ANALYSIS OF ESTERIFICATION REACTION UNDER MICROWAVE IRRADIATION

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ABSTRACT

The organic synthesis is one of the major roles of research in chemistry, which is used to improve everyone life. The use of microwave assisted organic synthesis (MAOS) has become increasingly popular within the pharmaceutical and chemical engineering areas. Sudden increase in Gibbs energy due to increase in temperature by microwave radiation, this is main reason to increase the rate of reaction. Esterification is the reaction which gives high conversion in microwave as compare to conventional heating. Study of esterification reaction is done with varying temperature, power and other parameters. Discover CEM is used to carry out reaction in microwave. Microwave synthesis is used for various applications in organic chemistry as well as analytical chemistry. Esters are one of the most common derivatives of carboxylic acids and are widely distributed in both nature and industry. Esterification is one of the major reactions which perform under microwave irradiation gives higher yield than conventional method. Analysis of variance, often abbreviated to ANOVA, is a powerful statistic and a core technique for testing causality in biological data and chemical data. Researchers use ANOVA to explain variation in the magnitude of a response variable of interest. This statistical analysis tells you whether that parameter is significant or not. The statistical analysis of conventional reaction data gives the significant parameters Based on that parameter experiments done in microwave assembly for higher conversion which gives optimize power for each parameter.

Index Terms—*MAOS, Esterification reaction, Analysis of variance, Optimize power*

INTRODUCTION

The organic synthesis is one of the major roles of research in chemistry from plastics to medication it participates in the improvements of everyone life. Over the past few decades many significant advances in practical aspects of organic chemistry have included novel synthetic strategies and methods as well as advent of a vast array of analytical techniques. In these environmentally conscious days, his developments in the technology are directed towards environmentally sound and cleaner procedures. Hence the present day chemists are no longer confined to using only thermal energy for driving chemical reactions. With increasing complexity of the problems and the availability of newer methods of activation of chemical reactions, chemist have restored to using wide variety of techniques such as photochemical, electrochemical, sonochemical, microwave and enzymatic methods[1]. Microwave has been used to speed up chemical reactions in the laboratories which led Scientists investigate the mechanism of microwave dielectric heating and to identify the advantages of the technique for chemical synthesis. During recent years, microwaves have been extensively used for carrying out chemical reactions and have become a useful non-conventional energy source for performing organic synthesis. The physical principles of microwaves are based on relatively simple laws. The wave-length l0 of a microwave (in this case 12.24 cm) is related to the frequency (2.45 GHz). The frequency indicates the number of oscillations of the electric or magnetic field in 1 sec the mechanism by which matter absorbs microwave energy is called dielectric heating. The important property is the mobility of the dipoles and the ability to orient them according

to the direction of the electric field. The orientation of the dipoles changes with the magnitude and the direction of the electric field.

REACTION, MATERIALS AND METHODS OF ANALYSIS

Esters are one of the most common deri- vatives of carboxylic acids and are widely distributed in both nature and industry. A typical procedure to synthesize esters is the Fischer esterification, wherein a carboxylic acid is treated with an alcohol in the pre- sence of a mineral inorganic acid catalyst or heterogeneous catalyst. Acetic acid can be converted in to ester which can be useful solvent, cosmetic, and flavour etc. Esters are also formed by a number of other reactions utilizing acids anhydries, amides, nitriles, unsaturated hydrocarbons, ethers, aldehydes, ketones, alcohols etc. Ester can be prepared by the reaction of carboxylic acid and an alcohol in presences of a catalyst such as concentrated sulphuric acid or ion exchange resin.

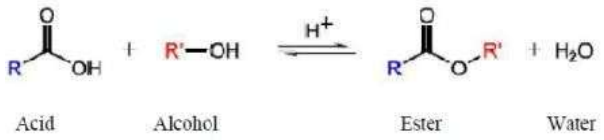


Figure 1: Esterification reaction mechanism.

Table-1Chemicals used for reaction

Chemicals	Purity
Acetic acid	99.5%
Methanol	99.5%
Sodium Hydroxide	99.0%
Amberlyst Wet 15	Sizes 600 to 800µm
Phenolphthalein	-

Samples were withdrawn from reactor at a regular time intervals and analysis is done using titration with 0.5N NaOH solution. With help of titration we calculate amount of acetic acid consume during reaction for that particular time. Experimental results thus obtained were within 3% experimental error. Total quantity of samples removed represented only a small fraction of total reaction mass and hence does not contribute significantly to change in the volume of reaction mass.

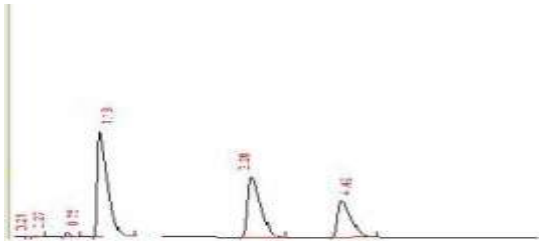
Conversion of Acetic acid (AA) is obtained:

$$\text{Conversion (\%)} = \frac{\text{Amount of Acetic acid reacted}}{\text{Amount of Acetic acid Charged}} * 100$$

Table-2 Calibration error chart for titration analysis

Burette Reading (ml)	Amount of samples	% Error
21.1	2	1.81
21.1	2	1.81
21.9	2	2.33
21.9	2	2.33

The liquid sample were weighted and analyzed with a gas chromatograph NUCON with thermal conductivity detector. Nucon Nuchrom software was used to analyze the data. A porapack-Q column (length 1.82m, OD 1/8 inch material -SS) was used for separation. For preparation of GC sample solution of collected samples with known amount of ethanol used for analysis. Ethanol used as internal standard. From prepared sample 0.5 micro liter sample injected into a column through syringe. The oven temperature program consists of 1500C constant for 1 min and ramp at 50C/min to get oven temp 2400C. Total rum time is 20 min. The injector and Detector temperature maintain at 2400C. Using standard calibration curve that were prepare for all the components, the integrated areas were converted to weight percentage for each component present in sample Figure shows the chromatograph obtain from GC analysis showing peaks for all components of the system i.e. water, methanol, ethanol, methyl acetate , and acetic acid.



0.75- water 1.1- methanol
3.26- methyl acetate 4.49- acetic acid

EXPERIMENTAL WORK

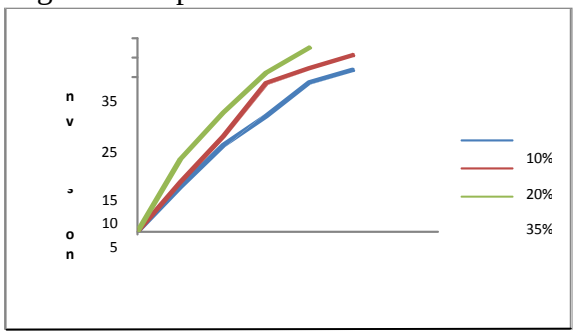
The system is consisting of a three necked glass batch reactor having capacity ±6 x10-4 m3 capacity. A constant temperature bath was used to control the temperature within 10^0C. Initially a known amount of acetic acid-water solution along with calculated quantity of methanol was taken in reactor and temperature was raised to 700^0C. The sample taken out at regular intervals and analyzed as detail above. Various batches are conducted by varying temperature and find out conversions.

Table 3 Conversion Calculation for different Time Interval.

Time (Hrs)	BR (ml)	Initial Normality	Conversion%
3	3.2	1.623	47.96
4	2.9	1.479	52.84
5	2.8	1.428	54.46
6	2.7	1.377	56.09
7	2.7	1.377	56.09

Effect of Temperature

In order to study the effect of temperature on reaction experiments were carried out over arrange of temperature.

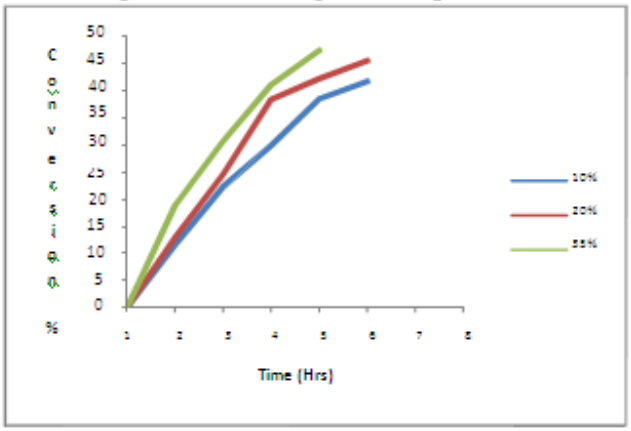


Graph-1 Effect of Temperature.

Effect of Speed of Agitation

The effect of external mass transfer across the solid liquid interface on the kinetics was studied by performing the reaction at various speeds of agitation.

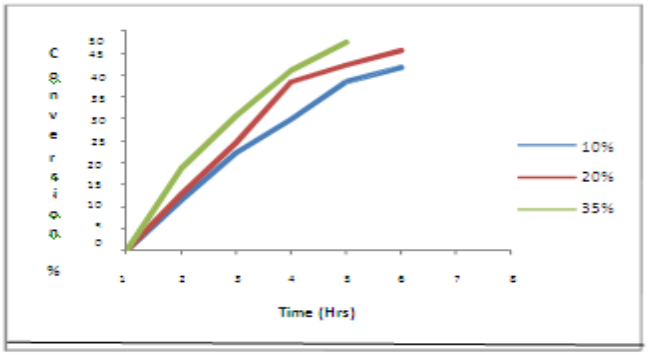
Graph-2 Effect of Speed of Agitation



Effect of Mole Ratio

In order to study the effect of mole ratio on the reaction, experiments were carried out at different mole ratio.

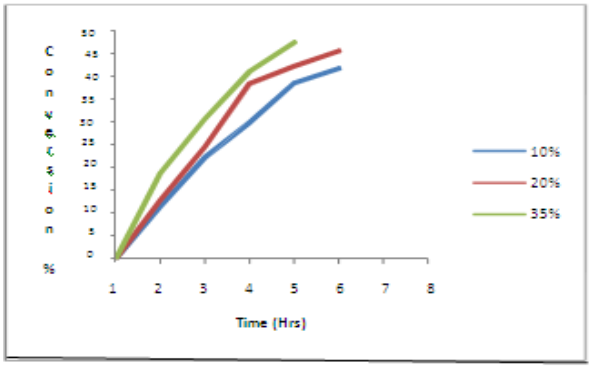
Graph 3 Effect of Mole Ratio



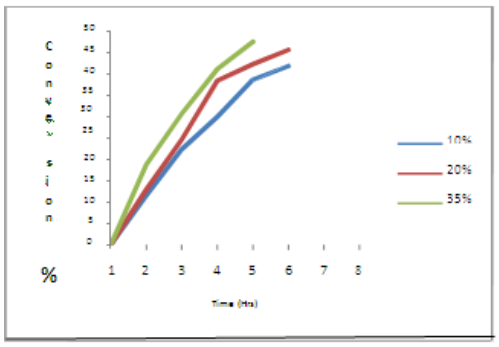
Effect of Catalyst Loading

The reactions were performing over a range of catalyst loading (5-15%w/w).

Graph 4 Effect of catalyst loading



Different Acid Concentration



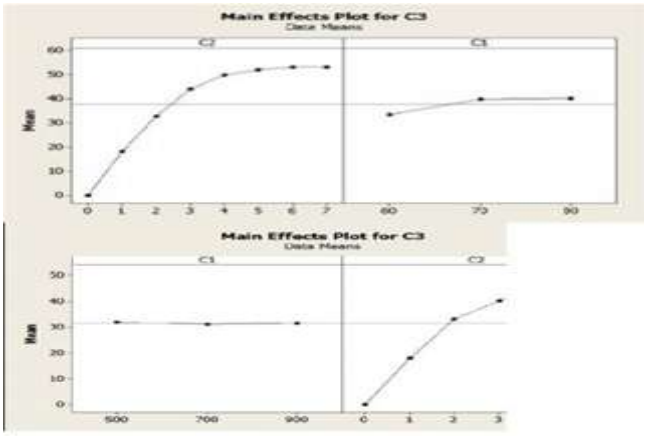
STATISTICAL ANALYSIS

Analysis of variance, often abbreviated to ANOVA, is a powerful statistic and a core technique for testing causality, in biological data and chemical data. Researchers use ANOVA to explain variation in the magnitude of a response variable of interest. This statistical analysis tells you whether that parameter is significant or not analysis of variance table. The most important statistics in analysis of variance table is p value. This p- value tells you whether the effect of the term is significant or not. If p- value is less than or equal to α-level you have selected (0.005 for all analysis) then this parameter is significant and if p value is greater than α-level then effect of parameter is not significant. This measure in the units of response variable and represents standard data value R2 describes smothe amount of variation in observed responses values that is explained by predictors. This value is always increases with predictors. Adjusted R2 that has been adjusted for the number of terms in the model. If R2 can be artificially high term adjusted R2 is small when you add some terms to model. For significant effect S should be minimum and R2 should be maximum. This analysis is performing in Minitab-15 which contains ANOVA tool in statistics main effect plot. This plot is visualization the effect of the factors on the responses to compare the relative strength of effect. If line is horizontal there is no main effect present that is responses is does not depends up on factor level and line is not horizontal main effect is present

Interaction plot-

It is used to visualize interaction effect of two factors on response and compares relative strength of effect. In this plot if lines are parallel to each other there is no interaction presents and lines are parallel then interaction is presents i.e response is depends on the factors.

Figure-3 Statistical analysis for Various Parameters.



Statistical analysis is checked for different parameters and only Speed of agitation is a parameter where gives no significant effect on reaction system.

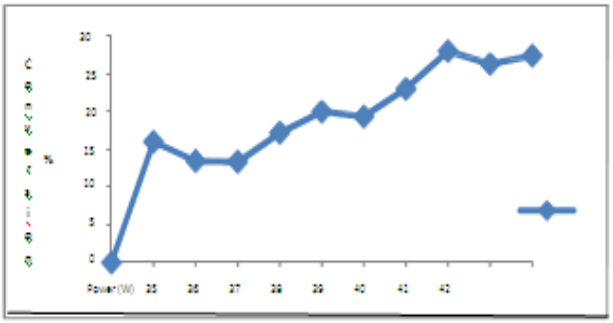
FOCOUSE MICROWAVE SYNTHESIS

The CEM Focused Microwave Synthesis System, Discover, is designed to enhance the ability to perform chemical reactions under controlled conditions on a laboratory scale. The systemfacilitates either homogeneous or heterogeneous solution phase chemistry, solid phase chemistry or chemistry conducted on solid

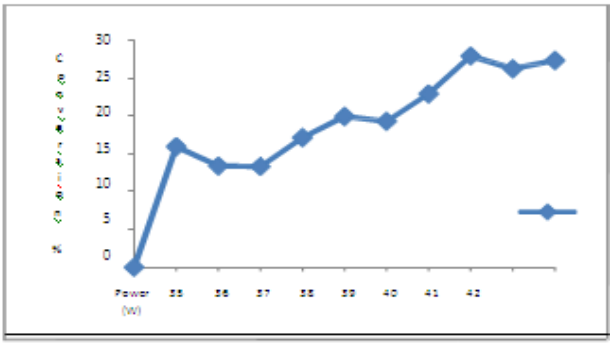
supports. Microwave energy is applied to the vessel contents (reactants, catalysts, solvents and/or solid supports) to accelerate the chemical reaction. The microwave absorbs some properties of liquid and solid material due to their polar and ionic characteristics have the capability to significantly enhance chemical reactions relative to traditional energy application (heating) techniques. The microwave interaction properties with the reactants, intermediates, catalysts, solid supports and salts provide unique opportunities for the synthetic chemist.

Experimental Work on Microwave synthesis is done by varying power required for different parameters for temperature.

Graph-5 Power Analysis for Temperature Parameter.



Graph-6 Power Analysis for Mole Ratio Parameter.



Likewise plot a graph for the each parameter and get optimized power for each parameter.

Parameter	Power (W)	Conversion (%)
Temperature	48	27.94
Acid Concentration	42	34.07
Mole Ratio	48	27.94
Acid Concentration	40	35.33

CONCLUSION

It is conclude that microwave assisted organic synthesis are having great potential to increase conversion as well as yield of product as compare to conventional heating method. Consideration of safety and other measurements like temperature and pressure, Microwave technology give easiest handling than conventional batch. Microwave heating is not used as industrial level because of efficiency. For controlling of power It was found optimized parameters which are studied in conventional procedure. By using analysis of variance I got significance each parameter which gives speed of agitation is not significant. So excluding that parameter Performs various experiments by varying power of microwave assembly and we get optimize power for each parameter.

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