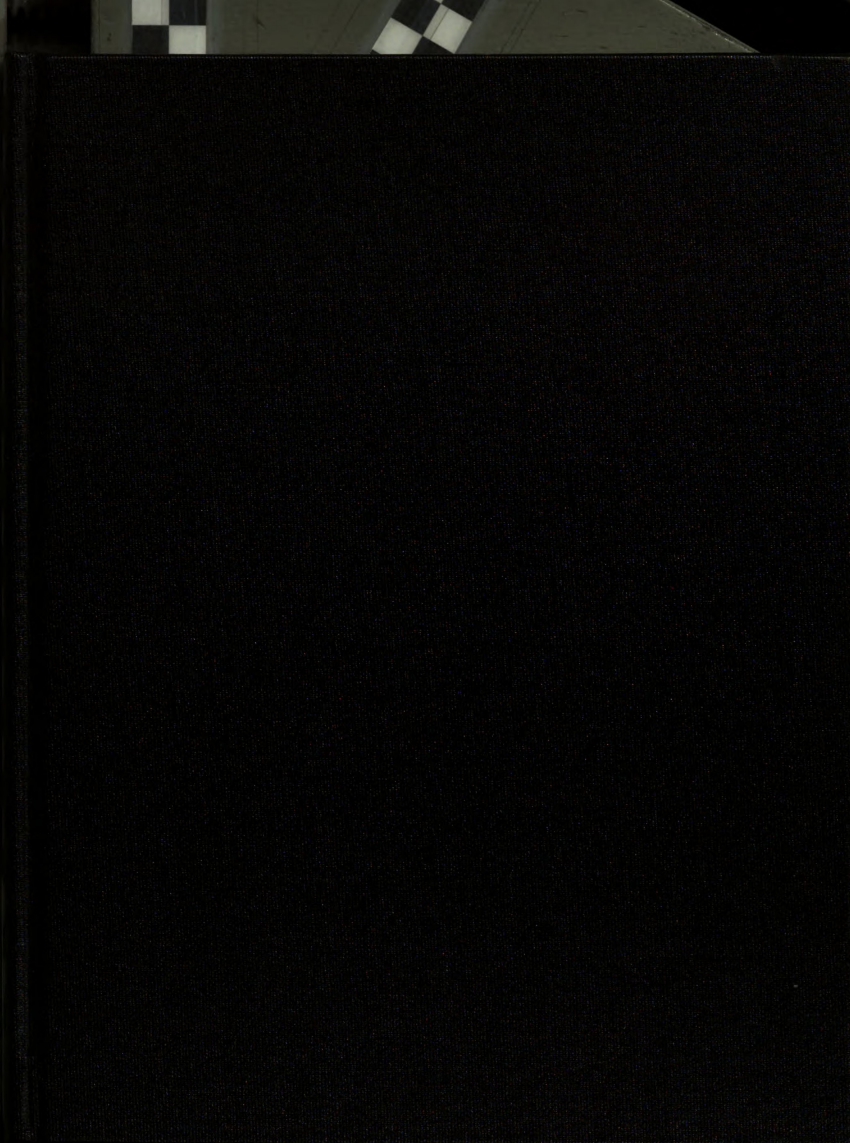




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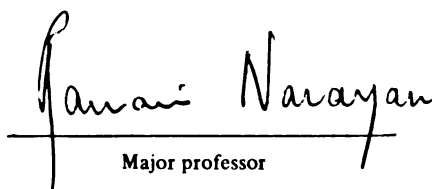
DESIGN AND ECONOMIC ANALYSIS OF A MALEATED
SOYBEAN OIL AND ESTER PRODUCTION FACILITY

presented by

KENNETH RANDALL SEYBOLD

has been accepted towards fulfillment
of the requirements for

M.S. degree in CHEMICAL ENGINEERING


Major professor

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**DESIGN AND ECONOMIC ANALYSIS OF A
MALEATED SOYBEAN OIL AND ESTER PRODUCTION FACILITY**

by

Kenneth Randall Seybold

A THESIS

**Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of**

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1997

ABSTRACT

DESIGN AND ECONOMIC ANALYSIS OF A MALEATED SOYBEAN OIL AND ESTER PRODUCTION FACILITY

By

Kenneth Randall Seybold

Many industrial applications for soybean oil have been developed, such as, drying oils for paints, epoxidized soybean oil for plastics, and stabilizers for synthetic resins. Unfortunately, in the past 30 years the market for drying oils has decreased and the use of epoxidized soybean oil has plateaued in the industry. Concurrently, environmental and life cycle considerations have excited interest in annually renewable feedstocks. The significance of the study was to investigate the reaction rate, processability, and characteristics of maleated soy products. Knowledge gained from laboratory experiments were applied to the design of a manufacturing process to produce maleated soy products. A maleated soy ester was produced in the laboratory and was found to be a good plasticizer for PVC. Two process designs were studied, continuous and batch, as possible routes to produce maleated soybean oil and the esterification of the oil. The continuous process was found to be superior to the batch by two methods of analysis, return on initial investment and internal rate of return.

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To my parents, sister, brother, and wife.

ACKNOWLEDGMENTS

I wish to thank my advisor, Dr. Ramani Narayan, for providing his uniquely styled guidance and support. I would also like to express my appreciation to everyone at the MBI International, BioPlastics Inc., and the Department of Chemical Engineering for providing an enjoyable working and learning environment.

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CHAPTER 1

INTRODUCTION

The United States has excess capacity for the production of food and feed crops, so new industrial uses for agricultural products are being sought. Production of industrial raw materials from agricultural feedstocks serves to extend our diminishing petroleum reserves, remedy trade imbalances, protect the environment, and expand market opportunities for rural economies.

Soybean seed is grown and processed using standard equipment to produce a wide variety of protein, carbohydrates, and oils. The current production of soybeans in the world is nearly 100 million metric tons per year with over half of this amount being raised in the United States¹. With this large amount of soybeans and soy products coming from this country a large opportunity exists to formulate new value-added products that can be used in the ever expanding plastic industry, two such potential areas are plasticizers and coatings.

1.1 Plasticizers

Plasticizers are organic compounds added to plastics to improve workability during fabrication and to extend or modify the natural properties of the original resin. Plasticizers are used in molding and shaping plastic resins into consumer end products,

such as bottles and plastic bags, easier. Plasticizers also improve flexibility and other desired properties in the finished product.

One of the most important uses of plasticizers is molding poly vinyl chloride (PVC). PVC resin is very brittle and cannot be molded without plasticizers. By the year 2000, PVC will be the leader with an annual volume of 17×10^9 metric tons according to the Stanford Research Institute². The widespread use of PVC arises from its high chemical resistance and a high solubility for additives to give a large number of reproducible compounds. Thus, with the properly chosen additives, a PVC formulation can have an enhancement in strength and workability.

For many years, bis (2-ethylhexyl) phthalate (DOP) was the accepted industry standard for a general-purpose plasticizer for PVC and a benchmark for comparisons of other plasticizers. DOP has an all around performance, eg, compatibility with the resin, and efficiency in flexibilizing that is so good, that it alone accounts for nearly one-fourth of all plasticizer production. Although DOP is a “work-horse” plasticizer for PVC, there are problems with its use. Phthalate plasticizers are moderately toxic (listed on the EPA section 313 Toxic Release Inventory or as a HAP), volatility can be a concern at higher temperatures, migration of DOP in the polymer matrix, and extraction under solvent and soapy water conditions.

Of the 1.6 billion pounds of plasticizers produced in the United States in 1990, only 230 million pounds, or 15 percent, were derived from plant matter. Most of these plant-based materials are from vegetable oil feedstocks (Table 1). Epoxidized soybean oil (ESO) accounted for 100 million pounds, while acrylic esters, which are derived from a variety of plant sources (including wood extractives and coconut oil), accounted for 74 million pounds. Over a dozen companies produce ESO. ESO is used as a secondary plasticizer to DOP as the primary plasticizer, only 2.5% ESO usage as opposed to 31% DOP usage.

Table 1: U.S. production of plasticizers from vegetable oil and petrochemical feedstocks, 1990

Category	Production	Million Pounds
Epoxidized soybean oil		100
Epoxidized linseed oil		6
Other epoxidized esters		14
Oleic acid esters		12
Stearic acid esters		8
Palmitic acid esters		6
Sebacic acid esters		6
Isopropylmyristate		4
Other acrylic acid esters		74
Total		230
Petrochemical-based plasticizers		1,324
Total Plasticizers	1,554	

Epoxidized soybean oil has many strong qualities but also many problems. As a plasticizer, ESO tends to lose compatibility due to photo-oxidation, high viscosity at ambient temperatures, and a relatively high cost. ESO is also difficult to produce because

of the use of preformed-peracetic acid techniques which employs an explosive hazard, acids, bases and solvents. These chemicals and techniques tend to increase both manufacturing and equipment costs. The high costs of the ESO process can be seen from the current market price of 1.1-1.3 dollars per pound. Therefore, an opportunity exists to increase plasticizer marketshare given DOP's problems if the properties of ESO or a new derivative can meet the requirements.

1.2 Coating materials from Soybean oil

In the U.S., thermoset coatings represent an 8 billion pound per year market. Alkyds, amino resins, epoxies, acrylics, and polyurethane systems are the most widely used coating materials. Thermoset coatings are almost entirely produced from petroleum feedstocks.

Drying oils, from plant matter, are the basis for corrosion resistant coatings, traffic paints, wire enamels, can linings, marine finishes, container and tube coatings, metal decorating, and aluminum paints. The drying oils provide: superior impact resistance; flexibility; gloss; chemical resistance; adhesion; flow and leveling.

The use of soybean oil in oil-based paints has steadily been declining in the past 30 years due to the rise of latex and other water-based systems. Since 1960 the use of paints

and varnishes have increased from 200 to 300 million pounds per year while the percent of oil based products have fallen from 50 to 15 percent of the market.

With the loss of oil based applications, there is a need to investigate the functionalized soybean oil applications with emphasis on the large market of plastics.

CHAPTER 2

LITERATURE BACKGROUND

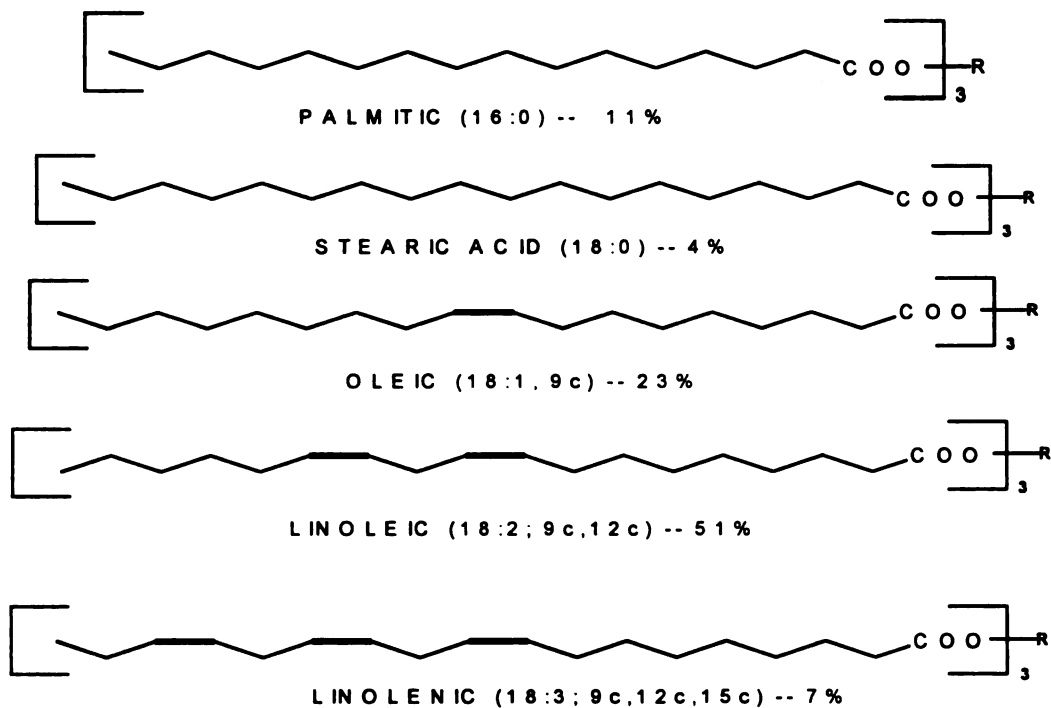
Soybean oil is a triglyceride of fatty acids. Soybean oil has the following composition and structures:

Table 2: Soybean Oil Composition

<u>Carboxylic acid^a</u>	<u>Chemical Acronym*</u>	<u>Wt% Soybean Oil^a</u>
<i>Fatty Acid</i>		
	<i>Saturated fatty acid</i>	
Palmitic acid	16:0	10.7
Stearic acid	18:0	3.87
	<i>Unsaturated fatty acid</i>	
Oleic acid	18:1	22.8
Linoleic acid	18:2	50.8
Linolenic acid	18:3	6.76

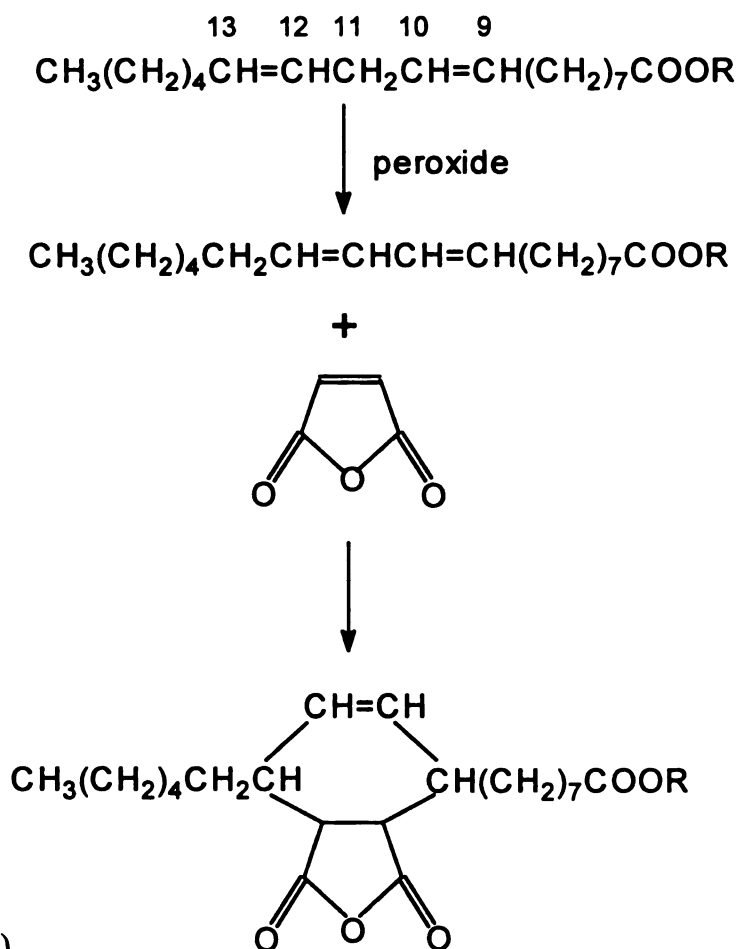
a -- Ref 1

*Chain length, number of double bonds, and functional groups, if any



COMPOSITION OF SOYBEAN OIL

Unfortunately, soybean oil contains mostly non-conjugated double bonds. Due to the prevalence of non-conjugated double bonds, a catalyst will be needed to facilitate the reaction. There is a great deal of literature discussing the addition of maleic anhydride to soybean oil using a peroxide catalyst. Root³ describes the use of benzoyl peroxide catalyst in a maleation reaction. Under these conditions the reaction takes place at a much lower temperature of 110 C as compared to 160-190 C without catalyst. Root postulates that soybean oil in the presence of a catalyst, like a peroxide, results in the conjugation of the non-conjugated double bonds. The conjugated double bonds can then undergo a 1-4 Diels-Alder type of reaction.

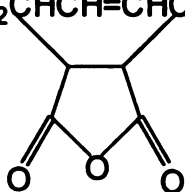
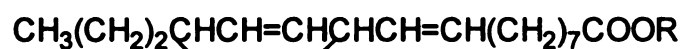


(Root et. Al.)

The resultant product is more viscous than that prepared at higher temperatures. The experimental work in this thesis was based on the peroxide catalyzed reactions discussed by Root³.

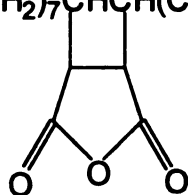
There is considerable study on the nature of the maleic anhydride addition reaction. Conjugated oil systems were the focus of Morrel and Samuels⁴ who showed that it was a diene addition. The study was of conjugated oil fatty acids from china wood and oiticica oils. The reaction product is a typical Diels-Alder 1-4 adduct:

(1)



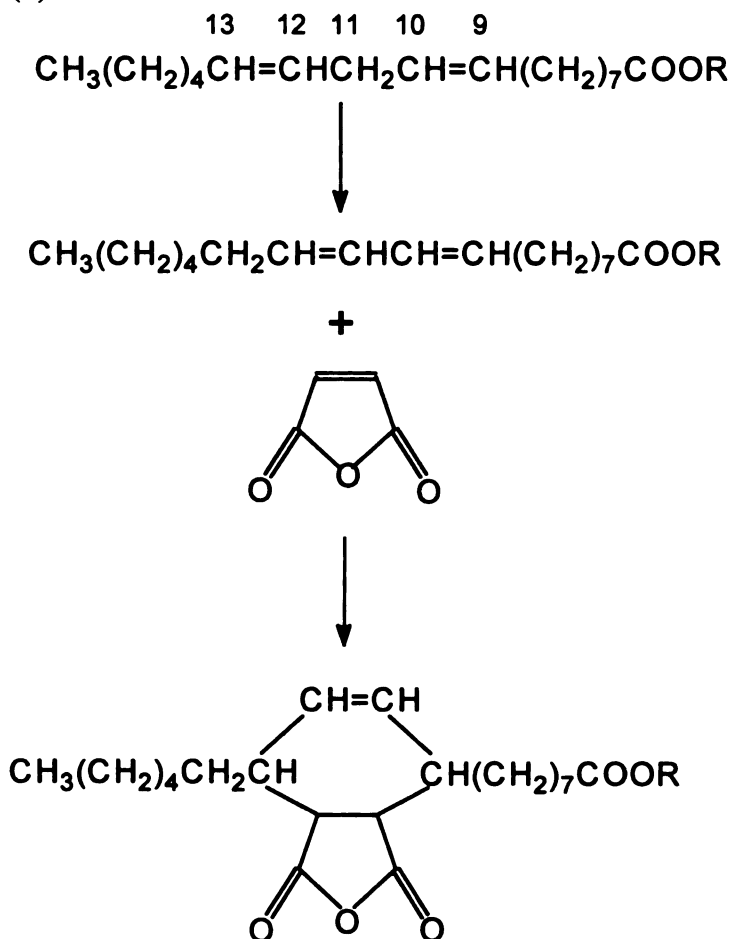
In the case of non-conjugated oils, the determination of the structure of the adduct has been more difficult. Structural information was indefinite for a long time, but this did not forestall the preparation and use of maleated oils. Thus, the patents of Bevan and Tervet⁵ admittedly make no attempt to define the nature of the reaction. Clocker⁶ postulated a cyclobutane structure for the oleic acid adduct:

(2)



In the case of polyunsaturated acids, a 1-4 diene addition similar to 1 for the conjugated oil has been suggested. This assumes that the reaction proceeds by a shift from the non-conjugated to conjugated forms. If maleic anhydride is present it can react to form a Diels-Alder adduct which in the case of linoleic esters occurs as follows:

(3)



High temperatures favor the conjugated structure.

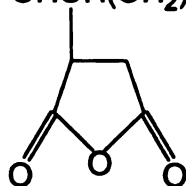
The formation of a substituted succinic type adduct is also possible for maleated oils. It is this structure that is the preference to the Diels-Alder adduct, although the

presence of a small amount of the latter has not been excluded. Bickford et al.⁷, Teeter et al.⁸ and Kappelmeier, and Van der Neut⁹ support the succinic type structure. Their work includes reactions of maleic anhydride with pure methyl oleate, methyl linoleate and methyl linolenate. From this work it appears that a hydrogen on a carbon atom α to a double bond become activated to form a compound of the succinic type with maleic anhydride.

The structures presented in the succeeding formula are suggestions of the above groups of investigators. Addition to oleic acid may occur at the eighth carbon atom.

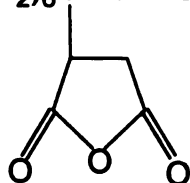
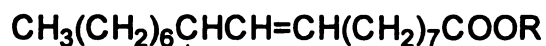
The adduct of oleic acid may be as follows:

(4A)



or at the eleventh carbon atom,

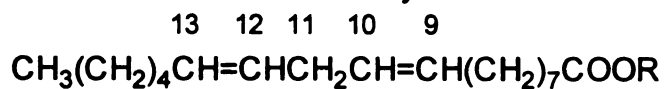
(4B)



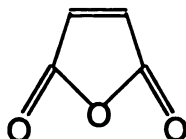
The majority of unsaturated acids in soybean oil is linoleic acid. The postulated reaction of linolate with maleic anhydride, in the presence of a catalyst, will result in three simple

succinic-type adducts with the reaction occurring at the 8, 11, 14 carbon atoms. Of these types the methylene at the 11 position is probably the majority (5B).

Lenoleic ester and maleic anhydride:

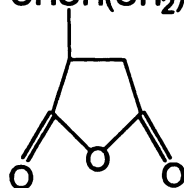
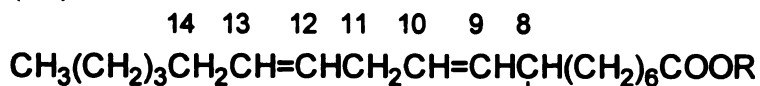


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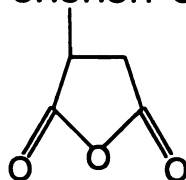


Reaction products:

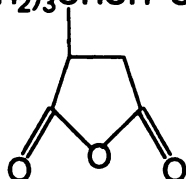
(5A)



(5B)

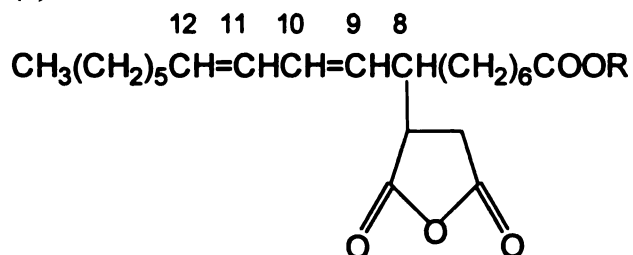


(5C)



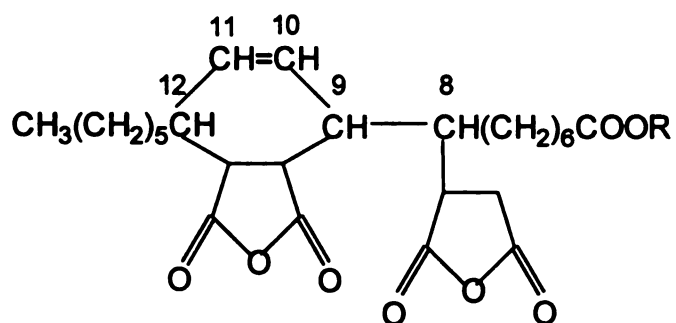
Kappelmeier and Van Den Neut⁹ suggest that conjugation may occur simultaneously with attack at a methylene carbon, or that the initial adduct such as 5A and 5C may rearrange to the conjugated structure as follows:

(6)



Diels-Alder addition of a second mole of maleic anhydride to the conjugated structure would give:

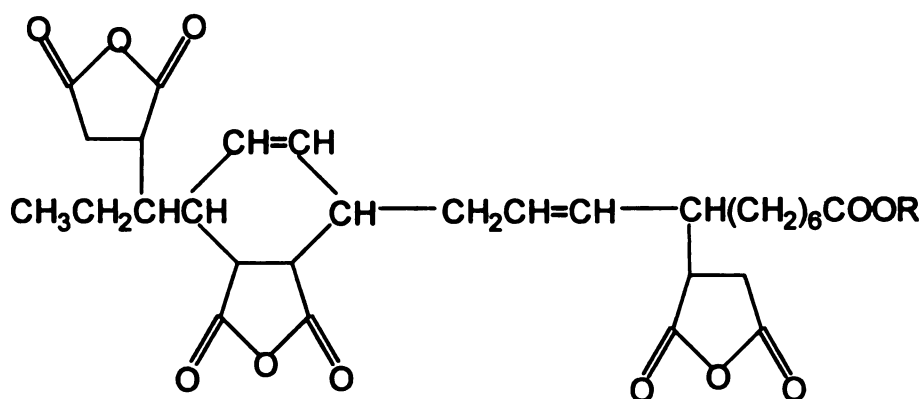
(7)



Alternatively the unconjugated structures 5A, B, and C may add a second mole of maleic anhydride at a methylene carbon to give a structure such as:

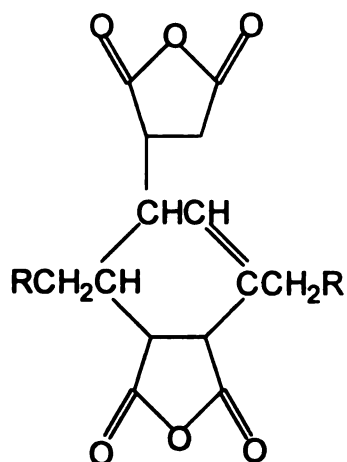
$$\text{CH}_3(\text{CH}_2)_4\overset{13}{\text{CH}}=\overset{12}{\text{CH}}\overset{11}{\text{CH}}-\overset{10}{\text{CH}}=\overset{9}{\text{CH}}-\overset{8}{\text{CH}}(\text{CH}_2)_6\text{COOR}$$

(9)



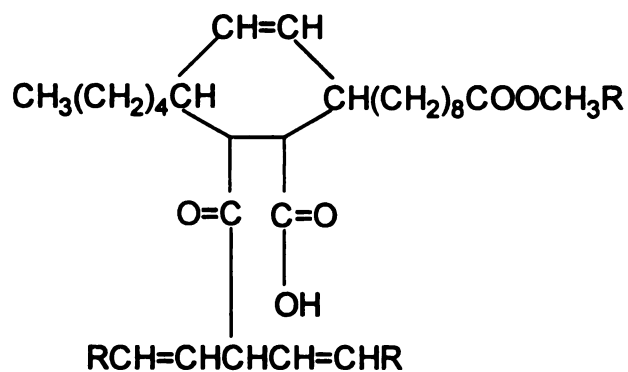
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(10)



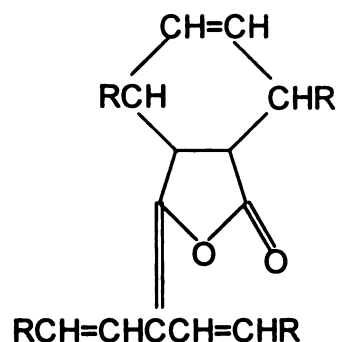
Considering differences in acid and saponification values, Plimmer¹⁰ also postulates a second type of structure, in which the maleic residue acts as a bridge between two acid chains. The Diels-Alder adduct (structure 1) reacts further as shown in 11 and 12 as follows:

(11)



This ketone, 11, enolizes and forms a lactone, thus:

(12)



According to Flett et al.¹¹, the succinic type adduct such as 4, 5, and 8 predominates over types represented by 6, 7, and 9.

The work to establish the identity of the various adducts described above were made from higher percentages of maleic anhydride than are used in the maleated oils of commerce. Most maleic additives do not exceed about 8 percent. This means that for 1 mole of drying oil (mol. wt. ca. 870) about 70 grams of anhydride would be required for an 8 percent modification. This is equivalent to about 0.72 mole of maleic anhydride for each mole of oil, or, for 3 moles of fatty acid in triglyceride form.

Though much work has been done to investigate the reaction of drying oils with maleic anhydride, no work has been done to design and engineer maleated soyproducts for their use as plasticizers, coatings, and composite matrix materials.

CHAPTER 3

GOALS AND OBJECTIVES

The goal of this thesis was to develop a new value-added product from soybean oil feedstock and to design an economical route for its production.

The reaction that was investigated was the addition of maleic anhydride to soybean oil via the use of a peroxide. Previous work outlines that non-conjugated double bonds in the presence of a peroxide allows for the conjugation of the bonds and thus addition via a Diels-Alder type reaction. Characterization of the maleated soybean oil (MSO) was performed by acid number, iodine values, viscosity, and FTIR spectroscopy.

The maleated soybean product was then modified to an ester for possible application as a plasticizer. Characterization of the ester product (MSOE) was performed by acid number and plasticization capability with poly vinyl chloride by the use of a differential scanning calorimeter.

A preliminary engineering and economical analysis was performed from the experimental data to determine the most effective and economical route. Two alternative process scenarios were investigated, continuous and batch. These two alternatives were then analyzed by a return on initial investment and internal rate of return determined by a

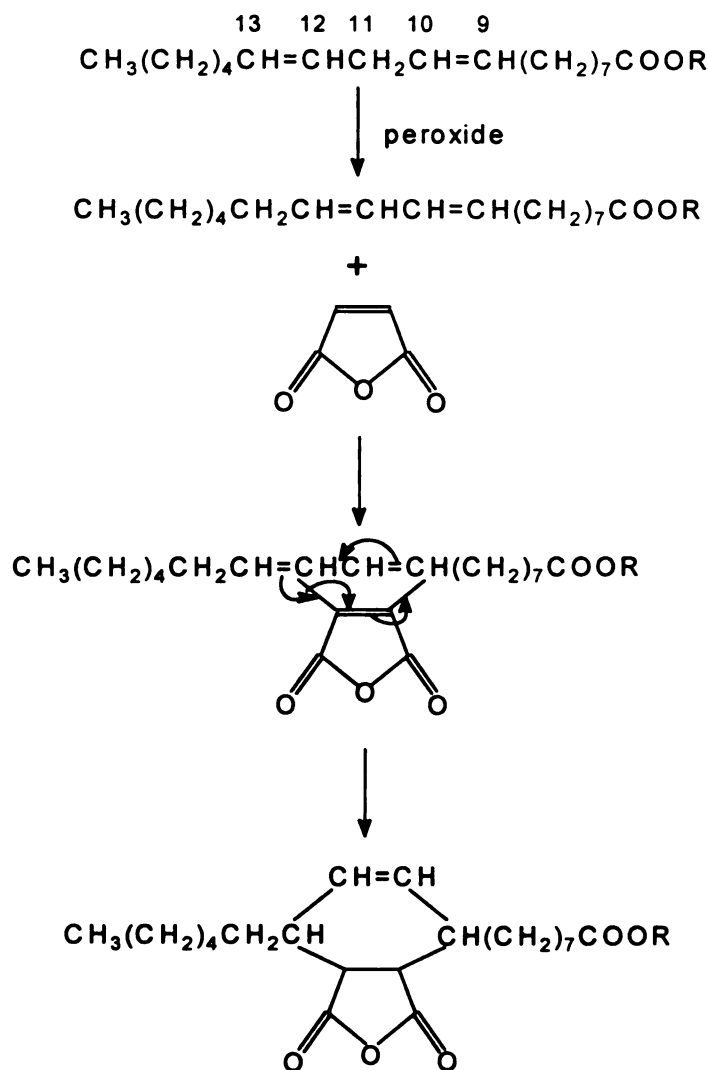
discounted cash flow. The best scenario for the production of maleated soybean oil ester was determined to be a continuous method.

EXPERIMENTAL METHODS AND RESULTS

4.1 Methods and Material

4.1.1 Maleation of Soybean Oil

The experimental procedure to determine maleation of soybean oil is as follows. The reaction includes refined soybean oil of approximately 872 gram molecular weight purchased from Cargill as a vegetable oil. The maleic anhydride was 99% pure reagent grade. The two catalysts used were Lupersol 101 (2,5-Dimethyl-2,5-di-tert-butylperoxy-hexane, Di-tert-butyl peroxide, 3,3,6,6-tetramethyl-1,2-dioxacyclohexane, 2,2,5,5-tetramethyl tetrahydrofuran) and tert-butyl peroxide (98% purity, reagent grade). Proposed reaction chemistry:



Measured quantities of the reactants were added to a 50 ml glass bottle with a magnetic stir bar. The bottle was sealed with a rubber septum and placed into an oil bath. To reduce oxidation, nitrogen was introduced to the reaction via a slow rate over the reaction contents by using needles (MA sublimes and some of it is lost by the Nitrogen flow).

The bottle was placed in an oil bath (at various temperatures) on a stir plate. After the desired time, a vacuum was applied to the bottle to remove excess anhydride and catalyst.

When the maleic anhydride and catalyst were fully removed, by visual inspection to confirm no bubble formation in the reaction, the bottle was removed from the oil, cooled

to room temperature, and refrigerated. The following figure shows the experimental apparatus.

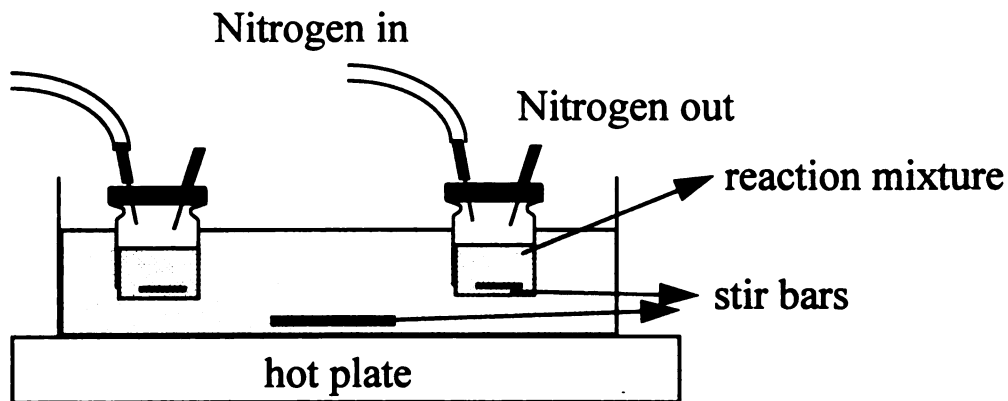


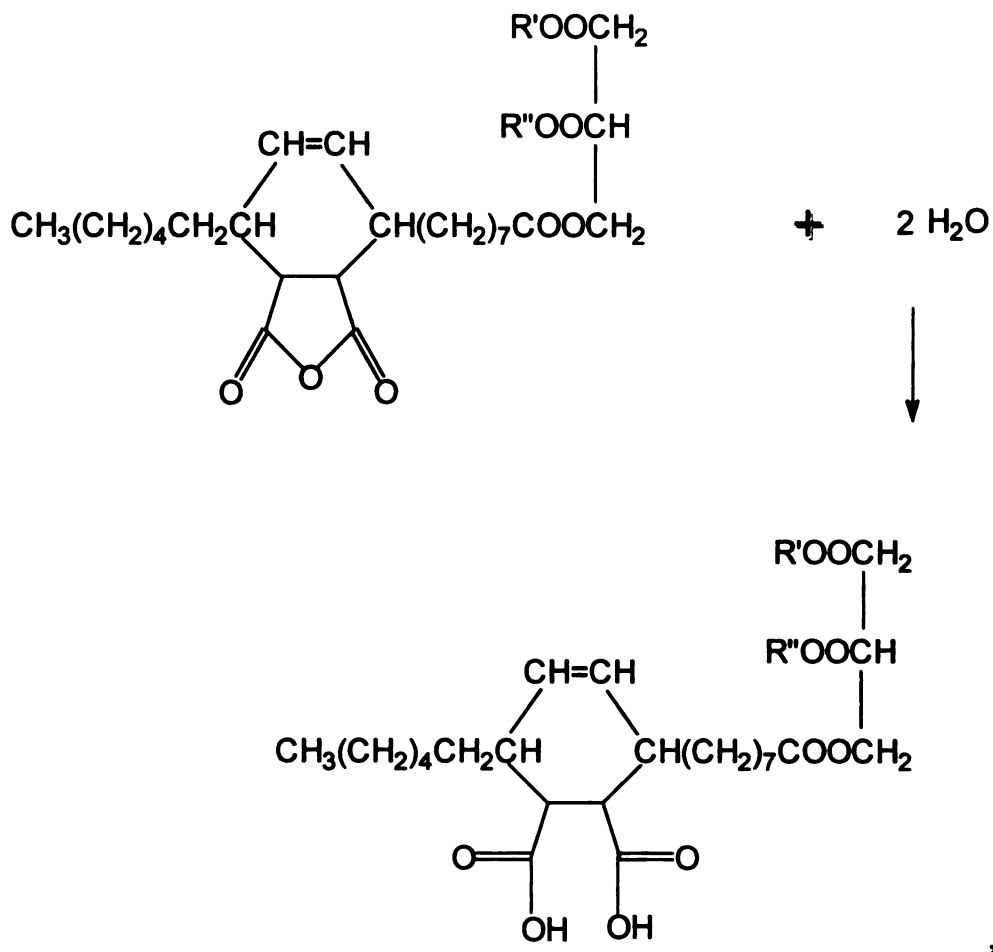
Figure 1: Experimental Apparatus for the Maleation of Soybean Oil

Table 3 shows the results of the maleation of soybean oil experiments. Included in the table are reaction conditions, acid numbers, iodine values, viscosity measurements, and yields of each experiment.

4.1.2 Esterification of Maleated Soybean Oil

The experimental procedure to produce the maleated soy product ester is as follows. The reaction includes a sufficiently high maleated soy product of approximately 1 mole of maleic anhydride per mole of soybean oil prepared in a manner outlined in section 4.1.1. A measured quantity of maleated soy product was added to a high pressure Parr reactor (refer to Figure 2) with a small amount of deionized water and a alcohol. The alcohol that was studied was 1-octanol of 99% pure reagent grade purchased from Aldrich Chemical. The reactor was sealed and placed into the heater mantle and the

thermocouple, water seal, and mixer were connected. The controller was set to 300 C and the contents of the reactor allowed to mix at temperature for various time. Proposed reaction chemistry:



4.2 Maleation of Soybean Oil Results

Table 3: Reaction Data for Soybean Oil and Maleic Anhydride

Sample	Soyoil gm	MA gm	Cat. gm	Cat. type	Rxn time min	Temp. C	Acid Number			Iodine V		Viscosity
							Mean Acid #	mol MA/ mol SO	% Yield	Iodine V	Viscosity cps	
1	40.5	1	0.5	Lup 101	60	150	13.51	0.17	78.63	144.20	80	
2	40.3	2.9	0.5	Lup 101	60	150	42.89	0.57	89.46	118.62	190	
3	40.4	5.7	0.4	Lup 101	60	150	79.62	1.12	89.63	98.70	3580	
4	40.4	1	0.2	Lup 101	60	150	13.96	0.18	81.13	139.59	80	
5	40.1	2.9	0.2	Lup 101	60	150	32.59	0.43	66.61	126.90	110	
6	40.4	5.5	0.2	Lup 101	60	150	81.24	1.15	95.02	106.71	650	
7	40.33	2.62	0	Lup 101	60	150	17.45	0.22	38.82	136.30	70	
8	40.39	1.005	0.54	Lup 101	60	120	15.80	0.20	91.60	134.83	55	
9	40.21	2.902	0.53	Lup 101	60	120	42.54	0.57	88.41	120.86	215	
10	40.19	5.7	0.57	Lup 101	60	120	81.18	1.15	91.14	96.44	32000	
11	40.61	2.922	1.04	Lup 101	60	150	42.68	0.57	89.00	106.60	310	
11B	40.31	2.85	0	Lup 101	720	amb.	7.21	0.09	14.53	140.26	50	
12	40.22	2.944	0.55	Lup 101	120	150	45.00	0.60	92.55	114.21	330	
13	40.45	2.943	0.56	Lup 101	240	150	43.28	0.58	89.34	113.98	400	
14	40.38	1.047	0	Lup 101	60	150	18.36	0.24	102.50	130.80	50	
15	40.41	5.691	0	Lup 101	60	150	40.98	0.55	43.55	128.17	60	
16	40.19	5.754	0.58	Lup 101	120	150	82.20	1.17	91.56	86.19	100000	
17	40.27	1.028	0.56	Lup 101	30	150	16.62	0.21	93.99	123.52	65	
18	40.74	5.766	0.55	Lup 101	30	150	74.09	1.04	82.42	86.88	67000	
19	40.68	2.871	0.56	Lup 101	30	150	35.28	0.47	74.18	107.87	355	
20	40.67	1.045	0.52	Lup 101	120	150	15.65	0.20	87.80	122.02	90	
21	40.12	1.075	0.59	Lup 101	60	100	15.21	0.20	81.81	131.98	110	
22	40.46	2.932	0.56	Lup 101	60	100	37.41	0.50	76.84	120.89	260	
23	40.93	5.8	0.51	Lup 101	60	100	61.89	0.85	67.47	102.79	3230	
24	40.35	1.072	0.53	Tert-but.	60	150	14.81	0.19	80.27	131.78	90	
25	40.14	2.956	0.55	Tert-but.	60	150	37.60	0.50	76.03	118.97	85	
26	40.4	5.754	0.52	Tert-but.	60	150	66.64	0.92	72.82	108.69	29000	
27	40.35	1.074	0.56	Tert-but.	30	150	14.52	0.19	78.52	133.58	60	
28	40.71	2.966	0.52	Tert-but.	30	150	36.13	0.48	73.67	107.56	210	
29	40.49	5.748	0.52	Tert-but.	30	150	68.10	0.94	74.82	102.58	900	
30	40.93	1.058	0.52	Tert-but.	120	150	16.72	0.21	93.39	130.60	65	
31	40.78	2.922	0.51	Tert-but.	120	150	38.35	0.51	79.78	110.51	350	
32	40.32	5.734	0.53	Tert-but.	120	150	71.98	1.00	79.42	107.59	500	
33	40.55	1.048	0.22	Tert-but.	60	150	14.89	0.19	82.99	129.95	75	
34	40.49	2.925	0.21	Tert-but.	60	150	37.74	0.50	77.79	130.19	65	
35	40.56	5.684	0.22	Tert-but.	60	150	73.08	1.02	81.98	103.64	1000	
36	40.36	2.913	1.06	Tert-but.	60	150	38.95	0.52	80.52	114.21	195	
37	40.59	1.083	0.5	Tert-but.	60	120	16.08	0.21	86.97	117.94	55	
38	40.61	2.943	0.51	Tert-but.	60	120	37.17	0.49	76.31	128.63	355	
39	40.46	5.717	0.51	Tert-but.	60	120	74.16	1.04	82.64	93.36	25600	
40	40.37	1.003	0.51	Tert-but.	240	150	14.26	0.18	82.60	127.75	80	
41	40.45	1.074	0.5	Tert-but.	45	150	17.17	0.22	93.47	130.07	50	
42	40.49	1.056	0.52	Tert-but.	5	150	22.39	0.22	95.10	133.25		
Soyoil							0.00	0.00		139.31	50	

4.2.1 Acid Number (Figure 3-6):

ASTM number 1045-86 was the basis for the experimental acid numbers. The data present three general conclusions.

1. All the acid numbers increased with initial maleic anhydride concentration and constant peroxide concentration. The reaction rate appeared to be first order in maleic anhydride and zero order in the peroxide catalyst. The reaction rates at these temperatures were very fast and experimental data at various points during the reaction were unattainable.
2. Peroxide concentration did not affect the acid number, experiments 1-3 (~0.5 grams Lupersol 101) and 4-6 (~0.2 grams Lupersol 101). The experiments in which no peroxide was present resulted in lower acid numbers, experiments 7, 14, and 15. Some residual maleic anhydride was apparent in these samples due to visual crystal formation which would have resulted in false high acid numbers. Experiment 11B was a reaction at ambient temperatures with no catalyst for 720 minutes which resulted in a very low acid number ($AN_{11B} = 7.2$).

The use of tert-butyl peroxide as the reaction catalyst gave similar results when compared with the Lupersol 101. At high initial maleic anhydride concentrations tert-butyl peroxide resulted in lower acid numbers than Lupersol 101.

3. Temperature had a slight affect on the acid number, as seen from experiments 21-23 (T=100 C) and 1-3 (T=150 C). The lower temperature reaction resulted in lower acid numbers at higher maleation. The reaction approaches completion within the first 30 minutes, experiments 17-19.

Figures 5 and 6 show that the maleation reaction was nearly complete for both catalysts. The final titrated amount of maleic acid (determined from a calibration curve of the KOH titration) was close to the initial amount of maleic anhydride added to the reaction, as seen from the diagonal line. The corresponding yields of the experiments were 80 to 100 percent.

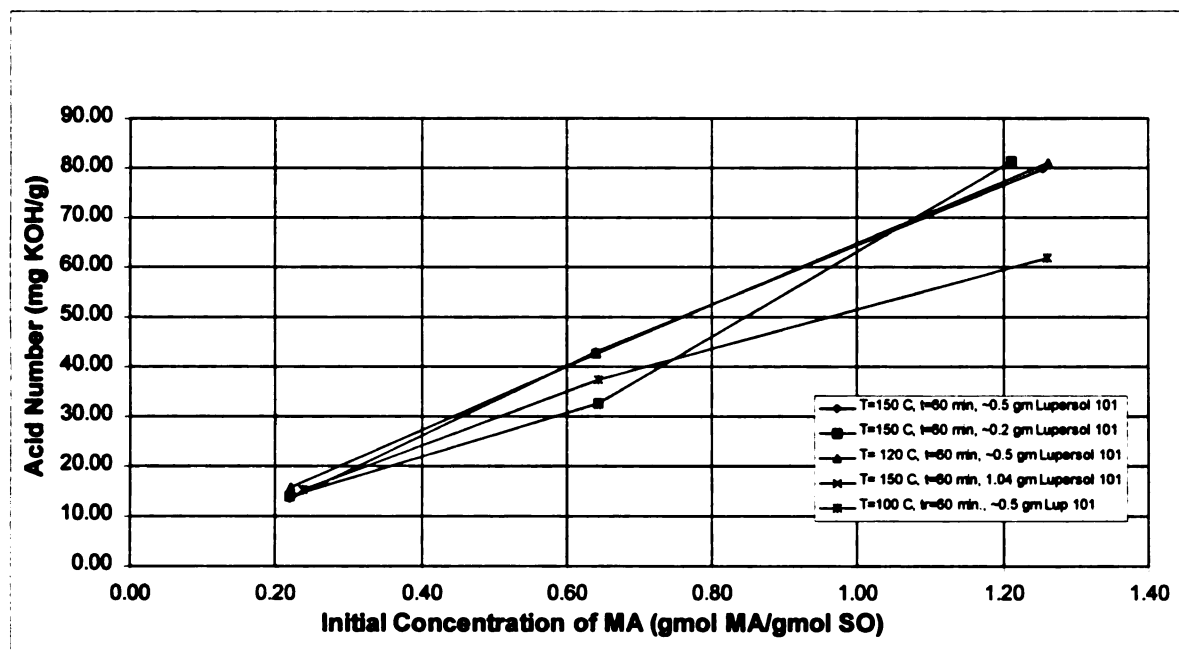


Figure 3: Comparison of Soybean Oil/Maleic Anhydride Acid Number and Initial Reaction MA Concentration using Lupersol 101

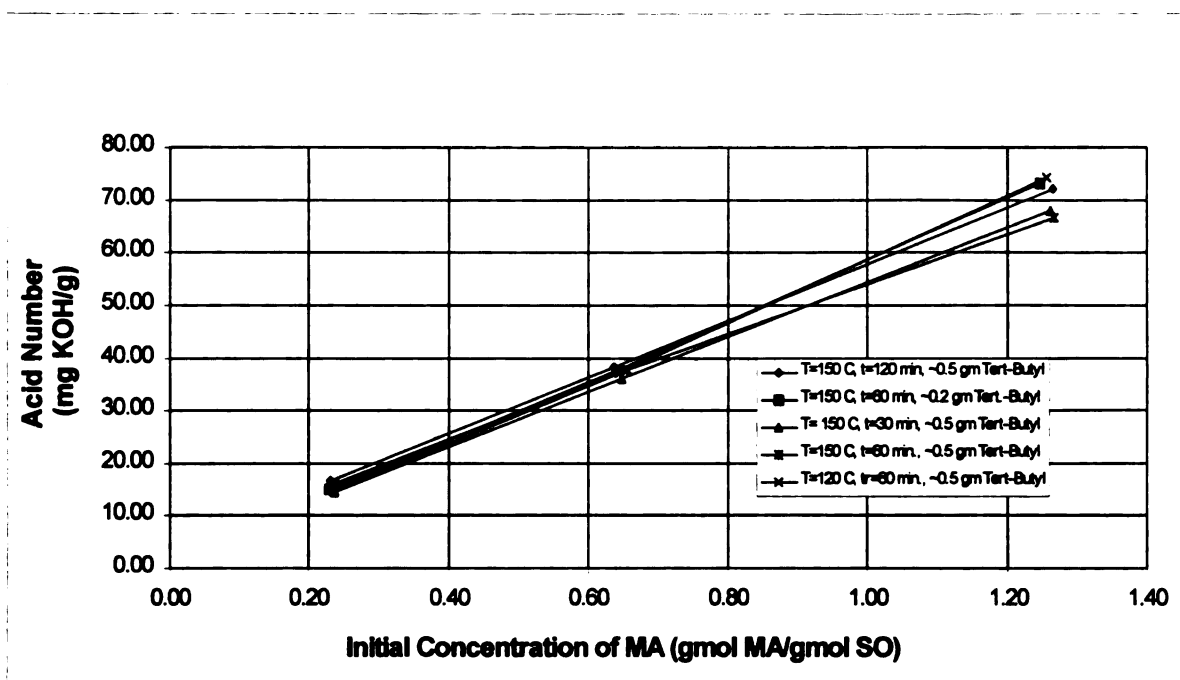


Figure 4: Comparison of Soybean Oil/Maleic Anhydride Acid Number and Initial Reaction MA Concentration using Tert-Butyl Peroxide

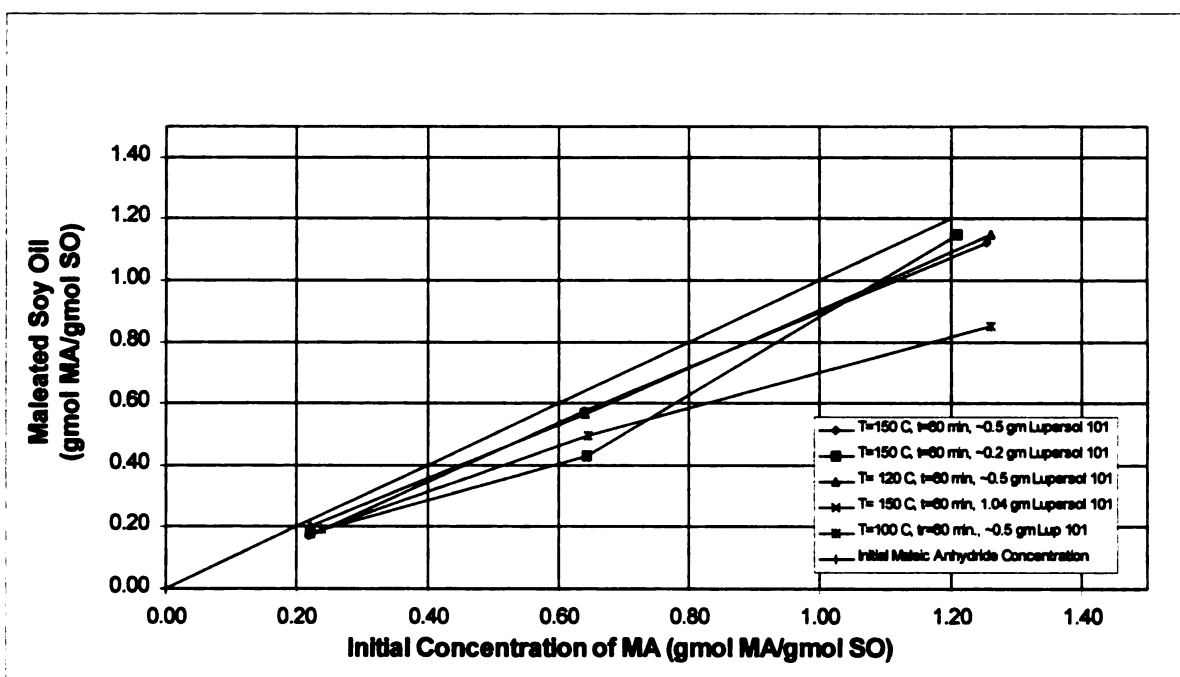


Figure 5: Comparison of Maleated Soybean Oil and Initial Reaction Concentration using Lupersol 101

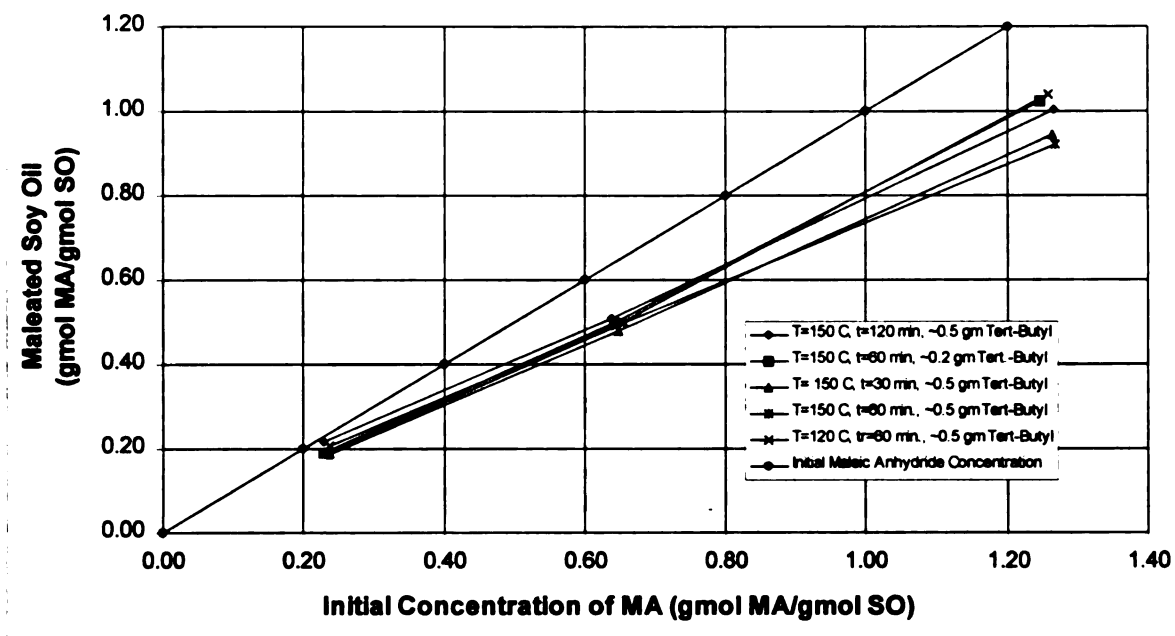


Figure 6: Comparison of Maleated Soybean Oil and Initial Reaction Concentration using Tert-Butyl Peroxide

4.2.2 Iodine Values (Figures 7-10):

A.O.C.S. methods Cd 1-25, Tg 1-64, Tg 2a-64 were the basis for the experimental iodine values. The data present three general conclusions.

1. All the iodine values decreased with increasing maleic anhydride content. The decrease in the iodine value is an indication of double bond saturation by the addition of maleic anhydride via a 1-4 Diels-Alder type reaction. Soybean oil contains approximately 4.3 double bonds per mole of soybean oil. The addition of 1 mole of maleic anhydride (using the proposed chemistry of Section 4.1.1) will reduce the total double bonds to ~3.3 bonds per mole of soybean oil.

2. Peroxide concentration only affected the iodine value in reactions that contained maleic anhydride. The experiments with no peroxide, only a small reduction in iodine values are apparent, experiments 7, 14, and 15. Experiment 11B was a reaction at ambient temperatures, with no catalyst, a reaction time of 720 minutes, with no apparent decrease in iodine value ($IV_{11B} = 140.3$ and $IV_{\text{soy oil}} = 140$). The reaction approaches completion within the first 30 minutes, experiments 17-19.

The use of tert-butyl peroxide as the reaction catalyst gave similar results when compared with the Lupersol 101. At high initial maleic anhydride concentrations tert-butyl peroxide resulted in higher iodine values than Lupersol 101. A higher iodine value would mean that fewer double bonds were attacked by the tert-butyl peroxide

3. Temperature did not significantly affect the iodine value as seen from experiments 21-23 ($T=100\text{ C}$) and 1-3 ($T=150\text{ C}$). Catalyst concentration did not affect the iodine value, experiments 1-3 (~0.5 grams Lupersol 101) and 4-6 (~0.2 grams Lupersol 101).

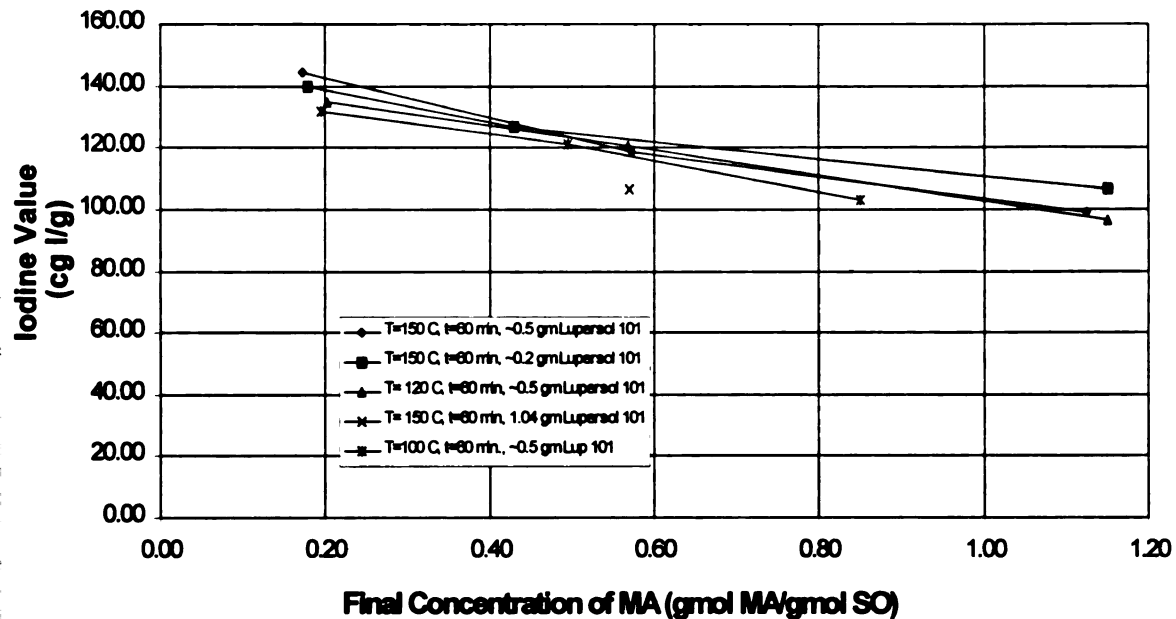


Figure 7: Comparison of Soybean Oil/Maleic Anhydride Iodine Value and Final Reaction MA Concentration using Lupersol 101

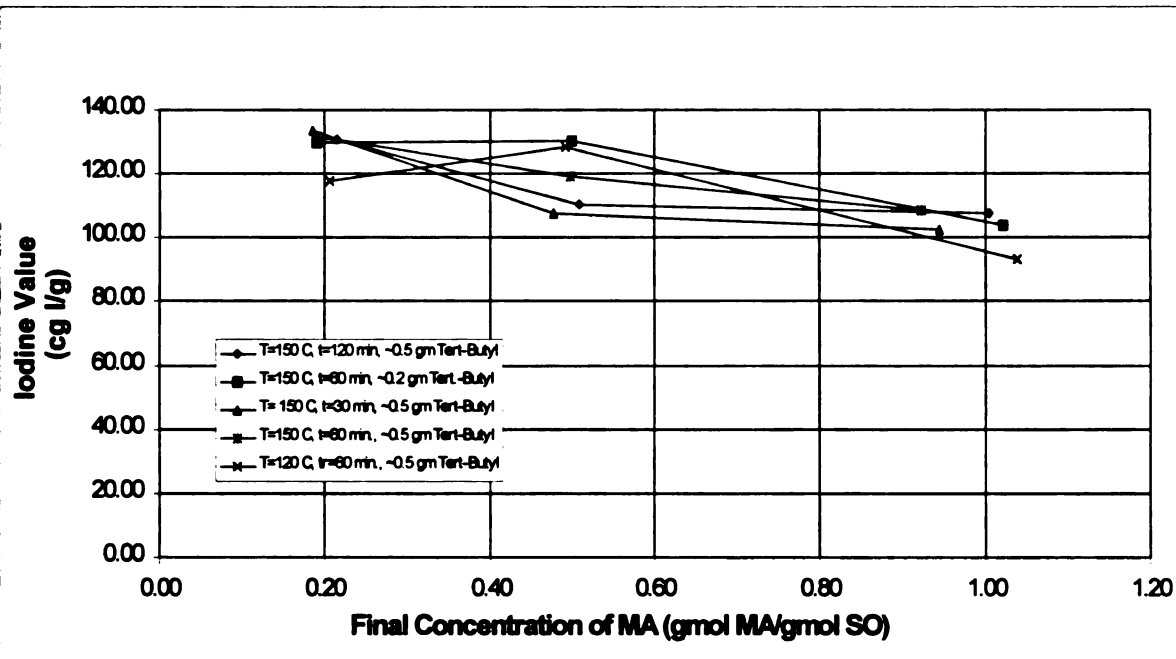


Figure 8: Comparison of Soybean Oil/Maleic Anhydride Iodine Value and Final Reaction MA Concentration using Tert-Butyl Peroxide

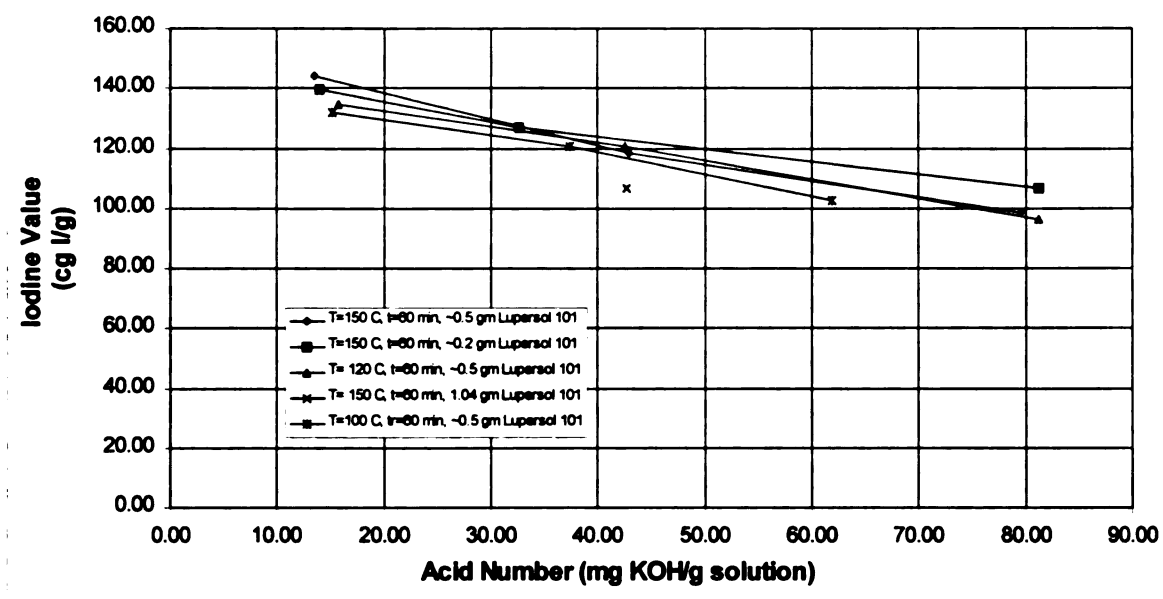


Figure 9: Comparison of Soybean Oil/Maleic Anhydride Iodine Value and Acid Number using Lupersol 101

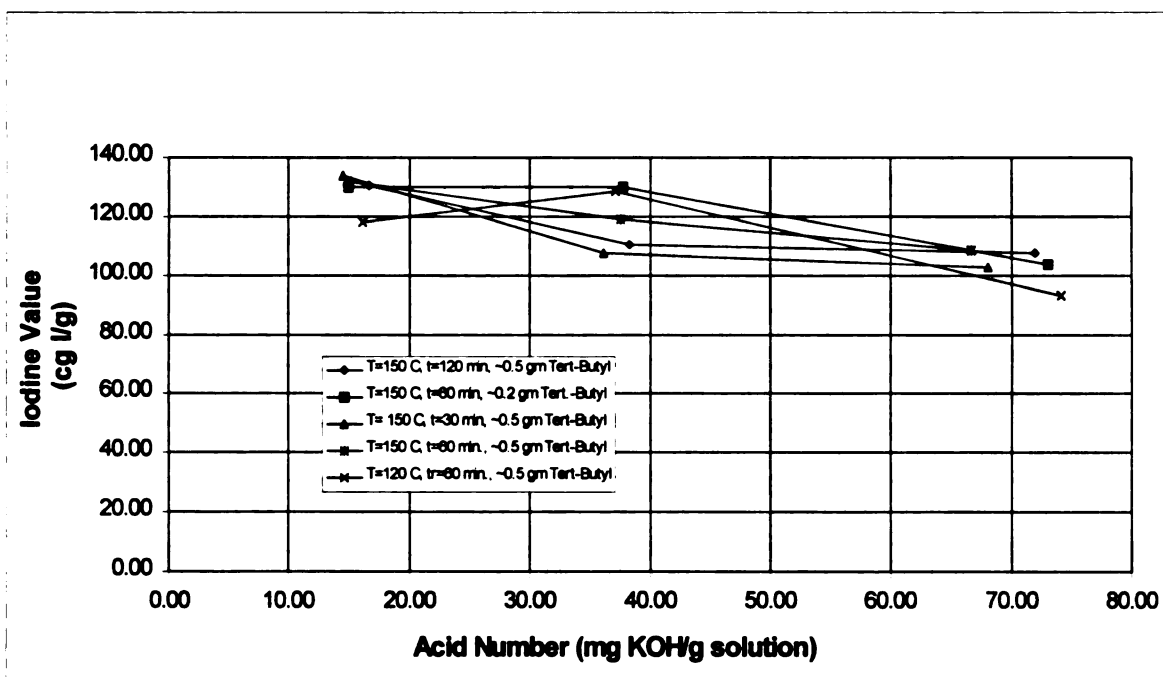


Figure 10: Comparison of Soybean Oil/Maleic Anhydride Iodine Value and Acid Number using Tert-Butyl Peroxide

4.2.3 Viscosity (Figures 11 and 12):

The equipment used for this experiment was a Brookfield, model EX100, viscometer, with a constant temperature bath.

The viscosity of the maleated soybean oil increases with the final maleic anhydride concentration. Viscosity of maleated soybean oil does not appear to be a function of reaction temperature, initial catalyst concentration, or duration of reaction.

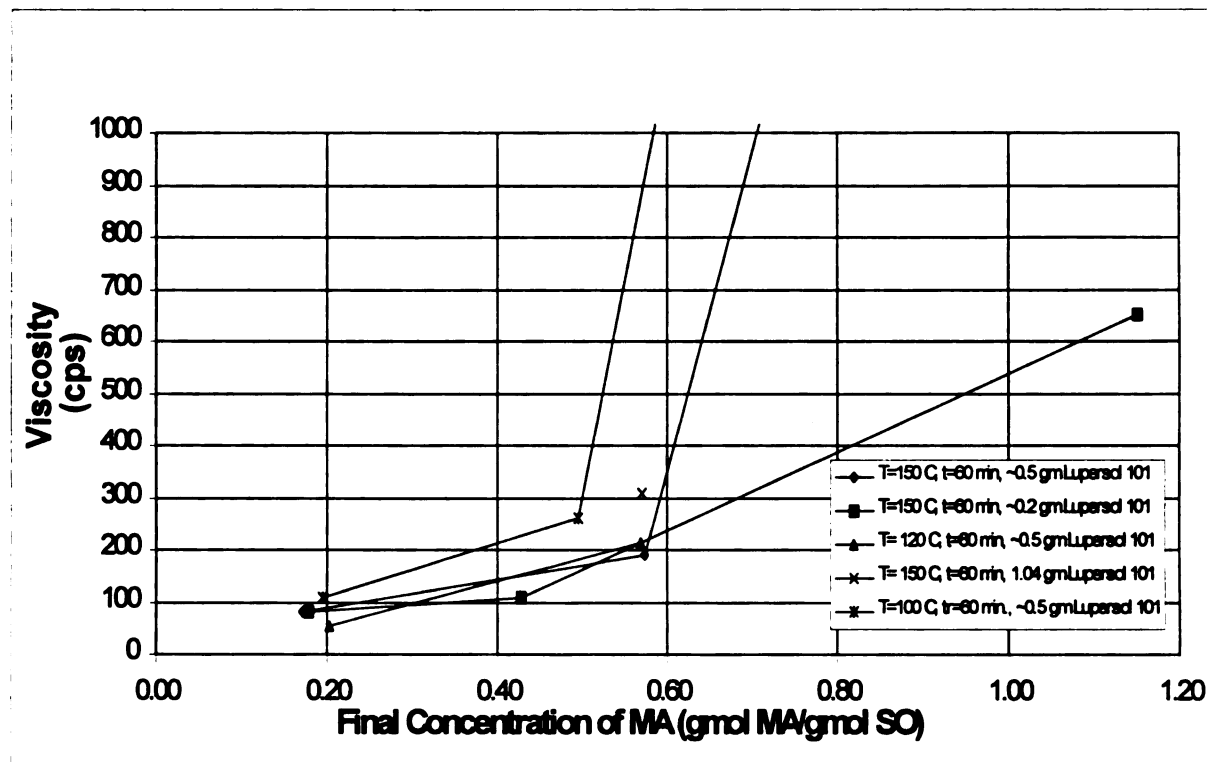


Figure 11: Comparison of Soybean Oil/Maleic Anhydride Viscosity and Final Reaction MA Concentration using Lupersol 101 at 25 C

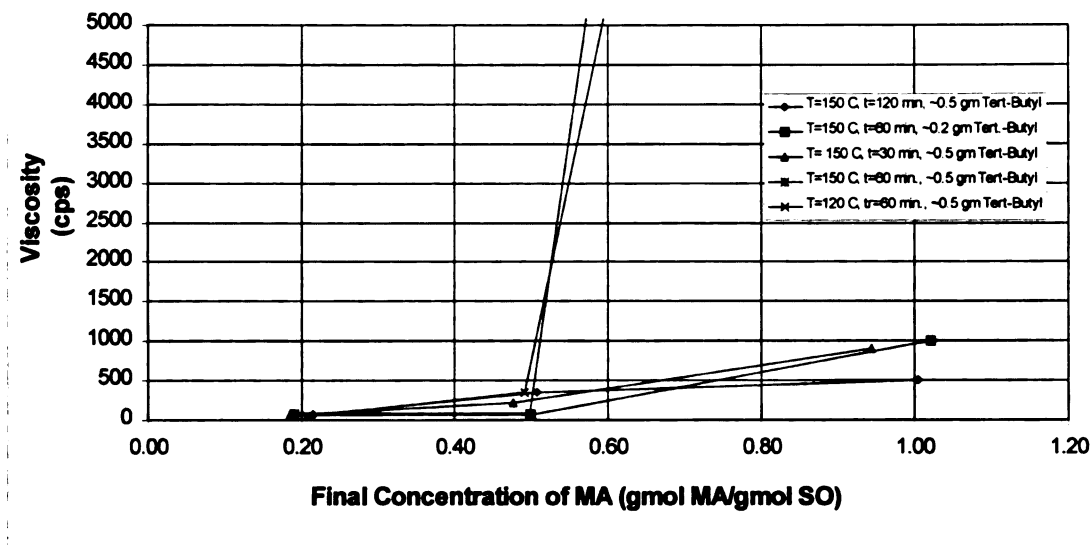


Figure 12: Comparison of Soybean Oil/Maleic Anhydride Viscosity and Final Reaction MA Concentration using Tert-Butyl Peroxide at 25 C

4.2.4 Fourier Transform Infra Red Spectrometer Results (FTIR)

The equipment used for this experiment was a Perkin-Elmer, model 1600, FTIR, with the horizontal ATR accessory. Sample fluid was applied to the ATR's sample crystal and measured by FTIR.

A strong correlation exists between the increase in maleated soybean oil and the area of two FTIR peaks at approximately 1775 cm^{-1} and 1850 cm^{-1} . In the case of soybean oil (Figure 13) both the peaks at 1775 cm^{-1} and 1850 cm^{-1} are not apparent; only the peak at 1740 cm^{-1} is apparent, most-likely the ester linkages from the triglyceride. An increase in maleic anhydride increases the peaks at 1775 and 1850 cm^{-1} as apparent on inspection of Figures 14-16. Apparently the peaks at 1775 and 1850 cm^{-1} are ester anhydride peaks

because hydrolysis of the sample will result in a broad peak above 3000 cm^{-1} , refer to Figure 17.

The maleated soybean oil was hydrolyzed (Figure 17) by the addition of excess water and mixed at temperatures of 150-160 C for 90 minutes. It can be noted that a reduction in both the anhydride groups and triglyceride are apparent due to the reduction in the ester peaks at 1740, 1775, and 1850 cm^{-1} .

The esterified, maleated soybean oil (Figure 18) was prepared with a maleated oil of 1.0 mole maleic anhydride per mol soybean oil, as in Figure 16, according to the procedure outlined in section 4.1.2. Figure 18 shows that the anhydride groups had been hydrolyzed, no apparent peaks at 1775 and 1850 cm^{-1} , with only a small amount converted to acid, small group of peaks above 3000 cm^{-1} . If the maleic anhydride was completely converted to acid the spectra would look similar to Figure 17. Though in the esterified samples the peak at $1740\text{-}1750\text{ cm}^{-1}$ became larger in size due to the ester linkages to the maleic acid groups and the triglyceride esters.

The conclusions from the FTIR data are similar to the previous analytical results. The extent of reaction does not appear to be a function of catalyst concentration, reaction temperatures (in the region of 100-150 C), or the type of peroxide (tert-butyl or Lupersol 101). The FTIR data also prove that the reaction of maleated soybean oil and 1-octanol result in a esterified, maleated product in the triglyceride form.

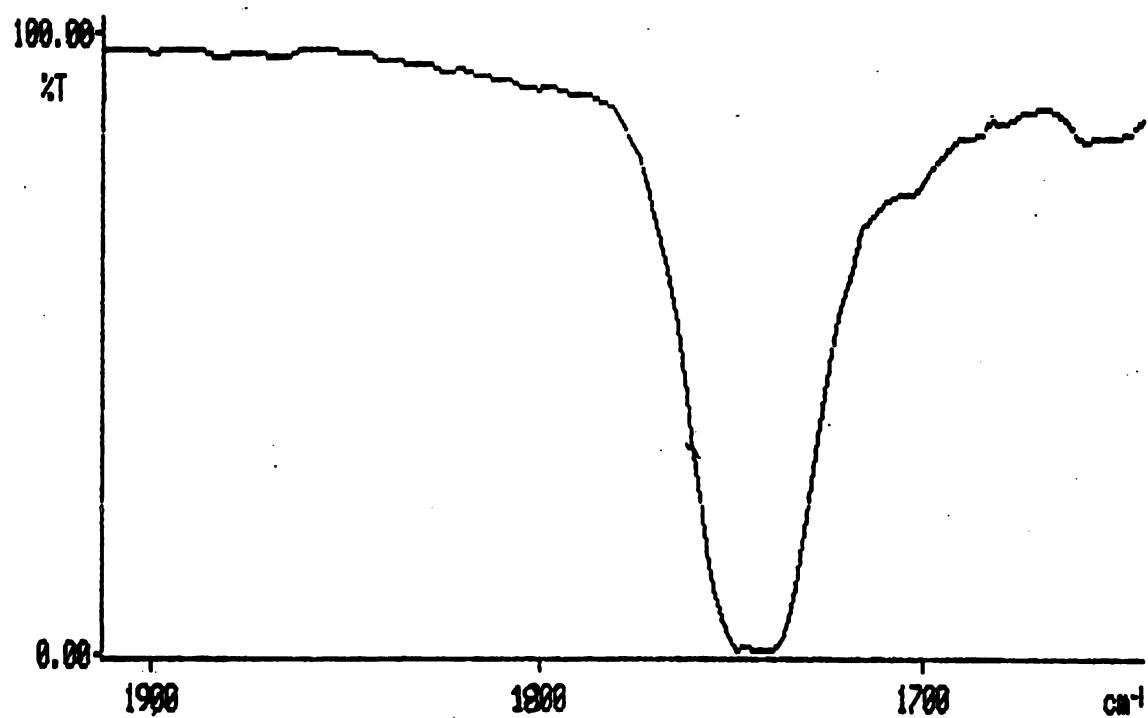
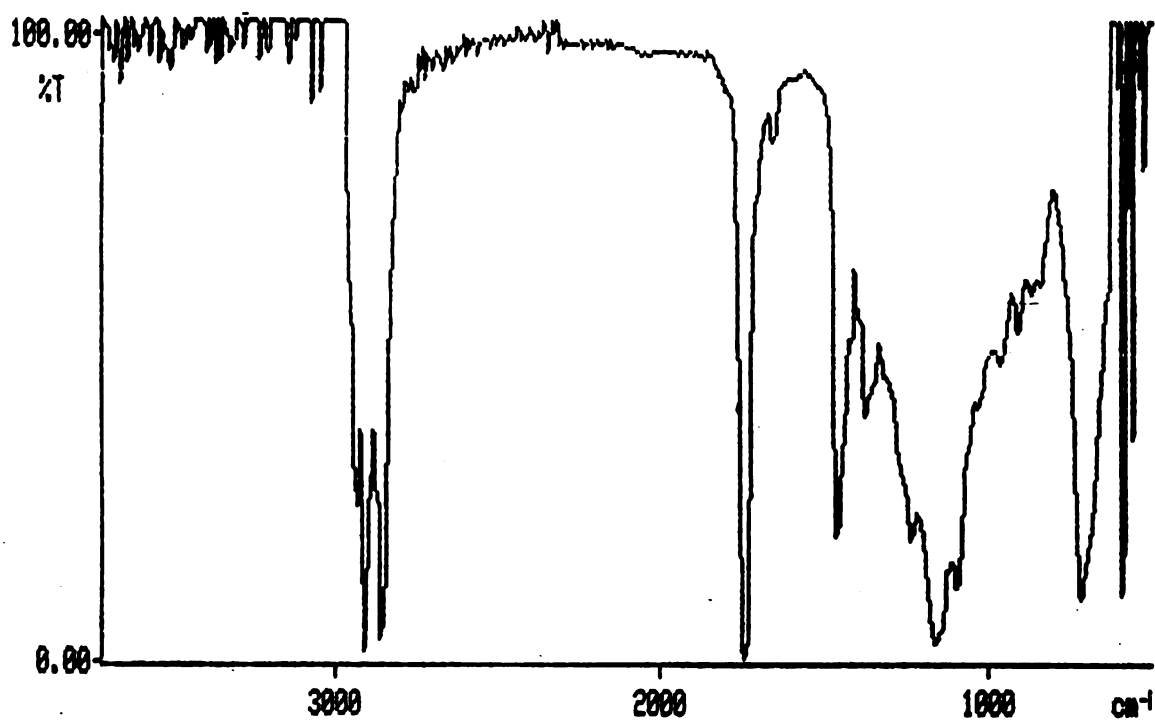


Figure 13: FTIR spectra of Soybean Oil

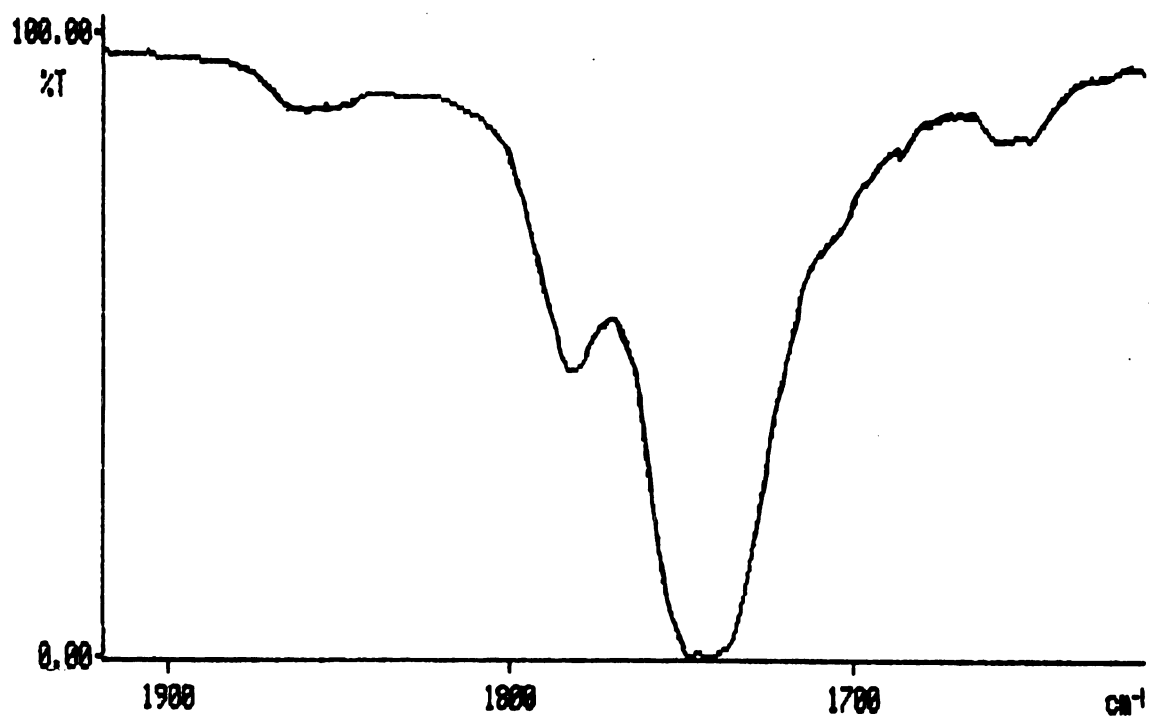
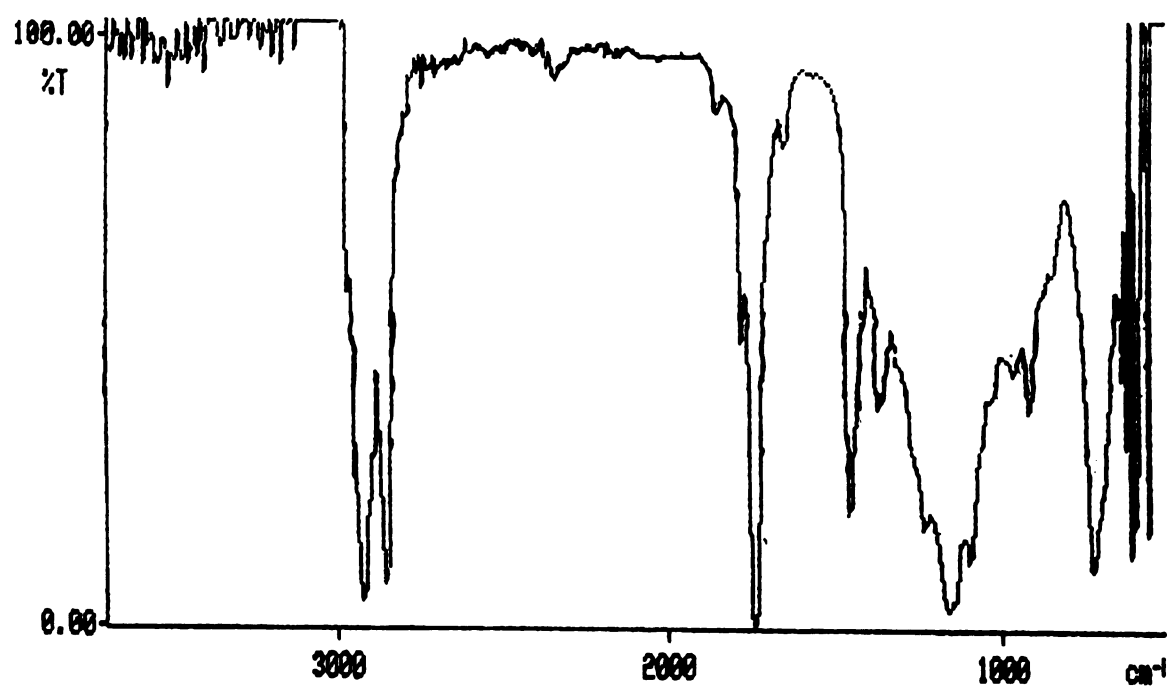


Figure 14: FTIR spectra of 0.2 mol MA/mol SO maleated soybean oil

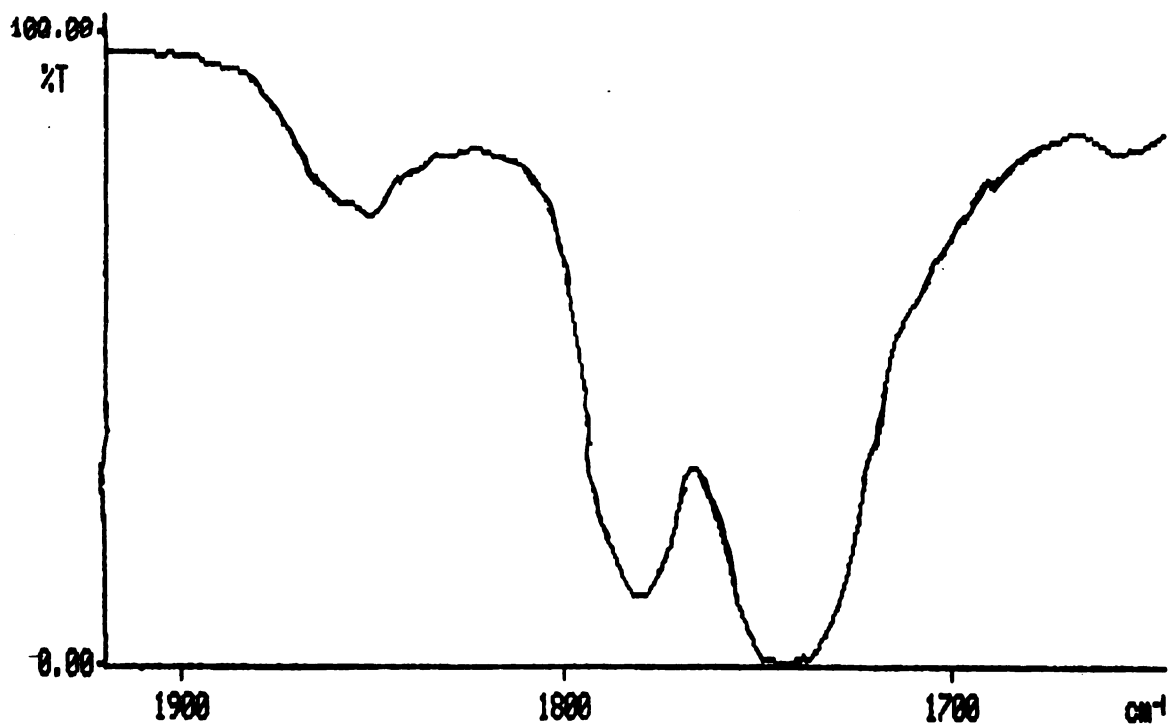
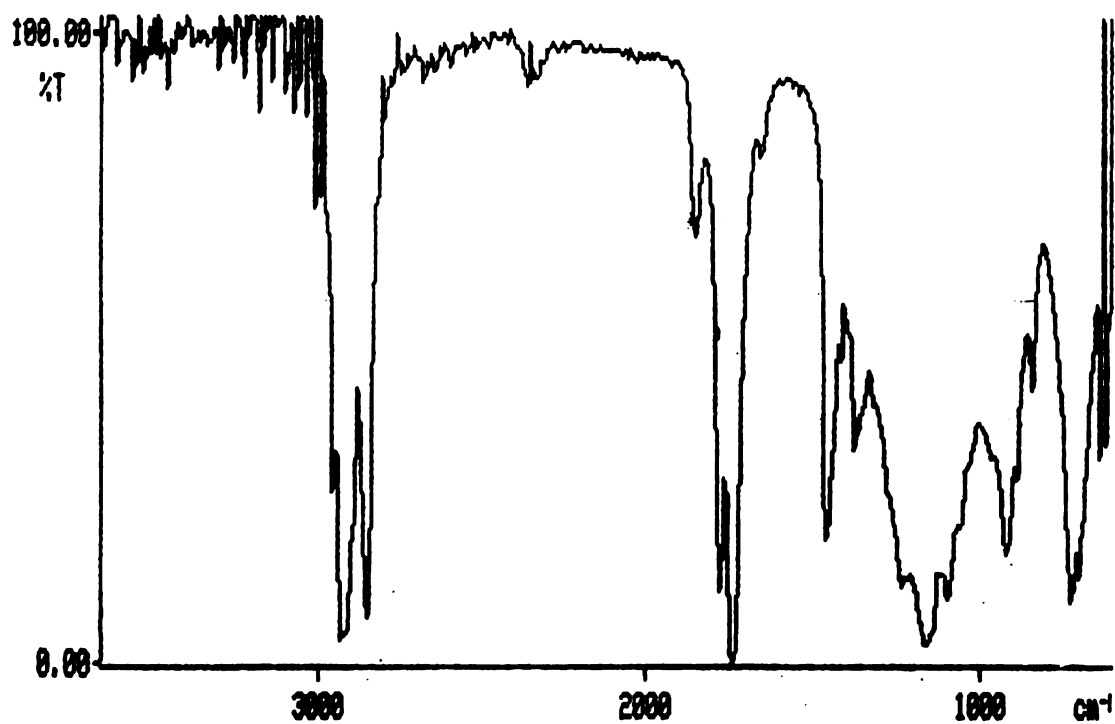


Figure 15: FTIR spectra of 0.5 mol MA/mol SO maleated soybean oil

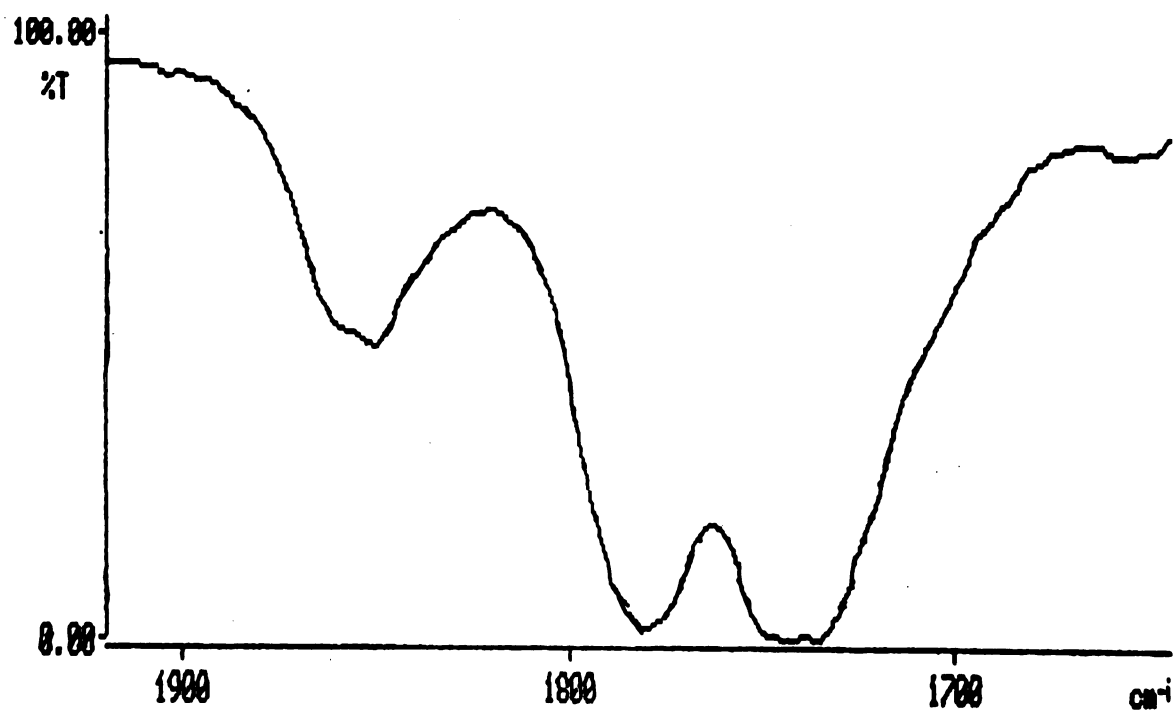
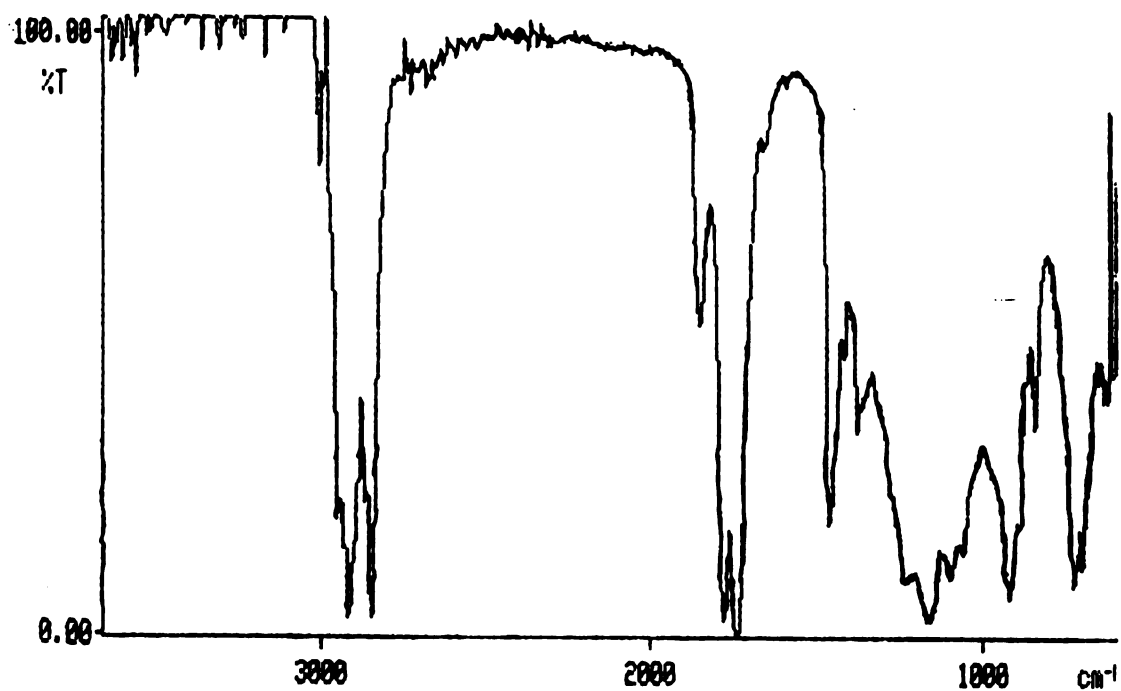


Figure 16: FTIR Spectra of 1.0 mol MA/mol SO maleated soybean oil

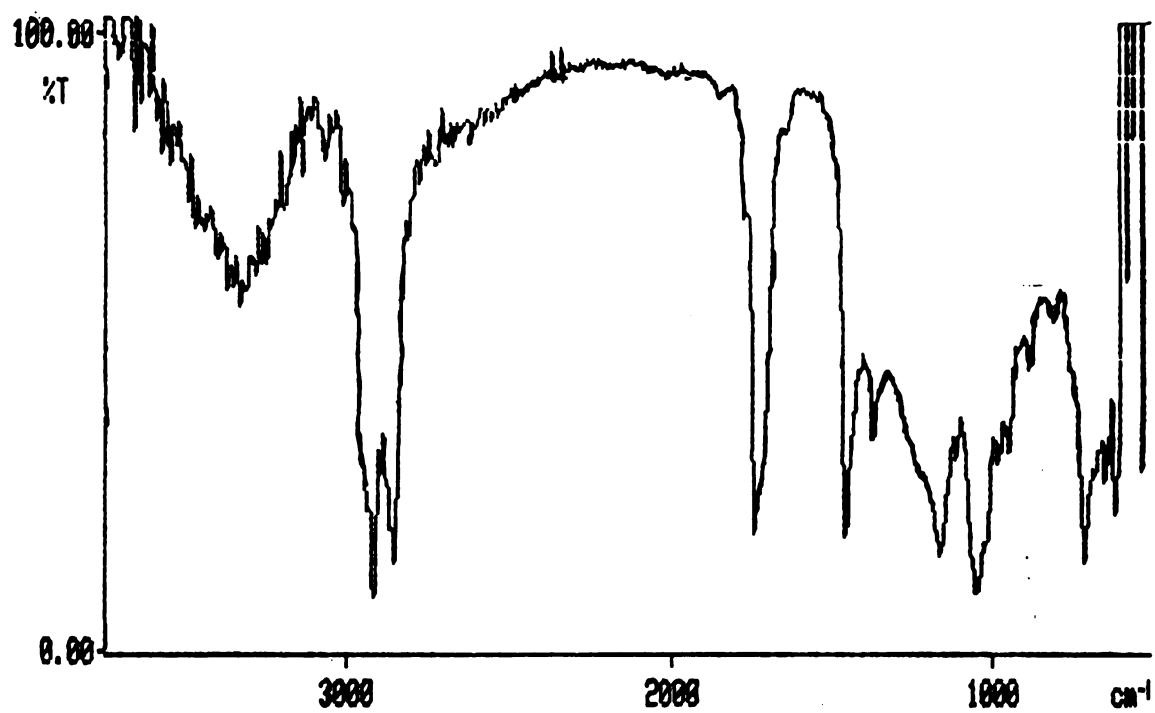


Figure 17: FTIR Spectra of 1.0 mol MA/mol SO maleated soybean oil, hydrolyzed

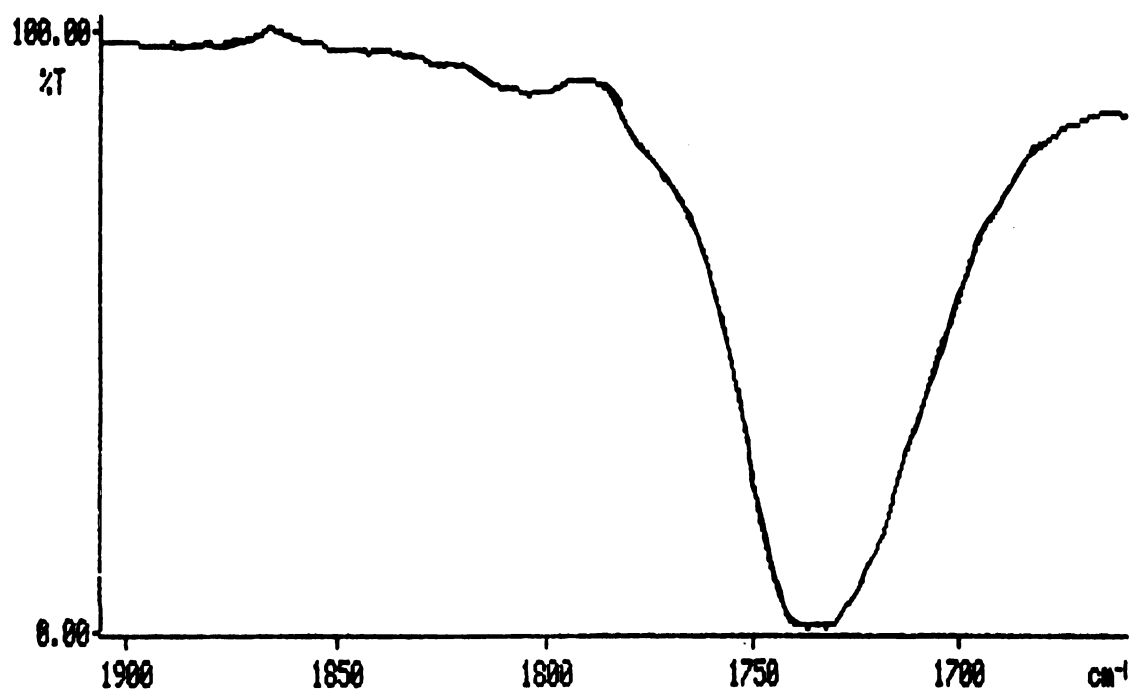
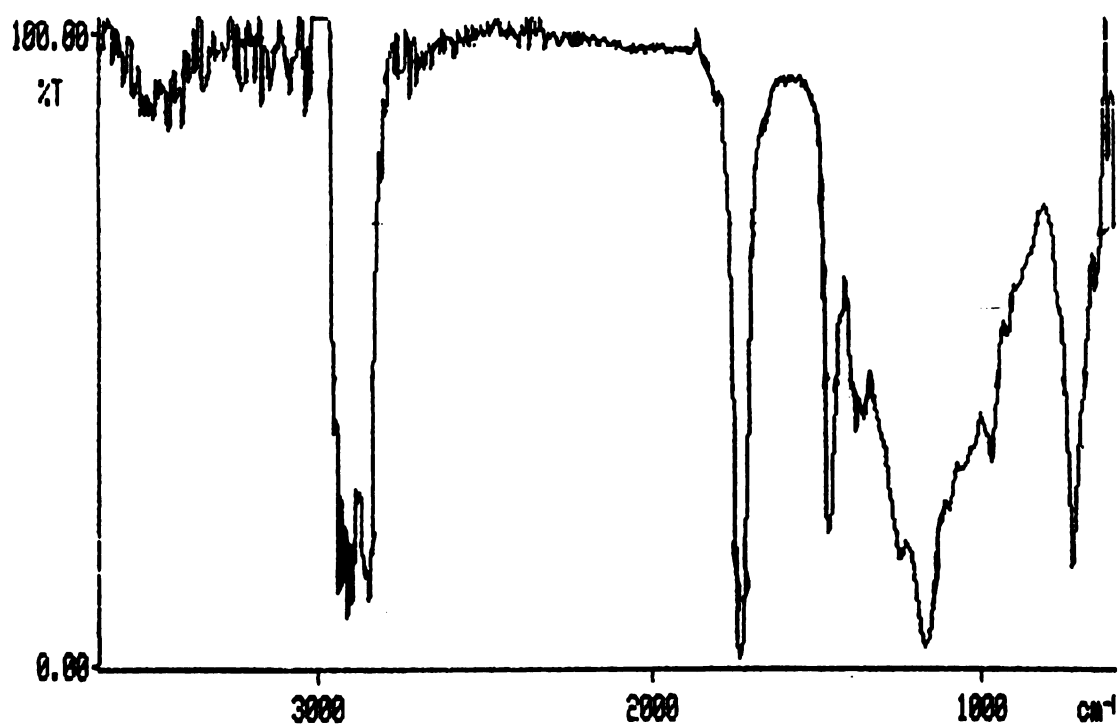


Figure 18: FTIR Spectra of 1.0 mol MA/mol SO maleated soybean oil, esterified

4.3 Esterification Results

The experimental results outlined in Table 4 were obtained by the procedure outlined in section 4.1.2. The results show some very interesting trends in the esterification data. Sample 44 represents a maleated soybean oil of approximately 1 mole maleic anhydride per mole of soybean oil. Esterification of sample 44 for 120 minutes resulted in a substantial decrease in acid number which can be attributed to the hydrolysis then esterification of the anhydride group. Sample 45 is also a maleated soybean oil of approximately 1 mole maleic anhydride per mole of soybean oil. Reactions of 60 and 180 minutes resulted in a substantial decrease in the acid number by esterification. Sample 46a show that if near stoichiometric quantities of alcohol are used in the experiment; the esterification of the anhydride groups are greatly reduced. Sample 54a was run with a stoichiometric amount of octanol without water and resulted in a significant reduction in initial acid number ($AV_{54} = 68.3 \text{ mg KOH/g}$). Sample 54c was run with 50% excess alcohol and nearly all anhydride was esterified as seen in the low acid number of 3.03 mg KOH/g. Sample 54b was run with 50% excess octanol and water but at a low temperature of 150 C instead of the normal temperature of 300 C. The lower reaction temperature resulted in a much lower amount of esterification. Sample 54b can be compared with sample 44d which had similar concentrations of reactants but was run at 300 C. Sample 44d had a much higher level of esterification than 54b as seen from the much lower acid number.

Samples 47 through 51 were obtained with soybean oil to verify the reactions of the triglyceride with various reactants under the given conditions. Sample 47 was conducted with only soybean oil and resulted in a near zero acid number showing that the triglyceride will not split apart in the absence of water. Comparison of sample 48 and 50 shows that soybean oil in the presence of octanol will result in a moderate amount of esterification of the glyceride over a sample in absence of octanol. Sample 51 was run with octanol but no water and resulted in a very low acid number thereby confirming a very low amount of triglyceride hydrolysis and thus esterification.

Table 4: Esterification Reactions

Sample	Rxn Time min	Rxn Temp. C	MSO gm	SO gm	1-octanol gm	DI H ₂ O gm	Mean Acid #	Stand. Deviation
44	na	na	na	na	na	na	65.57	0.74
44d	120	300	220.00	0.00	102.10	12.90	9.33	0.04
45	na	na	na	na	na	na	62.06	0.24
45b	60	300	70.70	0.00	40.90	5.00	18.43	0.26
45c	180	300	80.40	0.00	45.60	5.00	10.01	0.12
46	na	na	na	na	na	na	62.99	0.54
46a	120	300	70.00	0.00	21.10	5.00	33.74	0.07
47	150	300	0.00	40.16	0.00	0.00	0.09	0.01
48	60	300	0.00	70.40	20.20	5.20	16.25	0.64
49	60	300	0.00	80.40	0.00	0.00	2.86	0.21
50	60	300	0.00	81.10	0.00	5.40	34.78	0.07
51	60	300	0.00	71.20	21.20	0.00	1.72	0.22
54	na	na	na	na	na	na	68.26	0.79
54a	120	300	71.10	0.00	21.40	0.00	25.17	1.04
54b	120	150	59.90	0.00	31.20	5.00	53.47	0.66
54c	120	300	52.50	0.00	27.00	0.00	3.03	4.29

Further tests of the ester products with the use of a differential scanning calorimeter revealed plasticization characteristics of the maleated soybean ester product as outlined in the following section.

4.3.1 Differential Scanning Calorimeter (DSC)

The differential scanning calorimeter used was a Perkin-Elmer DSC 7 connected to a DECstation Personal Workstation via a TAC 7/DX Thermal Analysis Instrument Controller. The personal workstation utilizes the Perkin-Elmer 7 series/UNIX Thermal Analysis System software. ASTM D3418-82 titled “Standard Test Method for Transition Temperatures of Polymers By Thermal Analysis” was the basis for the experimental procedure.

Several samples of maleated soybean oil (MSO) were tested with the DSC to determine any plasticization qualities. The MSO resulted in no measurable reduction in the glass transition temperature, thus MSO offers no advantage as a plasticizer

Figure 19 shows the results of DSC experiments with PVC resin and maleated soybean oil ester (section 4.3). The maleated oil, deionized water, and 1-octanol reacted at 300 C in a pressurized reactor for 60 minutes. Vacuum removal of excess water and alcohol. Refrigerate the sample until the DSC test.

The DSC results include four samples, pure PVC, 12% MSOE in PVC, 33% MSOE in PVC, 52% MSOE in PVC. Figure 20 is the inversion of glass transition temperature as the dependent variable and ester concentration as the independent variable. The resulting graph revealed a regressed line of $R^2=0.97$, which would mean MSO ester is a plasticizer for PVC.

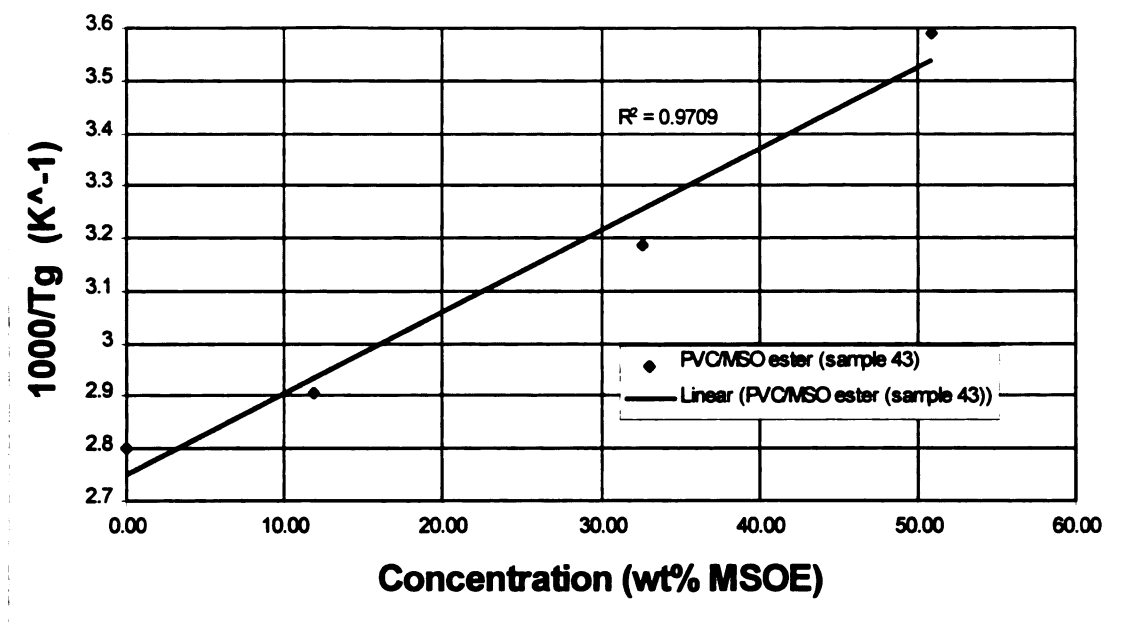


Figure 19: Differential Scanning Calorimeter results for PVC/MSO Ester (Sample 43)

Figure 20 shows the results of DSC experiments with PVC resin and maleated soybean oil ester, prepared in a manner outlined in section 4.1.1. The soybean oil, diethyl maleate, and Lupersol 101 reacted at 150 C in a pressurized reactor for 60 minutes. Vacuum removal of excess water and ester, refrigerate the sample until the DSC test.

The purpose of the experiment was to investigate the reaction of soybean oil and an alkyl maleate. The alkyl maleate reaction could offer a cost saving over the maleic anhydride reaction with soybean oil. The savings could be attributed to material and reduced labor costs. The reduction in manufacturing cost and capital equipment cost could reduce the selling price of the maleated soybean oil ester.

Three samples were prepared for the DSC test, pure PVC, 30% MSOE in PVC, 50% MSOE in PVC. The glass transition temperature of each sample was inverted and graphed using concentration as the independent variable. The resulting graph revealed a regressed line of $R^2=0.93$, which would mean the MSO ester is a plasticizer for PVC. This MSO ethyl ester did not plasticize the PVC to the degree of the MSO octyl ester reduced the glass transition temperature. This may be due to the interpenetrations of the octyl chains into the PVC matrix.

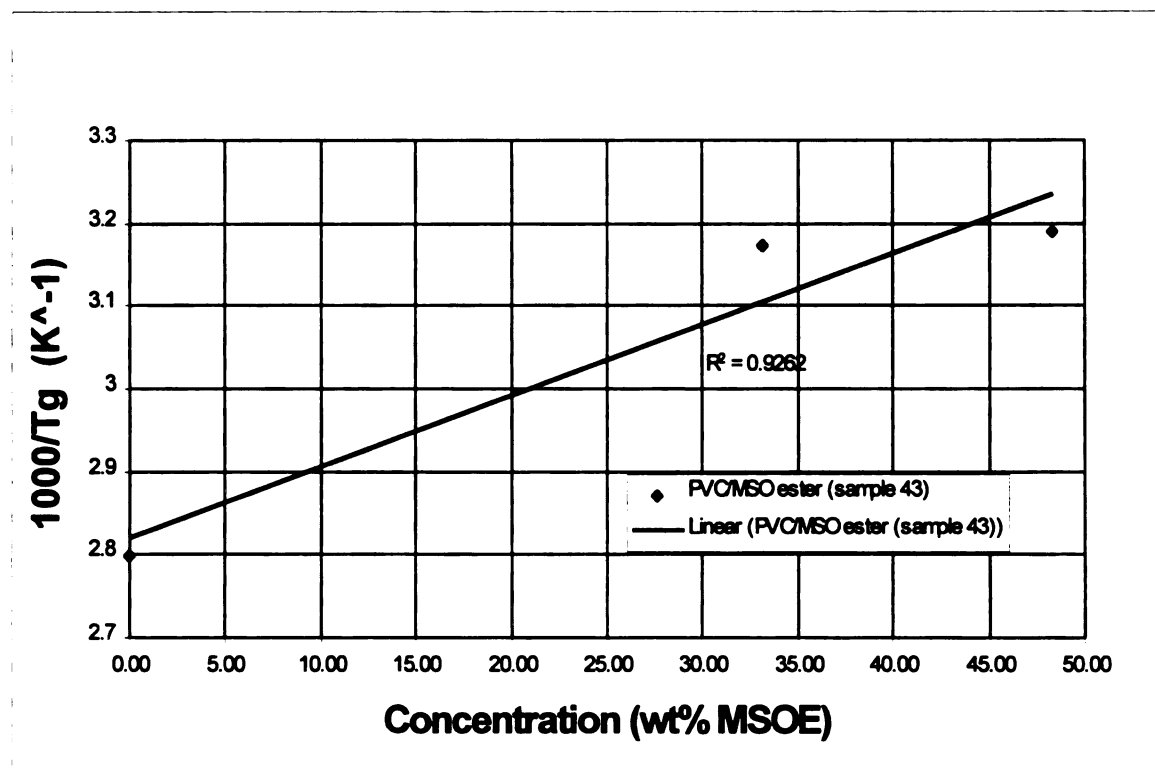
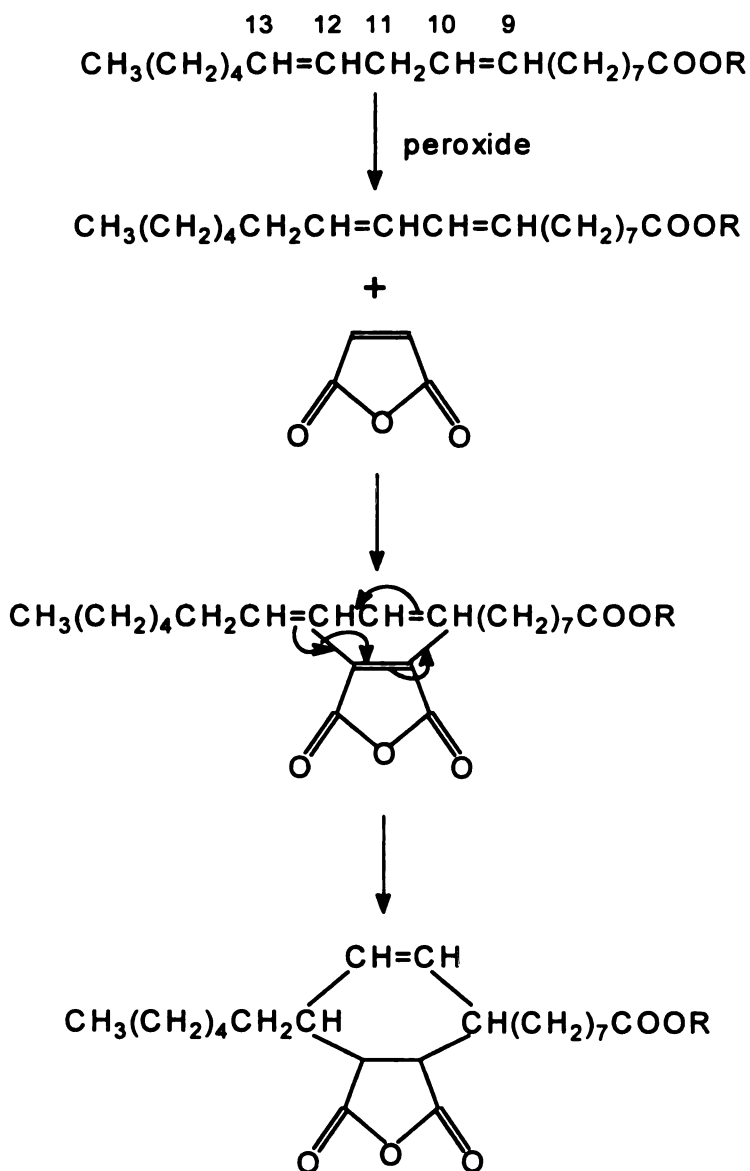


Figure 20: Differential Scanning Calorimeter results of PVC/MSO Ester (sample 44) blends

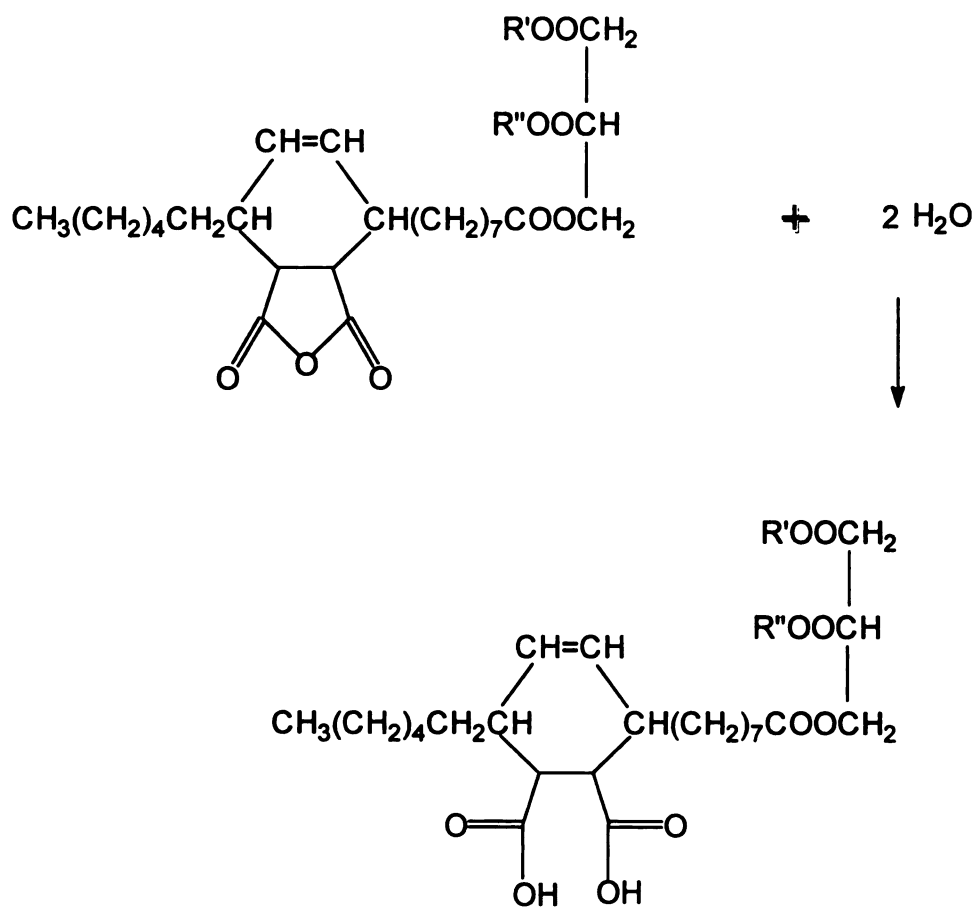
4.4 Experimental Conclusions

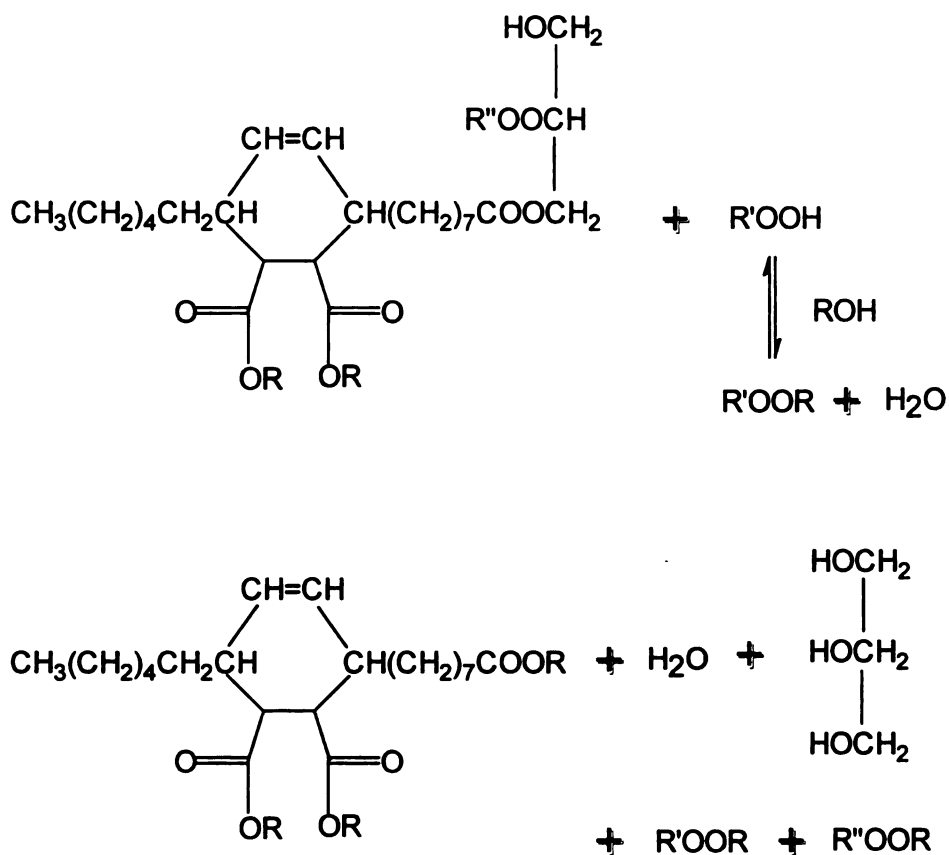
Maleated soybean oil (MSO) was produced relatively quickly and easily in the laboratory. Results of acid number, iodine number, viscosity, and FTIR show that the maleic anhydride was bonded to the soybean oil. The maleic anhydride was bonded to the soybean oil by the use of a peroxide catalyst which allowed the conjugation of double bonds and in turn allowed for a 1-4 Diels-Alder type reaction³.



Any of the afore mentioned analytical techniques can be used to determine the degree of maleation with good accuracy.

The maleated soybean oil can then be reacted with alcohols to produce an ester (MSOE), that in turn can be used as a resin plasticizer.





By-products from the mono- and diglyceride reactions may further react into light weight esters. The differential scanning calorimeter experiments showed that these “splintered” triglycerides show no real limitation in the plasticization characteristics of the overall product and perhaps may increase plasticization.

Thin layer chromatography seems to support the conclusion that a certain amount of the triglyceride is reduced to the mono- and di-glyceride state.

CHAPTER 5

PRELIMINARY PROCESS DESIGN

5.1 Continuous Process Design

A flow diagram and material and energy balances (refer to figure 22, 23, and Table 5) of a soybean maleation and a esterification process was determined from experimental data. The basis for the design was:

- 5000 ton per year of maleated soybean oil (MSO).
- 2500 ton per year of MSOE will be produced which translates into a raw material requirement of 2005 ton per year of maleated soybean oil.
- operation of 8000 hours per year.

Due to the relatively fast reaction rate of the soybean oil and maleic anhydride, a continuous stirred tank reactor could be used in the process. A reaction rate was determined from the experimental data to be $r_{MA} = (N_{MA(o)} - N_{MA}) / (t * V) = -1.9$ mol/hr*L. From the design basis the maleic anhydride feed rate was determined to be 729 gmol/hr and the conversion was determined from experiment to be approximately 90%. The volume of the continuous stirred tank reactor for the design basis would be $V = F_{MA(o)} X / -r_{MA} = 345.3$ L or 92 gallons.

Reactants will be added to the reactor from storage tanks. The soybean oil tank will be 25,000 gallons in size and constructed out of stainless steel, with an internal nitrogen atmosphere to prevent oxidation of the oil. The soybean oil will be added to the continuous reactor by a centrifugal pump, a pneumatic control valve, and flowmeter that will allow real-time process control. The catalyst tank will operate with a similar control configuration as the soybean oil tank. The maleic anhydride vessel will be placed on electronic load cells to record the loss of material gravimetrically. The maleic anhydride will be added to the reactor by a auger. The continuous reactor will be 100 gallons, constructed of stainless steel, internal baffles, external steam jacket, and mounted with a 10 horsepower motor and agitator. The temperature control will consist of a remote temperature device (RTD) that will be inserted into the reactor by the use of a stainless steel thermal well. The thermal well will allow for access to the RTD without contamination of the reactor contents. The RTD will monitor temperature and relay the information to the control computer which will adjust steam to compensate any deviation from temperature setpoint.

The maleated soybean oil will be removed from the reactor by an overflow well which will be connected to the devolatilizer. The difference in pressure from the reactor (0-5 psig) and the devolatilizer (vacuum, 0.1 atmosphere) will be the driving force for the transfer. The MSO will be depressurized through a pneumatic control valve with the flow monitored into the devolatilizer. Any residual maleic anhydride will sublime and the catalyst will evaporate and removed via a compressor. At 150 C the maleic anhydride

and catalyst will be compressed to 10 psig, a 10% purge stream removed and sewared, and the remaining reinjected into the reactor. The devolatilizer will also consist of a stainless steel mixing vessel with a steam jacket, RTD with thermal well, and a 5 horsepower agitator and assembly. The maleated soybean oil will be removed by centrifugal pump, flowmeter and control valve. The MSO will be cooled in a stainless steel, tube and shell heat exchanger to 25 C and pumped into a 25,000 gallon, stainless steel storage tank.

All control valves and meters will be piped with a bypass in the event of failure (refer to Figure 24). The bypass valves will allow for quick removal and replacement with a minimal disturbance of the overall process.

The esterification reactor volume was determined using a similar procedure as used in the maleated soybean oil reactor. The experimental alcohol reaction rate for esterification of the maleated soybean oil was determined to be 6.15, 1.88, and 0.87 mol/hr/L at 5, 30, 90 minutes, respectively. The reaction rates were graphed over time and integrated to determine the plug flow reactor volume.

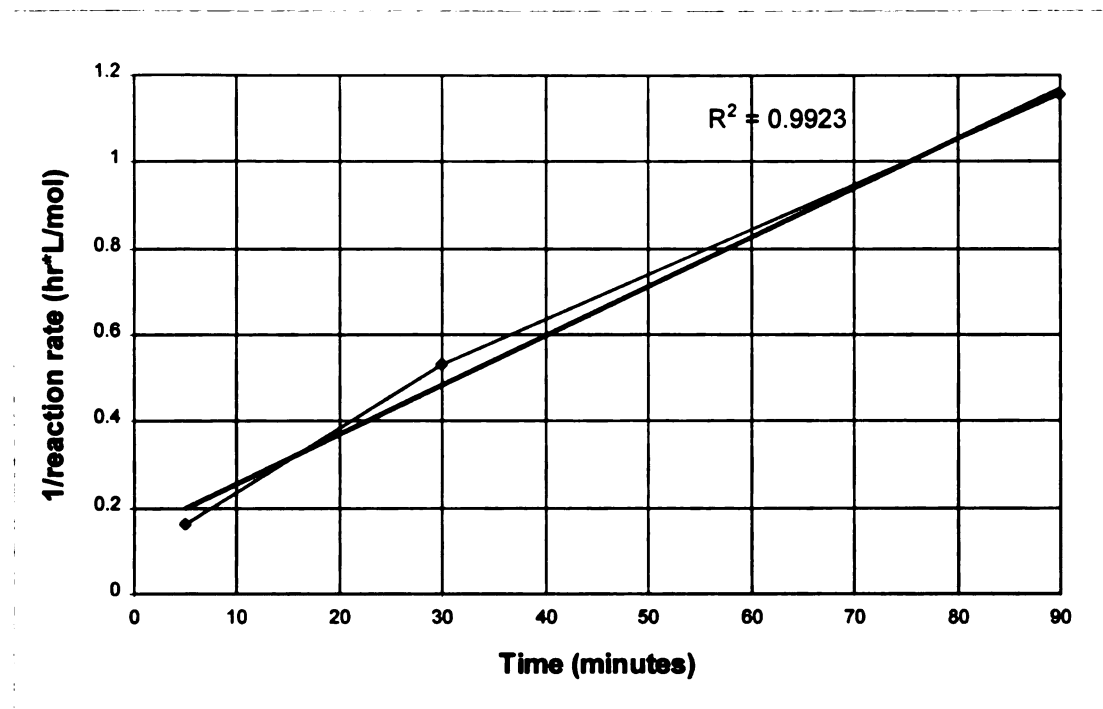


Figure 21: Esterification Reaction Rate versus Time for PFR Volume Determination

The alcohol for the esterification reaction will be set at a 20% excess to assure good esterification. The feed rate of the alcohol will be 510 gmol/hr and the conversion of alcohol will be 80%. Integration of the area beneath the curve in Figure 21 and the molar flow of the reactant will result in the PFR volume, $V = F_{MA(0)} \int dX / -r_{MA} = 458 \text{ L}$ or 122.1 gallons. This volume will equal a PFR of 6 inch diameter pipe of 83 ft in length which would be fabricated according to the given plant lay out.

A market determined amount of maleated soybean oil ester (MSOE) will be produced in an operation next to the MSO process. MSO, deionized water, and alcohol are added to a 50 gallon, stainless steel, agitated reactor. The reactor will heat the

contents to 250-300 C. The contents are then metered into a continuous stainless steel loop that will represent a plug flow reactor. The PFR will be of sufficient volume to represent a 90 minute residence time and will be well insulated to maintain a 250-300 C temperature. The MSOE and excess alcohol and water will be metered into a devolatilizer that will remove the excess alcohol and water. The alcohol and water are then condensed in a heat exchanger and sewared. The MSOE is then pumped through a heat exchanger and cooled to 20 C for storage in a 15,000 gallon stainless steel tank.

Control of the system will originate from a computer interface to the process. Flowmeters and RTDs will operate at a 4-20 mA signal which will then be interrupted by the computer into the corresponding process variables. The computer will operate a control program such as "Paragon" manufactured by Intel Inc., which can emulate a proportional, integral, derivative controller. The program will evaluate the incoming signal, evaluate, and send out the response based on PID parameters set by the plant engineers. The response signal will be transmitted to a I/P transducer which will convert the electronic signal of 4-20 mA to a pneumatic signal of 3-15 psig. The pneumatic signal will control the corresponding control valve. A pneumatic signal is desired over a electronic signal to an electric actuator because of the fire hazard associated with an electric actuator failure. The description of the control system sounds complex but offers many advantages over a manual control system. Advantages include process data collection/management, a very consistent product quality, and a minimization of operator input.

Figure 22: Continuous Process Flow Diagram of a Soybean Oil Maleation Facility

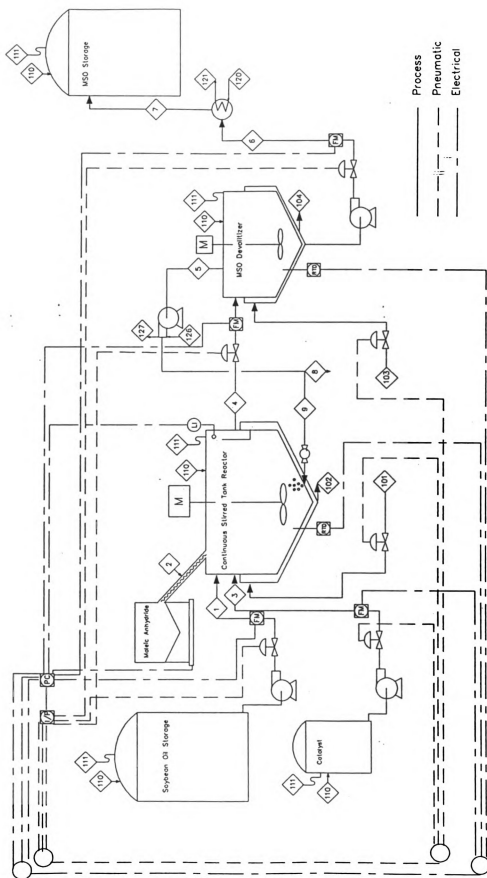


Figure 23: Continuous Process Flow Diagram of a Malated Soybean Oil Esterification Facility

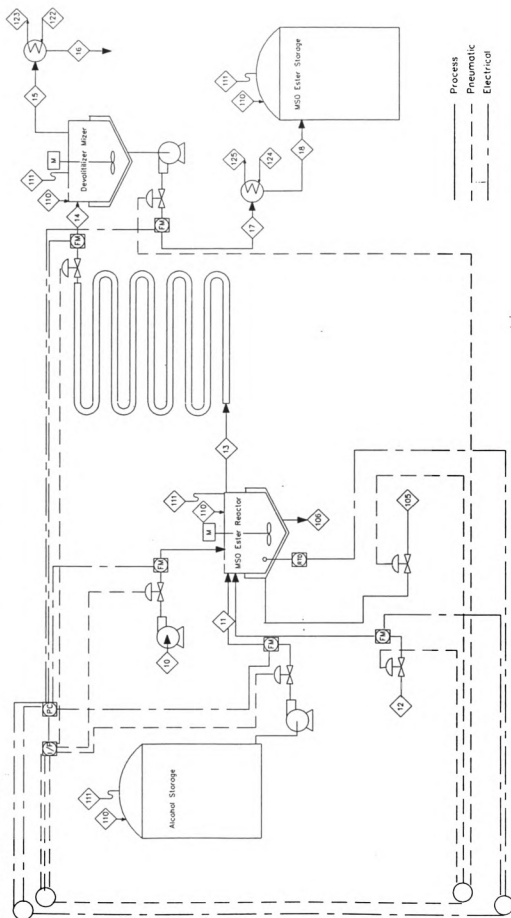


Figure 24: Process Flow Diagram of Valve, Meter, and Pump Bypasses

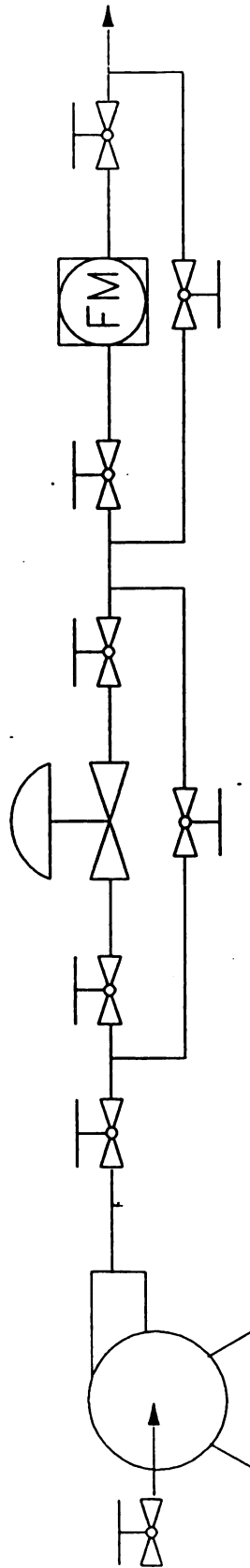


Table 5: Material and Energy Balances for a Maleated Soybean Oil Esterification Continuous Process (Cont.)

Material and Energy Balance for Maleated Soybean Oil Production
Continuous Process

Prepared by: Ken Seybold
Date: 4/1/97

Basis 10000000 #/yr
1250 #/hr
Maleation Level 0.125 #MA/#SO
Catalyst Level 0.0125 #cat./#SO
Yield 95 %

Material Balance:

Stream No.	13	14	15	16	17	18	101	102	103	104	120	121
Component (lb/hr)	MSO ester	MSO ester e	water/alch	water/alch	MSO ester	MSO ester	STM Rxn	Cond.	STM Rxn	Cond.	CWS	CWR
Assume												
Soybean Oil	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Maleic Anhydride	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Catalyst	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MSO	501.40	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Water	11.03	20.23	20.23	20.23	0.00	0.00	116.38	116.38	0.16	0.16	2343.75	2343.75
MSO ester	0.00	625.00	0.00	0.00	625.00	625.00	0.00	0.00	0.00	0.00	0.00	0.00
Alcohol	148.07	13.28	13.28	13.28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	658.51	658.51	33.50	33.50	625.00	625.00	116.38	116.38	0.16	0.16	2343.75	2343.75

Enthalpy Balance:

Stream No.	13	14	15	16	17	18	101	102	103	104	120	121
Composition	MSO ester	MSO ester e	water/alch	water/alch	MSO ester	MSO ester	STM Rxn	Cond.	STM Rxn	Cond.	CWS	CWR
Phase												
Temperature (deg C)	150	150	150	25	150	25	150	150	150	150	10	50
Pressure (psig)												
Heat of Vapor (BTU/#)	0.6	0.6	750				1185.2	290.4	1185.2	290.4		
Cp (BTU/lb-deg F)	162	162	0.4	0.4	0.6	0.6	1	1	1	1	1	1
Enthalpy (BTU/lb)	1.58E+04	1.58E+04	8.04E+02	8.04E+02	1.50E+04	1.50E+04	2.79E+03	2.79E+03	3.75E+00	3.75E+00	2.34E+03	2.34E+03
Flow Rate (lb/day)	2.58E+06	2.58E+06	6.90E+05	1.45E+04	2.43E+06	4.05E+05	3.31E+05	8.11E+05	4.44E+03	1.09E+03	4.22E+04	2.11E+05
Total Enthalpy (BTU/day)												

Table 5: Material and Energy Balances for a Maleated Soybean Oil Esterification Continuous Process (Cont.)

Material and Energy Balance for Maleated Soybean Oil Production

Continuous Process

Prepared by:

Ken Seybold

Date:

4/1/97

Basis 10000000 #/yr

Maleation Level 1250 #/hr

Catalyst Level 0.125 #MA/#SO

Yield 0.0125 #cat./#SO

95 %

Material Balance:

Stream No.	105	106	122	123	124	125	126	127
Component (lb/hr)	STM Rtn	Cond.	CWS	CWR	CWS	CWR	CWS	CWR

Assume

Soybean Oil	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Maleic Anhydride	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Catalyst	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MSO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Water	99.13	99.13	390.89	390.89	937.50	937.50	86.47	86.47
MSO ester	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Alcohol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	99.13	99.13	390.89	390.89	937.50	937.50	86.47	86.47

Enthalpy Balance:

Stream No.	105	106	122	123	124	125	126	127
Composition	STM Rtn	Cond.	CWS	CWR	CWS	CWR	CWS	CWR

Phase	V	L	150	150	10	50	10	50	10	50	10	50
Temperature (deg C)												
Pressure (psig)												
Heat of Vapor (BTU/#)	1185.2	290.4	1	1	1	1	1	1	1	1	1	1
Cp (BTU/lb-deg F)	270	270	18	18	18	18	18	18	18	18	18	18
Enthalpy (BTU/lb)	2.38E+03	2.38E+03	3.91E+02	3.91E+02	9.38E+02	9.38E+02	9.38E+02	9.38E+02	8.65E+01	8.65E+01	8.65E+01	8.65E+01
Flow Rate (lb/day)	2.82E+08	6.91E+05	7.04E+03	3.52E+04	1.69E+04	8.44E+04	1.56E+03	7.78E+03				
Total Enthalpy (BTU/day)												

5.2 Batch Process Design

Flow diagrams and material and energy balances of a batch process to produce maleated soybean oil and ester are shown in Figure 25, 26, and Table 6, respectively. The basis for the design was:

- 5000 ton per year of maleated soybean oil.
- 2500 ton per year of MSOE will be produced which translates into a raw material requirement of 2005 ton per year of maleated soybean oil.
- operation of 8000 hours per year.

Reactants will be added to the reactor from storage tanks. The soybean oil tank will be 25,000 gallons, constructed out of stainless steel, and blanketed with nitrogen to prevent oxidation of the oil. The soybean oil will be added to the batch reactor by a centrifugal pump and a manual on/off valve. The catalyst tank will operate with a similar pump and valve as the soybean oil tank. The maleic anhydride will be added to the reactor by an auger. The batch reactor will be 500 gallons, constructed of stainless steel, internal baffles, external steam jacket, and mounted with a 10 horsepower motor and agitator. The volume of the reactor allows for batches to be completed in 3 hour cycles which would include charging, reaction, and cleaning of the reactor. A temperature indicator will be inserted into the reactor by the use of a stainless steel thermal well. The thermal well will allow for access to the temperature indicator without contamination of the reactor contents. The reactor will be mounted on load cells so that the mass can be measured.

The maleated soybean oil will be removed from the reactor by a valve and pump. The MSO will be removed at the end of a run to the devolatilizer. Any residual maleic anhydride will sublime and the catalyst will evaporate and removed via a compressor. At 150 C the maleic anhydride and catalyst will be compressed to 10 psig, a 10% purge stream removed and sewared, and the remaining reinjected to the next batch run. The devolatilizer will also consist of a steam jacket and a temperature indicator for operator assisted temperature control. The maleated soybean oil will be removed by centrifugal pump. The MSO will be cooled in a stainless steel, tube and shell heat exchanger to 25 C and pumped into a 25,000 gallon, stainless steel storage tank.

A market determined amount of maleated soybean oil ester (MSOE) will be produced in an operation next to the MSO process. MSO, deionized water, and alcohol are added to a 500 gallon, stainless steel, agitated reactor. The reactor will heat the contents to 250-300 C for 60-120 minutes. The excess alcohol and water will be removed by vacuum, condensed in a heat exchanger, and sewared. The MSOE is then pumped through a heat exchanger and cooled to 20 C for storage in a 15,000 gallon stainless steel tank.

Control of the system will be by operator only. All materials will be weighed by addition to the reactor and recording the load cell measurement. Agitation will be started

and steam applied manually to the reactor jacket to bring the reactor to 150 C. The reaction will proceed for 30 to 60 minutes at 150 C. Operators will remove the reaction product from the reactor by a pump to the devolatilizer and prepare the reactor for another cycle. The reactor will then be cleaned and prepared for the next reaction. Soybean oil, maleic anhydride, and catalyst will then be heated to reaction temperature and the recycle from the devolatilizer will be added back to the reaction. The maleic anhydride and catalyst recycle pipe will be well insulated to prevent any crystallization of maleic anhydride. A check valve on the recycle line will prevent any of the reactor contents to fill the recycle pipe. A ten percent purge will be used to minimize any undesirable contaminants. The devolatilizer will be constructed of stainless steel, well insulated, a exterior steam jacket, and a agitator with motor and assembly. When the MSO has been devolatilized of the catalyst and maleic anhydride, the vessel will be adjusted to ambient pressure, and the contents removed by a pump. The MSO will be cooled to 25 C in a heat exchanger before being pumped into a storage tank.

Figure 25: Batch Process Flow Diagram of a Soybean Oil Maleation Facility

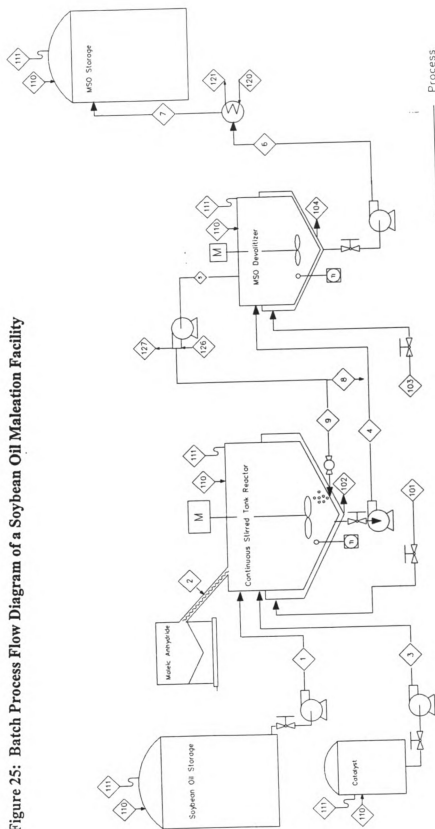
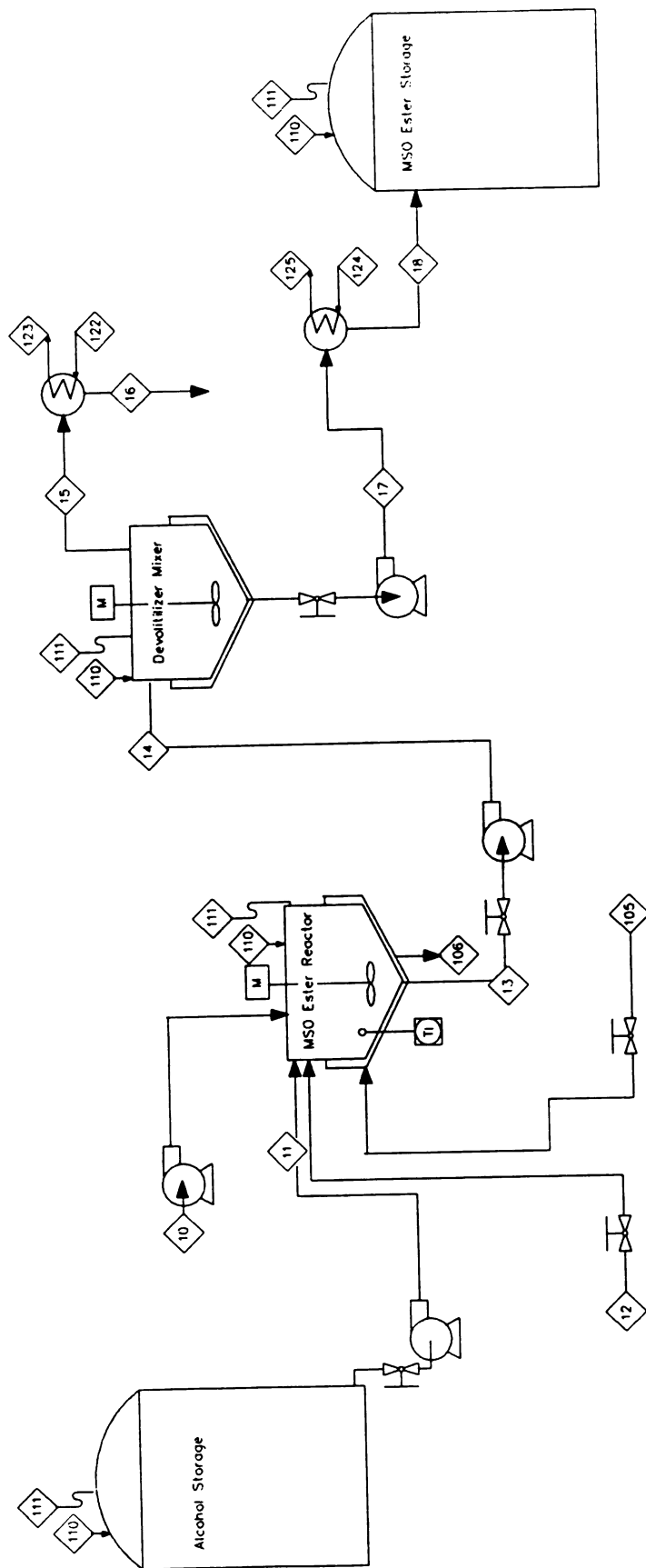


Figure 26: Batch Process Flow Diagram of a Maleated Soybean Oil Esterification Facility



_____ Process

Table 6: Material and Energy Balances for a Maleated Soybean Oil Esterification Batch Process

Material and Energy Balance for Maleated Soybean Oil Production												
Batch Process												
Prepared by:		Ken Seybold										
Date:		4/1/97										
Basis		10000000 #/yr										
Batch Capacity		3750 #/batch										
Number of Batches		2667 #										
Maleation Level		0.125 #MA/#SO										
Catalyst Level		0.0125 #cat./#SO										
Yield		95 %										
		1.11156435 mol MA/mol SO										
		Total										
		MSO										
		1.023										
Material Balance:												
Stream No.	1	2	3	4	5	6	7	8	9	10	11	12
Component (lb/batch)	SO	MA	Catalyst	Product	Vacuum	MSO	MSO	10% Purge	recycle	MSO rxn	Alcohol	DI Water
Assume												
Soybean Oil	3281.25	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Maleic Anhydride	0.00	472.17	0.00	23.61	23.61	0.00	0.00	2.36	21.25	0.00	0.00	0.00
Catalyst	0.00	0.00	21.59	21.59	21.59	0.00	0.00	2.16	19.43	0.00	0.00	0.00
MSO	0.00	0.00	0.00	3750.00	0.00	3750.00	3750.00	0.00	0.00	1504.20	0.00	0.00
Water	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	33.10
MSO ester	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Alcohol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	438.22	0.00
Total	3281.25	472.17	21.59	3795.20	45.20	3750.00	3750.00	4.52	40.68	1504.20	438.22	33.10
Enthalpy Balance:												
Stream No.	1	2	3	4	5	6	7	8	9	10	11	12
Composition	SO	MA	Catalyst	Product	Vacuum	MSO	MSO	10% Purge	recycle	MSO rxn	Alcohol	DI Water
Phase												
Temperature (deg C)	25	25	25	150	150	150	25	150	150	25	25	25
Pressure (psig)					-14.6			10	10			
Heat of Vapor (BTU/#)					222.71			222.71	222.71			
Cp (BTU/lb-deg F)	0.6	0.4	0.4	0.4	0.4	0.6	0.6	0.4	0.4	0.6	0.6	1
Enthalpy (BTU/lb)	27	18	18	108	331	182	27	331	331	27	27	45
Flow Rate (lb/batch)	7.88E+04	1.13E+04	5.18E+02	9.11E+04	1.08E+03	9.00E+04	9.00E+04	1.08E+02	9.78E+02	3.61E+04	1.05E+04	7.94E+02
Total Enthalpy (BTU/batch)	2.13E+06	2.04E+05	9.33E+03	9.84E+06	3.59E+05	1.46E+07	2.43E+06	3.59E+04	3.23E+05	9.75E+05	2.84E+05	3.57E+04

Table 6: Material and Energy Balances for a Maleated Soybean Oil Esterification Batch Process (Cont.)

Material and Energy Balance for Maleated Soybean Oil Production

Batch Process

Prepared by:

Ken Seybold

Date:

4/1/97

Basis 10000000 #/yr
 Batch Capacity 3750 #/batch
 Number of Batches 2667 #
 Maleation Level 0.125 #MA/#SO
 Catalyst Level 0.0125 #cat./#SO
 Yield 95 %

Material Balance:

Stream No.	13	14	15	16	17	18	101	102	103	104	120	121
Component (lb/batch)	MSO ester	MSO ester e	water/atch	water/atch	MSO ester	MSO ester	STM Rxn	Cond.	STM Rxn	Cond.	CWS	CWR
Assume												
Soybean Oil	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Maleic Anhydride	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Catalyst	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MSO	1504.20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Water	33.10	60.68	60.68	60.68	0.00	0.00	349.13	349.13	0.47	0.47	7031.25	7031.25
MSO ester	0.00	1875.00	0.00	0.00	1875.00	1875.00	0.00	0.00	0.00	0.00	0.00	0.00
Alcohol	438.22	39.84	39.84	39.84	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	1975.52	1975.52	100.51	100.51	1875.00	1875.00	349.13	349.13	0.47	0.47	7031.25	7031.25

Enthalpy Balance:

Stream No.	13	14	15	16	17	18	101	102	103	104	120	121
Composition	MSO ester	MSO ester e	water/atch	water/atch	MSO ester	MSO ester	STM Rxn	Cond.	STM Rxn	Cond.	CWS	CWR
Phase												
Temperature (deg C)	150	150	150	150	150	25	150	150	150	150	10	50
Pressure (psig)												
Heat of Vapor (BTU/#)			750				1185.2	290.4	1185.2	290.4		
Cp (BTU/lb-deg F)	0.6	0.6	0.4	0.4	0.6	0.6	1	1	1	1	1	1
Enthalpy (BTU/lb)	162	162	858	18	162	27	270	270	270	270	18	90
Flow Rate (lb/batch)	4.74E+04	4.74E+04	2.41E+03	2.41E+03	4.50E+04	4.50E+04	8.39E+03	8.39E+03	1.12E+01	1.12E+01	7.03E+03	7.03E+03
Total Enthalpy (BTU/batch)	7.98E+06	7.98E+06	2.07E+06	4.34E+04	7.29E+06	1.22E+06	9.93E+06	2.43E+06	1.33E+04	3.27E+03	1.27E+05	6.33E+05

Table 6: Material and Energy Balances for a Maleated Soybean Oil Esterification Batch Process (Cont.)

Material and Energy Balance for Maleated Soybean Oil Production

Batch Process

Prepared by:

Ken Seybold

Date:

4/1/97

Basis 10000000 #/yr
 Batch Capacity 3750 #/batch
 Number of Batches 2667 #
 Maleation Level 0.125 #MA/#SO
 Catalyst Level 0.0125 #cat./#SO
 Yield 95 %

Material Balance:

Stream No.	105	106	122	123	124	125	126	127
Component (lb/batch)	STM Rtn	Cond.	CWS	CWR	CWS	CWR	CWS	CWR
Assume								
Soybean Oil	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Maleic Anhydride	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Catalyst	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MSO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Water	297.38	297.38	1172.67	1172.67	2812.50	2812.50	259.41	259.41
MSO ester	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Alcohol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	297.38	297.38	1172.67	1172.67	2812.50	2812.50	259.41	259.41

Enthalpy Balance:

Stream No.	105	106	122	123	124	125	126	127
Composition	STM Rtn	Cond.	CWS	CWR	CWS	CWR	CWS	CWR
Phase	V	L						
Temperature (deg C)	150	150	10	50	10	50	10	50
Pressure (psig)	1185.2	280.4						
Heat of Vapor (BTU/#)	1	1	1	1	1	1	1	1
Cp (BTU/lb-deg F)	270	270	18	90	18	90	18	90
Enthalpy (BTU/lb)	7.14E+03	7.14E+03	1.17E+03	1.17E+03	2.81E+03	2.81E+03	2.59E+02	2.59E+02
Flow Rate (lb/batch)	8.48E+08	2.07E+08	2.11E+04	1.06E+05	5.00E+04	2.53E+05	4.67E+03	2.33E+04
Total Enthalpy (BTU/batch)								

PRELIMINARY ECONOMIC ANALYSIS

6.1 Continuous Process Economics

Table 7 lists the assumptions that were used in the economic evaluation of the proposed plant. Many of the assumptions made for non-manufacturing labor and utilities came from Peters and Timmerhaus¹². Material costs for given chemicals were determined from the current addition of Chemical Marketing Reporter¹³. The plant will produce 5000 tons per year of maleated soybean oil. Approximately 2005 ton per year of maleated soybean oil will be converted to an ester for use a resin plasticizer. The plant will operate 8000 hours per year. The total capital investment will return a rate of 15 % after taxes. The plant will operate for 10 years at which time the salvage value will be considered ten percent of the initial fixed capital investment. The depreciation will be straight-line over the 10 year period for 90% of the fixed capital investment. Labor will be paid \$15 per hour. Two operators will be required per shift for the continuous plant and six operators for the batch plant. Supervision, maintenance, and local taxes and insurance will be 8%, 7%, and 2% of fixed capital investment, respectively. Future R & D, marketing, and general, sales, administration expenses will be 5%, 5%, and 4% of total manufacturing costs, respectively.

Utility costs will be purchased at \$0.07 per Kilowatt hour for electrical power, \$2.5 per 1000 pounds of 90 psig steam, and deionized water will cost \$0.001 per pound. Cooling water will be purchased at \$0.15 per 1000 gallons, chilled water at \$0.25 per 1000 gallons and sewer will cost \$0.015 per gallon.

Purchased chemicals will cost \$0.3 per pound for soybean oil, \$0.51 per pound maleic anhydride, \$2.5 per pound for the peroxide catalyst, and \$0.925 per pound alcohol.

Table 7: Assumptions for Economic Evaluation

Built plant next to an existing bean elevator with the desired utilities

Plant capacity factor:	8000 hours per year
Maleated Soybean Oil Production	5000 ton/year
Maleated Oil Ester	2500 ton/year
Long-term return on investment:	15 percent after taxes
Depreciation:	9 percent, straight-line
Total Federal taxes:	34 percent
Working capital:	15 % Total Capital
Plant lifetime	10 years
Base rate operating labor:	\$ 15 per hour
Supervision:	8 percent fixed capital investment
Maintenance	7 percent fixed capital investment
:	
Local Taxes and Insurance:	2 percent fixed capital investment
R & D:	5 percent total manufacturing costs
Marketing:	5 percent total manufacturing costs
General, Sales, Admin. Expense:	4 percent total manufacturing costs

Utilities Costs:

Purchased electric power:	0.070	per Kwhr
Steam: 90 psig:	2.500	per 1000 pounds
DI Water:	0.0004	\$ per pound
Tower Cooling Water @ 60 F:	0.150	\$ per 1000 gallons
Chilled Water @ 10 C	0.25	\$ per 1000 gallons
Sewer:	0.015	\$ per gallon

Purchased Chemicals:

Soybean Oil	0.3 \$ per pound
Maleic Anhydride	0.51 \$ per pound
Catalyst	2.5 \$ per pound
DI Water	0.001 \$ per pound
Alcohol	0.925 \$ per pound

Table 8 shows the equipment description and cost adjusted to 1995 for the proposed process in Figures 22, 23 and 22, 23. Equipment costs (1990) were taken from Peters and Timmerhaus¹² and adjusted to 1995 using a Marshall and Swift Index¹⁴.

Table 8: Equipment List for Maleated Soybean Oil and Maleated Soybean Oil Ester

FLOW-SHEET NUMBER	EQUIPMENT DESCRIPTION	Total Cost 1995 \$
1	Reactor, 100 gal., 316-SS, w/ 10 Hp motor and mixing shaft	\$44,810
1	Agitator kettle. 50 gal., 316-SS w/ 5 Hp and mixing shaft	\$11,202
1	Soybean Oil Storage, 25000 gal., 304-SS	\$56,012
1	Maleated Soybean Oil Storage, 25000 gal., 304-SS	\$56,012
1	Catalyst Storage Tank, 250 gal., 304-SS	\$5,601
1	MSO Heat Exchanger, 10 ft ² , 316-SS	\$5,044
1	Gravimetric Feeder, 100 gal, 316-SS	\$50,436
1	Soybean Oil Feed Pump, 10 gpm, 50 ft head, 316-SS	\$2,240
1	Maleated Soybean Oil Feed Pump, 10 gpm, 50 ft head, 316-SS	\$2,240
1	Catalyst Pump, 1 gpm, 50 ft head, 316-SS	\$1,120
1	Vacuum Compressor, 150 CFM	\$16,804
1	Flow Meter	\$4,428
1	Pneumatic control valve	\$2,214
1	I/P Transducer	\$554
1	Computer w/ control program	\$16,804
2	Agitator kettle. 50 gal., 316-SS w/ 5 Hp and mixing shaft	\$22,405
2	PFR, 316-SS, 90 minute residence time	\$28,006
2	Flow Meter	\$3,321
2	Alcohol Feed Pump, 10 gpm, 50 ft head, 316-SS	\$2,240
2	DI Water Feed Pump, 10 gpm, 50 ft head, 316-SS	\$2,240
2	Maleated Soybean Oil Feed Pump, 10 gpm, 50 ft head, 316-SS	\$2,240
2	Alcohol/water condenser Heat Exchanger, 10 ft ² , 316-SS	\$5,044
2	MSE Heat Exchanger, 10 ft ² , 316-SS	\$5,044
2	Alcohol Storage, 1000 gal., 304-SS	\$5,601
2	Maleated Soybean Oil Ester Storage, 15000 gal., 304-SS	\$39,209
	Total Purchased Cost	\$390,874
	Delivery	\$19,544
	Total Cost	\$410,417

Table 9 shows the total capital investment that would be needed to construct a facility capable of producing 2500 tons of maleated soybean ester and 5000 ton per year of maleated soybean oil (2995 tons per year to be sold for cast film production). All costs are industrial averages for new plant fabrication based on work by Peters and Timmerhaus¹².

The total capital investment is calculated using the equipment cost as a basis and industrial averages for needed accessories. The equipment installation is 39% of equipment cost, instrumentation and controls installation will be 13% of the equipment cost, piping will be 31% of the equipment cost. Electrical, buildings, and yard improvements will be considered 10%, 29%, and 10% of equipment costs, respectively. Installed service facilities and land will be considered 55% and 6% of equipment costs, respectively. Indirect costs such as engineering and supervision, and construction expenses will be 32% and 34% of equipment costs. Contractor's fees and contingency will be 5% and 10% of direct and indirect costs. The above mentioned expenses will be defined as fixed capital investment. The working capital will be 15% of the total capital investment. The total capital investment will be the fixed capital investment and working capital.

Table 9: Total Capital Investment for a Maleated Soy Oil and Ester Production Facility¹²

<i>Production Plant Capacity (MSO)</i>	10,000,000 #/yr
<i>(MSOE)</i>	5,000,000 #/yr
Direct	Estimated \$
Costs:	
Purchased Equipment:	410,417
Purchased Equipment installation	160,063
Instrumentation and controls (installed)	53,354
Piping (installed)	127,229
Electrical (installed)	41,042
Buildings (including services)	119,021
Yard Improvements	41,042
Service facilities (installed)	225,730
Land (if purchase is required)	24,625
Total direct plant cost	1,202,523
Indirect Costs:	
Engineering and supervision	131,334
Construction expenses	139,542
Total direct and indirect plant costs	270,876
Contractor's fee (5% of direct and indirect plant costs)	73,875
Contingency (10 % of direct and indirect plant costs)	147,750
Fixed Capital Investment	1,695,024
Working Capital	
Working Capital (~15% of TCI)	
Total Working Capital	299,122
Total Capital Investment	1,994,146

Table 10 shows a manufacturing cost breakdown of the proposed production facility. Included in Table 10 are the variable and material for the facility, determined from mass and energy balances of Table 5. The fixed costs include process operators at 2 per shift for the required 8000 hour year. Supervision, maintenance, depreciation, and local taxes and insurance will be 8%, 7%, 10%, and 2% of the fixed capital investment. R & D,

Marketing, and GS & A are 5%, 5%, and 4% of total manufacturing costs, respectively.

It should be noted that the manufacturing cost is most sensitive to the cost of the raw materials. Energy and labor costs are fair less then the cost of raw materials.

Table 10: Manufacturing Cost Breakdown of a 2500 ton/yr MSO Ester and 5000 ton/yr MSO

	\$/unit	Quantity year	Cost \$/year
Variable Cost (excluding material cost)			
Utilities (unit)			
Steam: 90 psig (1000 lb)	2.5	1725281	4,313
Industrial Water (1000 gal)	0.75	1000000	750
Chilled Water (1000 gal)	0.25	30068898	7,517
Sewer (gal)	0.015	2000000	30,000
Electricity (Kwhr)	0.07	50557	5,308
Total Variable Costs			47,889
Material Cost			
Soybean Oil	0.3	8750000	2,625,000
Maleic Anhydride	0.51	1259129	642,156
Catalyst	2.5	57566	143,914
DI Water	0.001	88257	88
Alcohol	0.925	1168588	1,080,944
Total Material Cost			4,492,103
Fixed Costs			
Labor, 2 person/shift	2	15	8000
Supervision (8% FCI)			135,602
Maintenance (7% FCI)			118,652
Depreciation (10% Salvage, 9% FCI)			152,552
Local Taxes and Insurance (2% FCI)			33,900
Total Fixed Costs			680,706
Total manufacturing cost			5,220,698
R & D (5% TMC)			261,035
Marketing (5% TMC)			261,035
General, Sales, Administration Expense (4% TMC)			208,828
Total operating cost			5,951,595

Table 11 shows the selling price of the maleated soy oil and the ester at 15 percent return on investment. The selling prices were determined from the total operating cost plus the required return and principal divided by the annual production of maleated soy oil and

ester. Using this approach the selling price of the maleated soybean oil consists of a portion of the alcohol costs associated in producing the ester.

Table 11: Estimated Selling Price of Maleated Soy Oil and Maleated Soy Oil Ester at 15% Return on Investment

Minimum Selling Price MSO = \$ (ROI = 15%)	0.5989
Minimum Selling Price MSOE = \$ (ROI = 15%)	0.7174

Note the cost of the maleated soybean oil ester at 15 % return on investment is \$0.717 \$/# compared to DOP at 0.52 \$/# and epoxidized soybean oil of \$1.1-1.3/#. The large difference in maleated versus epoxidized soybean oil is due to the reduction in process difficulty.

6.2 Batch Process Economics

The assumptions for the batch process are identical to the continuous process with one exception. The reactor size will allow for 3750 pounds of MSO to be produced in one reaction. The reactor capacity will allow for a three hour cycle time for the MSO reactor with 2,667 reactions per year to produce the desired ten million pound per year production.

Table 12 shows the equipment description and 1995 cost estimate the proposed batch process in Figures 25, 26, and Table 6. Equipment costs (1990) were taken from Peters and Timmerhaus¹² and adjusted using a Marshall and Swift Index¹⁴.

Table 12: Equipment List for Maleated Soybean Oil and Maleated Soybean Oil Ester

FLOW-SHEET NUMBER	EQUIPMENT DESCRIPTION	Total Cost 1995 \$
1	Reactor, 500 gal., 316-SS, w/ 10 Hp motor and mixing shaft	\$112,025
1	Agitator kettle, 500 gal., 316-SS w/ 5 Hp and mixing shaft	\$89,620
1	Soybean Oil Storage, 25000 gal., 304-SS	\$56,012
1	Maleated Soybean Oil Storage, 25000 gal., 304-SS	\$56,012
1	Catalyst Storage Tank, 250 gal., 304-SS	\$5,601
1	MSO Heat Exchanger, 10 ft ² , 316-SS	\$5,044
1	Maleic Feeder, 100 gal, 316-SS	\$50,436
1	Soybean Oil Feed Pump, 10 gpm, 50 ft head, 316-SS	\$2,240
1	Maleated Soybean Oil Feed Pump, 10 gpm, 50 ft head, 316-SS	\$2,240
1	Catalyst Pump, 1 gpm, 50 ft head, 316-SS	\$1,120
1	Vacuum Compressor, 150 CFM	\$16,804
2	Reactor, 500 gal., 316-SS, w/ 10 Hp motor and mixing shaft	\$112,025
2	Agitator kettle, 500 gal., 316-SS w/ 5 Hp and mixing shaft	\$89,620
2	Alcohol Feed Pump, 10 gpm, 50 ft head, 316-SS	\$2,240
2	DI Water Feed Pump, 10 gpm, 50 ft head, 316-SS	\$2,240
2	Maleated Soybean Oil Feed Pump, 10 gpm, 50 ft head, 316-SS	\$2,240
2	Alcohol/water condenser Heat Exchanger, 10 ft ² , 316-SS	\$5,044
2	MSOE Heat Exchanger, 10 ft ² , 316-SS	\$5,044
2	Alcohol Storage, 1000 gal., 304-SS	\$5,601
2	Maleated Soybean Oil Ester Storage, 15000 gal., 304-SS	\$39,209
	Total Purchased Cost	\$660,418
	Delivery	\$33,021
	Total Cost	\$693,439

Table 13 shows the total capital investment that would be needed to construct a facility capable of producing 2500 tons of maleated soybean ester and 2995 tons of maleated soybean oil for cast film production. All costs are industrial averages for new plant fabrication based on work by Peters and Timmerhaus¹².

Table 13: Total Capital Investment for a Maleated Soy Oil and Ester Production Facility¹²

<i>Production Plant Capacity (MSO) (MSOE)</i>	<i>10,000,000 #/yr 5,000,000 #/yr</i>
Direct Costs:	Estimated \$
Purchased Equipment:	693,439
Purchased Equipment installation	270,441
Instrumentation and controls (installed)	90,147
Piping (installed)	214,966
Electrical (installed)	69,344
Buildings (including services)	201,097
Yard Improvements	69,344
Service facilities (installed)	381,391
Land (if purchase is required)	41,606
Total direct plant cost	2,031,775
Indirect Costs:	
Engineering and supervision	221,900
Construction expenses	235,769
Total direct and indirect plant costs	457,670
Contractor's fee (5% of direct and indirect plant costs)	124,819
Contingency (10 % of direct and indirect plant costs)	249,638
Fixed Capital Investment	2,863,902
Working Capital	
Working Capital (~15% of TCI)	
Total Working Capital	505,394
Total Capital Investment	3,369,296

Table 14 shows a manufacturing cost breakdown of the proposed production facility. Included in Table 14 are the variable, material, and fixed costs for the facility determined from mass and energy balances of Table 25, 26, and Table 6. Additional labor was included in the batch process, 6 persons per shift, compared to the continuous process which used just 2 operators per shift. The manufacturing cost of the batch process is still most sensitive to the cost of the raw materials. Energy and labor costs are fair less then the cost of raw materials.

Table 14: Manufacturing Cost Breakdown of a 2500 ton/yr MSO Ester and 5000 ton/yr MSO

	\$/unit	Quantity year	Cost \$/year
Variable Cost (excluding material cost)			
Utilities (unit)			
Steam: 90 psig (1000 lb)	2.5	2417040	6,043
Industrial Water (1000 gal)	0.75	1000000	750
Chilled Water (1000 gal)	0.25	30068898	7,517
Sewer (gal)	0.015	2000000	30,000
Electricity (Kwhr)	0.07	50557	5,308
Total Variable Costs			49,618
Material Cost			
Soybean Oil	0.3	8750000	2,625,000
Maleic Anhydride	0.51	1259129	642,156
Catalyst	2.5	57566	143,914
DI Water	0.001	88257	88
Alcohol	0.925	1168588	1,080,944
Total Material Cost			4,492,103
Fixed Costs			
Labor, 2 person/shift	6	15	8000
Supervision (8% FCI)			229,112
Maintenance (7% FCI)			200,473
Depreciation (10% Salvage, 9% FCI)			257,751
Local Taxes and Insurance (2% FCI)			57,278
Total Fixed Costs			1,484,614
Total manufacturing cost			6,006,335
R & D (5% TMC)			300,317
Marketing (5% TMC)			300,317
General, Sales, Administration Expense (4% TMC)			240,253
Total operating cost			6,847,222

Table 15 shows the selling price of the maleated soy oil and the ester at 15 percent return on investment. The selling prices were determined from the total operating cost plus the required return and principal divided by the annual production of maleated soy oil and ester.

Table 15: Estimated Selling Price of Maleated Soy Oil and Maleated Soy Oil Ester at 15% Return on Investment

Minimum Selling Price MSO = \$ (ROI = 15%)	0.7441
Minimum Selling Price MSOE = \$ (ROI = 15%)	0.8912

Note the cost of the maleated soybean oil ester produced by the batch process at 15 % return on investment is \$0.891 \$/# compared to the continuous process MSO ester at 0.717 \$/#. The large difference in the batch versus continuous process maleated ester is due to increased labor force and total capital investment. The selling price depends a great deal on the purchase price of the proposed equipment. Therefore, the purchase of used equipment rather than new could greatly reduce the equipment costs and thus reduce the required selling price of the products.

6.3 Determination of the Internal Rate of Return by a Discounted Cash Flow

In industrial operations, it is often possible to produce equivalent products in different ways. The method for a profitability evaluation by discounted cash flow takes into account the time value of money and is based on the amount of the investment that is unreturned at the end of each year during the estimated life of the project. A trial-and-

error procedure is used to determine a rate of return which can be applied to annual cash flow so that the original investment is reduced to zero or to salvage and land value plus working capital. Thus, the rate of return by this method is equivalent to the maximum interest rate (normally after taxes) at which money could be borrowed to finance the project under conditions where the net cash flow to the project over its life would be just sufficient to pay all principal and interest accumulated on the outstanding principal. The specific discount method used in this thesis is a net present worth or a venture worth method. All discount factors used are continuous.

As a basis for this method the selling price of the maleated soybean oil and the ester were set at \$ 0.6/# and \$ 0.8/#, respectively. The capacity was held constant at 2995 ton/year of maleated soybean oil and 2500 ton/year maleated soybean oil ester. The cash flow was then determined using the given capacity and selling price of each product. The land, fixed capital cost minus the land, working capital, salvage, and cash flow were then used to determine a discounted cash flow.

Determination of cash position at zero time must be calculated in terms of the unknown profitability index r .

The land will be purchased one year before the zero reference point of plant start-up. Therefore, the land value at zero time is the future worth after one year with continuous compounding, e^r .

The total construction cost in this case is the fixed capital investment minus the land purchase and will occur one year before plant start-up in a uniform series over that year. The compounded construction cost at zero time, therefore, is the future worth after one year flowing uniformly throughout the year with continuous compounding, $(e^r - 1)/r$.

The working capital investment must be supplied at the time of plant start-up or at the reference point of zero time.

The resulting cash position at the reference point will be:

$$CP_{\text{zero time}} = \text{Land} (e^r) + \text{Construction} (e^r - 1)/r + \text{working capital}$$

After plant start-up, the annual cash flow to the project (net profit plus depreciation) will flow continuously and uniformly at a constant annual level through the life of the project. At the end of each year, the compounded cash flow to the project, with continuous flow and continuous compounding will be:

$$S_{\text{cash flow, annual}} = \text{Cash Flow} (e^r - 1)/r$$

At the end of 10 years, the total future worth (S) of the cash flows to the project becomes

$$(A) \quad S = \text{Cash Flow} (e^r - 1)/r (e^{9r} + e^{8r} + e^{7r} + \dots + e^r + 1)$$

The future worth of the total flow to the project after 10 years must be equal to the future worth of the total cash position at zero time ($CP_{\text{zero time}}$) compounded continuously for 10 years minus the salvage value, land value, and working capital investment.

$$(B) \quad S = (CP_{\text{zero time}})(e^{10r}) - \text{Salvage} - \text{Land} - \text{Working Capital}$$

Equating equation (A) and (B) gives the following result with r as the only unknown, and a trial-and-error solution will give the profitability index r .

$$\text{Cash Flow } (e^r - 1)/r (e^{9r} + e^{8r} + e^{7r} + \dots + e^r + 1) - (CP_{\text{zero time}})(e^{10r}) + \text{Salvage} + \text{Land} + \text{Working Capital} = 0$$

This equation can be simplified by dividing by e^{10r} and substituting the expression for $CP_{\text{zero time}}$ to give the present value or discounted cash flow equation as follows:

$$\text{Cash Flow } (e^r - 1)/r (e^{9r} + e^{8r} + e^{7r} + \dots + e^r + 1)(1/e^{10r}) - (\text{Land } (e^r) + \text{Construction } (e^r - 1)/r + \text{Working Capital}) + (\text{Salvage} + \text{Land} + \text{Working Capital})(1/e^{10r}) = 0$$

For the case of continuous cash flow and interest compounding:

$$(e^r - 1)/r (e^{9r} + e^{8r} + e^{7r} + \dots + e^r + 1) = (e^m - 1)/re^m$$

The resulting discounted equation:

$$(C) \quad \text{Cash Flow } (e^m - 1)/re^m (1/e^{10r}) - (\text{Land } (e^r) + \text{Construction } (e^r - 1)/r + \text{Working Capital}) + (\text{Salvage} + \text{Land} + \text{Working Capital})(1/e^{10r}) = 0$$

Equation (C) is then used to determine the profitability or internal rate of return of the proposed process'.

The assumed values that were used for this calculation are given below.

Table 16: Discounted Cash Flow Assumptions

Item	Continuous	Batch
Project Life, n, years	10	10
MSO Capacity, #/yr	5,990,000	5,990,000
MSOE Capacity, #/yr	5,000,000	5,000,000
Selling Price MSO, \$/#	0.6	0.6
Selling Price MSOE, \$/#	0.8	0.8
Land, \$	24,625	41,606
Construction of FCI-land, \$	1,670,399	2,822,295
Working Capital, \$	299,122	505,394
Salvage, \$	167,040	282,230
Cash Flow,\$/yr	1,031,012	403,693

Equation (C) was then used by trial and error with the above assumptions to produce the diagrams of the net present value. The internal rate of return is the point at which the net present value is equal to zero. This rate of return is equivalent to the maximum interest rate (normally after taxes) at which money could be borrowed to finance the project under conditions where the net cash flow to the project over its life would be just sufficient to pay all principal and interest accumulated on the outstanding principal.

Figure 27 shows several different discounted rates and the net present value as determined from equation (C) for the proposed continuous process. The internal rate of return for the proposed continuous process with the assumptions of Table 16 is approximately 53 percent.

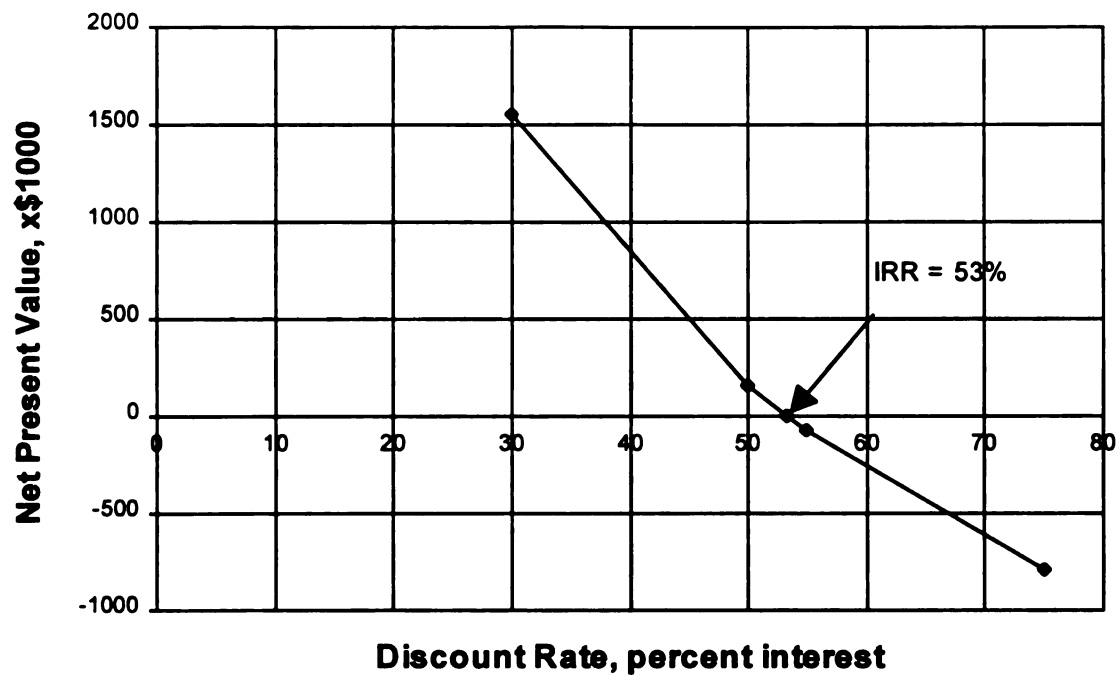


Figure 27: Determination of the Internal Rate of Return by a Discounted Cash Flow for the Proposed Continuous Process

Figure 28 shows several different discounted rates and the net present value as determined from equation (C) for the proposed batch process. The internal rate of return for the proposed batch process, with the assumptions of Table 16, is approximately 6.7 percent.

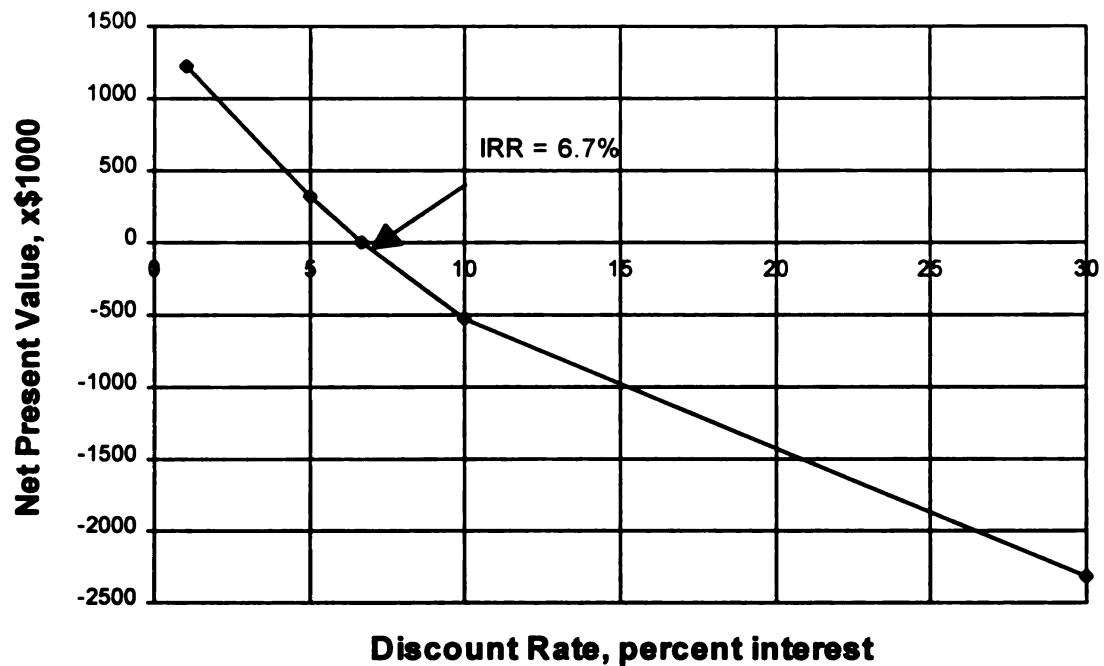


Figure 28: Determination of the Internal Rate of Return by a Discounted Cash Flow for the Proposed Batch Process

The resulting internal rates of return of the two proposed process' show that a continuous process would generate a higher return than the batch process given the selling price of the products. Therefore, the best alternative process is the continuous and not a batch production facility. The reason that the batch process is far less profitable is the high cost of the land, construction, working capital and the low annual cash flow compared to the continuous process.

6.4 Sensitivity and Production Capacity Analysis

The assumptions made for the sensitivity analysis were:

- Production capacity of 5 million pounds per year maleated soy ester and 5.9 million pounds per year maleated soybean oil.
- Condition of zero reflects the proposed economical analysis of 6.1, the proposed continuous process.
- Return on Investment of 15%.

A sensitivity analysis of the maleated soybean oil's selling price to variations in key manufacturing cost variables is shown in Figure 29.

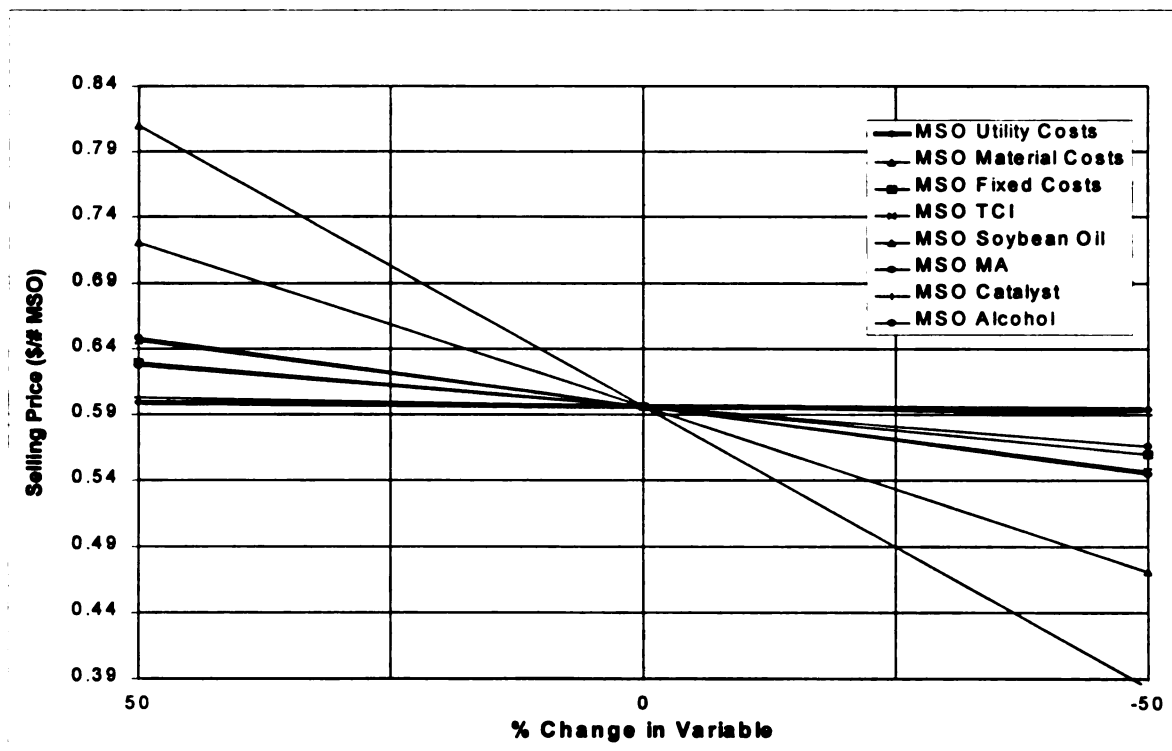


Figure 29: Sensitivity Analysis of the Selling Price of Maleated Soybean Oil at 15 % ROI

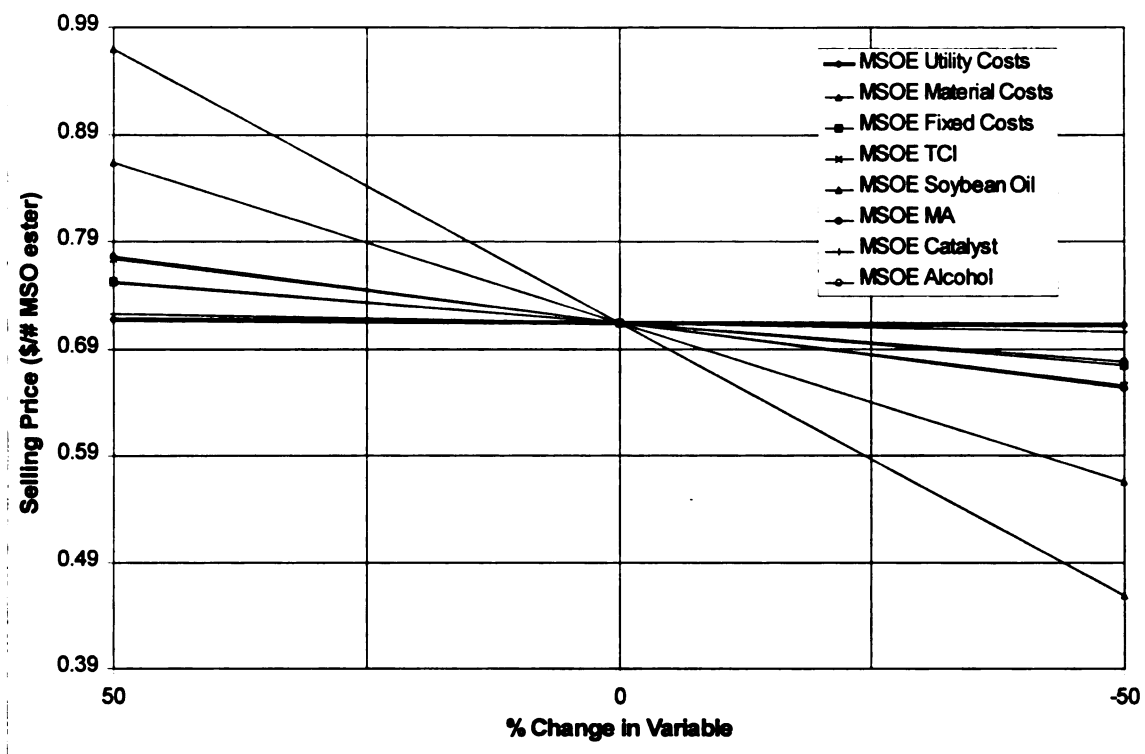


Figure 30: Sensitivity Analysis of the Selling Price of Maleated Soybean Oil Ester at 15 % ROI

Both the maleated soybean oil and ester exhibit a high sensitivity in selling price to variations in material cost, in particular to soybean oil. Variation in other quantities such as utility and fixed costs, exhibit little effect on the selling price of the two products because of the low energy and labor costs associated with the proposed process.

Figure 31 shows similar results for the process that only produces maleated soybean oil. Note the reduction in selling price for maleated soybean oil from a process that only produces maleated soy oil (\$ 0.59/# MSO) to a process that also produces the

soy ester (\$0.60/# MSO). This reduction in selling price can mainly be attributed to no cost associated with the alcohol needed for esterification.

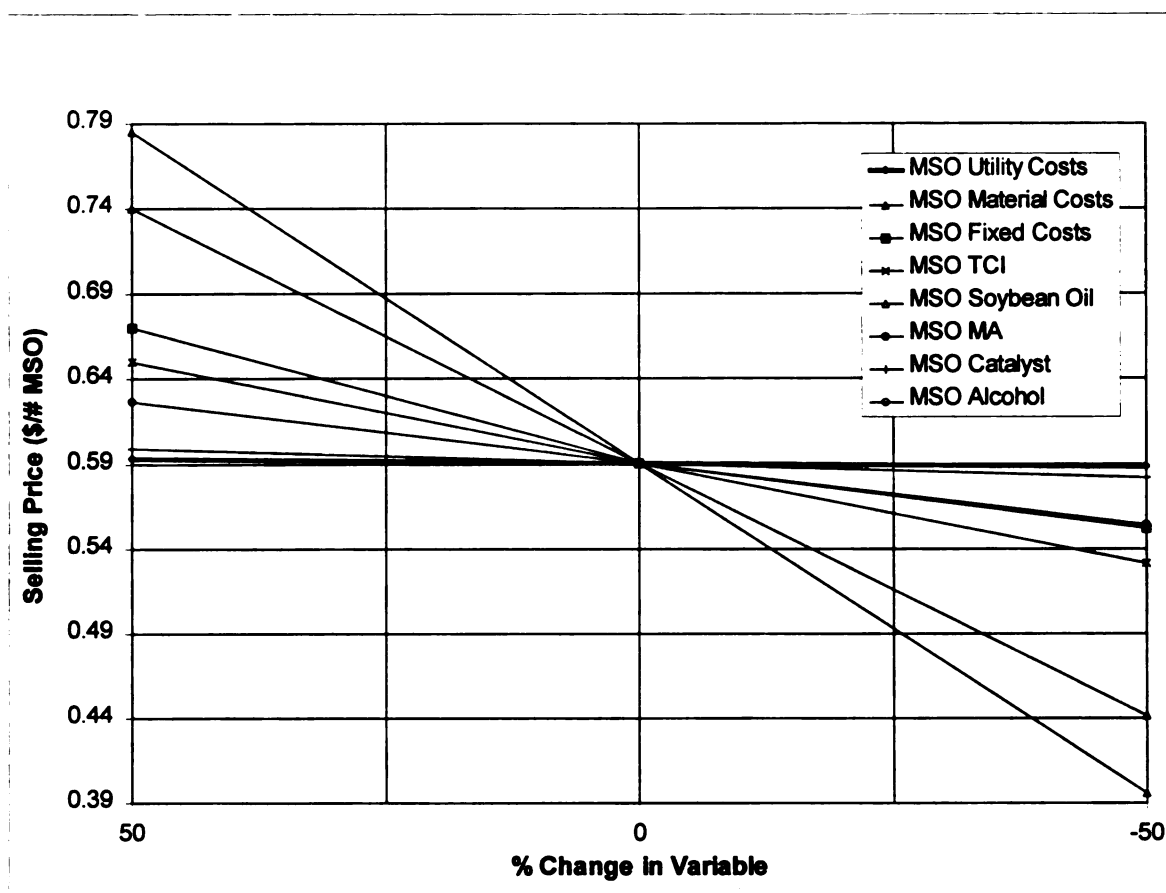


Figure 31: Selling Price of Maleated Soybean Oil at 15% ROI (Plant Capacity = 100% MSO)

Figure 32 shows a sensitivity analysis of a process that produces only maleated soybean oil ester. In the case of a process producing only maleated soy oil ester there will be an increase in selling price (\$0.721/# MSO ester) over a process that can sell both products (\$0.7143/# MSO ester). The process that can sell two products can distribute the extra material cost over two products instead of just the one.

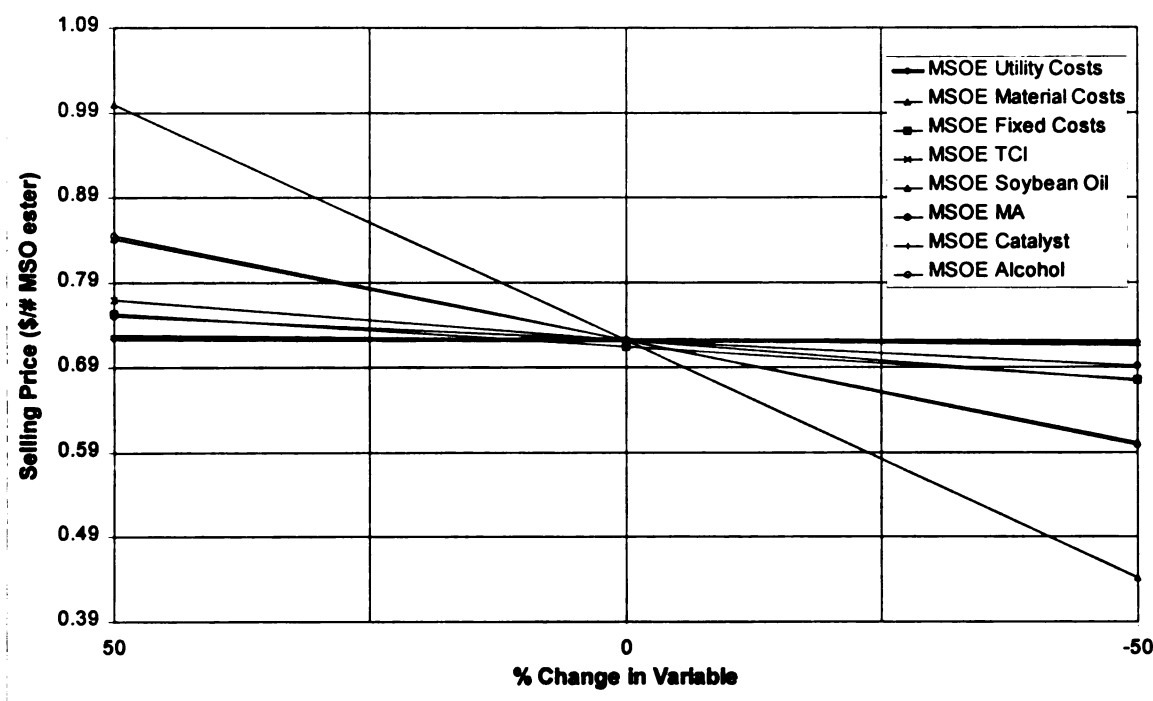


Figure 32: Selling Price of Maleated Soybean Oil Ester at 15% ROI (Plant Capacity = 100% MSO)

The most important conclusion that can be drawn from this type of analysis is the high sensitivity of the selling price to the price of soybean oil. Therefore, profit margins for the selling price of the products should be set high enough, so that an increase in soybean oil price does not adversely effect the profitability of the proposed process.

Production capacity is also an important variable to determine the optimum size of plant. This analysis will investigate the selling price that can be achieved for the incremental increase in manufacturing cost and capital investment.

Table 17 shows the change in product selling price (at 15% ROI) versus the production capacity.

Table 17: Comparison of MSO and MSO ester Selling Price versus Production Capacity

Capacity (x M# MSO)	MSO	MSOE
1	1.03	1.23
10	0.6	0.72
100	0.492	0.59
1000	0.456	0.55

The change in selling price of the products are due to the slower increase in equipment cost versus the faster increase in production from such equipment. Equipment cost will roughly follow the 0.6 rule of scaling, shown below.

$$\text{Cost of Equipment B} = \text{Cost of Equipment A} * (\text{Capacity B/Capacity A})^{0.6}$$

This equation was used to determine the various equipment costs and then the total capital investments shown in Table 18.

Table 18: Comparison of Production Capacity versus Total Capital Investment

Capacity (xM# MSO)	Total Capital Inv.
1	0.506
10	1.99
100	7.87
1000	31.11

Table 19 shows the change in manufacturing cost versus the production capacity.

Table 19: Comparison of Production Capacity versus Manufacturing Cost

Capacity (xM# MSO)	Manf. Cost
1	2.17
10	5.24
100	48.8
1000	462.7

From tables 17-19 the comparisons show that at a capacity of ten million pounds per year, a sizable reduction in the selling price of the products can be achieved with a moderate increase in both the total capital investment and manufacturing cost. From the ten million pounds per year capacity, significant increases in total capital investment and manufacturing costs would only result in a small decrease in the product selling price. Therefore, ten million pounds per year production facility would be the optimum size given the limited knowledge of market share displacement and availability of capital investment.

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

The proposed continuous process offers a more economical route for maleated soybean oil and ester products over the alternative batch process. The continuous process was found to have a selling price (15% ROI) of maleated soybean oil and ester of \$0.61 and \$0.71 per pound compared to \$0.75 and \$0.89 for the batch process, respectively. A discounted cash flow of the continuous and batch process designs (at a selling price of maleated soy oil of \$ 0.6 per pound and \$ 0.8 per pound for the ester) revealed an internal rate of return of 53% and 7%, respectively.

The continuous process offers a number of important advantages for soybean oil.

- The process will add value to soybean oil, thus improving the soybean market for American farmers.
- The addition of maleic anhydride to soybean oil is a low temperature reaction thus reducing oil oxidation problems and the need for exotic equipment design in a large scale process.
- The maleation process is less hazardous and energy intensive than the current process for the production of epoxidized soybean oil.
- The process is continuous, thereby minimizing processing time while maximizing process reliability.

- The proposed process automation will require a minimum of operator control and judgment.
- The new low-cost process can be retrofitted in an existing production facility.

The maleated soybean oil ester was found to have a good plasticization capability for poly vinyl chloride. The attractive selling price coupled with its non-toxic and low ability to leach will make maleated soybean oil ester very competitive with dioctyl phthalate. Though the price of dioctyl phthalate is lower than maleated soybean oil ester, dioctyl phthalate is considered toxic and can leach under various conditions. The selling price of maleated soybean oil ester could be further reduced if used equipment rather than new equipment could be purchased. Therefore, a small displacement of dioctyl phthalate's market (estimated at 1.0×10^9 metric tons per year) could generate a terrific opportunity for maleated soybean oil esters.

7.2 Recommendations

Further research should incorporate three thrusts of optimizing the soybean oil/maleic anhydride reaction, developing coating formulations suitable for industrial applications, and suitability of maleated soy oil ester as a resin plasticizer. Closely integrating these thrusts will facilitate more rapid progress and a better overall understanding of the commercialization potential of modified soybean oil. The specific objectives of further research:

- (1) Design, fabricate, and operate a pilot scale plant to produce maleated soybean oil and ester at optimum conversion for extended periods of time.
- (2) Develop in detail the continuous modification of soybean oil by maleic anhydride and ester maleate.
- (3) Esterify maleated soybean oil with an alcohol to produce a novel plasticizer
- (4) Formulate modified soybean oil coating materials.
- (5) Characterize reaction with maleic anhydride, soybean oil, and peroxide.

Details of the research to be conducted in pursuit of the above objectives follow in the next section.

7.2.1 Task 1: Design, Fabrication, and Operation of a Pilot-Scale Production Line

The objectives of this task are to design, fabricate, and operate a pilot-scale process to produce maleated soybean oil and ester. The maleated soybean oil and ester pilot-process will be similar to Figures 22 and 23 for the plant design. The information gathered from the pilot plant will allow for the optimization of unit operations and the elimination of any process flow bottle necks. The data from the pilot plant would be vital for process scale-up.

7.2.2 Task 2: Modification of soybean oil

The addition of maleic anhydride to soybean oil should be a continuous process. Also to be tested would be the use of an ester maleate and catalyst to produce the maleated ester directly. The optimization of reaction temperature, duration, and ratio of maleic anhydride to soybean oil should be within the following ranges:

- Reaction temperature: 100°C ---150°C.
- Reaction duration : 10 minutes to 1 hours.
- Ratio of maleic anhydride/ soybean oil: 0.1/1.0 to 2.0/1.0.

Additional comparisons of vacuum operation, nitrogen purge, and addition of oxidation inhibitors should be performed. The goal would be to produce high functionality and low bulk viscosity, and reduce or eliminate oxidation of double bonds in soybean oil during the modification. Results in this thesis indicated that by increasing the extent of maleation, the bulk viscosity of modified soybean oil increases. It is possible that oxidative crosslinking of double bonds in soybean oil occurs during the modification. Suitable inhibitors should be added to prevent oxidation of double bonds.

Characterization of the modified soybean oil should include the determination of acid value (carboxyl group content), acid anhydride content, bulk viscosity, iodine value, percent unreacted maleic anhydride, molecular weight and molecular weight distribution of modified and unmodified soybean, and FTIR and NMR spectroscopy.

7.2.3 Task 3: Esterification of maleated soybean oil

The maleated soybean oil should be modified using an alcohol that would produce the best plasticization capability of the resulting ester. Plasticization should be determined using a differential scanning calorimeter (ASTM # D3418-82) to scan various concentrations of the ester in poly vinyl chloride. Reaction temperature, duration, and ratio of alcohol and water to maleated soybean oil should be optimized within the following ranges:

- reaction temperature: 200°C ---300°C.
- reaction duration : 1 minutes to 3 hours.
- ratio of alcohol and water/maleic content in the maleated soybean oil: 0.5/1.0 to 2.5/1.0.

Additional comparisons of vacuum operation, nitrogen purge, and addition of oxidation inhibitors should be performed. The goal would be to produce high esterification at high alcohol conversion and reduce or eliminate oxidation of double bonds in soybean oil during the modification.

Characterization of the modified soybean oil should include the determination of acid value (carboxyl group content), acid anhydride content, bulk viscosity, iodine value, percent unreacted alcohol, and FTIR and NMR spectroscopy.

The production of maleated soybean oil ester should allow for the evaluation of the product in end-user trials as a resin plasticizer.

7.2.4 Task 4: Formulation of modified Soybean oil coating materials

In order to demonstrate the commercial applicability of modified soybean oil, some preliminary coating formulations should be created. Various curing agents, catalysts, and polymers containing reactive groups, such as epoxy, amino, amide, thiol, hydroxyl, and chlorosulfonic, could be used to form multi-component, multi-phase, interpenetrating polymer networks (IPN's). Optimization of formulation and curing profile must be determined.

When formulations are determined, extrusion and calendering experiments would need to be conducted to determine processing conditions for commercial development.

7.2.5 Task 5: The Peroxide Reaction of Soybean Oil

Experiments should be conducted to fully characterize the reaction of soybean oil and maleic anhydride with the use of a peroxide. The complex chemistry of this system was not fully investigated due to the goals and objectives of this work. The proposed method was chosen on the merit of the chemistry and the good fit of the data.

The reaction should be investigated with electron spin resonance (ESR) and the products fully analyzed by high pressure liquid chromatography (HPLC).

CHAPTER 8

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