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OPTIMIZATION STUDY OF ESTERIFICATION USING LOW COST CATALYST

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Abstract

This Experiment aims to reduce the cost of catalyst and with the help of optimizing parameter study the kinetics of esterification of n-butanol and acetic acid. Catalyst used in this esterification was prepared from waste egg shells which are easily available. Making a fine powder of required size, calcination is done under 900°C. With the help of FTIR analysis it is found that CaO was available at wavelength of 724-924Cm-1. For better catalytic activity, esterification reaction is carried between 323-343K. Effect of catalyst concentration, effect of molar ratio, effect of temperature is studied to find out the optimized parameter

Keywords: *N-butanol, Acetic acid, n-butyl acetate, Calcium oxide (CaO),*

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1. INTRODUCTION

Esterification is one of the most important reactions in chemical industry where a number of industrially important organic esters are produced which have various applications in areas of cosmetics, perfumes, pesticides, solvents, flavors, pharmaceuticals and plasticizers. Esterification can be carried out in both liquid phase as well as vapor phase reactions in presence of homogeneous or heterogeneous catalysts. Environmental and corrosion problem are generated due to use of homogeneous acid-catalyzed reaction. Therefore, heterogeneous catalyzed esterification reactions are attracting every one because they provide advantage of easy separation of products from the reaction medium without any contamination[7].

Butyl acetate one of the product of esterification is a solvent with a fruity banana aroma that is used in a variety of household and industrial formulations. It is a low viscous compound, having high miscibility with other solvents and low miscibility with water. It has many applications in various chemical processes. It was used in Paints and lacquer industries. It was also used in photography and leather processing processes.

There are some limitations in using the homogeneous catalysts for the process, due to which, the technology is being shifted to heterogeneous catalysis in availing the post reaction benefits. The heterogeneous solid catalysts are non-corrosive, easy to separate from the reaction mixture and a variety of reactor types and configurations can be adopted on industrial scale. They can also be used repeatedly over prolonged periods of time without any difficulty in handling and storage. Amberlyst 15, Dowex 50, TULSION T-62, T-63, T-66MP, $(Ce(S_2O_8)2/SBA\text{-}15$, $NH_4Fe(SO_4)_2\cdot 12H_2O)$ and oxide (MoO_3/SiO_2) are some heterogeneous catalysts used for the reaction. Most of the catalysts listed above are having industrial applications and are expensive, so it is proposed to develop the catalysts which are derived from solid waste materials and can be availed for low cost.

The catalytic activities of calcium oxide obtained from natural sources (eggshell) were characterized and evaluated in the esterification of n-butanol and acetic acid. These catalysts are mainly composed of calcium carbonate, which is partially converted into CaO after calcination (900°C for 2h). The catalysts have some advantages, such as abundant occurrence, low cost, porous structure, and nontoxic. The materials was characterized by FTIR. The thermal treatment produces small particles of CaCO3 and CaO that are responsible for the catalytic activity[7].

Also it is found heterogeneous catalysts have the advantage the separation and regeneration of the catalyst is easy and cheap . Heterogeneous basic catalysts include alkaline earth metal oxides such as calcium oxide (CaO), magnesium oxide (MgO) and hydrotalcites . Eggshells are comprised of a network of protein fibers, associated with crystals of calcium carbonate ($CaCO_3$), magnesium carbonate ($MgCO_3$), calcium phosphate ($Ca_3(PO_4)_2$) and organic substances and water. $CaCO_3$, the major constituent of the egg shell (96%), is an amorphous crystal that occurs naturally in the form of calcite (hexagonal crystal)[7]. Other components include 1.4 % magnesium carbonate, 0.76 % phosphate, 4 % organic matter and trace amounts of sodium, potassium, zinc, manganese, iron and copper.

1.1 Esterification

Conversion of carboxylic acids to esters using acid and alcohols (Fischer Esterification) by James. Description: When a carboxylic acid is treated with an alcohol and an acid catalyst, an ester is formed (along with water). This reaction is called the Fischer Esterification.

2. METHODOLOGY

2.1 Material Required for Catalyst Preparation

Eggshells are waste materials from hatcheries, homes and fast food industries and can be readily collected in plenty. Eggshell waste disposal contributes to environmental pollution. The composition of the egg shell is approximately 98.2 % (phosphate) respectively. Shell membranes comprises of 69.2% protein, 2.7% fat, 1.5% moisture and 27.2% ash. Shell membranes protein comprises of approximately 10% collagen. In the present work non-conventional heterogeneous catalyst i.e. Calcium Oxide has been prepared from chicken eggshell. The use of a catalyst in a reaction is still being developed. Chicken eggshell is household waste and it utilization is still relatively small, such as used as art or handcraft. Eggshell containing calcium carbonate (94%), calcium phosphate (1%), organic compounds (4%), and magnesium carbonate (1%)[7].

The high contains of calcium in eggshells can be converted as a CaO catalyst by calcinations process at temperature around 800ºC for 2 hours where the reaction takes place as exothermic reaction.

2.2 Experimental setup for catalyst preparation

1) The chicken eggshell was collected from the local area restaurant. To remove impurity and interference material, the eggshell was rinsed several times with deionised water. Then, the eggshell was dried at 100 °C in the dry oven.

2) The dried eggshell was crushed and sieved to pass 60 meshes.The experimental were carried out using equipment namely, oven, furnace, FT-IR spectrophotometer 60 mesh sieve, and analytical balance.

3) Amount of 100 g of the chicken eggshell that pass 60 mesh sieves was calcined in a furnace at atmospheric oxygen conditions at 800^{o}C and 900^{o}Ctemperatures for 3 h, after calcinations process completed a cold solid is obtained and stored in a desiccator for 24 hours.

4) The results also have differences lost weight of the samples before and after calcination. The $CaCO_3$ which is the main component of eggshells are known to have a decomposition temperature at 900 ºC.

5) While at 800 ºC the sample weight was reduced by 26%, perhaps at this temperature the CaCO3has been converted into CaO and CO_2, but only in slightly amounts.

6)The calcination temperature at 900 ºC reduced the sample weight by 46% indicated that the decomposition temperature of $CaCO_3$ to CaO and CO_2.

2.3 Materials required for esterification reaction

1) Acetic acid (99.5%) were purchased from SDFCL Fine Chemlimited; Mumbai.

2) Butanol-1-ol LR (n-butanol) was purchased from SDFCL Fine Chemlimited; Mumbai.

3) Sodium Hydroxide used for titration was purchased from LobaChemiePVT LTD, Bombay, India.

4) Phenolphthalein indicator used was from Qualigens fine chemicals Mumbai.

2.4 Experimental setup for esterification reaction

1) First, three-neck flask arranged with condenser.

2) Before acetic acid and n-butanol were reacted, 0.5% wt.CaO (%wt of rxn mixture) was added to acetic acid, and both of raw materials were heated according to variable temperature on separated place.

3) After acetic acid and n-butanol reach the temperature variable, both of them put into three neck flask for esterification process.

4) Reaction time began after materials were poured into three neck Flask and every 5 minutes 5 ml samples were taken for analysis of residual acetic acid and stopped after 55 minutes.

5) The temperature which gave highest conversion from experiment of temperature variable was used as fix temperature for catalyst loading variable.

6) Conversion was determined by titrating unreacted AA with 0.5N NaoH soln.and applying stiochiometry for determining equilibrium conversion of AA, BtOH, BA and water.

*Normality of residual acetic acid calculated by this equation

$V_{NaOH} \times N_{NaOH} = V_{sample} \times N_{sample}$

*Acetic acid conversion is calculated by:

Conversion, $X = (C_{Ao}-C_A)/C_A$

3. RESULT AND DISCUSSION

3.1 FTIR of calcium oxide

1) Identification of chemical compounds using FT-IR spectrophotometer in general divided into two areas for the uptake and absorption of inorganic compounds to organic compounds. The region for inorganic compounds is in the wave number range between 400-600 cm^{-1} and for organic compounds ranging in wave numbers above 1000cm^{-1}.

2) The existence of absorption in the region 1000 - 4000 cm-1 in eggshell powder with calcination temperature at 900 ºC preparation results in an absorption of background on the FT-IR spectra shown in Figure 1, whereas the wave number 3641.60 cm^{-1} showed absorption bands of O-H from $Ca(OH)_2$.

3) This happens because the CaO containing water, the water is filling the cavities of CaO crystal lattice that exist in the form of metal oxide base catalyst which is proof by appearing absorption spectra characteristic for metal oxide CaO in the area range 250-600 cm^{-1}

4) In the FT-IR spectra at Figure 1 shows that the width peak at wave number 393.48 cm-1 suggests indicate as broad band vibration of Ca-O metal oxide the absence of a sharp absorption in the region around 724-924 cm^{-1}.Indicates that the $CaCO_3$ as the basic components of the eggshell are no longer present as it already converted to CaO.

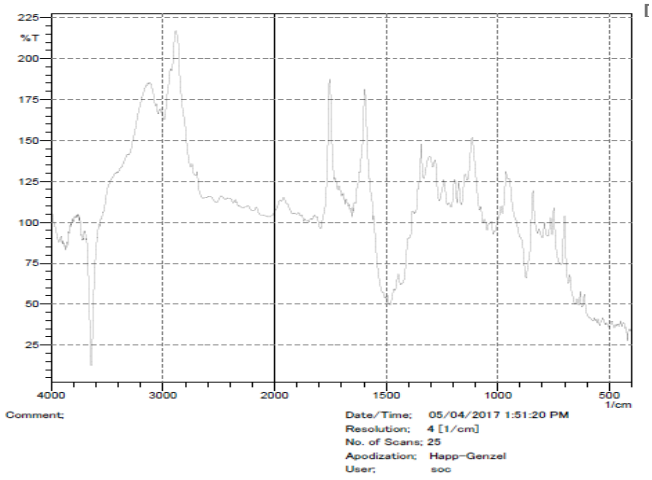

Fig-1: FT-IR Spectra for Metal Oxide CaO Obtain in the range of wave number at 300-1000 cm^{-1}

3.2 Mechanism of CaO transesterification

For primary alcohols reacting with unhindered carboxylic acids, K_{eq} = 4. If equal quantities of 1-butanol and acetic acid are allowed to react, at equilibrium the theoretical yield of ester is only 67%. To upset the equilibrium we can, by Le Chatelier's principle, increase the concentration of either the alcohol or acid, as noted above. If either one is doubled, the theoretical yield increases to 85%. When one is tripled, it goes to 90%. But note that in the example cited the boiling point of the relatively nonpolar ester is only about 8°C higher than the boiling points of the Polar acetic acid and 1-butanol, so a difficult separation problem exists if either starting material is increased in concentration or the product is isolated by distillation.

3.3 Optimization

Butanol to acid molar ratio is one of the most important aspects affecting conversion and usually excess of Butanol is needed particularly in the conventional approach, to drive the reaction in the desired direction.. The mole ratio of Butanol to acetic acid M was varied between 2.5 and 3.5. Theoretically, butyl acetate synthesis reaction requires one mole of Butanol for each mole of acetic acid. However, in conventional ester synthesis, alcohol is used in excess (M greater than 1) to drive the reaction toward completion as the esterification is reversible.

3.4 Catalyst conversion concentration

After optimizing initial molar ratio at 1:2.5 (AA : n-butanol), the effect of catalyst concentration on conversion was studied for this three batches were taken at 0.5%, 1% and 1.5% (w/w), constant stirring speed at 600 r.p.m., temperature at 70^{O}C. The conversion was been determined by titrametric determination of unreacted acetic acid and stoichiometric proportion of n-butanol for the same.

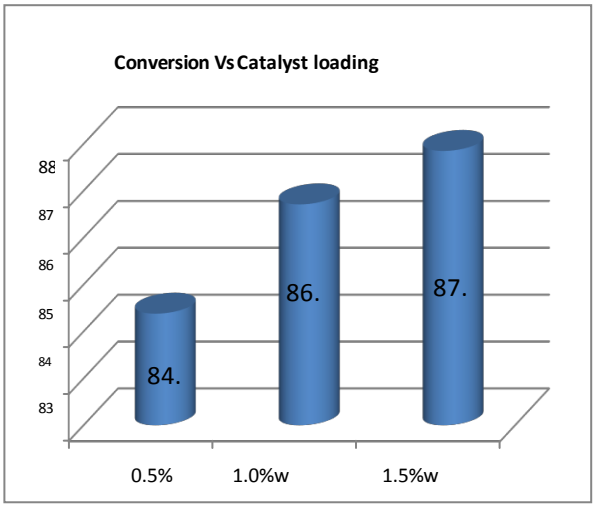

Fig-2: % conversion of various catalyst loading

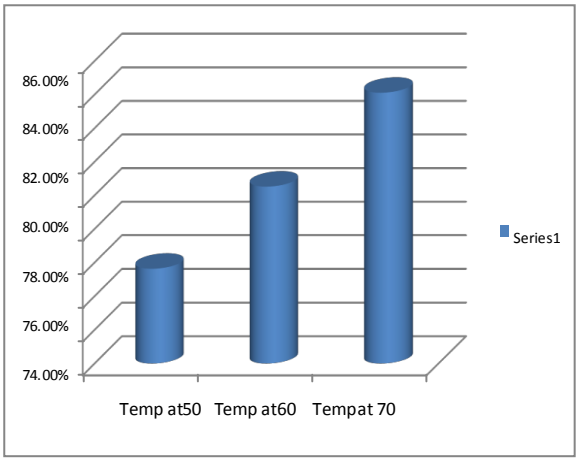

Fig-3: Effect of temp on conversion

3.4 Effect of Temperature on conversion

After optimizing initial molar ratio at 1:2.5 (AA : n-butanol) and effect of catalyst concentration at 1.5% (w/w), the effect of temperature was determined for this three batches at temperatures 50, 60 and 70^{O}C was taken and the stirring speed was keep constant at 600 r.p.m.

Table-1: comparision between various temperature in terms of % conversion

Temperature	% Conversion
50	73.63
60	78.52
70	84.11

3.5 Thermodynamics and kinetics

Acetic acid undergoes a reversible reaction with n-butanol to form Butyl acetate and water in presence of solid CaO catalyst. The effects of temperature on the equilibrium constant are usually expressed using the classical Van't Hoff relation. This equation gives information about the d After optimizing initial molar ratio at 1:2.5 (AA : n-butanol) and effect of catalyst concentration at 1.5% (w/w), the effect of temperature was determined for this three batches at temperatures 50, 60 and 70^{O}C was taken and the stirring speed was keep constant at 600 r.p.m. The conversion was been determined by titrametric determination of unreacted acetic acid and stoichiometric proportion of n-butanol for the same.ependency of equilibrium constant on temperature. The Van't Hoff equation can be derived from the Gibbs–Helmholtz equation. ΔH is the standard enthalpy change of a reaction and ΔS is the change in entropy of the reaction system.

Determination of activation energy:-

Esterification reactions are known to be second order reversible reactions.

$$CH_3COOH + C_4H_9OH \Leftrightarrow C_4H_9COOCH_3 + H_2O$$

With the restrictions that $C_{A0} = C_{B0}$ and $C_{C0} = C_{D0} = 0$,

$$-r_B = -\frac{dC_B}{dt} = C_{B0}\frac{dX_B}{dt}$$

$$= k_1 C_A C_B - k_2 C_C C_D = k_1 C_{B0}^2 (1 - X_B)^2 - k_2 (C_{B0} X_B)^2$$

Where, A,B,C and D refer to acetic acid, n-butanol, butyl acetate and water respectively. k_1 and k_2 are the forward and backward reaction rate constants respectively.

At the equilibrium, - r_B = 0. Hence, from the above equations, we find the fractional conversion of B at the equilibrium conditions by

4. CONCLUSION

Following points are concluded to finalize optimum parameters

1) Initial molar ratio of 1:2.5, Temperature of 70 ^{o} C, Catalyst concentration of 1.5 % (w/w) result in to conversion up to 87.34 % in 45 min.

2) Heat of enthalpy is found to be –ve so it is affirmed that reaction is exothermic for given set of conditions.

3) Activation energy for forward reaction is found to be 11.47 KJ/mole & Activation energy for backward reaction is found to be 14.08KJ/mole.

4) From this it was concluded that the use of calcium oxide result in increase of yield than the conventional method. Hence prove to bebeneficial.

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