was purchased from Sigma-Aldrich (99%), xylene was acquired from Panreac (98.5%) and triphenyl phosphite was purchased from BDH Laboratory Reagents.

2.1.1 Commercial samples of ASA

The commercial samples of ASA used in this work were given by Portucel and identified from A to F.

2.2 Synthesis of ASA

It was studied the influence on ASA synthesis of temperature ranging from 180 °C to 230 °C, reaction time between 1 hour and 24 hours, olefin : maleic anhydride ratio from 0.5 to 2.0 and were studied the effects of additives between 0.5 and 5.0% weight/weight of the amount of maleic anhydride used. In a three-neck flask equipped with a thermometer, reflux condenser and with

a nitrogen input, was added the olefin (1-hexadecene or 1-octadecene) and a given amount of maleic anhydride depending on the experiment. The mixture was stirred and heated at a variable temperature during a predetermined amount of time. At the end of the experiment, the sample remained at room temperature until the temperature inside the flask reached 60 °C. The medium was vacuum-distilled to remove residual maleic anhydride and olefin. In reactions with additives, they were added after stirring the olefin and maleic anhydride. After distillation all samples were analyzed by gas chromatography-mass spectrometry (GC-MS).

2.3 Thin layer chromatography

The reactions were followed with thin layer chromatography with the use of aluminium foils in a silica gel matrix with fluorescent indicator 254nm purchased from Fluka. For the elution

were used various mixtures of solvents, like petroleum ether, toluene, dichloromethane and ethyl acetate., toluene, dichloromethane and ethyl acetate. The aluminium foils were revealed under ultraviolet light with wavelength of 254nm. For compounds that did not appear under ultraviolet light, it was used a iodine chamber, and the compounds appear as a brown spot.

2.4 Side reaction products

Side reaction products were partially determined by a gravimetric method. For this, 135 mL of xylene were added to 7.5 g of sample, and some of the side reactions products precipitated in the solvent. The mixture was stirred for 30 minutes, after which it was filtered to recover the solid. After drying, the solids were weighed and the side reaction products were calculated as the ratio between the weight of the solid recovered and the total weight of the sample.

2.5 Gas chromatography-mass spectrometry (GC-MS)

The samples were diluted in ethyl acetate in a 1:20 ratio and analyzed by a Finnigan Trace GC Ultra gas chromatograph coupled to a Finnigan Trace DSQ mass spectrometer. The apparatus was equipped with a TR-5 MS from Thermo Fischer Scientific (30 m x 0.25 mm). Helium was used as carrier gas at a constant flow rate of 1 mL/min. The temperature programming was as follows: 10 °C/min from 90 °C to 310 °C and 5 min at 310 °C. The injector temperature was 250 °C.

3 Results and discussion

3.1 Distillation of commercial samples of ASA

All 6 commercial samples of ASA were submitted to distillation under vacuum with a pressure between 0.05 and 0.1 mm Hg. The objective was the isolation of the different compounds of the samples, but analysis of the chromatograms (Figure 3) showed that all the fractions obtained from the distillation under vacuum contained all the fractions so the separation is not effective. During the distillation of the different samples it was observed the formation of a gas inside the system. This gas is carbon dioxide that was formed from the decarboxylation of the maleic anhydride. This process proves that during the distillation under vacuum occurs the degradation of the ASA samples.

3.2 Characterization of the commercial samples of ASA by GC-MS

The 6 commercial samples of ASA were analyzed by GC-MS and it was calculated the relative percentage of each peak present in the chromatograms. This was achieved by peak integration obtaining the area of each individual peak and in relation to the total area it was possible to obtain the relative percentage of every peak in the commercial samples. Due to some limitations it was not possible to determine the exact chemical structure from the mass spectrums obtained. The results are shown in the Table 1.

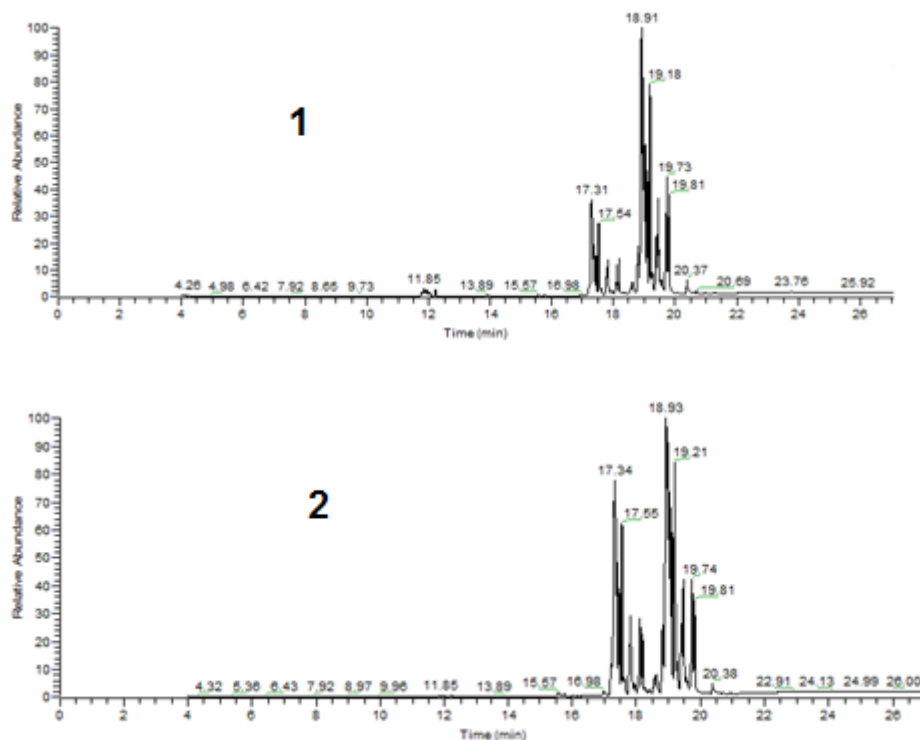


Figure 3. Chromatograms of commercial sample E (1) and second fraction of commercial sample E (2) obtained by distillation under vacuum.

Table 1. Relative percentage of the compounds in the commercial samples of ASA.

Sample	Hexadecene	Octadecene	16-ASA	18-ASA	20-ASA
A	0.00	0.68	17.86	81.46	0.00
B	0.00	0.59	3.75	95.66	0.00
C	0.11	1.76	19.79	78.34	0.00
D	0.00	1.65	1.54	96.81	0.00
E	0.00	1.13	18.62	79.80	0.45
F	0.09	1.56	19.00	79.35	0.00

3.3 Synthesis of ASA

In the literature ^[12] it is mentioned that low yield and formation of side products are influenced by the temperature, reaction time, additives and olefin : maleic anhydride molar ratio.

3.3.1 Temperature

The influence of the temperature was studied with a olefin : maleic anhydride molar ratio of 1.0 during 6 hours and no additives. The temperature used was between 180 °C and 220 °C. After each

experiment it was determined the yield and side products (Table 2 and 3).

Table 2. Synthesis of 16-ASA at a variable temperature.

T (°C)	Yield (%)	Side Products (%)
180	38.4	0.0
190	44.1	0.0
200	58.6	0.1
210	71.5	0.3
220	76.1	0.8

Table 3. Synthesis of 18-ASA at a variable temperature.

T (°C)	Yield (%)	Side products (%)
180	40.1	0.0
190	46.9	0.0
200	56.1	0.1
210	72.3	0.3
220	74.8	0.8

To a temperature higher than 210 °C, it was observed a considerable increase in the formation of side products for both 16-ASA synthesis and 18-ASA synthesis. Despite obtaining a higher yield at 220 °C, a good compromise between yield and side products is a temperature at 210 °C.

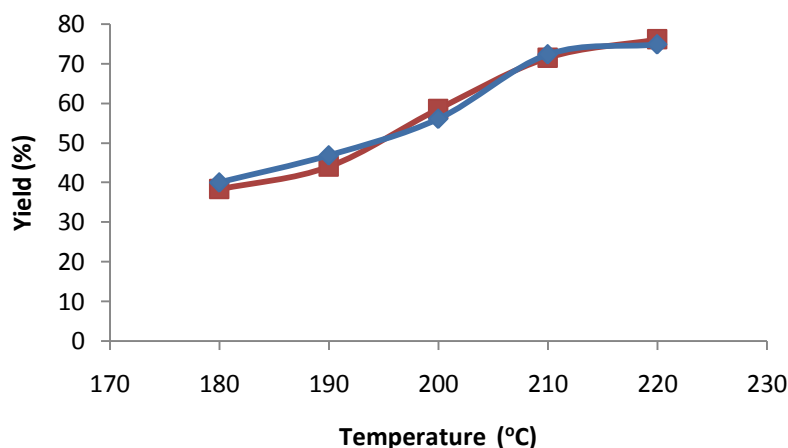


Figure 4. Yield of 16-ASA and 18-ASA synthesis with a variable temperature.

3.3.2 Reaction time

The influence of the reaction time was studied with a olefin : maleic anhydride molar ratio of 1.0 with a temperature at 210 °C and no additives.. After each experiment it was determined the yield and side products (Table 4 and 5).

Table 4. Synthesis of 16-ASA at a variable reaction time.

Time (h)	Yield (%)	Side products (%)
2	34.0	0.0
4	60.3	0.0
6	71.5	0.3
8	73.9	0.5
12	75.4	1.2
16	76.1	1.9
24	77.0	3.1

Table 5. Synthesis of 18-ASA at a variable reaction time.

Time (h)	Yield (%)	Side products (%)
2	37.8	0.0
4	58.1	0.0
6	72.3	0.3
8	75.0	0.5
12	75.8	1.5
16	76.6	2.0
24	77.2	3.5

The results show an increase in the yield for a higher reaction time but also more side products. Since the increase of the yield is not significant to a reaction time higher than 8 hours for both 16-ASA and 18-ASA synthesis, a good compromise for the reaction time is 6 to 8 hours.

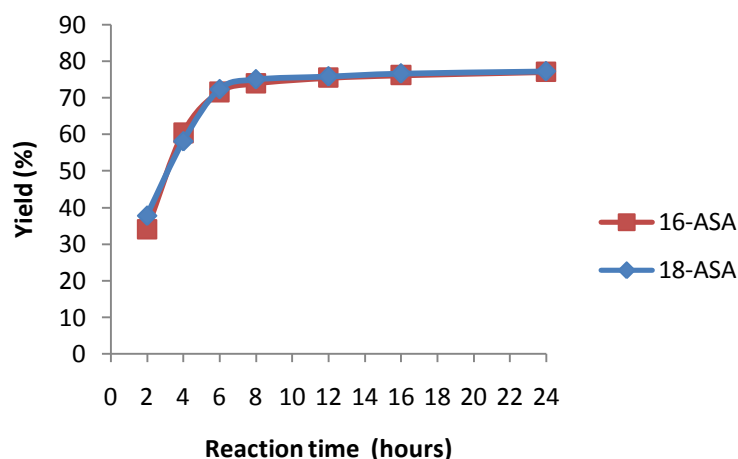


Figure 5. Yield of 16-ASA and 18-ASA synthesis with a variable reaction time.

3.3.3 Olefin : maleic anhydride molar ratio

The influence of the olefin : maleic anhydride molar ratio was studied with with a temperature at 210 °C during 6 hours and no additives. After each experiment it was determined the yield and side products (Table 6 and 7).

Table 6. Synthesis of 16-ASA with a variable olefin : maleic anhydride ratio.

HD/MA Ratio	Yield (%)	Side products (%)
0.5	75.2	0.8
1.0	71.5	0.3
1.5	68.6	0.2
2.0	65.0	0.3

HD – 1-hexadecene; MA – Maleic anhydride.

Table 7. Synthesis of 18-ASA with a variable olefin : maleic anhydride ratio.

OD/AM Ratio	Yield (%)	Side products (%)
0.5	74.4	1.1
1.0	72.3	0.3
1.5	69.8	0.1
2.0	64.2	0.2

OD – 1-octadecene; MA – Maleic anhydride.

This results show that the yield of the reaction is higher when the olefin : maleic anhydride molar ratio is lower despite the fact that a lower molar ratio also results in more side products in the product. Using an excess of maleic anhydride leads to the presence of this reagent in the final product, which is a problem in a industrial environment because of the difficulty to extract the maleic anhydride which will lead to an increase in the production costs. For all of the above reasons, the better compromise for the olefin : maleic anhydride molar ratio between 1.0 and 1.5.

3.3.4 Additives

In this study it was used phenothiazine, hydroquinone, xylene and triphenyl phosphate as additives in the synthesis of ASA. The influence of the additives were studied with a temperature at 210 °C during 6 hours and a olefin : maleic anhydride molar ratio of 1.0. After each experiment it was determined the yield and side products.

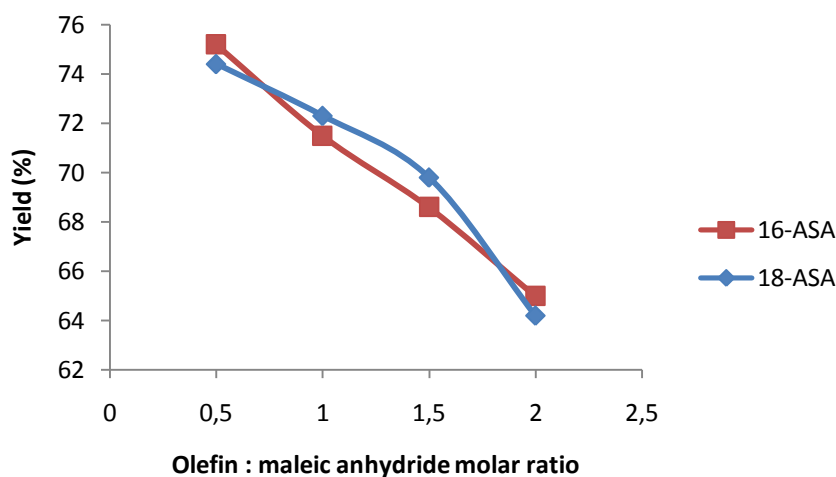


Figure 6. Yield of 16-ASA and 18-ASA synthesis with a variable olefin : maleic anhydride molar ratio.

In the synthesis with hydroquinone the yield and side products (Table 8 and 9) shows an increase of the yield and less side products formation to a higher quantity of hydroquinone used.

Table 8. Synthesis of 16-ASA with hydroquinone.

%wt HQ/MA	Yield (%)	Side products (%)
0.0	71.5	0.3
0.5	71.2	0.1
1.0	73.8	0.0
2.5	76.2	0.0
5.0	77.7	0.0

HQ – hydroquinone; MA – Maleic anhydride.

Table 9. Synthesis of 18-ASA with hydroquinone.

%wt HQ/AM	Yield (%)	Side products (%)
0.0	72.3	0.3
0.5	73.0	0.0
1.0	74.1	0.0
2.5	77.8	0.0
5.0	78.0	0.0

HQ – hydroquinone; MA – Maleic anhydride.

This results show that the hydroquinone have a positive impact in the synthesis of ASA. Since the increase in yield is not significant to a weight/weight percentage higher than 2.5, this is the recommended quantity of hydroquinone to be used in the synthesis of ASA.

In both synthesis with phenothiazine and triphenyl phosphite it was observed that the products obtained were darker and because of this fact, it is not suitable as a paper sizing agent. It was also observed that both additives did not have an impact in the yield of the synthesis.

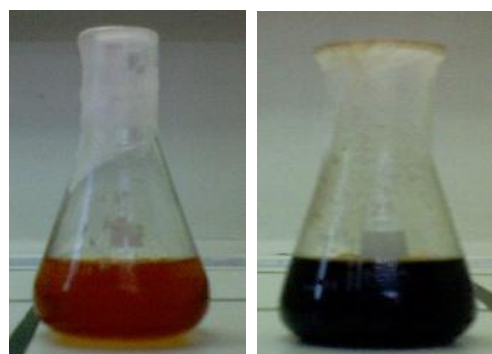


Figure 7. Products of synthesis with hydroquinone (left) and phenothiazine (right).

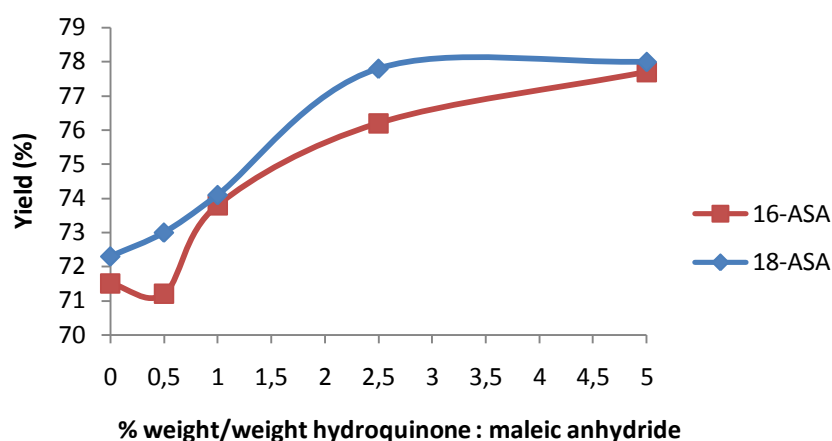


Figure 8. Yield of 16-ASA and 18-ASA synthesis in the presence of hydroquinone.

The reactions with xylene were unsuccessful because of the lower temperature of the reaction. It was not possible to achieve a higher temperature than 160 °C.

3.3.5 Optimized synthesis

The optimized synthesis were realized with a temperature at 210 °C during 7 to 8 hours, with a molar ratio of olefin : maleic anhydride between 1.0 and 1.5 and with 2.5% of hydroquinone weight/weight. After each experiment it was determined the yield and side products (Table 10 and 11).

Table 10. Optimized synthesis of 16-ASA.

Ratio HD/MA	Time(h)	Yield (%)	Side products (%)
1.0	6	76.2	0.0
1.0	8	77.6	0.0
1.5	6	74.2	0.0
1.5	8	76.5	0.0

HD – 1-hexadecene; MA – Maleic anhydride.

Table 11. Optimized synthesis of 18-ASA.

Ratio OD/MA	Time(h)	Yield (%)	Side products (%)
1.0	6	77.8	0.0
1.0	8	79.5	0.1
1.5	6	74.0	0.0
1.5	8	78.4	0.0

OD – 1-octadecene; MA – Maleic anhydride.

This results shows that with the optimized conditions it is possible to obtain a product without side products and a good yield. It was also observed that when the reaction lasts 2 more hours that do not have a great impact in the yield to justify the difference in reaction time. Analysis by GC-MS showed that the products obtained with the optimized synthesis and after being submitted to a distillation under vacuum were pure and correspond to 16-ASA and 18-ASA with the double bond in the β -carbon of the hydrocarbon chain.

4 Conclusion

It was possible to determine the relative percentage of the compounds present in the commercial samples of ASA by GC-MS. The results indicate that all commercial samples have 18-ASA as the main compound with a relative percentage between 78.34% and 96.81%. Only one sample revealed traces of 20-ASA and all of them have residual olefins in their composition with a relative percentage lower than 2%.

After optimization it was possible to conclude that the optimized conditions for the synthesis of ASA are: temperature at 210 °C, reaction time of 6-8 hours, olefin : maleic anhydride molar ratio of 1.0-1.5 and 2.5% of weight of hydroquinone. In these conditions are produced 16-ASA and 18-ASA with minor content of side products and with a yield between 74.2% and 77.6% for the 16-ASA synthesis and 74.0% and 78.4% for the 18-ASA synthesis.

Acknowledgements

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