Design, fabrication and Characterization of a 7 Litre Esterification Reactor

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ABSTRACT

The purpose of this research work is to characterize an Esterification Reactor (CSTR). The tracer experiments were carried out to validate the effectiveness of the reactor by using the beaker and stop watch method. Experimental data obtained at 0.6M of Nacl concentration and 160rpm gave a curve that is in close agreement to that of the model. In other words, the results obtained at a concentration of 0.6M and 160rpm is in close agreement with that of early researchers. Thus confirming the classification of the reactor as a CSTR. To carry the work further, an esterification process involving the reaction of ethanol and acetic acid catalyzed by sulfuric acid was chosen in this work. In this experiment, the direct synthesis of ethyl acetate was chosen. For a normal operation, the reactant concentration and catalyst concentration were set respectively to be 6M and 3M. The reaction was carried out at room temperature with 5% catalyst volume and without cooling water.

Key Words: Design, fabrication, Esterification Reactor, Beaker and Stop watch

INTRODUCTION

Continuous stirred tanks are used ubiquitously in the chemical process industry for mixing, reactions, and crystallizations. The mixing in a continuous stirred tank is often not ideal.

A type of reactor used commonly in industrial processing is the stirred tank. It is referred to as the continuous-stirred tank reactor (CSTR) or vat, or back-mix reactor; and is used primarily for liquid phase reactions. It is normally operated at steady state and is assumed to be perfectly mixed: consequently, there is no time dependence or position dependence of the temperature, the concentration or the reaction rate inside the CSTR. That is, every variable is the same at every point inside the reactor (Marina and Alfredo, 2004).

Because the temperature and concentration are identical everywhere in the reaction vessel, they are the same at the exit point as they are elsewhere in the tank. Thus the temperature and concentration in the exit stream are modelled as being the same as those inside the reactor (Laurence, 2002). In reactor design one has to know what size and type of reactor and method of operation that is best for a given job. Because this may require that the conditions in the reactor vary with position as well as time, this question can only be answered by a proper integration of the rate equation for the operation (Robert and Don, 2006).

This may pose difficulties because the temperature and composition of the reacting fluid may vary from point to point within the reactor, depending on the endothermic or exothermic character of the reaction, the rate of heat addition or removal from the system, and the flow pattern of fluid through the vessel. In effect, then, many factors must be accounted for in predicting the performance of a reactor (Robert and Don, 2006).

How best to treat these factors is the main problem of reactor design. Equipment in which homogeneous reactions are effected can be one of three general types; the batch, the steady-state flow, and the unsteady-state flow or semi batch reactor

METHODOLOGY

The general mole balance is as given below (Lawrence, 2002). When the general mole balance equation;

$$F_{j0} - F_j + \int^V r_j dV = \frac{dN_i}{dt} \qquad 1.1$$

Is applied to a CSTR operated at steady state (i.e**.,** conditions do not change with time),

$$\frac{dN_j}{dt} = 0 \qquad 1.2$$

In which there are no spatial variations in the rate of reaction (i.e., perfect mixing),

$$\int^V r_j \, dV = Vr_j \qquad 1.3$$

It takes the familiar form known as the *design equation* for a CSTR:

$$V = \frac{F_{j0} - F_j}{-r_j} \qquad 1.4$$

The CSTR design equation gives the reactor volume necessary to reduce the entering flow rate of species j, from *Fj*, to the exit flow rate, when species j is disappearing at a rate of *-rj*. We note that the CSTR is modelled such that the conditions in the exit stream (e.g. concentration, temperature) are identical to those in the tank. The molar flow rate *is* just the product of the concentration of species j and the volumetric flow rate *v*, (Lawrence, 2002).

$$F_j = C_j . v \qquad 1.5$$

Consequently, we could write a balance on species A as

$$V = \frac{V_0 C_{AO} - vC_A}{-r_A} \qquad 1.6$$

For continuous-flow systems, this time usually increases with increasing reactor volume. Example, the bigger/longer the reactor, the more time it will take the reactant to flow completely through the reactor and thus, the more time to react. Consequently, the conversion X is a Function of reactor volume *V*. If F_A, is the molar flow rate of species A fed to a system operated at steady state. The molar rate at which species A is reacting within the entire system will be F_{AO} (Fogler, 2006).

$$[F_{AO}][X] = \frac{moles\ of\ A\ feed}{time} . \frac{moles\ of\ A\ reacted}{mole\ of\ A\ feed} \qquad 1.7$$

$$[F_{AO} . X] = \frac{moles\ of\ A\ reacted}{time} \qquad 1.8$$

The molar feed rate of A *to* the system minus the rate of reaction of A within the system *equals* the molar flow rate of A leaving the system F_A . The preceding sentence *can* be written in the form of the following mathematical statement:

$$\begin{bmatrix} molar\ flow\ rate \\ at\ which\ A\ is \\ feed\ to\ the\ system \end{bmatrix} - \begin{bmatrix} molar\ rate\ at \\ which\ A\ is\ consumed \\ within\ the\ system \end{bmatrix} = \begin{bmatrix} molar\ flow\ rate \\ at\ which\ A \\ leaves\ the\ system \end{bmatrix} \qquad 1.9$$

$$[F_{AO}] - [F_{AO}X] = [F_A] \qquad 1.10$$

Rearranging

$$F_A = F_{AO}(1 - X) \qquad 1.11$$

Continuous stirred tank reactors (CSTRs) are typically used for liquid-phase reactions. As derived, the following design equation for a CSTR holds (Fogler, 2006)

$$V = \frac{F_{AO}X}{(-r_A)_{exit}} \qquad 1.12$$

Which gives the volume V necessary to achieve a conversion X**.** The space time**,** is a characteristic time of a reactor**.** To obtain the space time τ as a function of conversion we first substitute for

$$F_{AO} = v_0 C_{AO} \qquad 1.13$$

in the equation above

$$V = \frac{u_0 C_{A0} X}{-r_A} \qquad 1.14$$

And then divide by u_0 to obtain the space time, τ, to achieve a conversion X in a CSTR

$$\tau = \frac{V}{v_0} = \frac{C_{A0}X}{-r_A} \quad 1.15$$

This equation applies to a single CSTR or to the first reactor of CSTRs connected in series.

We could also combine Equations (1.13) and (1.14) to find the exit reactor concentration of A, C_{AO},

$$C_A = \frac{C_{A0}}{1+\tau k} \quad 1.16$$

Esterification is one of the popular processes in chemical engineering. Various important products are produced from this reaction and their applications are varying. Esterification process can be classified as exothermic reaction where in every reaction; a few amount of heat will be released to the surrounding. Hence it is a quite simple reaction.

Esterification of carboxylic acids with alcohol in the presence of acid catalyst has been the subject of investigation by many research workers. Both homogeneous and heterogeneous catalyst had been used for this purpose. Mineral acids can be given as the example of homogeneous catalyst and a cation-exchange resin in the acid form can serve as heterogeneous catalyst (Lipnizki *et al*, 1999).

Esterification process involved the reaction of ethanol and acetic acid catalysed by sulfuric acid were chosen in this work. The stoichiometry reaction of the process is as below;

$$CH_3CH_2OH + CH_3COOH \rightarrow CH_3COOCH_2CH_3 + H_2O \quad 1.17$$

Ethanol reacts with acetic acid in producing ethyl acetate. This reaction is called a homogeneous liquid phase.

Normally, in the absence of a catalyst, the reactions are very slow and require typically several days to attain the equilibrium (Domingues *et al*, 1999). Therefore, a catalyst was added to enhance the reaction. The catalyst could be heterogeneous or homogenous. In this reaction, sulfuric acid acted as a homogeneous catalyst. This catalyst is already known as an efficient mineral acid catalyst (Domingues *et al*, 1999).

The reaction was selected because it is a well-known reaction, simple and moderately exothermic [Heat or reaction, H= -0.0114kJ/mol] with no danger of decomposition reaction. Furthermore, this type of reaction also got the attention of other researchers in studying the possible runaway reaction on different chemical types (Krupiczka and Koszorz, 1999).

The commercial production of ethyl acetate is mainly by two processes: The Tischenko reaction produces ethyl acetate by direct conversion of ethanol via acetaldehyde using an aluminum alkoxide catalyst and the production of ethyl acetate by direct esterification of ethanol with acetic acid and sulfuric acid catalyst. In this experiment, the direct synthesis of ethyl acetate was chosen. For a normal operation, the reactant concentration and catalyst concentration were set respectively to be 6M and 3M. The reaction was carried out at room temperature with 5% catalyst volume and without cooling water.

Furthermore, the product from this reaction (i.e., ethyl acetate) is a very important solvent and is used in many products and industries (Hasanoglu *et al*, 2009). It is used extensively as a solvent for high-resolution printing inks and laminating adhesives. It is also an important solvent in paints, resin coatings and varnishes and also used in the pharmaceutical industry as a process and purification solvent.

The reaction was selected because it is a well-known reaction and is moderately exothermic reaction with no danger of decomposition reactions and for which accurate kinetic exist; the reaction exhibits second-order kinetics when no strong acid is present and a kind of autocatalytic behavior when the acid is introduced.

Material Balances with Chemical Reactions
Chemical reactions play a vital role in manufacturing process. For design of chemical process equipment, the operating conditions such as pressure, temperature, composition and flow of the streams should be known. The material balance and energy balance calculations come to the rescue of the designer and allows him to calculate the various flow rates and temperature of the streams. Assuming that the kinetic data of the reaction is available, the overall material balance of the steady state condition will be discussed here.

Material Balances
The general mathematical statement can be written as:

Total mass entering the unit = Total mass of products leaving the unit 1.18

It should be noted that in chemical reactions, the total mass of the input remains constant, but the total moles may or may not remain constant.

For the Process in consideration

Generally, calculations should be based on limiting reactant and quantity of new products formed should be calculated with the help of chemical reactions and number of limiting reactants reacted.

For any reactant material the balance of material can be written as

Material entering = material reacted + material un-reacted 1.19

For products we can write

Material leaving = material produced by the reaction 1.20

If the material is produced by more than one reaction, then the material leaving is sum of the materials produced by all the reactions.

Stoichiometric equation of a chemical reaction is a statement indicating relative moles of reactant and products that take part in the reaction. Any balanced reaction equation is a stoichiometric equation.

Model Formulation
Assumption
The esterification reaction between the acetic acid and ethanol follows a first order kinetics with respect to each reactant but overall follows second order reaction kinetics. The fluxes of all other elements except ethyl acetate present at any time are assumed to be zero.

Governing Equations
The governing equations for the esterification of acetic acid and ethanol are given below (Hasanoglu *et al.*, 2009). Esterification reaction of acetic acid and ethanol to give ethyl acetate and water can be schematically represented by:

$A+B \leftrightarrow R+W$ 1.21

Where:
A = Acetic Acid
B = Ethanol
R = Ethylacetate
W = Water

Acetic acid Ethanol Ethyl acetate Water

The rate of ethyl acetate formation by esterification reaction can be written as:

$$r_R = k_1 C_A C_B - K_1 C_R C_W \quad (1.22)$$

The variation of volume of the reactor is neglected. Hence the ethyl acetate balance in esterification reactor can be:

$$\frac{dC_R}{dt} = (k_1 C_A C_B - k_2 C_R C_W) - \frac{S}{V} J_R \quad (1.23)$$

The relation between flux and ethyl acetate concentration is nonlinear and not constant throughout the reaction, the following relation can be used.

$$J_R = k_{pv1} C_R - k_{pv2} C_R^2 \quad (1.24)$$

Hence the material balance for the water, acetic acid and ethanol can be:

$$\frac{dC_W}{dt} = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = (k_1 C_A C_B - k_1 C_R C_W) \quad (1.25)$$

Above equation represents the homogeneous esterification reaction rate equation without catalyst and the reaction with catalyst can be written as:

$$A + B + C \leftrightarrow R + W + C \quad (1.26)$$

The reaction also occurs without the catalyst and the rate of the reaction with catalyst is directly proportional to the catalyst concentration. Hence, the overall rate of disappearance of component B can be given by:

$$-\frac{dC_B}{dt} = k_{obs}\left(C_A C_B - \frac{C_R C_W}{k}\right) \quad (1.27)$$

The value of k_{obs} depends on the catalyst concentration and reaction temperature. Also the balance equation for ester becomes,

$$\frac{dC_R}{dt} = k_{obs}\left(C_A C_B - \frac{C_R C_W}{k}\right) - \frac{S}{V} J_R \quad (1.28)$$

The conversion of ethanol can be given by:

$$X_B = \frac{C_{BO} - C_B}{C_{BO}} \quad (1.29)$$

The values of rate constants were taken from available thermodynamic and experimental data (Hasanoglu *et al*, 2009).

PROCEDURES

The experiment was carried out in a pilot plant batch reactor. The schematic diagram for the pilot-plant batch reactor is as shown in Figure 1.

The pilot-plant batch reactor consists of reaction vessel, electric heating sensor, variable speed stirrer, temperature indicator, feed vessel, gas feed pipe and solid discharge pipe. The maximum capacity of the reaction vessel is 7 litres. 2.5L of ethanol and 2.5L of ethyl acetate were charged to the reaction vessel via the feed vessel and charge port.

The reaction vessel was fitted with a manually adjusted variable speed (0-800 rpm) stirrer enabling the degree of mixing to be varied; the reaction temperature was indicated by a dial thermometer in the reaction vessel.

The reaction vessel was also fitted with an internal cooling coil allowing the reaction mixture to be cooled. By varying the heating and cooling, exothermic reaction could be studied.

During all the experiments, the process temperature and conductivity were recorded using a temperature indicator and conductivity meter. On the other hand, the concentration of product (ethyl acetate) was measured from the titration process.

Experimental procedure
(i) Ethanol (reactant B) was weighted and loaded into the reactor vessel using feed vessel.
(ii) Acetic acid (reactant A) was weighted and loaded into reactor vessel.
(iii) Sulfuric acid (catalyst) is added to the reactor vessel.
(iv) When the reaction had finished, the reactor contents were discharged.
(v) The experiment can be repeated with different catalyst concentration.

Shutdown procedure
1. Turn the CSTR impeller speed setting to 0 RPM.
2. Turn OFF the CSTR ON/OFF switch.
3. Close the Reactants control valve.
4. Turn OFF the motor control Switch
5. Turn OFF the mains control Switch.

RESULTS

The geometry of the 7L laboratory stirred tank reactor is as shown in Figure 1 with all internal dimensions given in Table 1

Table 1 Design Correlations and Dimensions Summary

S/N	Standard Correlations Used (from Geankoplis, 1993)	Dimensions (in mm)
1	$D_a/D_t = 0.5$	89.00
2	$C/D_t = 1/3$	59.33
3	$W/D_a = 1/5$	17.80
4	$D_d/D_a = 2/5$	35.60
5	$L/D_a = 1/4$	22.25
6	$J/D_t = \frac{1}{12}$	14.83
7	$D_t/72$	5.17
8	D = 0.10J = 0.15 x 5.17	19.40
9	H	356
10	D_t	178
11		

(Source: Geankoplis, 1999)

The feed tube dead-ends at the top of the reactor vessel, and a temperature sensor.

The ratio of liquid level to the tank diameter (*H*/*Dt*) of the vessel in Figure 1 is 1.48mm and is within the general range of 1.0 to 1.5 for most industrial stirred tank precipitators. To reduce the energy input to the system while maintaining mixing uniformity, a standard baffle design was used consisting of four flat vertical plates, radially directed (i.e., normal to the vessel wall), spaced at 90° around the vessel periphery running the length of the vessel's straight side. Standard baffle widths are between 1/10 and 1/12 of the vessel diameter (J/10 or J/12, for this work, the ratio J/12 was used), see Table 1 for details. The gaps with the vessel wall and base are left to allow the flow to clear the baffles. Recommended gaps are equal to 1/72 of the vessel diameter (/72) between the baffles and the vessel wall, and 1/4 (L/to one full baffle width between the bottom of the baffles and the vessel base. The dimensions of the turbine are also given in Table 1. (The reference text adopted is, Geankoplis, 1999)

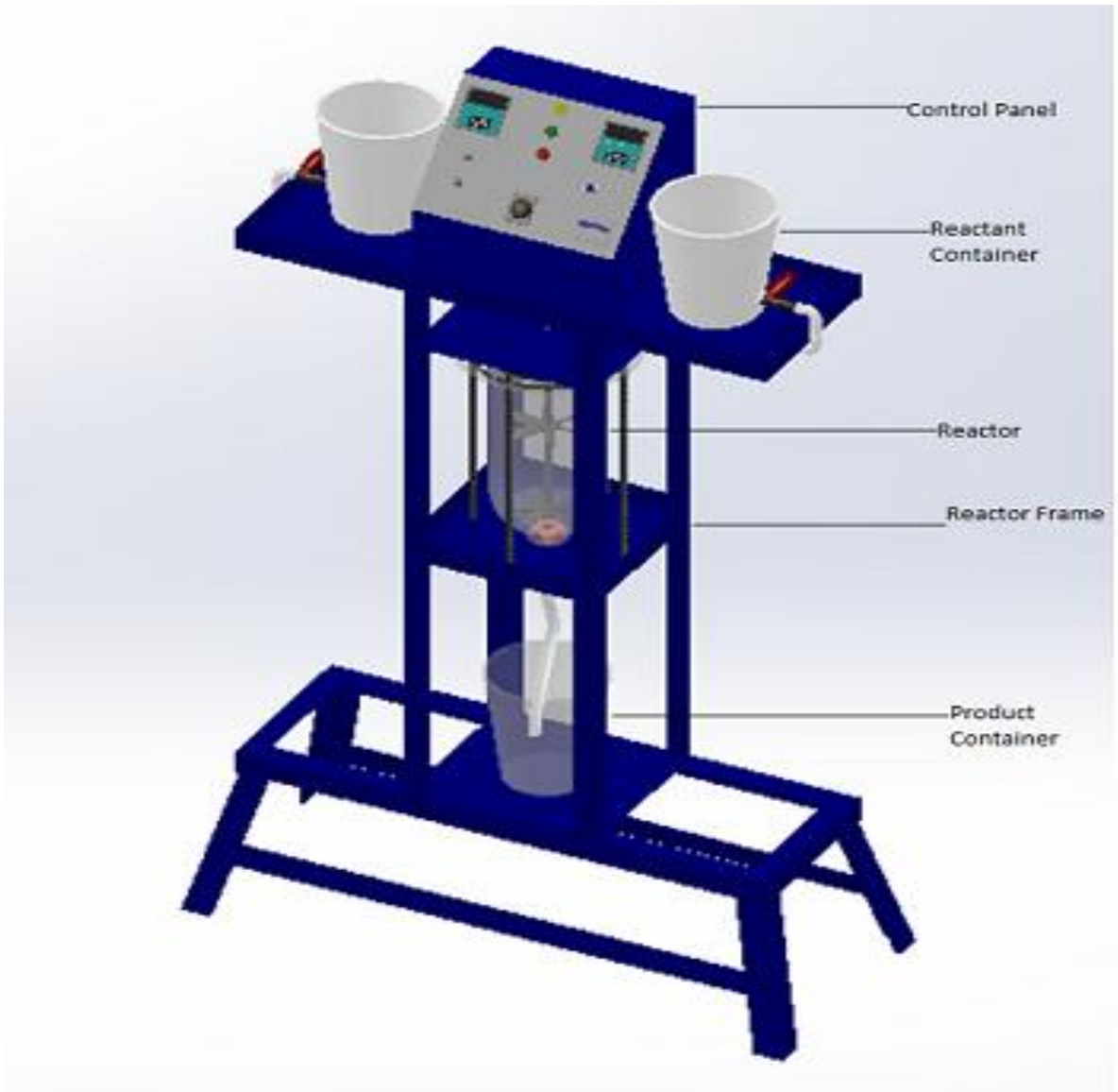

Figure 1 A labelled 3 Dimensional solidworks drawing of the reactor

The rpm of the geared motor is controlled by a carefully fabricated control system establishing the proper mixing and agitation of the solution in the tank. The variables temperature, pH and conductivity, as well as sodium ion concentration, were taken with the aid of accurate digital tools for their measurements respectively.
The calibration for all of these systems was done before each run to ensure measurement accuracy. The RTD measured was the combination of process dynamics and sensor dynamics.

DISCUSSION

The tracer experiments were carried out to validate the effectiveness of the reactor, the effect of different parameters such as stirring speed, concentration and time were studied. In performing the tracer test experiments, standard solutions of NaCl were prepared in 0.2M, 0.4M, 0.6M, 0.8M and 1.0M with methyl blue as the tracer. However, on the course of the experimentation, it was discovered that the 0.8M and 1.0M solution conductivity values were beyond the range of the conductivity meter used, as such they were discarded, thus, the series of experiments were conducted with the 0.2M, 0.4M, and 0.6M solutions at 80rpm, 100rpm, 120rpm, 140rpm and 160rpm, at 20 seconds intervals, twenty eight number of value were taken for each rpm and each concentrations, thus, generating a total number of twenty five curve plots for each 20 seconds interval at a particular rpm(600 second in total for each rpm).

Experimental data obtained at 0.6M and 160rpm gave a curve that is in close agreement to that of the model. In other words, the results obtained at a concentration of 0.6M and 160rpm is in close agreement with that of early researchers.

Esterification process involving the reaction of ethanol and acetic acid catalysed by sulfuric acid was chosen in this work. In this experiment, the direct synthesis of ethyl acetate was chosen. For a normal operation, the reactant concentration and catalyst concentration were set respectively to be 6M and 3M. The reaction was carried out at room temperature with 5% catalyst volume and without cooling water

CONCLUSION

The equipment so designed and developed though at laboratory scale gave a good yield in the production of ethylacetate which is a very important industrial product used extensively as a solvent for high resolution printing inks and laminating adhesives. The product also finds ready markets for the production of paints, resin coatings and vanishes.

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