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CHEMICAL REACTION ENGINEERING ON ISOMERIZATIONOF OLEIC ACID: CLAY CATALYST

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ABSTRACT

Isomerization reaction was carried out and was studied in detail. Porous Clay is the catalyst for isomerization of oleic acid .The reaction kinetics are estimated for 5wt% catalyst concentrations, temperature was from 260^0C to 280^0C .The reaction was carried out for several duration of hours and product was obtained as iso-oleic acid (IOA) along with dimer as simultaneous product. Kinetic studies based on rate data is proposed based on multiple reactions. Residence time distribution for reactant is plotted for F curve and E curve. Yield and conversion has determined **50.5258%**and **66.309%**respectively.

KEYWORDS: iso-oleic acid, isomerization kinetics, residence time distribution

INTRODUCTION

Oleic acids are mono unsaturated compound commercial known as cis – 18 octadecanoic acid having a polar carboxylic acid head group and an alkyl chain.

Oleic acid as its sodium salt is a major component of soap as an emulsifying agent . It is also used as an emollient **[1]**. Small amounts of oleic acid are used as an emulsifying agent or products**[2]**.

This straight chain naturally occurring compound and its isomers for many beneficiaries and to obtain much desired properties into products which could not be fulfilled by oleic acid.

Hence an isomer named , Iso-oleic acids are branched compounds that are non-toxic and biodegradable in nature. They are predominantly used in cosmetics because of their superior moisturizing properties as they are odorless, provides smooth spreading and non-tacky feeling when applied onto skin**[3]**.

COMMERCIAL ISO-OLEIC ACIDS

Isomerization reaction at industrial scale with proper reactor choice , reactor design and the choice of catalyst. All theparameters requires the kinetic study and theoretical calculations of process related terms. This all is studiedin this research work .

EXISTING METHODOLOGY FOR ISO OLEIC ACID

The accepted process includes the porous clay as a catalyst . The process conditions been employed in this experimentation are optimum and isomer obtained is at maximum production.

EXPERIMENTAL PROCEDURE

MATERIALS

Oleic acid is the sole main reactant and porous clay catalyst plays a selective role, inert gas nitrogen is being employed to maintain the pressure .

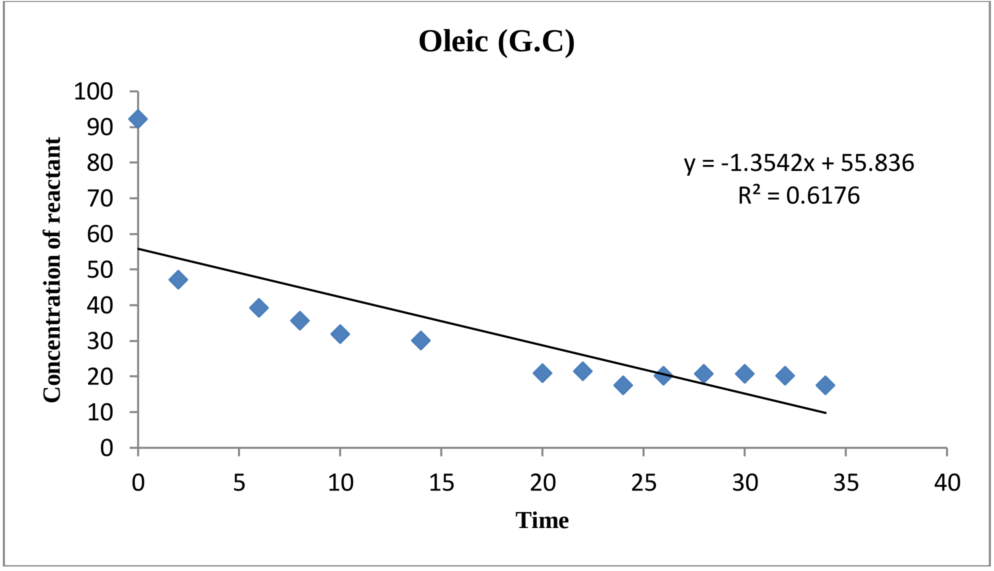
METHODS

Oleic acid obtained is subjected to isomerization reaction and a clay catalyst activated with ammonium nitrate of about 5%,at a temperature of about 260^{0}C to about 280^{0}C, under nitrogen pressure of about 1 hours to about 34 hours .During this process the straight chain unsaturated fatty acids are converted into branched chain compounds . Dimers are also formed during the process. Process was monitored and samples were taken for analysis .Then said sample mass is cooled gradually to 90^{0}C temperature where filtration of mass for removal of clay catalyst. Finally the reaction mass is dried.

The autoclave is charged with reaction mixture. It is supported by mechanical stirrer into it and accessorized with temperature controller along with pressure gauge.

THE REACTION MECHANISM

Thereaction proceeds as time passes; the reactant gets it consumed on conversion into products . The rate of decreasing of reactant from the graph is follows :



Oleic acid with respect to time decreases linearly which is depicted by equation:

$$\mathbf{y = -1.3542x + 55.836}$$

and value of square of R is stated as:

$$\mathbf{R^2 = 0.6176}$$

Products of this reaction yields the isomer along with dimer. Hence form of this reaction and progress of this reaction along with kinetic equation can be proposed. Here, materials convert into multiple products hence it is a multiple type of reaction with parallel reactions with products forming competitively**[4]**where in a single reactant converts into two different products simultaneously. Thus, the one product is desired and the other one undesired. The competitiveness of the formation of products depends on controlling of process parameters.

This particular isomerization reaction is catalyzed reaction. Wherein the catalyst is the clay porous material. Presence of this catalyst enhances the formation of desired product. This particular behaviorof catalysis is known to be as selectivity.

FORMATION OF PRODUCTS

As stated earlier the formation of products can be obtained by the kinetic models and kinetic constants and stoichiometric equation.

The reaction goes on continuously the rate of formation of product can be obtained from the graph by finding the order of reaction for both the products.The rate equation will differ as follows:

KINETIC MODEL FOR ISOMERIZATION

Qualitative Discussion**[5]**about product distribution : Consider the decomposition of A by either one of two paths :

$\xrightarrow{K_1}$ A   R (desired product)

$\xrightarrow{K_2}$ A   S (undesired product)

With corresponding rate equations

$$r_R = dC_R /dt = K_1 C_A^{a1}$$
$$r_S = dC_S /dt = K_2 C_A^{a2}$$

Relative rate of formation of R and S

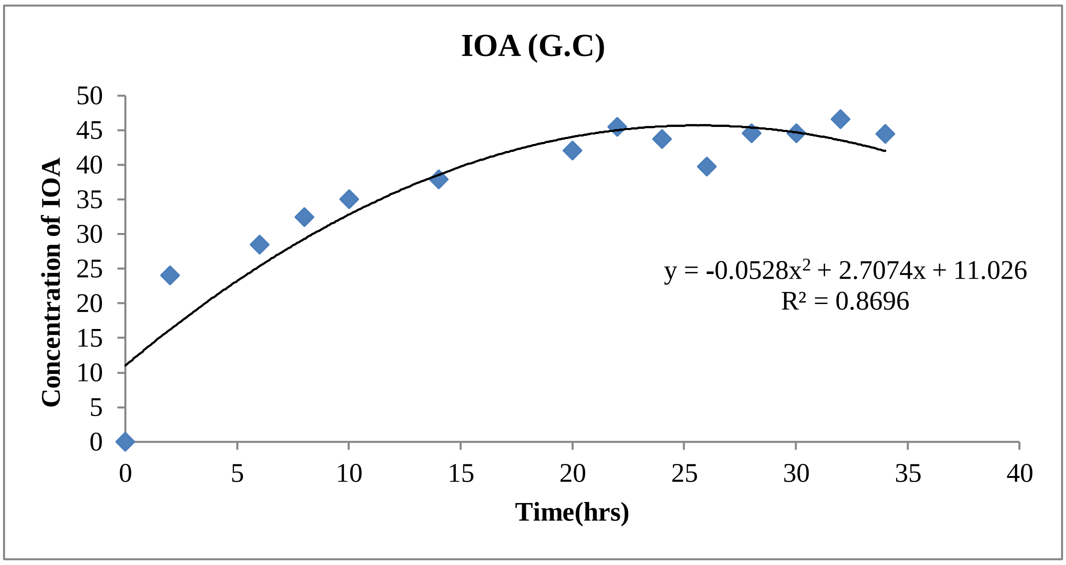
$$r_S/r_R = (dC_S /dt) / (dC_R/ dt) = K_2 C_A^{a2} / K_1 C_A^{a1}$$
$$r_S/r_R = dC_S / dC_R = K_2 C_A^{(a2 - a1)} / K_1$$

this above ratio should be as small as possible.

Now C_A is the only factor in this equation which can be adjusted and control .This concentration of A depends on the stoichiometric value of a_1 and a_2 for products R and S respectively.

For finding the values of a_1 and a_2 which also suggests the order of reaction can be calculated using graphical method as follows:

For value of a_1



The graph depicts the relation between concentration of Iso-Oleic acid and the time of reaction. As time increases the isomerization continues and desired product is obtained.

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

$$\mathbf{Y = -0.0528x^2 + 2.7074x + 11.026}$$

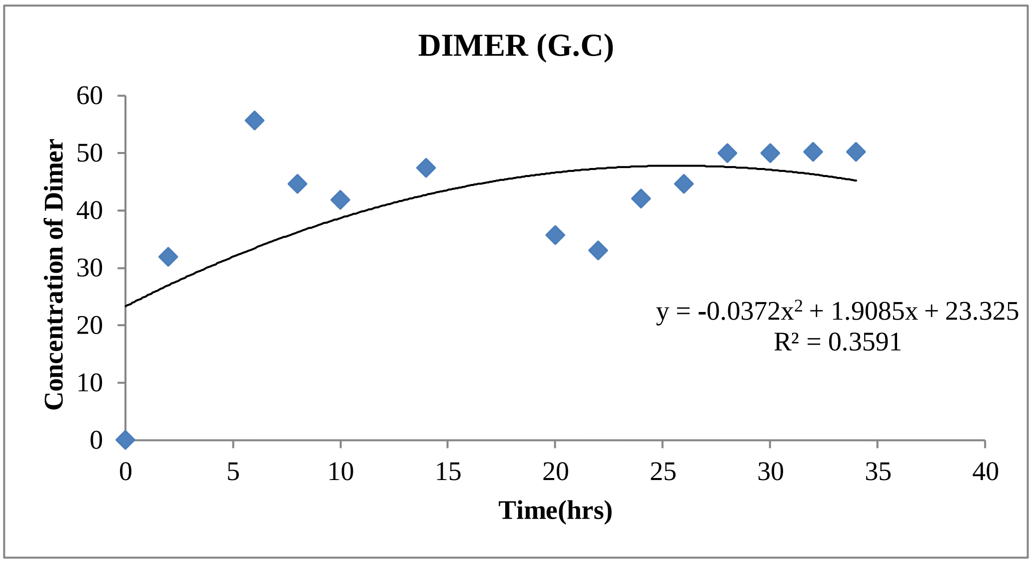
The above equation can be inferred as it is equation in power of 2. Hence the overall order of equation is second. Therefore the isomerization of oleic acid is a second order reaction.

Also:

$$\mathbf{a_1 = 2}$$
$$\mathbf{R^2 = 0.8696}$$

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 .

For value of a_2



The graph depicts the relation between concentration of dimer formed and the time of reaction. As time increases the dimerization continues and undesired product is obtained competitively.

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

$$y = -0.0372x^2 + 1.9085x + 23.325$$

The above equation can be inferred as it is equation in power of 2. Hence the overall order ofequation is second. Therefore the dimerization reaction is a second order reaction.

Also:

$$a_2 = 2$$

$$R^2 = 0.3591$$

This value states that it deviates from the ideality that is the value of R^2 has to be nearer to 1, inferred that the reaction proceeds competitively. But the process conditions maintained for the dimerization reaction are not apt which ultimately results into the reaction conditions in the favor of isomerization reaction hence isomer obtained is more in this experimentation and dimer in lesser quantity which desired.

Now,

$$a_1 = 2 = a_2$$

$$a_1 = a_2$$

Hence,

a_1 and a_2 are equal or the two reactions are of the same order , the last equation of kinetic model becomes

$$r_S / r_R = dC_S / dC_R$$

$$= K_2 / K_1 = \text{Constant}$$

Hence product distribution is fixed by k_2 / k_1 alone and is unaffected **[6]**by type of reactor used . Thus the reactor volume requirement will govern the design .

Besides this method , the product distribution is varied by two ways:

1. By changing the temperature level of operation.
2. By using catalyst. One of the most features of a catalyst is its selectivity in accelerating the desired specific reaction.

Thus far all design of equipment’s are restricted to two idealized flow patterns and mixed flow. Though real reactors never fully follow these flow patterns**[7]** . in other cases deviation from ideality are considerable. This deviation can be caused by channeling of fluid , by recycling of fluid , or by creation of stagnant regions in the vessel. The problems of non-ideal flow are intimately tied to those of scale -up because the question of whether to pilot -plant or not rests in large part on whether it is a major concerns to control all process parameters.

RESIDENCE TIME DISTRIBUTION OF FLUID IN VESSELS

Precisely within the vessel , if we have a complete velocity distribution map for the fluid , then its apt to predict the behavior of a vessel as a reactor.

The least concept about flow which will be useful for design is how long the molecules stay in the vessel , or more precisely , the distribution of residence time of flowing fluid **[8]**. this information can be determined easily by widely used method of stimulus response experiment.

E , THE AGE DISTRIBUTION OF FLUID LEAVING A VESSEL

It is evident that elements of fluid taking different routes through the reactor may require different lengths of time to pass through the vessel**[9]** . The distribution of these time for the streams of fluid leaving the vessel is called the exit age distribution E, or the residence time distribution RTD fluid.

Theoretically , it is convenient to represent the RTD in such a way that the area under the curve is unity , or

$$\int E = 1$$

FINDING RTD BY EXPERIMENTATIONS

The area under the concentration – time curve , can be obtained as **[10]**

$$Q=\sum C\Delta t$$

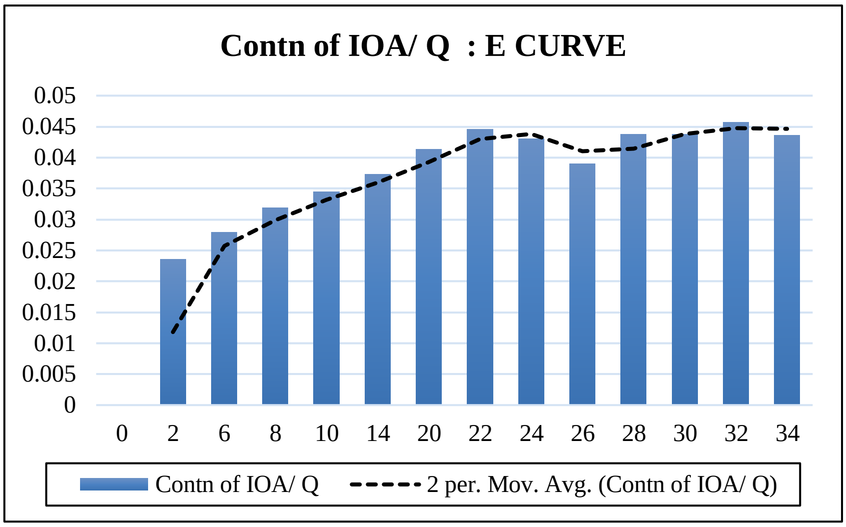
$$= 509.35 * 2$$

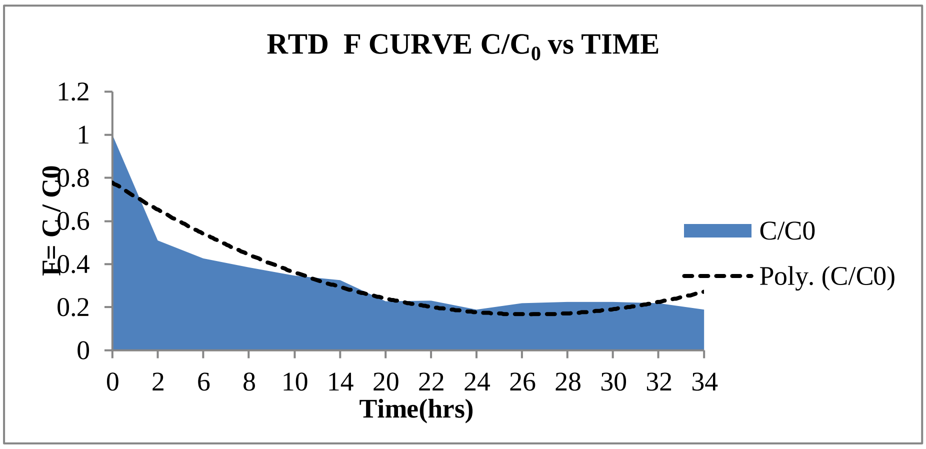
$$Q=1018.7 \text{ gm hr / ltr}$$

The area under curve gives total amount of tracer inside the vessel . To find E , the area under this curve must be unity ; hence the concentration readings must each be divided by Q , giving

$$E= C / Q$$

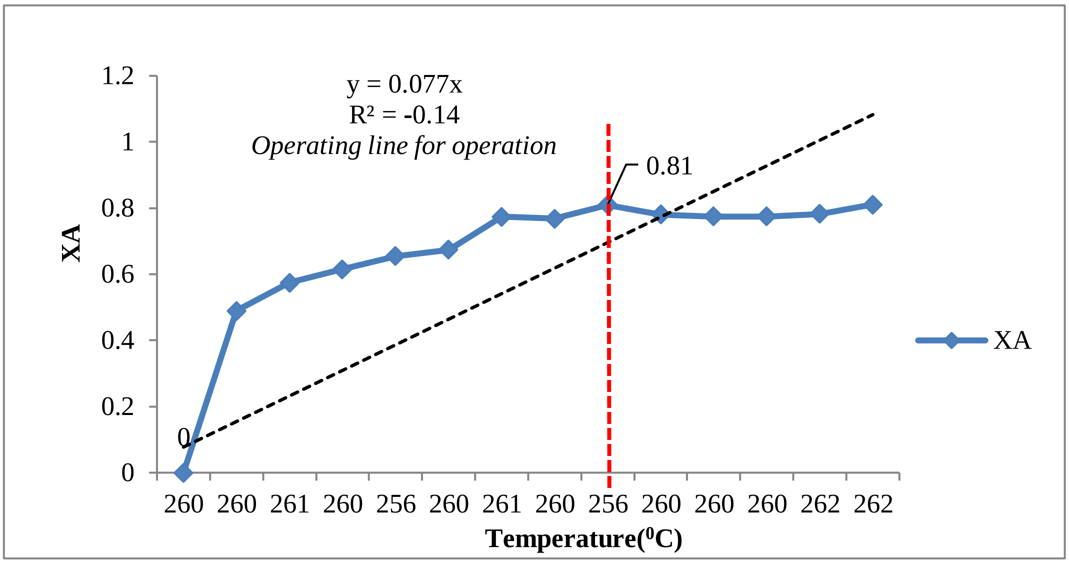
Thus we have ,The following is the plot of this distribution: E vs Time graph





THE F CURVE

With no tracer initially present anywhere impose a input and concentration C_0 on the fluid stream charged into the vessel , **measured as C / C_0 ,** is called the F curve **[11]**.The following graph sketches this curve and shows that it always starts from 0.



RELATION AMONG THE F , C AND E CURVES AND “ MEAN TIME” FOR CLOSED VESSELS

To relate E and C for the steady – state flow note that RTD for any batch of entering fluid must be the same as for any leaving batch**[12]** . If this were not so , material of different ages would accumulate in the vessel , thus violating the steady state assumption .

We know

$$\int C\,dt = \int (C / Q)\,dt$$

Where ,

$$Q = \int C\,dt$$

The C curve for the tracer then records when these molecules leave , distribution of ages . Since the C curve represents the RTD for the particular batch of entering fluid , it must also be the RTD for that particular batch of entering fluid , it must also be the RTD for any other batch , in the particular , any batch in the exit stream**[13]** .

So we have ,

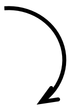
$$C=E$$

Thus the C curve gives directly the exit age distribution which is depicted in graph above of E curve.

FINDING THE REACTOR SIZE AND OPERATING LINES FOR MINIMUM REACTOR SIZE

The condition for the optimum temperature progression in a given type of reactor is as follows :Whatever the composition , always have the system at the temperature where the rate is a maximum **[14]**.

The graph for conversion vs Temperature is plotted as follows:



Graph : Operating lines for minimum reactor size

From the above graph it is inferred that the reaction Reversible and endothermic in nature**[15]**. For a endothermic reactions a rise in the temperature increases both equilibrium conversion and the rate of reaction .

The red line depicts T_{max} , allowable after that the conversion remains unaltered .

ANOVA STATISTICAL ANALYSIS

The ANNOVA analysis data gives following equation:

IOA = 47.343 + (0.1072 *Time) – (Oleic Acid * 0.5592) + (Acid Value *0.0210)

For each incremental time unit the concentration of Iso-Oleic acid (Y) increases by 0.1072 and for each decrease in reactant that is oleic acid the concentration increases by a factor of 0.5592 and for each change in acid value the concentration of product increases by 0.0210 for the proposed isomerization process.

Also for the choice of the reactor from the available types, three important parameters are used **[16]** to describebetheir performance:

Conversion

$$= \frac{\text{limintingreactantconsumed inthereactor}}{\text{limitingreactantfedtoreactor}}$$

Overall conversion = 0.66309*100

Conversion=66.309%

STOICHIOMETRIC FACTOR

It is the stoichiometric moles of reactant required per mole of product. Here for this reaction it is 1:1.

SELECTIVITY

$$\frac{\text{desiredproductproduced}}{\text{reactantconsumedinthereactor}} \times \textbf{stoichiometric factor}$$

(Desired product / Reactant consumed)* stoichiometric Factor[16]

= (46.6 / 74.8)* 1

Selectivity=0.622994

YIELD

$$\frac{\text{desiredproductproduced}}{\text{reactantfedtothereactor}} \times \text{ stoichiometric factor}$$

=46.6 / 92.23

=0.50525

=0.50525*100

Yield =50.5258%

CONCLUSIONS

- Both the rate equation of for isomer and dimer formation are second order reactionwith reversible in nature and endothermic in nature .
- Also the experimentation yields isomerin larger amount as desired which is confirmed by the value of square of R of graph of 2 that is 0.6176 .
- The kinetic model followed by the systemis of multiple type reaction with samestoichiometric value, this states that the product distribution is alone dependent upon the ratio of rate constant of dimer to the rate constant of isomer formation.
- The product distribution is hence unaffected by the type of reactor and only the reactor volume will govern the design .

- The residence of molecules inside the reactor plays a vital role. Here from graph of E curve states that at 256^0C and time of 24 hours the molecules have maximum value of E stating the equilibrium conditions have been attained at this process conditions .
- As stated above reactor volume governs the design hence the minimum size of reactor should be calculated which is given by graph 5 stating the operating line for the reactor design it also states the maximumconversion of 0.81 at the same temperature of 256^0C and 24 hours .
- Overall conversion was 66.309% and selectivity for isomer was 0.62294 and yield was 50.5258%.
- Hence optimum temperature to be maintained has to be 256^0 C (with increase up to 10 degrees) and process time of 24hours (+ 2 hours if required) is sufficient and aptwhich gives maximum conversion and yield .

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