A KINETIC STUDY ON MALENISATION OF SOYBEAN OIL

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ABSTRACT

Malenisation of soybean oil with maleic anhydride was investigated.The effect of variations in weight percent ratio of reactants on rate of reaction has been studied.

Sodium bisulphate and sodium bisulphite are used as catalyst for the malenisation of soybean oil. The reaction kinetics is estimated for soybean oil – maleic anhydride ranging from 75:25 to 90:10. The optimum conditions are found to be 85:15 soybean oil:maleic anhydride weight percent ratio and 2 % catalyst at 230^0C for 330 minutes with conversion of 82.48% and yield of 95%.

KEYWORDS: malenisation, catalyst, kinetics, conversion, yield.

INTRODUCTION:

Modification of vegetable oil in the recent years has gained a lot of momentum because of its known modified[1] properties. Polymer based on vegetable oils dates to as early 20th century[2]. Research activity throughout world is concentrated to produce eco friendly product from biodegradable polymer. Sustainable and eco friendly product has to be synthesized so that it is biodegradable in the nature. Its availability for future generation should be there. With synthesis of these polymers is believed to replace the raw material obtained from petroleum origin of crude oil. Literature reports various works on the synthesis of novel chain polymer based on sorbitol, phthalic anhydride, maleic anhydride and benzoic acid which was used into formulation of liquid and powder detergent[3].

A number of methods have been proposed for improving the properties of vegetable oil. The methods most generally used are segregation, reaction with unsaturated compounds, mono and diglycerides of fatty acids[4]. The unsaturated compounds used are those which react with double bonds present in fatty acids chains of oils.

Among various stated processes of modification, malenisation reaction of oil is considered in this study. The reaction process to be scaled up needs process engineering. The chemical kinetics for malenisation process has been studied here. The details of kinetics aspect are discussed in this research work.

A reaction mechanism consisting of an initial mass transfer controlled region followed by a kinetically controlled region is proposed. The experimental data for the latter region (kinetically controlled region) proposed during mechanism appear to be a good fit into a second order kinetic model. The data presented was analyzed by **ANNOVA** to evaluate the level of statistical significance.

Soybean oil and maleic anhydride are the main reactants used for malenisation process to obtain malenised oil. The variables affecting the malenisation process have been investigated as widening industrial uses.Molar ratio of vegetable oil to maleic anhydride, type of catalyst, temperature and viscosity of the product and acid value has been studied.

EXPERIMENTAL SECTION
MATERIALS

Soybean oil and maleic anhydride was procured from the local industry. All chemicals used in experimentation such as bisulphate and bisulphite both (98%) pure were of laboratory grade and were procured from Merck Chemicals and used such.

Also benzene, isopropyl alcohol few such organic solvents were also used during experimentation and calculation of few terms.

ANALYTICAL METHODS

Acid value of oil and maleic anhydride were found using AOCS method[5]. The extent of reaction conversion was based on solvent extraction and titrimetric analysis of the free fatty acids in the samples and viscosity of product was measured using the standard methods and reaction extent was decided.

EXPERIMENTAL PROCEDURE

A 2000 ml glass kettle with three neck openings was used. Centre opening was equipped with mechanical stirrer. Thermometer was installed for temperature measurement and a condenser system was employed. System was heated by heating mantle of power 400 watt. For the typical experiment, soybean oil (85% by wt) and maleic anhydride (15% by wt) was added and mixed at 150^0C. The speed of agitator was maintained constant and could be varied using a regulator. Samples were withdrawn at regular time interval of 30 min and were analyzed for various parameters such as acid value and viscosity.

The reaction starts with the choice of raw materials. The malenisation reaction was studied in detail with all parameters and the variables of reaction. Each chemical reaction has its own chemistry and the chemical reaction engineering part[6]. Both aspects of the reaction lead to chemical reactor designs and the integration of various unit operation equipments to scale up into a pilot plant.

CHOICE RAW MATERIALS

Reactions that use the cheapest raw materials and produce the smallest by products[7] are to be preferred. Some other factors also includes such as:

1. Future prices of raw materials
2. Technical aspects, such as safety and energy consumptions.
3. The lack of suitable catalyst is the common reason exploiting the novel synthesis.

Here the choice of oil whether edible oil, non –edible oil, minor oil is the main concern.Also choice of catalyst which would enhance the rate of reaction.

Hence, in this study following main reactants were chosen

1. Soybean oil
2. Maleic anhydride
3. And the catalyst
   a. sodium bisulphate
   b. sodium bisulphate

REASONS TO CHOOSE SOYBEAN OIL ARE AS FOLLOWS

- The ground beans are extracted with solvent extraction method.
- Refines with less loss[8]
- Has a high iodine value that permits hydrogenation of base stocks for a wide variety of products[9].
- Has high essential fatty acids content[10].
- Soya Fatty acid was found to contain 23.5% oleic acid and 54.6% linoleic acid and 8.3 % linolenic acid.

SINGLE AND MULTIPLE REACTIONS

We have a single reaction[11]

FEED 1 + FEED 2 ⟶ PRODUCT

From the above reaction it can be seen that a single stoichiometric equation gives the product formation. Also no other competitive by product is formed during the malenisation process. Hence the multiple reactions do not occur. Hence here the reaction is termed to be a single stoichiometric reaction.

ELEMENTARY AND NON – ELEMENTARY REACTIONS

A single reaction with stoichiometric equation

$$\longrightarrow A+B \quad P$$
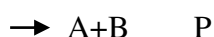
Reactions in which the rate equation corresponds to a stoichiometric equation are called elementary reactions[12].

As observed during the process of malenisation the single molecule of double bonded site of soybean oil is attacked by a single molecule of maleic anhydride and product is formed. Hence the reaction is elementary in nature.

REVERSIBLE AND IRREVERSIBLE REACTIONS

The reaction product formation from raw materials is a forward reaction. Here the polymerized adduct formation takes place, which is a hardened solid mass and does not result into formation of reactants i.e. soybean oil and maleic anhydride. Hence it is a irreversible reaction in nature.

MECHANISM OF REACTION

It is addition polymerization reaction giving a adduct formation. Few points regarding mechanism of reaction can be highlighted as:

- Chemical reaction occurs between the double bond of maleic anhydride and the non-conjugated double bond of linoleic acid[13].
- This is followed by -ene synthesis mechanism by hydrogen abstraction[14].
- According to molecular orbital conservation principle, oleic acid present in soybean oil cannot undergo cyclo addition involving 2pi + 2pi orbitals with maleic anhydride under thermal condition[15].
- 1, 4 linoleic acid (nonconjugated) present in soybean oil does not go Diels -Alder reaction[16].
- The reaction undergoes – ene synthesis with cycloaddition of 2s +2pi +2pi orbitals involving highest occupied mol. Orbital and the allylic part of linoleic acid with lowest unoccupied molecular orbital[17].
- *Molecularity:* One mole of soyabean oil reacts with one mole of maleic anhydride to give desired product hence only two important reactants play vital role for synthesis of reaction therefore it is observed to have bimolecularity.
- *Reaction phases involved:* Soybean oil is liquid phase, maleic anhydride and catalyst used are solid in phase and the desired resin product is highly viscous in nature along with vapors of water and sulphur dioxide. Hence, it is a heterogeneous reaction.
- *Catalyst:* It is an acid catalyzed reaction.

It involves formation of two sigma bonds and pi -bond at expense of three original pi bonds. The product obtained from this mechanism at end is known to be adduct.

MOLECULARITY AND ORDER OF REACTION

Molecularity refers only to an elementary reaction. Since the order refers to the empirically found rate expression and rate data[18] which can be obtained for the malenisation of reaction as:
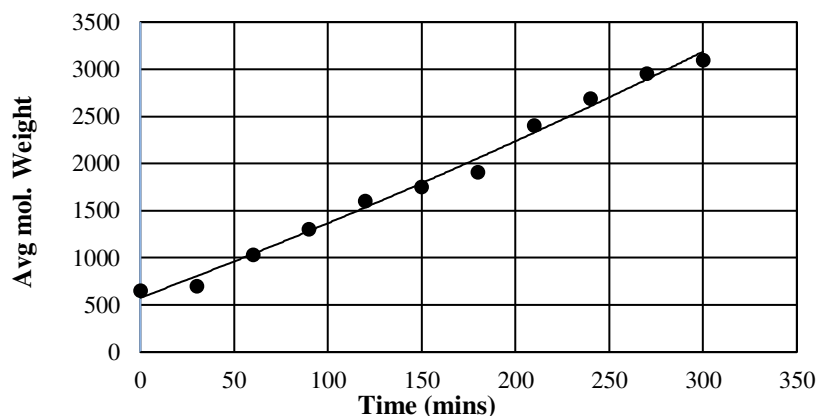
The graph depicts the relation between Average molecular weight of adduct and the time of reaction. As time increases the polymerization continues and dense mass is obtained of novel resin.

Also, the trade line in the graph gives the relation as:

$$y = 0.004x^2 + 7.503x + 576$$

The above equation can be inferred as it is equation in power of 2. Hence the overall order of equaton is second. Therefore the malenisation of soybean oil is a second order reaction. Also:

$$R^2 = 0.991$$

This value states that it is nearer to value of 1, inferred that the reaction order calculated has least error into its value and calculation.

STOICHIOMETRIC FACTOR
It is the stoichiometric moles of reactant required per mole of product[19]. Here for this reaction it is 1**:**1.

RATE CONSTANT K
The dimensions of the rate constant k for the nth order reaction are

$$(time)^{-1}(concentrations)^{n-1}$$

Here n=2,

$$= (time)^{-1}(concentration)^{2-1}$$
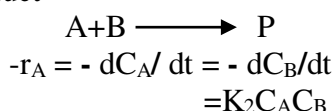
Dimensions of reaction rate k =

$$(time)^{-1}(concentration)^{1}$$

KINETIC MODEL
Malenisation of soybean oil hence is an irreversible second order reaction with bimolecular in nature and its kinetic model[20] satisfying the rate data of experimentation can be stated as:

Soybean oil+Maleic anhydride $\longrightarrow$ Adduct

$$A+B \longrightarrow P$$
$$-r_A = - dC_A / dt = - dC_B/dt$$
$$=K_2 C_A C_B$$

At any time t,

$$C_{A0} * X_A = C_{B0} * X_B$$
$$-dC_A = C_{A0} * dX_A$$

We have,

$$-r_A = dC_A / dt = K_2 C_A C_B$$
$$-r_A = d (C_{A0} * X_A) = K_2 C_A C_B$$
$$= C_{A0} * (dX_A / dt) = K_2 C_A C_B$$
$$-r_A = C_{A0} (dX_A/dt) = K_2 (C_{A0} - C_{A0} * X_A) (C_{B0} - C_{A0} * X_A)$$
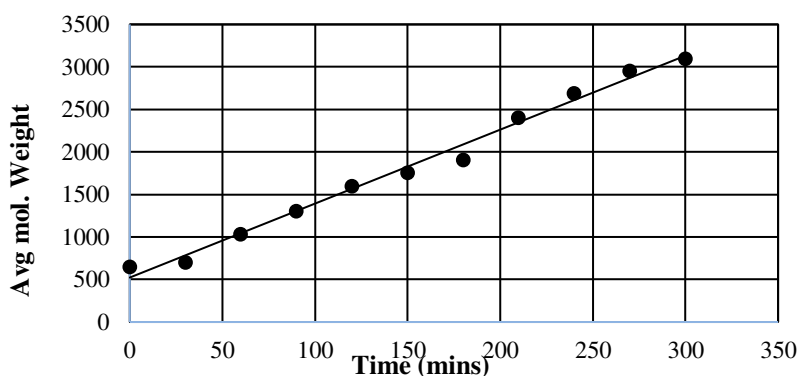
The initial molar ratio of reactants

$$M = (C_{B0} / C_{A0})$$
$$-r_A = C_{A0} * dX_A / dt = K_2 C^2_{A0}(1 - X_A) (M - X_A)$$

On integrating within limits from conversion 0 to X_A and time changing from 0 to t, we get,

$$ln(1- X_B / 1- X_A) = lnC_{A0}(M-1) K_2 * t = (C_{B0} - C_{A0})K_2 * t$$

THE ABOVE KINETIC MODEL CAN BE RESULTED INTO PLOTS GRAPHICALLY AS FOLLOWS:

The relation between average molecular weight and time can be stated with a standard equation.

$$y = 8.6985x + 522.9$$

This equation depicts the straight-line equation. This equation can be used to predict the average molecular weight of resin at particular time of reaction

$$R^2 = 0.9895$$

This value states that the reaction is carried with least error and tending the value towards 1 is inferred to have good adduct formation.

CHOICE OF REACTOR

For the choice of the reactor from the available types, three important parameters are used[21] to describe their performance:

conversion

$$= \frac{\text{liminting reactant consumed in the reactor}}{\text{limiting reactant fed to reactor}}$$

Selectivity =

$$\frac{\text{desired product produced}}{\text{reactant consumed in the reactor}} \times \text{stoichiometric factor}$$

Yield =

$$\frac{\text{desired product produced}}{\text{reactant fed to the reactor}} \times \text{stoichiometric factor}$$

FOR CALCULATION OF CONVERSION: EXPERIMENTAL PROCEDURE

Soybean oil and maleic anhydride were taken into 90:10 ratios by weight percent. During reaction, the temperature maintained was 45^0C as above that Reactants are homogenized for one and half hour. The reaction mixture was kept overnight. The dense mass of polymer was obtained and the unreacted portion was separated from the dense mass.

Unreacted portion was weighed and the solvent; benzene; was added to it in 1:1 ratio, as same that of the weighed portion. Organic solvent and the unreacted mass are homogenized for 1 hour for proper extraction of maleic anhydride.

On mixing, the complete mass is weighed and poured to separating flask and left undisturbed for 48 hours. White colored maleic anhydride is obtained at lower portion of flask and unreacted oil and benzene liquid mixture is obtained at top.

The mass is filtered and weighed on oven drying. Also the liquid part of unreacted and solvent were analysed for acid value which gave the value of traces of maleic anhydride present into that liquid portion. Total mass of unreacted maleic anhydride and sublimed quantity are calculated and noted for various samples of batches.

CALCULATION:

Acid value of unreacted mass before employing to solvent extraction had 106.7971 and that of resin obtained on reaction was found to be 174.55.Also the acid value of mixture of benzene and unreacted oil after solvent extraction is 170.6447.Sum of acid value of mixture of benzene, unreacted oil after solvent extraction is the value obtained in terms of alcoholic potassium anhydride.

Table 1: Weight of maleic anhydride calculated

Weight of maleic anhydride calculated	Sample 1	Sample 2
	5.561221 mgms	3.0886 mgms

Total unreacted maleic anhydride calculated as:

Weight of maleic anhydride obtained on solvent extraction + Weight of maleic sublimed + Weight of maleic anhydride calculated as from formula was found to be 2.20308 gms.

Conversion=

$$\text{Sample} = \frac{10 - 2.20308}{10} = 0.779692$$

Average conversion found to be

$$= 0.824846 * 100 = 82.48\ \%$$

Conversion = 82.48%

SELECTIVITY OF REACTION

As there is single product formation hence selectivity does not play vital role here.

YIELD OF REACTION

The weight of product obtained in the reaction as = 213.75 gms

Limiting reactant fed to the reactor 225 gms

$$\text{Yield} = \frac{213.75}{225} = 0.95 * 100 = 95\ \%$$

Yield = 95 %

ANNOVA STATISTICAL ANALYSIS OF MALENISATION REACTION

The above ANNOVA analysis data gives following equation:

Y = 855.3312 + (8.1155 *time) – (0.99367 *Acid Value)

For each incremental time unit the molecular weight (Y) increases by 8.1155 and for each decrease in acid value the weight increases by a factor of 0.99367 for the proposed malenisation process.

Choice of idealized reactor model

From the study of rate data, single reaction type system and various parameters[22] considered above following points can be highlighted:

1. The highest rate of reaction is maintained by the highest concentration of the limiting reactant that is maleic anhydride.
2. The rate of reaction is lower in mixed flow reactor than in the ideal batch and plug flow reactors, since it operates at the low reaction rate corresponding with the outlet concentration feed.
3. Thus, a mixed flow reactor requires a greater volume than an ideal batch or plug flow reactor.
4. Consequently, for single reactions, an ideal –batch or plug – flow reactor is preferred.

CONCLUSION

A single stoichiometric bimolecular reaction is studied for malenisation of soybean oil. Single molecule of double bonded site is attacked by a single molecule of maleic anhydride and product is formed .hence the reaction is elementary in nature. Molecularity and order of reaction is calculated as two. Stoichiometric ratio is stated as 1:1.It follows a kinetic model for elementary bimolecular irreversible reaction with a maximum conversion of 82.48% and yield of 95%.

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