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Investigation into the Effects of Surfactant on Itakpe Iron Concentrate Magnetic Fluids

By Lukman Y, Anakhu E. A., Ajayi P. R., Audu L. M. & Sule T.U.N
Ahmadu Bello University (ABU)

Abstract- This research work encompasses the potentials of Itakpe Iron concentrate for Magneto-rheological behavior under the effect of a liquid soap as surfactant. The concentrate was first ball milled to size reduce it then subjected to magnetic strength from a locally made electromagnet, with the iron concentrate in-situ the magnetic fluid. Magnetic fluid potential increased as iron concentrate increased in the fluid but viscosity of the fluids was affected by increased surfactant concentration. These positive signs of magneto-rheology under low magnetic influence puts Itakpe Iron concentrate a candidate material for magnetic fluid potential and application in automobile shock absorbers, brakes etc.

Keywords: *magneto-rheological, itakpe iron concentrate, temperature, in-situ, magnetic bits.*

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Investigation into the Effects of Surfactant on Itakpe Iron Concentrate Magnetic Fluids

Lukman Y [α], Anakhu E. A. [σ], Yesufu I. S. [ρ], Ajayi P. R. [ω], Audu L. M. [¥] & Sule T.U.N [§]

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I. Introduction

Magnetic fluids are stable colloidal homogenous suspensions of magnetic nanoparticles around 10 nm in diameter) in an appropriate carrier (aqueous or non-aqueous) liquid. They are super magnetic because they are attracted by a magnetic field but retain no residual magnetism after the field is removed. Typical magnetic fluid consists of three main elements: magnetic particles, carrier liquid and surfactant. The quality of each determines the performance of the final product. The technological advances made in the last few years have greatly increased the quality of magnetic fluids and variously enhanced properties to serve the requirements of brakes, seismic dampers, human prosthesis [http://en.wikipedia.org/wiki/Magnetorheological_fluid, 2013], etc. The whole family of magnetic fluid consists of a large number of different types. The two most common magnetic fluids that have been widely used commercially are ferrofluid (FF) and Magneto-rheological fluid (MR fluid) [Wang, 2014]. Another smart fluid, the Electro rheological fluid (ER fluid) which has almost the same function as MR fluid.

The history of MR fluids dates to the 1940s when it was discovered by Jacob Rabinow of the US National Bureau of Standards fluids. Rabinow was inspired by Willis Winslow following a seminar on electrorheological (ER) Fluids (Rao, 2001). A decade later saw MR patents surpassed that of the ERs and by the 1990s MR fluids moved from research and development to industrial application in areas of Shock absorbers and polishing machine (Claracq *et al*., 2003). In recent times, MR fluids have found application in automobile and aerospace technology and they possess higher field induced particles than ER fluids, hence the preference for ER fluids (Jolley *et al*., 1996; Wereley, 1999).

Magnetic fluids can be made into solid structures at room temperature and turned liquid at slightly elevated temperature when paraffin based ferrofluid is used as the carrier liquid. Heating the fluid and cooling in the presence of a magnetic field will find application in solid magnetic nanostructures such as the gear-like structure (Jolley *et al*., 1999). Magneto-rheological applications are generally classified as Shear mode where clutches and breaks are used; flow mode which includes shock absorbers and damper in medical devices and squeeze mode in vibration isolation systems in artificial limbs (Choi and Han, 2013). Several studies on magnetic fluid have been carried out with great engineering interest at room temperatures and more focus on the external magnetic field (electromagnets). However, other works have reported findings in small temperature ranges of 40 – 45°C in biomedical applications. This research therefore focuses on the effect of temperature (from room temperature to 70 °C and Iron concentrate of up to 25%) on permanent magnetic influenced ferrous particles in-situ Motor oil.

II. Material and Methods

a) Equipment used

The Materials and Equipment used in this research work are listed in Table 1.

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Table 1

S/NO.	MATERIAL/EQUIPMENT	MANUFACTURER	SOURCE
1	Motor Oil	Ammasco synthetic 5w/30	Zaria Market
2	Magnetic Stirrer bars	3 mm (1/8") x 12 mm (½"),VWR Octagon Spinbar	Chemical Engineering Department, ABU Zaria
3	Weighing Balance	Sauter Mode	Chemical Engineering Department, ABU Zaria
4	Thermometer		Chemical Engineering Department, ABU Zaria
5	Viscometer	Fann Instrument Company, Model 35	Chemical Engineering Department, ABU Zaria
6	Iron Concentrate		Itakpe Iron Mining Site, Kogi state Nigeria
7	Ball milling Machine	Kere Soesterberg, 057748	Chemical Engineering Department, ABU Zaria
8	Scanning Electron Microscope	Q30	Kaduna Geological Centre.

b) Ball-milling the Iron ore

Iron ore concentrates at different sizes were put in a milling machine and milled for approximately 50 hours until the size of the sample was reduced to very tiny(nano) particles.

c) SEM Analysis

A scanning electron microscope (SEM) analysis was conducted to get the following information about the sample (iron ore concentrate); external texture, chemical composition, crystalline structure, orientation of materials making up the sample.

d) Experimental Procedure

First a basis of 100g was taken as the primary measurement for the process. According to literature, the volume of a typical magnetic fluid is 5% magnetic solids, 10% surfactant and 85% carrier but for the purpose of this research work, different ratios will be experimented to get a relationship between the viscosity of the magnetic fluid and volume of surfactant.

100g (100% loading) of oil with 0g (0% loading) of the iron concentrate and 0g of surfactant was measured, the behaviour of the oil without magnetic solids or surfactants at 200 RPM of the oil was then taken at room temperature using the viscometer. An external magnetic field in form of an electromagnet was wound around the cup of the viscometer. It was then placed on the magnetic stirrer which also served as the heat source with constant temperature.

III. Results and Discussions

The viscometer used for this process measured shear rates in millipascal-seconds (mpa-s) equivalent to centipoise (cP).

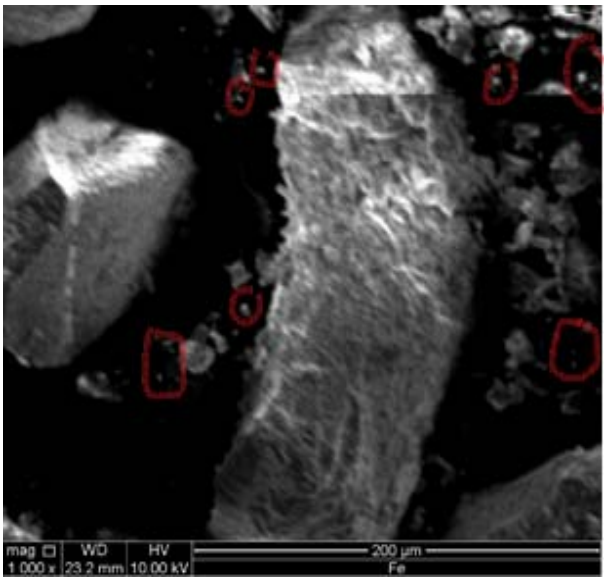

Figure 1: SEM Surface Image of Itakpe Iron Concentrate

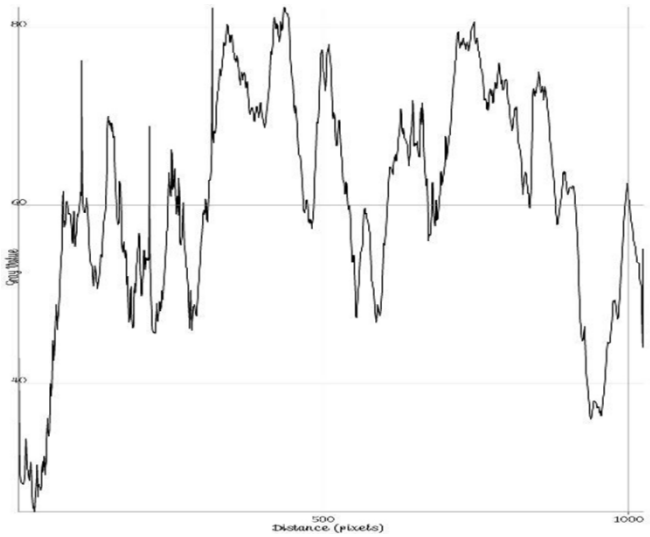

Figure 2: Profile plot of SEM analysis of the iron concentrate

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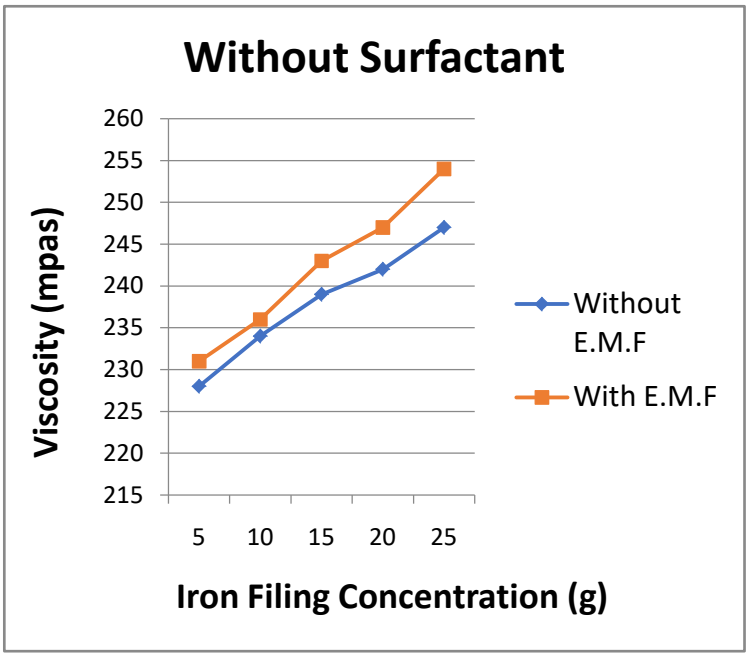

Figure 3: Effect without surfactant on the viscosity of the magnetic fluid under the influence of electromagnetic field

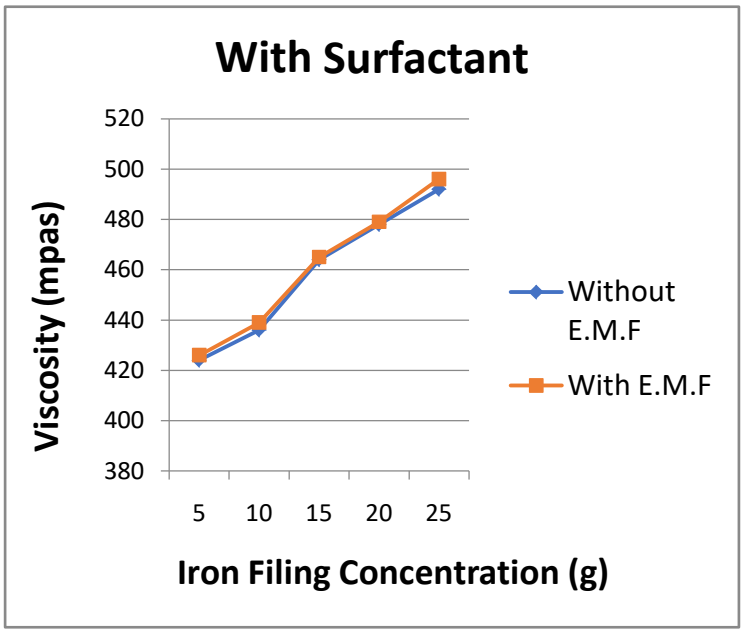

Figure 4: Effect of Surfactant on Magnet Influenced Iron concentrate in Motor Oil

Figures 1 shows the morphology of the ball milled iron concentrate. Particles size distributing varies from about <5 to 100 μm as seen from the scale of the microscopic image. The smaller particles (< 10 μm, circled in red) fall in the range of particles generally used for magnetorheological studies (Joseph and Suresh, 2014). Figure 2 shows the total dispersion of the iron particles inside the iron concentrate. This gives the microscopic overview of the relationship between the distance and gray value of the iron concentrate particles.

Figure 3 showed that at different loading (i.e. concentration) of the iron filings in the magnetic fluid, its viscosity also changed. From the experimental procedure, as the loading was increased, the fluid naturally became denser and it was assumed that the increase in density meant the viscosity will increase. The figure above confirmed that assertion as it is seen that as the iron filing concentration increased, the viscosity also increased without the effect of an electromagnetic field (E.M.F), and with the effect of an E.M.F. This implies that an influence of an E.M.F affects the

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hydrodynamic behavior of a magnetic fluid by increasing its density and hence its viscosity. From the figure 4, just like figure 3 it was seen that at different loading (i.e. concentration) of the iron filings in the magnetic fluid, its viscosity also changed. Also from the experimental procedure, as the loading was increased, the fluid naturally became denser and it was assumed that the increase in density meant the viscosity will increase. But in this case, it was quite different because of the addition of liquid soap which served as the surfactant. As the iron filing concentration increased, the viscosity also increased as usual even similar to figure 2 but here it was more uniform because of the influence of the surfactant.

The addition of the surfactant reduced the surface tension of the fluid and also prevented aggregation or clumping of the iron particles at the bottom of the fluid, allowing them to be suspended and stable in all parts of the fluid (i.e. there's no separation between the solid and liquid nor agglomeration of particles is seen even under a strong magnetic field [www.sigma-hc.co.jp, 2015]. Also, it increases the shear stress (thickness) of the fluid and hence the viscosity.

IV. Conclusions and Recommendations

1. The Iron concentrates although with wide distribution of particle size showed prospects of magneto-rheology.
2. Magneto-rheology increases with Iron concentrate content in the motor oil up to 25%.
3. Surfactant has more influence on the viscosity of the fluid when under influence of weak magnetic effect.

a) Recommendations/Future work

1. A more efficient method to size-reduce the iron concentrate to uniform size in Nano scale rather than ball-milling for plenty hours.
2. Electromagnetic effect with higher and known magnetic strength will be used for future studies.

Conflict of Interest

There is no conflict of interest associated with this work.

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Assessment of Separation Processes for Recovery of 1-Butanol from its Dilute Aqueous Solution

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Keywords: 1-butanol, aqueous solution, fermentation, separation.

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Assessment of Separation Processes for Recovery of 1-Butanol from its Dilute Aqueous Solution

Shreya Akshay Thakkar [α], Atharva Shashank Chikhalikar [σ] & Neha Amol Padwal [ρ]

Abstract- Microbial fermentation yields aqueous solutions with concentrations of 1-3 % by weight of organic compounds. Moreover, the presence of organics in water may lead to hazardous effects on health and the environment. Separation and recovery of these organics from water poses difficulties for industries as several energy-intensive operations such as distillation prove to be uneconomical when compared with the energy content of 1-butanol. Fermentation broth concentrations upto 70 kg/m^3 are required to produce an effective liquid-liquid split. The paper aims at assessing several unit operations for recovering 1-butanol from water in terms of their recovery, purity, energy input and evaluating their applicability. Separation processes studied are freeze crystallization, adsorption, pervaporation, reverse osmosis, phase separation using salts and ionic liquids. Some adsorbents were found to be efficient for extracting 1-butanol from the solution. Multiple stages of pervaporation were capable of providing a high purity stream of 1-butanol. Likewise, freeze crystallization and reverse osmosis also offer feasible alternatives to overcome the separation crisis. The ability of ionic liquids and salts to alter the equilibrium even at low 1-butanol concentrations can be potentially utilized for separation. A comparison of these operations reveals that we need to make a compromise between energy efficiency, recovery, and purity.

Keywords: 1-butanol, aqueous solution, fermentation, separation.

Highlights

- Evaluating feasibility of unit operations based on energy, recovery, and purity.
- Based on recovery, freeze crystallization and salting are potential options.
- Adsorption and reverse osmosis were found to be the least energy intensive.
- Hybrid separation processes could be the key to solve separation crisis.

I. Introduction

1-butanol has a plethora of uses in the manufacture of commodity as well as specialty chemicals. It possesses numerous advantages as a biofuel. Firstly, it has a higher organic content than ethanol which makes it more compatible to mix with gasoline. Secondly, its energy content is similar to petrol making it a suitable replacement. Moreover, high energy density, low vapor pressure, and low corrosiveness result in easier handling making it a promising bio-fuel [1, 2, 3, 4].

1-butanol production on industrial scale occurs via microbial fermentation yielding concentrations of 1-3% by weight. Above concentrations of 2 wt % of 1-butanol, process inhibition occurs, and fermentation is stopped [4, 5, 6]. Its separation and recovery is a crucial step in the industry. Although distillation is the most widely practiced separation process, its energy requirement is comparable to the energy content of 1-butanol rendering it uneconomical [7, 8]. Much higher fermentation broth concentrations are required to produce an effective liquid-liquid split [9]. This paper assesses alternative separation methods for 1-butanol recovery such as freeze crystallization, adsorption, pervaporation, reverse osmosis and phase splitting using salts or ionic liquids, and evaluates them on the basis of recovery, purity, and energy-input.

We have considered a concentration of 20 kg/m^3 1-butanol in aqueous solution and a flow rate of 1000 kg/hr for the continuous unit operations for calculations. Uniform basis for each unit operation evaluated ensures that this paper provides an effectual comparison amongst the separation methods studied.

II. Freeze Crystallization

Freeze crystallization (FC) is a separation method based on the difference in melting points of the components in the mixture. It is a relatively newer method which has not found much application in the industry due to difficulty in operation. There is a considerable difference in latent heat associated with evaporation and fusion. While distillation exploits the former which is much higher, FC is based on the latter leading to lower energy requirements [8]. In the last few decades, the principles of FC have been applied for the purification of water [10, 11].

FC is based on the solid-liquid equilibrium of the mixture. As the temperature is lowered, the component with higher melting point crystallizes to give a product with very high purity [12] resulting in a change in concentration of the solution. A typical equilibrium

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diagram showing the cooling temperature on the Y-axis and composition of the solution in the liquid phase is depicted in Figure I. This phase diagram enables us to calculate the quantity of crystals formed using lever rule and the amount remaining in the liquid phase and its composition.

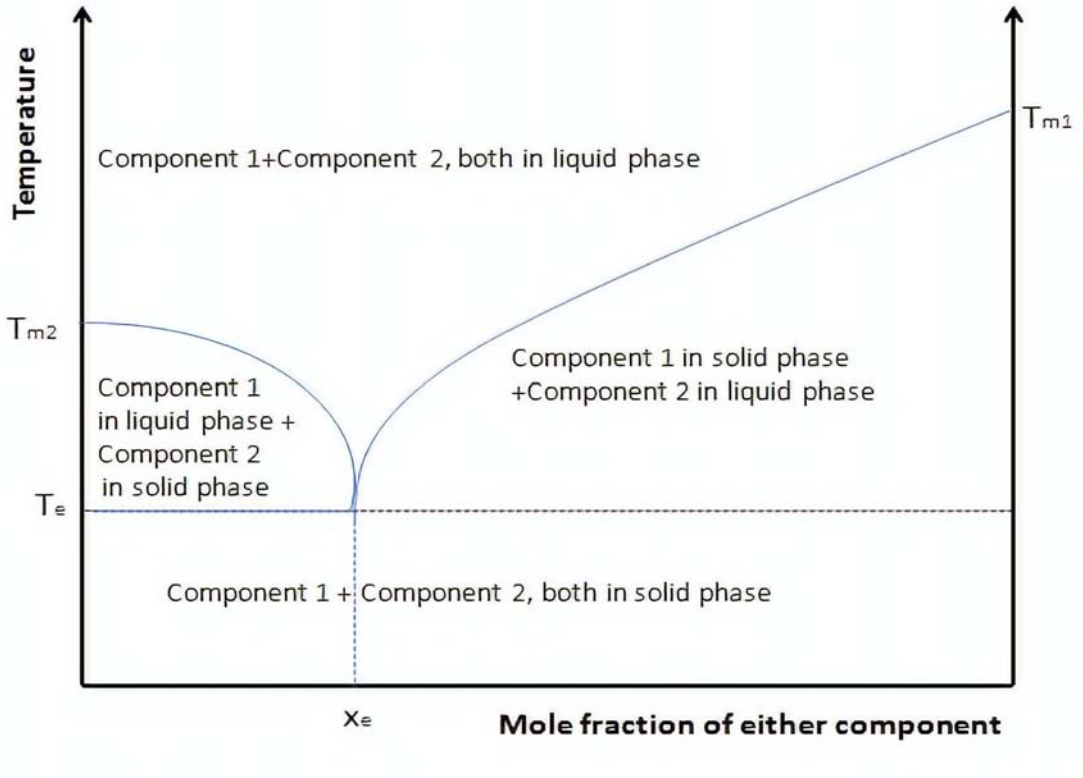

Figure I: Solid-Liquid phase equilibrium for binary mixtures (where T_{m1} and T_{m2} represent melting point temperatures of component 1 and 2 respectively; T_e represents eutectic temperature, and X_e represents eutectic composition)

The above concept was used to calculate the mole fraction of 1-butanol remaining in the liquid phase after crystallization of water from the aqueous solution. The solid-liquid equilibrium data for this system is represented in Figure II [13].

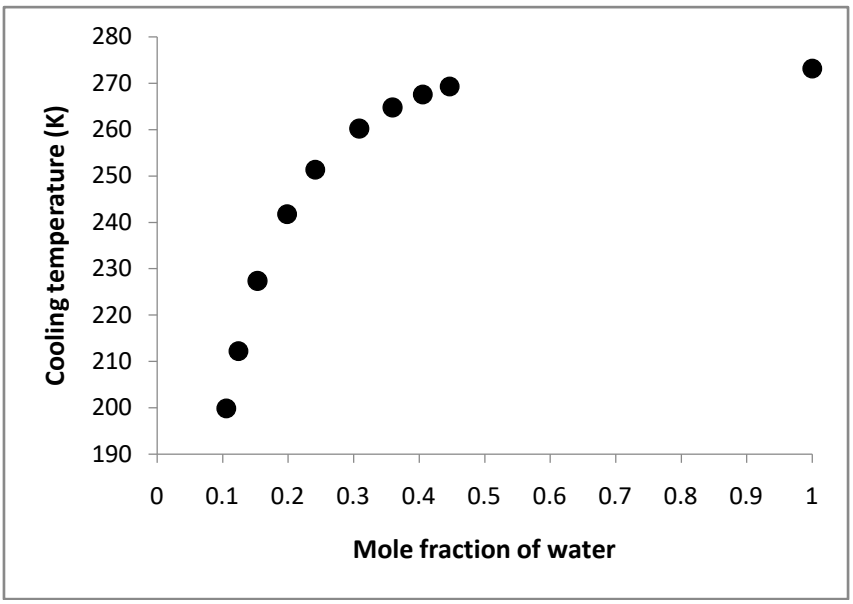

Figure II: Solid-Liquid equilibrium data for 1-butanol and water mixture

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The pure component melting point of water is 273.16 K and that of 1-butanol is 183.3 K. Since the data in Figure II is above 183.3 K, it represents right-hand side of the curve in Figure I where component 1 would be water and component 2 would be 1-butanol.

The data points between 269.28 K to 199.89 K were regressed to obtain cooling temperature in K (y) as a function of mole fraction of water in the liquid phase (x) with $R^2 = 0.998$

$$y = 2694x^3 - 2993x^2 + 1160x + 108.5 \quad \text{(I)}$$

Using equation (I) and applying lever rule, the variation of 1-butanol concentration in the liquid phase with cooling temperature was calculated and represented in Figure III.

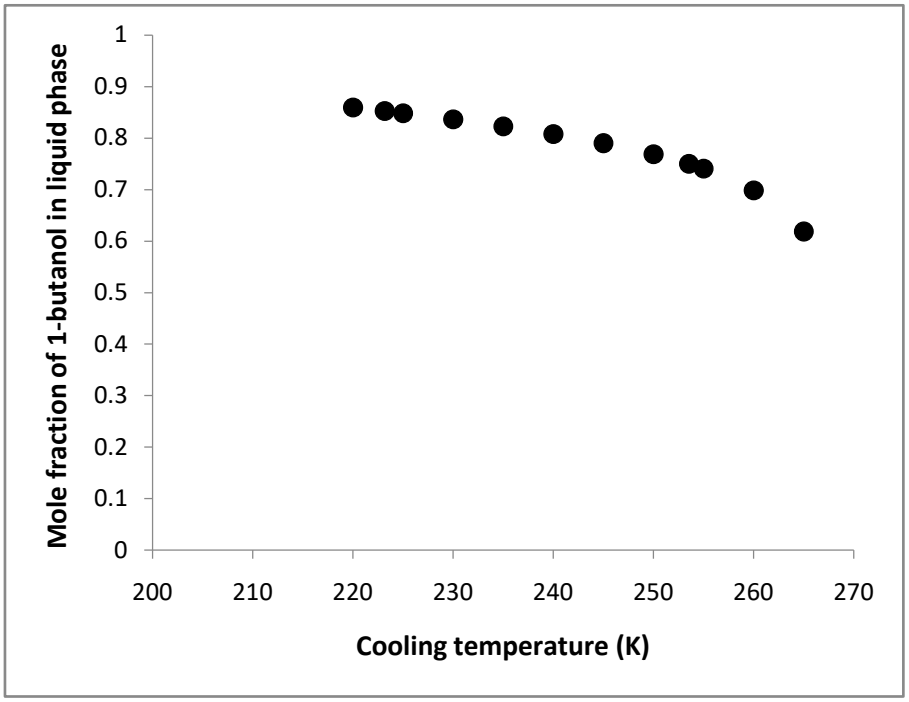

Figure III: Plot of how mole fraction of 1-butanol decreases with an increase in cooling temperature

Cooling to 253.53 K yields a concentration of 0.75 mole fraction 1-butanol in the liquid stream and 99.83% of water fused to form ice. This temperature is attainable, and there is a significant improvement in 1-butanol concentration from an inlet of 0.005 mole fraction to 0.75 mole fraction in the outlet. More concentrated outlet stream can be obtained at lower temperatures. But, it is not feasible to use a cooling agent to attain such low temperatures at an industrial scale. Cooling agents such as liquid nitrogen, solid carbon dioxide or even glycols at very high concentrations can achieve significantly low temperatures but possess handling difficulties.

At 253.53 K, ethylene glycol in water can be used as a cooling agent at a concentration of 45% by weight. Other cooling agents such as propylene glycol brine can be used, but it has very high viscosity. Calcium chloride can also be used but it is highly corrosive [14] and has a relatively low specific heat[15].

Hence, the energy requirements for crystallization using 45% by weight ethylene glycol brine were calculated at a cooling temperature of 253.53 K.

Table I: Feed properties assumed for calculations

Feed flow rate (1-butanol+water)	1000 kg/hr
Feed concentration	20 kg/m^3 1-butanol in water
Feed temperature	293.16 K

Under the conditions mentioned in Table I, the overall heat load on the system is calculated to be 495.05 MJ/hr by energy balance which is equivalent to 24.75 MJ/kg of 1-butanol whereas the combustion enthalpy of 1-butanol is 36 MJ/ kg of 1-butanol [16].

The temperature to which the solution is to be cooled will determine the energy required for crystallization, purity of product and coolant selection. At a higher cooling temperature, ethylene glycol brine at lower concentrations is suitable since it has better heat capacity and lower viscosity. Table II summarizes the ethylene glycol properties required, the energy required to cool the feed and 1-butanol concentration in the liquid phase at various cooling temperatures.

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Table II: Effect of cooling temperature on coolant properties, energy requirement, and purity

Cooling temperature (K)	Concentration by % weight of ethylene glycol	Specific heat capacity (kJ/kg K)	Viscosityx1000 (Pa s)	Energy required to cool 1000 kg/hour feed (MJ/hour)	Liquid phase 1-butanol mole fraction in after crystallization
upto 264	35 [15]	3.60[15]	6.8 [15]	451.04	0.62
upto 253	45 [15]	3.31[15]	17.2 [15]	495.05	0.75
upto 239	55 [15]	3.06[15]	75 [15]	558.16	0.81

Table II suggests that a compromise among energy requirement, ease of handling and purity needs to be made. Maintaining sub-zero temperatures and handling a large quantum of ice crystals are the key challenges posed to the application of FC for 1-butanol and water separation. But, high recovery and lower energy requirements than conventional distillation process provide an incentive for encouraging pilot plant trials. With the advancement in technology to overcome the practical difficulties in operation, FC is expected to be a promising technology for separating low concentrations of 1-butanol in water.

III. Pervaporation

Pervaporation is a novel membrane technology which has a dual effect of two processes combined in one set-up: namely reverse osmosis and membrane gas separation [17]. Pervaporation consists of a selective membrane through which different entities present in a liquid mixture diffuse according to their permeabilities through the particular membrane [18]. Thus, the mechanism of separation is the difference in the affinities of the components in the mixture for the specific membrane [19]. The process is purposefully carried out at a very low pressure to ensure that the components evaporate and are collected on the downstream as purified gaseous products which then can be removed with the help of vacuum pump or with the use of chillers [17, 18, 19].

Pervaporation being a membrane-based process, some factors such as permeabilities, flux, separation factors depend upon the type of membrane utilized. Separation of 1-butanol and water has been performed by a variety of membranes each with one modification over another to get higher flux and permeate concentrations. According to Vane [19], poly dimethyl siloxane (PDMS) is a widely used membrane for separation. Vane [19] effectively tested various PDMS membranes with certain modifications such as integration of membrane with octadecyldiethoxymethy-lsilane, and PTFE (poly tetra fluoro ethylene) or PP (polypropylene) which were found to have higher separation factor and selectivity than usual PDMS membranes. Liu et al. [20] performed a separation of water and 1-butanol using ceramic membranes. Li et al. [21] introduced a new membrane: tri-layer PDMS for effective separation of 1-butanol and water. Wang et al. [22] took the PDMS one step ahead by generating a zeolite, PDMS matrix membrane for the separation which helps in generating better interface compatibility. Fouad and Feng [23] evaluated the properties of PDMS membrane filled with silicalite particularly adapted to separate 1-butanol and water.

A recent advance in membrane materials consists of hyper-branched structure to enhance the properties of the membranes like low package density, negligible crystallinity, etc [24, 25, 26]. Bai et al. [26] developed a highly efficient modification of PDMS membrane which consisted of cross linkers in the form of hyper branched polysiloxane. Due to the novelty of the membrane and performance characteristics depicted, this membrane was utilized for further calculations.

Table III: Stage-wise parameters and values

Parameter	Stage I	Stage II	Stage III
Temperature (K)	313.16	318.16	363.16
1-butanol Permeability (mol.m/(m^2.s.Pa)	$8.88*10^{-11}$	$8.04*10^{-11}$	$4.69*10^{-11}$
Water Permeability (mol.m/(m^2.s.Pa))	$1.34*10^{-11}$	$1.34*10^{-11}$	$1.34*10^{-11}$
Permeate Pressure (Pa)	1333.22	1333.22	133.22

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The water permeability remains the same while, the 1-butanol permeability decreases with temperature, as seen from the data in Table III. In case of pressure driven pervaporation, the concentration of a component at the permeate side would depend upon the permeability at that temperature and activity coefficient of the component [18]. The driving force in such cases is the pressure difference between the feed and the permeate stream which is kept maximum to obtain better separation.

In the case of linear systems where permeability value is assumed to be constant, flux equation for binary mixture can be written as follows:

$$J_A = Q_A(\gamma_A * x_A * P_A^* - y_A * P_2) \quad \text{(II)}$$

In a similar manner, we can write equations for the other component.

Where, J_A is the flux of component A through the membrane, Q_A is Ratio of permeability to membrane thickness for component A, γ_A is Activity coefficient of component A, x_A is Mole fraction in feed of component A, y_A is the mole fraction of A in permeate, P_A^* is Vapour pressure of component A at the given temperature, P_2 is Permeate Pressure.

For the estimation of activity coefficient, Redlich-Kwong model was used to calculate Gibb's free energy of both liquid and gas phase which were used to estimate the values of fugacity coefficients in the liquid phase as well as gaseous phase respectively. Further, modified Raoult's law was applied to determine activity coefficient at Vapor-Liquid Equilibrium data points which then was regressed concerning1-butanol mole fraction to obtain activity coefficient at any concentration.

Pressure ratio and modified selectivity has been defined in the following manner: [18]

$$R_A = \frac{P_2}{\gamma_A * P_{A2}^*};\ R_B = \frac{P_2}{\gamma_B * P_{B2}^*} \quad \text{(III)}$$

$$\alpha' = \frac{Q_A * \gamma_A * P_A^*}{Q_B * \gamma_B * P_B^*} \quad \text{(IV)}$$

Separation factor in any pervaporation set-up is defined as follows:

Where R_A is Pressure Ratio for component A, R_B is Pressure Ratio for component B, α' is Modified selectivity.

$$\beta = \frac{\frac{c_{iP}}{1-c_{iP}}}{\frac{c_{if}}{1-c_{if}}} \quad \text{(V)}$$

With the knowledge of permeate pressure (P_2), the initial conditions and the permeabilities, equations (III), (IV) and (V) can be solved simultaneously to obtain the permeate composition of 1-butanol at different stages. The results obtained are stated in Table IV.

Table IV: Pervaporation results

Parameter	Stage I	Stage II	Stage III
Temperature (K)	313.16	318.16	363.16
Permeate Mole Fraction of 1-butanol (y_b)	0.21	0.81	0.81
Permeate Flux of 1-butanol (kg/m^2 s)	0.017*10^{-3}	0.45*10^{-3}	1.6*10^{-3}
Permeate Flux of water (kg/m^2 s)	0.016*10^{-3}	0.025*10^{-3}	0.21*10^{-3}

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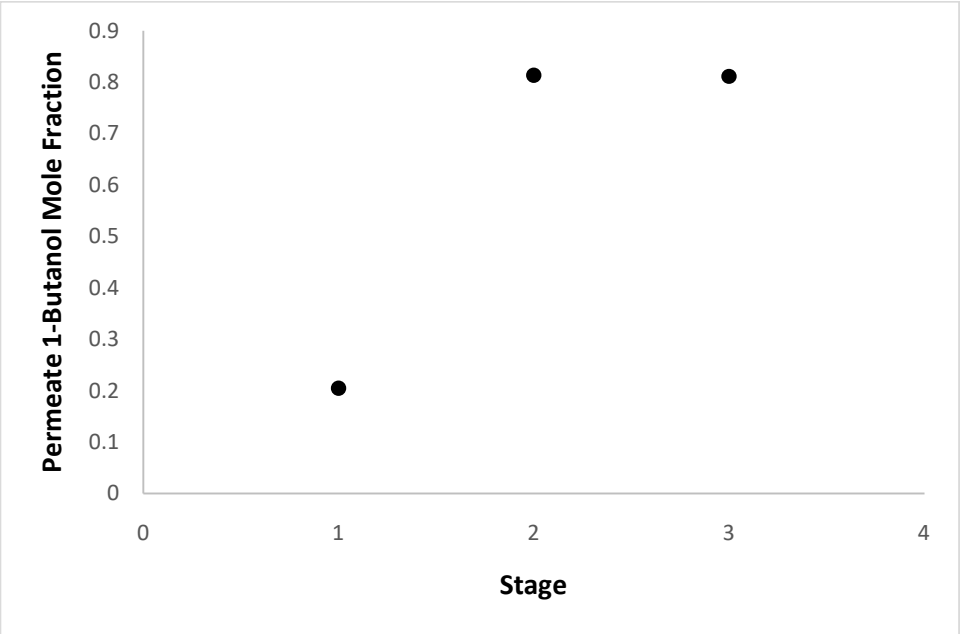

Figure IV: Plot of permeate 1-butanol mole fraction versus Stage number

With the increase in the number of stages from 1 to 2, the output mole fraction of 1-butanol increased. Further increase in the number of stages reduces the output concentration but increases the flux as seen in Table IV. The initial increase in the output concentration can be attributed to the rise in the temperature of the feed and high activity coefficient of 1-butanol at the feed concentration, which is not the case for the subsequent stage.

The flux of 1-butanol was found to increase along with the process temperature because of the fact that, with an increase in temperature, the saturated pressure of both the components increase while the permeate pressure remains constant. This increases the driving force to which the flux is proportional as shown in Equation (IV). Thus, the flux increases with increase in temperature, even though the permeability decreases.

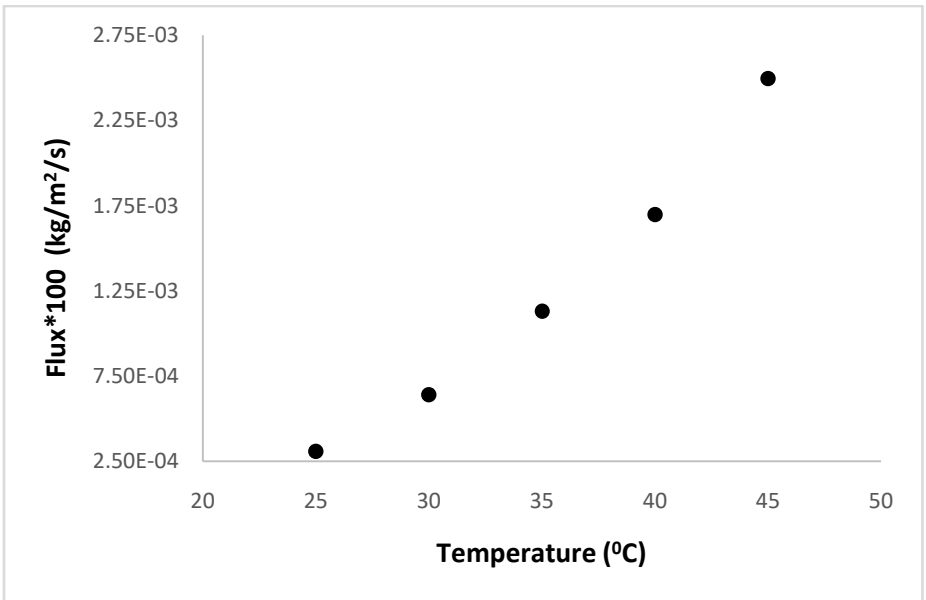

Figure V: Plot of flux variation with temperature

Pervaporation resulted into permeate mole fraction of about 0.82 at the second stage. Moreover, pervaporation is an environment-friendly alternative which separates the components without affecting microbe activity and growth, which allows for in-situ operation. Thus, pervaporation seems to be a practical alternative for separation of 1-butanol from the water.

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IV. Reverse Osmosis

Reverse osmosis (RO) provides an efficient solution for the removal of low molecular weight organic compounds from their low concentration aqueous solutions. Several studies have been conducted to separate organic compounds from their dilute aqueous solutions with the help of reverse osmosis [27, 28, 29].

Rejection of compounds by the membrane is dependent on the combination of membrane materials and solute to be separated. Several membranes have been fabricated and qualified for seawater desalination, but the membranes most suitable for desalination are not always useful for organic-aqueous separation [30]. Solute and solvent diffusivity through the membrane is used to describe the influence of solvent, solute and membrane interaction on the performance of the membrane. Notably two commercially available RO membranes have been studied extensively for 1-butanol separation from water, namely the cellulose acetate membrane and the composite polyamide membrane. Different scientists have attempted to correlate the rejection coefficients for cellulose acetate and aromatic polyamide membranes with polar and steric parameters, molecular size or with solubility parameters [29, 21, 32, 33]. The rejections obtained by cellulose acetate membrane for organic-aqueous solutions are relatively low, especially for low molecular weight organic compounds [28]. Polyamide membranes have exhibited rejection rates as high as 98% and have a potential application in 1-butanol-water separation [34, 35].

For estimation of rejection and permeate fluxes at target feed concentration and flow rate, the MSCB2521 R99 spiral-wound aromatic polyamide membrane was considered, and the preferential sorption-capillary flow model was employed. Alvarez et al.[36] provided the required membrane and feed parameters, pure water permeability, and 1-butanol transport parameter ($D_{AM}/K\delta$) through the membrane. Table V reports the above values.

Table V: Constants, membrane and feed parameters (where: a=solute; b= water)

Parameter	Value	Parameter	Value
Temperature (T)	298.16 K	Equivalent hydraulic diameter (d_h)	$9.6*10^{-4}$ m
1-butanol transport parameter ($D_{AM}/K\delta$)	$1.91*10^{-6}$ m/s	Molar volume of pure water (V_w)	18.07 m^3/kmol
Feed density (ρ)	1000 kg/m^3	Permeability of pure water (A)	$7.83*10^{-12}$ $m^3/s\ m^2\ Pa$
Feed viscosity (μ)	0.001 Pa s	Diffusivity of 1-butanol in water (D_{ab})	$9.6*10^{-10}$ m^2/s[37]
Feed flow rate (Q)	1 m^3/hr	Effective area tangential to the feed flow (A_t)	0.001 m^2

Kimura et al. have proposed an empirical equation for the estimation of osmotic pressure as a function of 1-butanol concentration [38].

$$\pi = -\frac{RT}{V_w} ln\left(\frac{\frac{1000-c_b}{M_w} - \frac{2c_b}{M_g}}{\frac{1000-c_b}{M_w} - \frac{c_b}{M_g}}\right) \quad \text{(VI)}$$

Where, T and R are the temperature and universal gas constant respectively; V_w is the molar volume of pure water; and M_w and M_g are the molecular weights of water and 1-butanol, respectively; π is the osmotic pressure.

Schock and Miquel's correlation, established for spiral-wound modules, was used to estimate the mass transfer coefficient of 1-butanol in the concentration polarization boundary layer (k_a)[39].

$$Sh = 0.065Re^{0.875}Sc^{0.25} \quad \text{(VII)}$$

Where Sc is the Schmidt number ($\mu/\rho D_a$), Re is the Reynolds number ($d_h v\rho/\mu$), and Sh is the Sherwood number ($k_a d_h/D_{ab}$). d_h is the equivalent hydraulic diameter; k_a is the mass transfer coefficient for species 1-butanol, v is the tangential flow velocity, D_a is the diffusion coefficient for species A, μ is the solution viscosity, and ρ is the solution density.

The concentration of solute on membrane surface was then determined by film theory.

$$C_{a2} = C_{a1} exp\left(\frac{N_b}{k_a C_1}\right) \quad \text{(VIII)}$$

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Where C_{a1} is the feed 1-butanol concentration; C_{a2} is the concentration of 1-butanol on the membrane surface; N_b is the molar flux of water; C_1 is the molar density of the feed solution.

The flux of water and 1-butanol through the membrane were then estimated using preferential sorption-capillary flow model and hence the solute rejection. Solute rejection, water flux as well as the solute flux increased with the applied pressure. Figure VI depicts the dependence of solute rejection on the applied pressure.

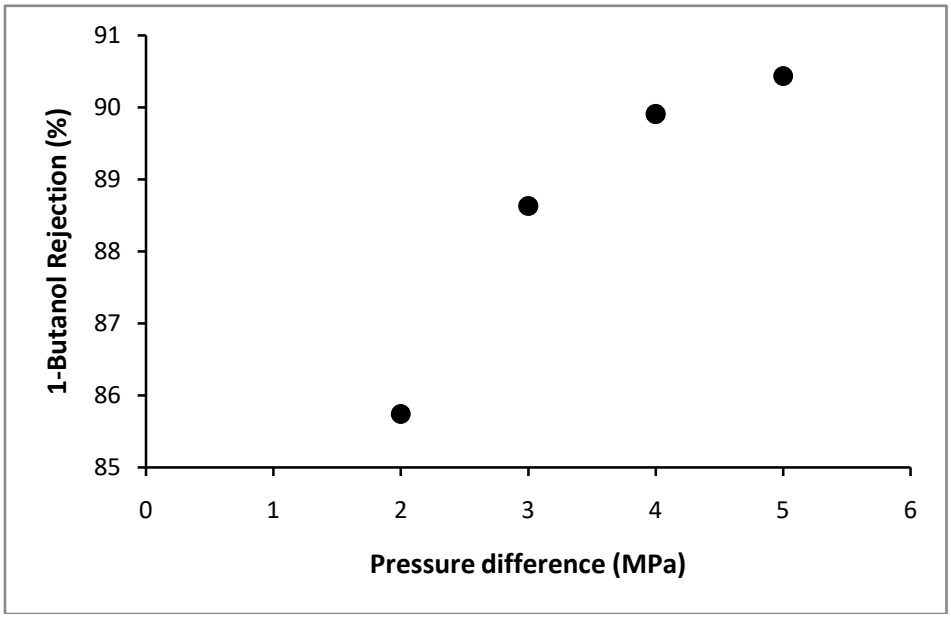

Figure VI: Plot of 1-butanol rejection (%) versus Pressure difference (MPa)

1-butanol rejection increased with pressure difference on account of a stronger dependence of molar water flux on the pressure difference than that of the molar solute flux.

Despite the restriction on rejection due to its strong dependence on applied pressure, higher rejection to some extent can be achieved by customizing specific membrane and feed parameters such as leaf width, spacer thickness, porosity, temperature among others. In a typical seawater reverse osmosis plant, 3 to 10 kWh of electric energy is required to produce one cubic meter of freshwater [40]. This energy requirement when calculated for our feed concentration comes out to be around 1.8 MJ/kg of 1-butanol. This value is much lower compared to the energy requirement of most other separation processes. Thus, reverse osmosis can provide us with an energy-efficient alternative, compared to the traditional unit operations for 1-butanol recovery.

V. Adsorption

1-butanol separation from aqueous solutions and its recovery by adsorption is an energy efficient method with promising results [7]. Multiple adsorbents like activated carbon, zeolite, amberlite have been studied for 1-butanol adsorption from water at very low concentrations of 1-butanol. Various studies have been performed to experimentally demonstrate the effectiveness of adsorbents for this separation [7, 41, 42].

Abdegagh et al.[7] found that Activated carbon(AC) F-400 was the most effective adsorbent amongst the adsorbents: ZSM-5, AC F-600, NaY, Silicalite, and multi-walled carbon nanotubes studied by them. Their study on the kinetics of adsorbents indicated that AC F-400 and AC F-600 had the fastest adsorption kinetics among others. In an adsorbent screening study by Milestone and Bibby[41], Zeolite: ZSM-5 with 4% alumina was found to have the highest adsorption capacity amongst ZSM-5 adsorbents with different concentrations of alumina. Raganati et al. [42] observed that adsorption capacity of 1-butanol on Amberlite XAD4, Amberlite XAD7, and Zeolite Y increased with temperature and maximum adsorption capacity was found at 318.16 K when temperatures were varied from 298.16 K to 318.16 K.

In this assessment, we have used the equilibrium data for adsorption from the above studies and calculated the 1-butanol concentration in the rejected stream. The calculations were performed for five adsorbents: ZSM-5 with 4% alumina, Amberlite XAD4, Amberlite XAD7, Zeolite Y, and AC F-400. Conditions mentioned in Table VI were used to calculate 1-butanol concentration in the rejected stream in case of a batch type contact operation.

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Table VI: Feed and adsorbent parameters

Amount of Feed	1000 kg
1-butanol concentration in feed	20 kg/m^3
Adsorbent mass required	300 kg
Initial concentration of 1-butanol in adsorbent	0 kg/m^3

Calculations were done for a single stage adsorption model by simultaneously solving the material balance equations and the adsorption isotherm equations. Table VII depicts the results.

Table VII: Capacity of various adsorbents

Adsorbent	Temperature (K)	Isotherm equation *	Concentration of 1-butanol in rejected stream (kg/m^3)
ZSM-5 with 4% alumina	Room temperature	$y = 0.079x^{0.082}$ #	4.48
Amberlite XAD4	318.16	$y=57.12x/(1+0.21x)$ [42]	1.37
Amberlite XAD7	318.16	$y=152.2x/(1+0.2x)$ [42]	0.46
Zeolite Y	318.16	$y=43.92x/(1+0.18x)$ [42]	1.79
AC F-400	Room temperature	$y=500x/(1+2130.5x)$ ##	0.18
* y represents amount of 1-butanol adsorbed per unit mass of adsorbent and x represents concentration of 1-butanol in solution			
# This equation has been obtained by regressing the data from work of Milestone and Bibby [42]			
## This equation has been obtained by regressing the data from work of Abdehagh et al.[7]			

The Table VII allows us to conclude that AC F-400 has the highest adsorption capacity for 1-butanol from the water. The time constant (time required for the 1-butanol concentration to vary by a factor of 0.6321) was reported to be 8.2 minutes for AC F-400 by fitting the experimental results in the study by Abdegagh et al. to the model obtained from Lagergren's pseudo-second order equation for adsorption kinetics. This indicates that AC F-400 also shows very high adsorption kinetics, making it a suitable choice of adsorbent for separation of 1-butanol from water [7].

The desorption of 1-butanol needs to be studied, if we want to evaluate the recovery by this process. Abdegagh et al. experimentally evaluated the recovery of 1-butanol on desorption on AC F-400. According to their study, it is possible to recover 84% of the total 1-butanol adsorbed via thermal desorption process. [43]. AC F-400 is a suitable adsorbent for 1-butanol separation of water since it possesses high adsorption capacity, favorable kinetics and allows desorption of 1-butanol with significant recovery.

The concentration of 1-butanol in the rejected stream varies considerably with a change in mass of adsorbent: AC F-400 as indicated by Figure VII.

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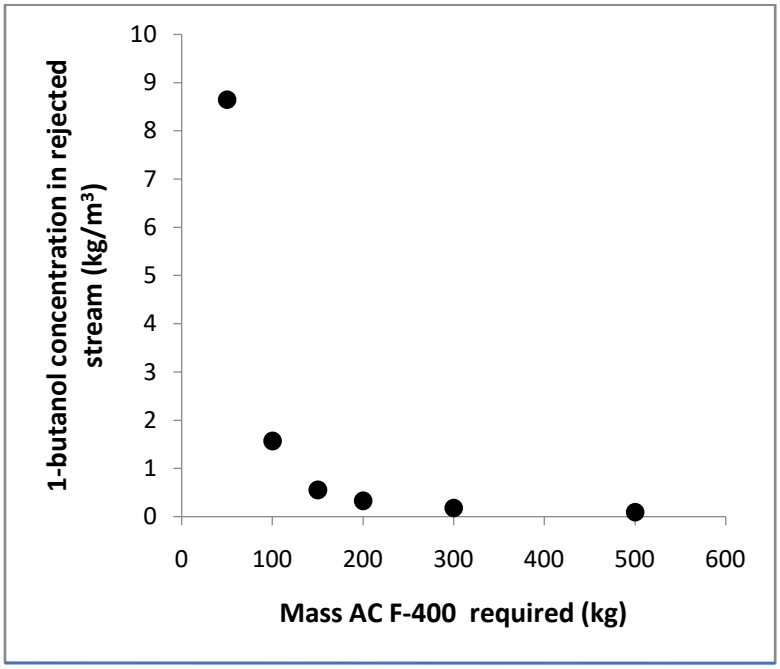

Figure VII: Plot of 1- butanol concentration in rejected stream versus Mass of adsorbent required

It is seen from Figure VII that the 1-butanol concentration in the rejected stream drastically drops with the increase in mass of adsorbent. Hence, enhanced recovery can be obtained with higher mass of adsorbent. The improvement in desorption recovery can be achieved by lowering the cold trap temperature which would increase the energy requirement and subsequently, the operating cost [43]. The increased amount of adsorbent required would also increase the capital cost. Hence, a compromise is required between cost and recovery while deciding the operating conditions.

Due to unavailability of literature, the energy efficiency of the process using AC F-400 could not be determined. However, Oudshroon et al. have evaluated the energy of adsorption-desorption process to be 1.3 MJ/kg of 1-butanol assuming heat capacity of the adsorbent to be 1 kJ/kg K. [44]. An energy requirement of 8.14 MJ/kg of 1-butanol was reported by Qureshi et al. using silicalite as adsorbent [45].

Furthermore, adsorption is the only separation technique besides pervaporation which provides for in-situ separation of fermentation broth resulting from ABE fermentation with an energy demand of about 10% of 1-butanol combustion enthalpy [46]. Many studies have evaluated the selectivity of adsorption of 1-butanol and its recovery from the fermentation broth using suitable adsorbents [7, 43].Use of adsorption for in-situ recovery of 1-butanol may improve the economics of the fermentation process [47]. Hence, adsorption is an efficient separation method for this separation. Lack of literature on desorption has held back the use of adsorption-desorption process on the industrial scale for separation of 1-butanol.

VI. Liquid-Liquid Extraction using Ionic Liquids

Liquid-Liquid extraction is seen as a potential alternative to energy-intensive techniques for 1-butanol-water separation such as distillation [48]. However, conventional liquid-liquid equilibrium techniques utilizing organic solvents as extractive phase, suffer from the fact that, separation is not high enough for concentration as low as obtained from the fermentation broth [9]. Moreover, organic liquids used as extractants such as tert-amyl ether, diisopropyl ether, and dibutyl ether result in significant damage and contamination [49]. Hence, the focus has now shifted from organic liquids to ionic liquids for extraction of 1-butanol from the water. Ionic liquids are the ones made up entirely of ions. The term ionic liquid is different from ionic solution as in; NaCl with water forms an ionic solution, while molten NaCl is ionic liquid [50]. Ionic liquids are advantageous due to various factors such as low vapor pressure, and high thermal and chemical stability [48]. Ionic liquids make way for enormous possible cation-anion combinations which can be utilized to prepare task-specific ionic liquids (ILs). However, following concerns should be addressed before selecting an ionic liquid [9]:

1. Toxic nature of the extractant.
2. High selectivity (1-butanol).
3. Loss of liquid to the aqueous phase.

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Various ionic liquids have emerged in the field of separation, and this paper attempts to review and evaluate some of them based on their potential for separation. Nann et al.[48], Domaska et al. [49], Davis et al.[9], Fadeev et al.[51], Garcia-Chevez[52], Ha et al. [53], came up with various ionic liquids for the separation of water from 1-butanol. Some of them are listed in Table VIII along with their distribution coefficients and selectivity. Distribution coefficient and selectivity are defined as:

$$S = \frac{w_1^{IL} * w_2^{aq}}{w_1^{aq} * w_2^{IL}} \quad \text{(IX)}$$

$$D = \frac{w_1^{IL}}{w_1^{aq}} \quad \text{(X)}$$

Where w_1 and w_2 denote the mass fractions of 1-butanol and water respectively; the superscripts IL and aq depict the phases rich in ionic liquid and water respectively.

Table VIII: Data of ionic liquids

Sr. No.	Ionic Liquid	Feed Concentration (%wt 1-butanol)	Temperature (K)	Selectivity	Distribution Coefficient with respect to 1-butanol	References
1	1-decyl-3-methylimidazolium tetracyanoborate $[Im_{10,1}]^+[tcb]^-$	<10	308.16	85	8	[48]
2	4-decyl-4-methylmorpholinium tetracyanoborate $[Mo_{10,1}]^+[tcb]^-$	<10	308.16	78	6	[48]
3	1-decyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)imide $[Im_{10,1}]^+[ntf2]^-$	<10	308.16	70	7.9	[48]
4	4-decyl-4-methyl morpholinium bis(trifluoromethylsulfonyl)-imide $[Mo_{10,1}]^+[ntf2]^-$	<10	308.16	73	6.1	[48]
5	trihexyltetradecylphosphonium tetracyanoborate [P14,6,6,6][TCB]	-	308.16	50-903	25-65	[49]
6	1-decyl-3-methylimidazolium tetracyanoborate [DMIM][TCB]	-	308.16	45-125	28-48	[49]
7	1-butyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)imide [bmim][Tf2N]	Higher than obtained in ABE fermentation	298.16	10-100	1.4-7.3	[9]
8	1-hexyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)imide [hmim][Tf2N]	Higher than obtained in ABE fermentation	298.16	0.3-77	0.2-8	[9]
9	1-butyl-3-methyl-1H-imidazol-3-ium hexafluoro phosphate [bmim][PF_6]	2.01	296.16	25.77	0.849	[51]
10	1-octyl-3-methyl-1H-imidazol-3-ium hexafluoro Phosphate [omim][PF_6]	2.01	296.16	55.37	0.923	[51]

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11	1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [hmim][ntf_2]	1	298.16	120	1.11	[52]
12	tetradecyl(trihexyl)-phosphonium bis-2,4,4-trimethyl pentyl-phosphinate Cyphos 104	1	298.16	55	9.21	[52]
13	Methyltrioctyl ammonium octanoate [MTOAOct]	1	298.16	49	11.29	[52]
14	Tetraoctylammonium2-methyl-1-naphthoate [TOAMNaph]	1	298.16	274	21	[52]
15	1-hexyl-3-methylimidazolium hexafluoro phosphate [Hmim][PF_6]	6	298.16	37.47	0.967	[53]
16	1-methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide [omim][Tf2N]	6	298.16	78.89	1.372	[53]
17	1-phenylpropyl-3-methylimidazolium trifluoromethane sulfonate [Pmim][TfO]	6	298.16	4.96	1.046	[53]
18	1-hexyl-3-methylimidazolium tetrafluoroborate [Hmim][BF_4]	6	298.16	3.906	0.902	[53]
19	1-methyl-3-octylimidazolium tetrafluoroborate omim][BF_4]	6	298.16	12.24	2.183	[53]

Table IX shows the performance of various ionic liquids in different conditions. Ionic liquids number 5, 6, 7, 11, 14 in the table show exceptional performance amongst the liquids reviewed.

The tie lines and the extraction data of both the phases specified in the papers were utilized to perform mass balance calculations and evaluate the performance of most of the ionic liquids. The tie lines were selected such that they offered the maximum selectivity as well as recovery of 1-butanol. Table IX gives details of the same.

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Table IX: Performance of several ionic liquids

Sr. No	Ionic Liquid	1-butanol Concentration in IL phase (wt %)	Water Concentration in IL phase (wt %)	1-butanol Recovery (%)	Ionic Liquid Requirement *1000 (kg)	Reference
1	[P14,6,6,6] [TCB]	12.6	14	90.35	108.16	[49]
2	[TOAMNaph]	0.95	7.65	97.943	1884.63	[52]
3	TDAMCH	0.75	6.5	96.338	2382.76	[52]
4	HMIMNTf2	0.56	0.92	76.004	2674.27	[52]
5	Cyphos 104	0.56	16.8	98.838	2917.14	[52]
6	OmimPF6	0.809	1.321	48.066	1167.25	[51]
7	Bmim PF6	0.724	2.4	42.43	1179.48	[51]
8	[bmPIP][NTf2]	4.4	28	86.91	267.91	[54]
9	[COC2mPIP] [NTf2]	36.9	9.7	72.02	81.16	[54]
10	[COC2mPYR] [NTf2]	36	2	96.84	601.02	[54]

From the calculation results in Table IX following conclusions can be drawn:

1. Separation with Cyphos 104 requires the largest amount of IL and also takes a substantial amount of water into the Ionic Liquid phase, in-turn giving the best 1-butanol recovery.
2. [TOAMNaph], TDAMCH, [COC2mPYR] [NTf2], show similar amount of 1-butanol recovery in the range of 95% and above.
3. [COC2mPIP] [NTf2] requires the lowest amount of liquid, but 1-butanol recovery is not attractive.
4. [P14,6,6,6] [TCB] on the other hand requires low amount of ionic liquid and achieves a remarkable recovery of 90.35 %.
5. [COC2mPYR] [NTf2], along with [COC2mPIP] [NTf2] and [P14, 6, 6, 6] [TCB] show significant amount of 1-butanol concentration in the IL phase.

Thus, selection of any Ionic Liquid is performed cumulatively based on of recovery achieved, amount of ionic liquid required and water content in the IL phase. Separation of water and 1-butanol using extraction techniques/ using ionic liquids gives rise to another phase of IL with 1-butanol. To obtain pure 1-butanol, this phase needs to be separated. Generally, pervaporation is used to separate the phases [51]. However, due to lower volume and higher mass of the ionic liquids, this separation is feasible and provides better results [51]. Finally, [TOAMNaph] seems to be the best choice based on the recovery of 1-butanol from water and is used for comparison in further stages.

Even though ionic liquids enjoy various advantages, the process is ridden with problems. Since water tends to enter the IL-rich phase; further complications can arise in subsequent operations. Ionic liquid at times enters the water-rich phase, and hence recovery of IL becomes a separate arduous task. A separate unit operation, like pervaporation or distillation, has to be employed to recover 1-butanol from the separated ionic liquid. With newer and more efficient ionic liquids, extraction of 1-butanol by ionic liquids is expected to be a cost-effective and energy-efficient technique for separating 1-butanol from its aqueous mixtures.

VII. Salting

Liquid−liquid phase splitting using salts, which takes place at atmospheric pressure and moderate temperature, has been explored to overcome the energy-intensive distillation for 1-butanol concentration. The influence of electrolytes and inorganic salts on the behavior of 1-butanol-water mixtures has been frequently investigated [55-61]. Dissolved salts in aqueous–organic mixtures would either decrease or increase the solubility of the organic species in water. Salting out is observed when the solubility of organic species in water reduces with increase in salt concentration, resulting in an enlarged heterogeneous region of the ternary mixture and hence a higher degree of immiscibility. Salting out is observed after the addition of a certain amount of salt to the solution. This effect is exploited in the extraction of organic compounds from solutions. A salting-out agent with the merits of cheapness, greenness, and stability takes advantage of its reutilization. Chawong et al analyzed the effects of salting-out mechanism of Na_2SO_4, NH_4Cl, NaCl, and $(NH_4)_2SO_4$. Na_2SO_4 appeared to be the most effective salt among the three, while NH_4Cl is the least effective. The temperature had no significant effect in the range studied on the Liquid-Liquid Extraction (LLE) behavior of these systems [55]. Measuring LLE data for the systems 1-butanol-water-KF and 1-butanol-water-K_2CO_3 at 25 °C, revealed that 1-butanol concentrations in organic phase can reach over 96% and 98% when the concentrations of K_2CO_3 and KF and in the aqueous phase are 52.5% and 50.40% respectively. 1-butanol was not detected in the aqueous phase by gas chromatography, resulting in 100% recovery. Thus, water can be separated efficiently from 1-butanol-water solution by adding K_2CO_3 or KF to the system [56]. Li et al. found that KCl has higher salting out efficiency than NaCl, with KBr being the least efficient in water+1-butanol+salt system [57]. In the case of NH_4Cl,

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it was found that the addition of ammonium chloride not only decreased 1-butanol concentration in the water-rich phase but also water concentration in the organic phase [58].

Mentioned in Table X are the salt requirements required to achieve a particular 1-butanol concentration in the organic phase per m^3 of the 1-butanol-water solution. The 1-butanol recovery is defined as the ratio of the amount of 1-butanol in the organic phase to the amount of 1-butanol originally present in the aqueous solution. The tie line data was taken from literature and utilized to perform mass balance calculations and hence evaluate the performance of various salts. The salt requirement to achieve a particular level of separation and recovery was estimated.

Table X: Performance of several salts

Salt	1-butanol Concentration (wt %)	Water concentration (wt %)	Temperature (°C)	1-butanol recovery (%)	Salt requirement (g/kg solution)	Reference
$NaNO_3$	90.25	9.34	25	15.15	635.08	[58]
Na_2SO_4	93.54	6.45	30	80.28	331.29	[55]
$(NH_4)_2\ SO_4$	94.63	5.36	30	63.	286.45	[55]
KI	82.04	9.74	25	62.58	1428.96	[59]
NaBr	91.61	6.23	25	81.88	924.55	[59]
KBr	90.2	9.11	25	49.03	655.57	[59]
NaCl	93.26	6.56	30	25.79	318.89	[55]
$CaCl_2$	88.5	1.5	25	61.72	544.87	[44]
KCl	90.4	9.45	25	86.76	342.86	[57]
KF	98.23	1.76	25	100	995.44	[56]
K_2CO_3	96.5	3.49	25	100	1082.36	[56]

No general trend was observed in the recovery and concentration of 1-butanol in organic phase for different salts. From Table X it can be seen that salting suffers from low recovery for most of the salts. Potential salts that can be employed are potassium fluoride and potassium carbonate. However, handling of potassium fluoride and potassium carbonate is hazardous and may add to the cost. The regeneration of the salt is another drawback of the process. On account of low concentrations of 1-butanol, high energy requirements in the range of 21.9 MJ/kg 1-butanol [60] to 28.5 MJ/kg 1-butanol [61] are required to evaporate off the unrecovered organics and water from the salt solution. Although process simplicity of salting operation is enticing, salt selection and handling is an arduous task, thereby challenging the economic tradeoff.

VIII. Conclusion

Despite extensive research and collective efforts towards overcoming limitations of low productivity and concentrations of fermentation, most of the technologies studied in this paper are not industrialized because of their techno-economic barriers. The primary optimization target for the downstream separation units is to achieve the lowest energy requirement possible at the highest possible recovery. Complete process designs with these specifications for the recovery of 1-butanol are scarce. Figure VIII is a graphical representation of calculations performed and literature cited in the above sections.

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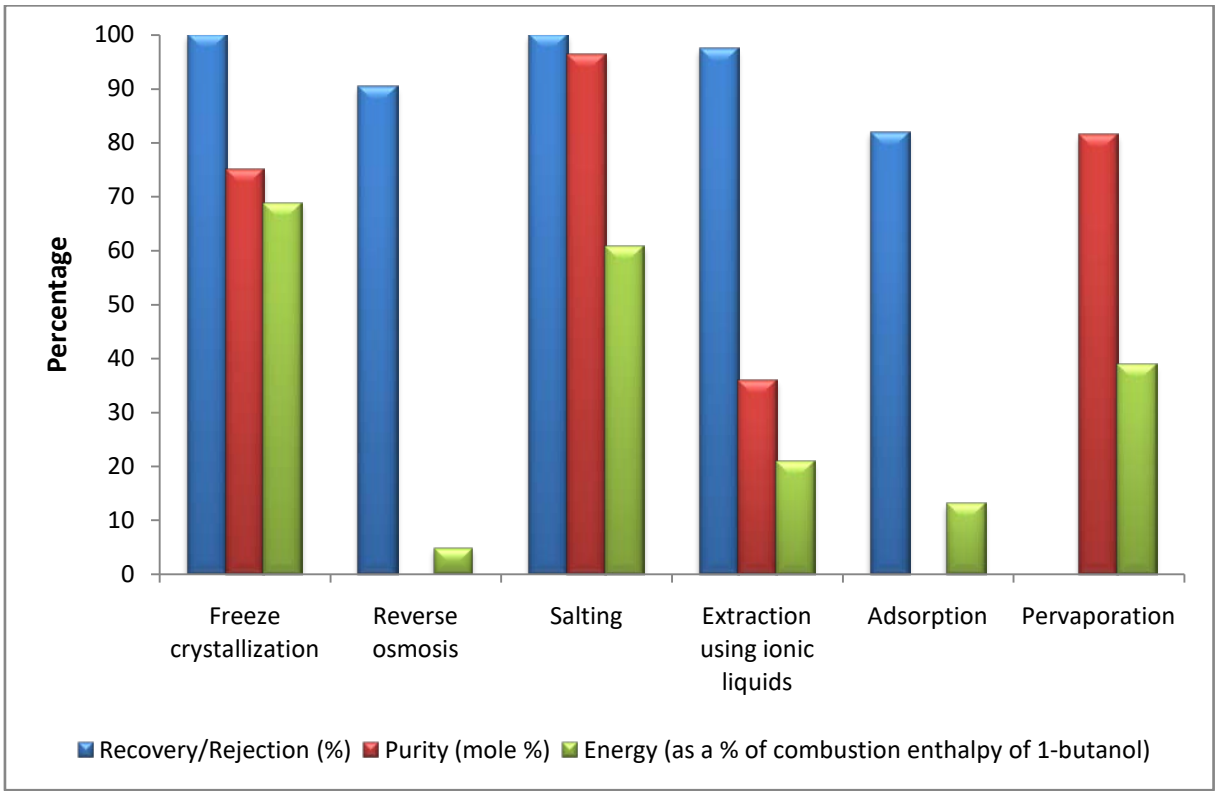

Figure VIII: Comparison of separation processes regarding recovery/rejection, purity and energy requirement

Freeze crystallization and salting provided with high recovery, but the energy associated with these is significant resulting in high operating costs. Besides, salt handling and its recovery are key issues related to salting and it is difficult to maintain sub-zero temperatures and to handle large quantities of ice in case of freeze crystallization. Regarding energy requirement, it is evident that adsorption and reverse osmosis are promising options. ILs are capable of providing high recovery at low energy requirements but need to be followed by a subsequent separation step for IL-1-butanol separation such as pervaporation. To devise an operational process that enjoys high selectivity, nontoxicity and that is energy-extensive, integration of different separation technologies such as pervaporation-distillation, RO-freeze crystallization, IL-pervaporation could be worth trying. Hence, an integrated separation operation to complement their positives and right their drawbacks could be the key. However, all potential options need further proof of industrial long time performance, to obtain additional insights about their operation and performance.

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Table of Symbols

J_A	Flux of component A through the membrane (kmol/s.m^2)
Q_A	Ratio of permeability to membrane thickness for component A (kmol/m.s.Pa)
γ_A	Activity coefficient of component A
P_A*	Vapor pressure of component A at the given temperature(Pa)
P_2	Permeate Pressure (Pa)
x_A	Mole fraction in feed of component A
y_A	Mole fraction in permeate of component A
R_A	Pressure Ratio for component A
α'	Modified selectivity
B	Separation factor
c_{iP}	Mole fraction of component in permeate
c_{if}	Mole fraction of component in feed
T	Temperature (K)
$D_{AM}/K\delta$	1-Butanol transport parameter (m/s)
ρ	Feed density (kg/m3)
μ	Feed viscosity (Pa s)
Q	Feed flow rate (m/s)
d_h	Equivalent hydraulic diameter(m)
V_w	Molar volume of pure water (m^3/kmol)
A	Permeability of pure water (m/s.Pa)
D_{ab}	Diffusivity of butanol in water (m^2/s)
A_t	Effective area tangential to the feed flow (m^2)
π	Osmotic pressure (Pa)
M_w	Molecular weights of water (kg/kmol)
M_b	Molecular weights of 1-butanol (kg/kmol)
C_b	Concentration of 1-butanol (kg/m^3)
Sh	Sherwood number

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Re	Reynolds number
Sc	Schmidt number
k_a	Mass transfer coefficient (m/s)
v	Tangential flow velocity (m/s)
C_{a1}	Molar feed 1-butanol concentration (kmol/m^3)
C_{a2}	Molar concentration of 1-butanol on the membrane surface (kmol/m^3)
C_1	Molar density of the feed solution (kmol/m^3)
N_b	Molar flux of water (kmol/s.m^2)
S	Selectivity
D	Distribution coefficient
w_1	Mass fractions of 1-butanol
w_2	Mass fractions of 1-butanol and water
x	Concentration of 1-butanol in solution (kg/m^3)
y	Amount of 1-butanol adsorbed per unit mass of adsorbent

Declarations of interest
None

Funding sources
None

Annexure: Calculations

Reverse Osmosis

To obtain the rejection of 1-butanol by reverse osmosis, the following calculations were done.

1. To estimate rejection and permeate flux of 1-butanol, the preferential sorption-capillary flow model was employed. The model assumes that all transport takes place through the 'pores' of the membrane skin layer. It defines pore as the space between non-bonded elements in the membrane matrix through which mass transport can occur. It also assumes that solute is rejected at the surface for physicochemical factors and water preferentially gets adsorbed onto the pore walls. The solvent and solute fluxes are,

$$N_A = \frac{D_{AM}}{K\delta}(C_{A2} - C_{A3}) \quad \text{(A1)}$$

$$N_B = A(\Delta P - \Delta\pi) \quad \text{(A2)}$$

Where, the subscript A refers to 1-butanol and the subscript B refers to water. N_B and N_A are the fluxes of water and 1-butanol through the membrane, respectively. A is the permeability of water through the membrane. $\Delta\Pi$ is the osmotic pressure difference across the membrane. ΔP is the pressure difference across the membrane. C_{A2} is the concentration of 1-butanol on the membrane surface at the feed side. C_{A3} is the concentration of 1-butanol on the membrane surface at the permeate side. $D_{AM}/K\delta$ is the 1-butanol transport parameter. A and $D_{AM}/K\delta$ were obtained from literature.

2. To predict the concentration of solute on the membrane surface at the feed side, the film theory was used.

$$C_{A2} = C_{A1}\exp\left(\frac{N_B}{k_g C_1}\right) \quad \text{(A3)}$$

Where C_1 is the molar density of the feed solution; k_A is the mass transfer coefficient; and X_{A1}, X_{A2}, and X_{A3} are the mole fractions of the 1-butanol in the feed solution, on the membrane surface at feed side, and in the permeate, respectively. k_A has been calculated using Schock and Miquel's correlation, established for spiral-wound modules and Reynolds numbers in the range of $100 < Re < 1000$.

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3. The osmotic pressure difference ($\Delta\Pi$) can be estimated from 1-butanol concentration at the two sides of the membrane (C_{A2} and C_{A3}). As the butanol concentration is quite low, the osmotic pressure will be low compared to the pressure difference applied and would be further lower at the permeate side. While calculating osmotic pressure difference, only the osmotic pressure at the feed side of the membrane was considered and that at the permeate side was assumed to be negligible. The osmotic pressure was estimated using the expression.

$$\Pi_A = -\frac{RT}{V_w} ln \frac{(1000 - C_{A2})/M_B - 2C_{A2}/M_A}{(10000 - C_{A2})/M_B - C_{A2}/M_A} \quad \text{(A4)}$$

Hence, solving equations (A2), (A3) and (A4) simultaneously the water flux can be estimated.

Where, T and R are the temperature and the universal gas constant, respectively; M_A and M_B are the molecular weights of 1-butanol and water respectively; V_w is the molar volume of pure water.

4. The mole fraction of solute in the permeate can be calculated as

$$X_{A3} = \frac{N_A}{N_A + N_B} \approx \frac{NA}{N_B} \quad \text{(A5)}$$

Equation (A1) has been rewritten in the following form,

$$N_A = \frac{D_{AM}}{K\delta}(C_2 X_{A2} - C_3 X_{A3}) \quad \text{(A6)}$$

Where, X_{A2} and X_{A3} are the molar fractions of 1-butanol on the membrane surface and in the permeate, respectively; C_2 and C_3 are the molar densities of the solution on the membrane surface and in the permeate, respectively.

The molar density C_2 was estimated from C_{A2}. The molar density of the permeate (C_3) was assumed to be equal to that of the water.

Hence, from X_{A3}, C_3, X_{A2}, C_2, the 1-butanol flux through the membrane can be estimated.

5. The rejection of 1-butanol (R) can be estimated from the following expression,

$$R(\%) = \left(1 - \frac{C_{A3}}{C_{A1}}\right) * 100 \quad \text{(A7)}$$

Pervaporation

Calculations to obtain the output mole fraction of the pervaporation process were carried in the following steps:

1. The permeability of the membranes was utilized from the paper of Bai et al. (2015).
2. The mole fraction of 1-butanol was evaluated by taking an initial concentration of 20 g 1-butanol in 1000 g solution. This turned out to be 0.004939.
3. The temperature of the system for the first stage was taken to be 40 ^{0}C, with permeate pressure of around 10 mm Hg.
4. Following factors were required to calculate the output mole fraction of the system: Flux equation concerning each component, modified pressure ratio of both the components and the modified selectivity of the system. The following equations were utilized to calculate the flux through the system.

$$J_A = Q_A(\gamma_A * x_A * P_A^* - y_A * P_2) \quad \text{(A8)}$$

$$J_B = Q_B(\gamma_B * (1 - x_A) * P_B^* - (1 - y_A) * P_2) \quad \text{(A9)}$$

Where J_A is the molar flux across the membrane, Q_A is the ratio of permeability of component through membrane and thickness of membrane, γ_A is the activity coefficient of the component, x_A is the mole fraction of component in the feed, $P_A^*$is the vapor pressure of the component at the system temperature, y_A is the mole fraction of the component on the permeate side, and P_2 is the pressure on the permeate side. Similar notations of other component named B.

5. To calculate the flux, mole fraction of the permeate is required. To estimate the mole fraction, pressure ratios (R_A, R_B) and modified selectivity (α') of the system is required, which is given by:

$$R_A = \frac{P_2}{\gamma_A * P_{A2}^*} ; R_B = \frac{P_2}{\gamma_B * P_{B2}^*} \quad \text{(A10)}$$

$$\alpha' = \frac{Q_A * \gamma_A * P_A^*}{Q_B * \gamma_B * P_B^*} \quad \text{(A11)}$$

6. Each value except the activity coefficient is known in the above equation. To calculate the activity coefficient, a code was created in python language which utilized the Soave-Redlich-Kwong model to evaluate the Gibbs free energy of real gas for the particular system. The following set of equations were utilized to estimate the activity coefficient of the system:

$$\varphi_i^L = \frac{G_{Li}^R}{R*T}; \varphi_i^V = \frac{G_{Vi}^R}{R*T} \quad \text{(A12)}$$

$$\gamma_i = \frac{P * y_i * \varphi_i^V}{x_i * \varphi_i^L * P_i^*} \quad \text{(A13)}$$

Where φ_i^L is the fugacity coefficient for liquid phase and φ_i^V is the fugacity coefficient for

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gaseous phase, G_{Li}^{R} is the Gibbs free energy of the component without any ideality in the liquid phase, and G_{Vi}^{R} is the Gibbs free energy of the component without any ideality in the vapor phase.

7. VLE data was taken from Dortmund Data Bank, which was utilized to calculate γ_i values for various inlet mole fractions. This data was then employed to interpolate gamma values for the specific mole fraction of the system. This process was performed for both the components and gamma values of both the components were incorporated.
8. Once γ_i were available, both modified pressure ratios and modified selectivity could be calculated. Equations (A8) to (A11) combined to give a quadratic equation explicit in γ_i as follows:

$$a * y_i^2 + b * yi + c = 0 \qquad \text{(A14)}$$

Where,

a= $\propto^{'} * R_A - R_B$

b=$R_B + x - 1 + \propto^{'} * (R_A + x)$

c=$\propto^{'} * x$

9. This quadratic was solved on excel using goal seek method to find out the mole fraction of the permeate which was then used to find the flux of the particular component through the membrane.
10. For the second stage, the output of the first stage was considered as the input of the second stage and similar calculations were performed.

Ionic Liquid

1. Calculations of ionic liquids were performed on the basis of tie-line data obtained from a variety of papers. One such data is shown below:

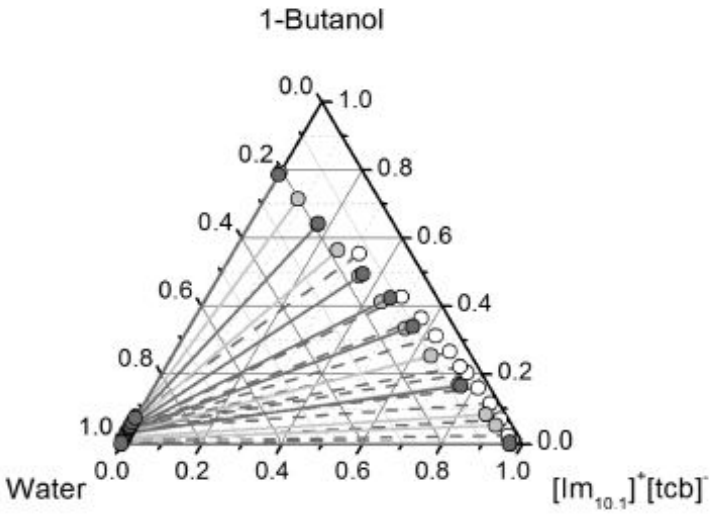

Figure IX: Ternary diagram of 1-butanol-water-ionic liquid system

2. The tie line chosen for each of the ionic liquid was the one providing highest selectivity. Based on the tie line, the mole fractions of the components were obtained in each phase. Let, ill denote the amount of ionic liquid in ionic liquid phase, bl denote the amount of 1-butanol in ionic liquid phase, wl denote the amount of water in ionic liquid phase. Similarly, ilw denotes the amount of ionic liquid in the water phase, ww denote the amount of water in the water phase, and bw is the amount of 1- butanol in the water phase.
3. So, the mole fraction of ionic liquid and water in ionic liquid phase can be written as:

$$x_{il}^{l} = \frac{ill}{ill + wl + bl} \qquad \text{(A15)}$$

$$x_{w}^{l} = \frac{wl}{ill + wl + bl} \qquad \text{(A16)}$$

4. Similarly, equations can be written for the water phase. Two more mass balance equations based on the initial concentration of water and 1-butanol can be written as given:

$$980 = wl + bl \qquad \text{(A17)}$$

$$20 = ww + bw \qquad \text{(A18)}$$

5. Above mentioned six equations were solved simultaneously to obtain the amount of each component in both the phases and amount of ionic liquid required for the separation. Based on the results, the ionic liquids were compared and analyzed.

Salting

Calculations similar to the one done for ionic liquids were performed for salting to obtain the amount of salt required for different systems and the output composition of each phase.

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Freeze Crystallization

1. The solid-liquid equilibrium data for the binary system of 1-butanol and water was obtained from the paper of Lohmann et al. (1997) which is as follows:

Table XI: Solid-liquid equilibrium data of 1-butanol-water system

$x_{1\text{-butanol}}$	T (K)
0	273.15
0.55354	269.28
0.59431	267.57
0.64055	264.76
0.69146	260.22
0.75861	251.37
0.80155	241.77
0.8468	227.4
0.87572	212.26
0.89422	199.89

2. The data points between 269.28 K to 199.89 K were regressed to obtain cooling temperature in K (y) as a function of mole fraction of water in the liquid phase (x) with $R^2 = 0.998$

$$y = 2694x^3 - 2993x^2 + 1160x + 108.5 \quad \text{(A19)}$$

3. Using the above function, mole fraction of water in the liquid phase was calculated to be 0.25 at 253.53 K. From this, the mole fraction of 1-butanol in the liquid phase was estimated to be 0.75 using the following equation.

$$x_{1-butanol} + x_{water} = 1 \quad \text{(A20)}$$

4. The heat load on the system was calculated assuming a feed flow rate of 1000 kg/hr having a concentration of 20 kg/m^3 1-butanol in water at 293.16 K. Hence, flow rate ($\dot{m}$) of 1-butanol in the feed was obtained to be 0.27 kmol/hr and water was 54.40 kmol/hr.
5. Initially, the system was cooled using chilled water upto 278.16 K. The specific heat capacity (c_p) of 1-butanol and water in the feed was taken as a function of temperature (T):

$$c_p = A + BT + CT^2 + DT^3 + ET^4 \quad \text{(A21)}$$

Where,

Table XI: Coefficients for estimating specific heat capacity

Compound	A	B	C	D	E
Water	2.76E+05	-2.09E+03	8.125	-1.41E-02	9.37E-06
1-butanol	1.91E+05	-7.30E+02	2.2998	0	0

6. The heat load (Q_1) for cooling the system upto 278.16 was calculated as:

$$Q_2 = \left(\dot{m}\int c_p dT\right)_{water} + \left(\dot{m}\int c_p dT\right)_{1-butanol} \quad \text{(A22)}$$

7. For further cooling from 278.16 K to 253.53 K, ethanol glycol which was 45 % by weight was used as a coolant. In this case, since the water will start fusing below 273.16 K, the term for latent heat of fusion of ice needs to be accounted for calculating the heat load (Q2). The latent heat of fusion of ice (L) was taken to be 6017.10 kJ/kmol.

$$Q_2 = \left(\dot{m}\int c_p dT\right)_{water} + \left(\dot{m}\int c_p dT\right)_{1-butanol} + \dot{m}_{water} * L \quad \text{(A23)}$$

8. The overall heat load(Q) on the system is:

$$Q_1 + Q_2 = Q \quad \text{(A24)}$$

Adsorption

1. The isotherm equation for adsorption on AC F-400 was obtained by regression of the data available in the paper of Abdegagh et al. (2013). The equation gave a relation between the amount of butanol adsorbed per unit mass of adsorbent (y) and concentration of 1-butanol in the feed solution (x) at equilibrium. The equation is as follows:

$$y_i = \frac{500x_i}{1 + 2130.5x_i} \quad \text{(A25)}$$

Where i= O or 1; Isotherm equations for other adsorbents were also obtained similarly.

2. Mass balance across a batch adsorption unit was carried out:

$$Lx_o + Sy_o = Lx_1 + Sy_1 \quad \text{(A26)}$$

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Where, L is the amount of water in the feed (kg); x is the concentration (kg 1-butanol/kg water); S is the amount of adsorbent (kg); y is the amount of 1-butanol adsorbed (kg 1-butanol/kg adsorbent). The subscript 'o' indicates inlet and '1' indicates outlet.

3. Assuming the value of L=980 kg; S=300 kg; $x_o = 0.02$; $y_o = 0$; and solving equations (A25) and (A26), the value of x_1 and y_1 was determined.

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Extractive Demetalization of Iraqi Crude Oil by using Zeolite A

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Abstract- The feasibility of removal vanadium (V) from Iraqi crude oil using zeolite A was investigated. Different operating parameters such as adsorbent loading, vanadium loading, and operating time were studied for their effects on metal removal efficiency. Experimental results of adsorption test show that Langmuir isotherm predicts well the experimental data and the maximum zeolite A uptake of V was 30 mg/g. XRD and EDX analyses revealed the noticeable uptake of zeolite for V. In crude oil, experimental results indicated that for zeolite loading at 1g/100ml oil and within approximately 5 h, the removal efficiencies of V were 60, 45, and 33% at vanadium loadings of 75, 85, and 95 ppm respectively. While at 10, 20, 40, and 50 h the removal efficiency was 68, 75, 78 and 78% for 75 ppm of V loading. The equilibrium concentration of V in crude oil was attained after 40 h of operation. Long term tests revealed the high stability of zeolite A for vanadium removal. Results depict that zeolite A could be advantageous for removal of V in the crude oil hydrotreating units.

Keywords: *vanadium; crude oil; demetalization; isotherm models.*

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Extractive Demetalization of Iraqi Crude Oil by using Zeolite A

Luma H. Mahmood [α] & Mohammad F. Abid [σ]

Abstract- The feasibility of removal vanadium (V) from Iraqi crude oil using zeolite A was investigated. Different operating parameters such as adsorbent loading, vanadium loading, and operating time were studied for their effects on metal removal efficiency. Experimental results of adsorption test show that Langmuir isotherm predicts well the experimental data and the maximum zeolite A uptake of V was 30 mg/g. XRD and EDX analyses revealed the noticeable uptake of zeolite for V. In crude oil, experimental results indicated that for zeolite loading at 1g/100ml oil and within approximately 5 h, the removal efficiencies of V were 60, 45, and 33% at vanadium loadings of 75, 85, and 95 ppm respectively. While at 10, 20, 40, and 50 h the removal efficiency was 68, 75, 78 and 78% for 75 ppm of V loading. The equilibrium concentration of V in crude oil was attained after 40 h of operation. Long term tests revealed the high stability of zeolite A for vanadium removal. Results depict that zeolite A could be advantageous for removal of V in the crude oil hydrotreating units.

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I. Introduction

In crude oil, traces of vanadium (V) are considered the most plentiful metals [1]. Serious problems can be evolved due to this metal through petroleum processing, such as catalyst poisoning which lead to acid rain, corrosion of equipment and low quality of product. It is well-known that metals in crude oils form complexes with asphaltenes [2]. Consequently, sever conditions have been applied for removal metals from crude oil in conventional technologies include; deasphalting, hydrocracking and hydrotreating [3]. Other removal processes are adsorption, acid attack, and solvent extraction [4-6]. Therefore efficient and effective-cost process is required to decrease the concentration of these metals before any subsequent processes. Zeolites have been utilized in many industrial implementations such as water softening, heterogeneous catalysis, separation, environmental remediation because zeolites possessing large surface area, remarkable catalytic and ionic exchange properties [7-8] and then it could be employed for the removal of these metal ions from crude oil. Zeolites are naturally occurring crystalline alumino-silicate minerals which are synthesized of 3-dimensional structures of tetrahedral molecules connected with the O_2 participated atoms [9]. Zeolites are assured ion exchangers and have been effectively utilized in the elimination of heavy metals from wastewaters, and as catalyst for the catalytic cracking of heavy oils [10-11]. Ikyereve et al. [12] investigated the eclectic sharing of the natural zeolites in the elimination of these toxic metals from crude oil. Ikyereve [13] reported that the ion substitution reaction between positive ion A_S^{Za}, at first in solution and B_Z^{Zb}, at first in a zeolite is shown as follows:

$$Z_b A_S^{Za} + Z_a B_Z^{Zb} \longleftrightarrow Z_b A_Z^{Za} + Z_a B_S^{Zb} \quad (1)$$

B_Z^{Zb} & A_Z^{Za} are the positive ions inside the zeolite crystal; Za & Zb are the valences of the seions; A_S^{Za} & B_S^{Zb} are positive ions in solution. The positive ionuptake capacity of a zeolite is a consequence of the degree of exchange of Alfor Si in the structure. Author concluded that the more the substitution of Al for Si, the higher the number of positive ions wanted to preserve electronic neutrality in the zeolites. Price et al. [14] conducted experimental study to investigate the adjustments in framework occurred after partly substituting the extra-framework Na^+ ions with monovalent, Li^+, K^+, Rb^+ and NH^{4+} and divalent, Ca^{2+} cations. Authors concluded that solid state Nuclear Magnetic Resonance detected alterations to the internal structure of the Linde Type A framework upon ion substitute with NH^{4+} and Ca^{2+}. Substitution with Li^+, K^+ and Rb^+ ions does not considerably influence the long-range crystal order. Substitution with NH^{4+} ions compensates some of the long-range order of the zeolite A crystals because of the wastage of some structure Al as can be observed from X-ray data. Substitution with divalent Ca^{2+} ions inserts some mono dentate carbonate kinds into the structure, but no change to the long-range crystal order is noticed. Published data on the usage of zeolites for the elimination of metal ions from crude oil are scarce. In Iraq crude oil of east Baghdad field contains higher amounts of vanadium (> 75 ppm) than other heavy metals [15]. The main objective of present work was to investigate the feasibility of Zeolite type A to remove vanadium ions from crude oil. Another objective was to study the kinetics of adsorption process.

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II. Materials and Methods

a) Materials

Zeolite A (Na_{12} $(AlO_2)_{12}$ $(SiO_2)_{12}$ x $27H_2O$) was purchased from GCMIL, India. Crude oil was received from Al-Daura Oil Refinery, Baghdad. Vanadium tetrachloride (VCl_4) and EDTA were supplied from Ava Chemicals Private Limited, India. Table 1 lists the physicochemical properties of crude oil of east Baghdad field

b) Experimental method

The experimental setup is shown in Figure 1. Zeolite A particles was grounded. Figure 2 shows the Zeolite A particles before and after grounding. 1 gram of the sieved zeolite A was added into 100 mL of the crude oil in a separating flask with 5mL of EDTA. This mixture was well mixed by a magnetic stirrer at 100 rpm for an hour at room temperature (~ 25°C). Zeolite A was separated from the mixture in a vacuum separator (Rocker 300A Vacuum Filtration System, New Star Environmental & Laboratory Products). The liquid mixture was then transferred to a high speed centrifuge (Type Centrisart® D-16C, Sartorius Co.) where the demetalized crude oil (DMCO) layer was separated and analyzed for the metal ions.

c) Analysis techniques

XRD-6000 Shimadzu (X-ray diffractometer with incident angle of 0.154nm using Cu-Kα radiation) was used to examine the phase ingredients. The topographical features were accomplished by utilizing Tescan VEGA 3SB scanning electron microscope with accelerating voltage: 200V to 30kV and the magnification power from 4X to 10^5X. The chemical composition of zeolite A was anatomized by utilizing energy dispersive X-ray analysis (EDX) Model; Inspect S50/FEI Company, Netherland. The concentration of vanadium in fluid before and after treatment was measured using atomic absorption type (AA-7000, Shimadzu, Japan) at the Petroleum Research and Development Center, Ministry of Oil, Baghdad/Iraq.

III. Results and Discussion

a) Kinetic study of adsorption

The maximum adsorption capacity of zeolite A was estimated by conducting adsorption experiments. Different concentrations (5, 10, 20, 30, and 50 mg/L) of an aqueous solution of VCl_4 in distilled water was prepared. Then 100ml of each concentration is placed in a 250ml flask separately with 1g of zeolite A. The amount of vanadium adsorbed at equilibrium, (mg/g) was estimated using Eq. 1.

$$q_e = \frac{(C_o - C_e)\,V}{W} \quad (1)$$

Where C_o and C_e: concentrations of vanadium at initial and at equilibrium (mg/ L), respectively, V: volume of the heavy oil used, and W: mass of zeolite A used (gm). The Freundlich and Langmuir equations are the most widely used models for isotherm [16], the correlation of Freundlich and Langmuir isotherms are represented by Eqns. 2 and 3, respectively.

$$q_e = K_F C_e^{1/n} \quad (2)$$

$$q_e = \frac{q_m \cdot K_L . C_e}{(1 + K_L . C_e)} \quad (3)$$

Where q_m: maxima quantity of metal V adsorbed per unit mass of zeolite (mg gm^{-1}), q_e: concentricity of V at equilibrium (mg L^{-1}). K_L is the Langmuir constant (L mg^{-1}) and K_F is Freundlich constant (mg gm^{-1}) (L $mg^{-1})^{-n}$. Figure 3 plots the experimental results of vanadium and nickel adsorption at equilibrium on zeolite A sample respectively. To predict which one of these two models will well represent the experimental data of metal (V) removal, a linearization technique would be applied on equations 2 and 3, respectively. Equations 4 and 5 represent the linearized form for equations 2 and 3 respectively.

$$\frac{1}{qe} = \frac{1}{qo} + \frac{1}{bqm\ Ce} \quad (4)$$

$$lnq_e = \ln K_F + \frac{\ln C_e}{n} \quad (5)$$

Figure (4a) represents a plot of $\frac{1}{q_e}$ vs $\frac{1}{C_e}$ with a correlation coefficient (R^2) = 0.9738. Mean while Figure (4b) represents a plot of lnq_e vs $\ln C_e$ with a correlation coefficient (R^2) = 0.9484. These results assure the viability of Langmuir isotherm in our study. This outcome depicts that the maximum uptake of V metal was ≈30mg g^{-1}, this may be attributed to the capability of the usable zeolite structural frame with high percentage of pore volume.

b) Influence of metal adsorption on zeolite characteristics

i. *XRD analysis*

Figure 5 shows XRD images of zeolite A before and after vanadium adsorption. According to [17], the XRD pattern (Fig. 5a) for the zeolite shows excellent match with typical zeolite A while the XRD image of the vanadium-zeolite (see Fig. 5b) shows a breakdown of structure which indicates an effective exchanger (zeolite A). This collapsing in peaks may be attributed to the replacement of Si ions by larger vanadiumions which could induce an extension in the unit cell. This attitude is compatible with the existence of vanadium in the structure of zeolite which caused by the difference between V-O and Si-O ligament tallness [18]. Gallezot and Leclerc [19] found that vanadium promotes the

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collapse of zeolite frame work because it joins with other ions which stabilize the framework of zeolite.

ii. *EDX analysis*

EDX analysis of the zeolites was carried out, before and after vanadium uptake, to estimate the percentage weight of elements existed. Moreover, the proportion of Si/Al in the zeolites can be determined. Table 2 presents the percentage weight of elements as measured by the SEM-EDX (XRD-6000 Shimadzu) and the proportion of Si/Al in the zeolites. Figure 6(a-b) shows EDX images of zeolite A before and after vanadium uptake. As be seen from images, that all Na, and some of Al and Si are ion exchanged with vanadium on the zeolite surface. The percentage weight of elements displays that the whole Na^{+} inside the zeolite were substituted and furthermore, about 76% of ions of silicon which formed the structure were also replaced by the ions of vanadium while only 26% of Al ions were exchanged. (Gomes et al., [20] stated that ion radius plays an important effect on the ionic exchange. Shannon [21] published a revised crystallographic data on ionic radii. He estimated the ionic radii of Na^{+}, Al^{3+}, Si^{4+}, and V^{4+} as equal to 116, 67.5, 54, and 72 picometer, respectively (1 Angstroms = 100 picometer). These values suggest that vanadium ions could exchange any ions of equal or larger of its size which clearly explains the drastic effect of Na and Si ions exchanged and breakdown of zeolite structure noticed after vanadium ion exchange.

c) *Removal of vanadium from crude oil*

A series of experiments was conducted to test the capability of Zeolite to remove Vanadium ions from crude oil. Figure 7 illustrates vanadium removal efficiency as a function of operating time at different loading of vanadium. As can be seen in Figure 6, a remarkable increase in vanadium removal within a short time was observed for all loadings of vanadium after then a slight increase with operating time was shown. Within approximately 5 h, the vanadium removal efficiencies were 33, 45, and 60% at vanadium loadings of 10, 30, and 40 ppm respectively. Further processing of crude oil with 10 ppm vanadium shows a continuous slight increase in metal removal with operating time. At 10, 20, 40, and 50 h the removal efficiency was 68, 75, 78 and 78%. As can be seen, an equilibrium concentration of the vanadium was attained after 40 h. For other vanadium loading (i.e., 30 and 40 ppm), the equilibrium concentration of vanadium was attained at approximately 20 h. Salman et al. [22] reported that the differences in zeolite adsorption capacities for heavy metal ions can be attributed to different factors i.e. physicochemical factors, hydration energy, and diameter. In general zeolites and ion exchanges prefer high valent ions [23]. Thus high selectivity of zeolite for vanadium was due to electrostatic attraction between high valent vanadium cations and cations of solid adsorbent. Fig. 8 plots the effect of zeolite loading (g/100ml oil) on vanadium removal (%). As can be seen in this Figure, zeolite loading has a positive impact on removal efficiency. The increase in vanadium removal with the zeolite A loading is due to the higher number of active sites available over the adsorbent [24]. It is interesting notice that at higher loading of zeolite a constant value of vanadium removal was attained. This may be attributed to that equilibrium is established between the adsorbed ions of vanadium onto zeolite and that which still existed into the treated crude oil.

IV. Conclusion

In present work different operating parameters such as vanadium loading, zeolite type A loading, and operating time were investigated for their effects on vanadium removal efficiency from crude oil. Results revealed that zeolite loading and operating time have positive impact on removal efficiency while vanadium loading showed different trend. Experimental results of adsorption test show that Langmuir isotherm predicts well the experimental data. RDX and EDX analyses confirm the high tendency of zeolite A to remove vanadium ions from crude oil. Long term tests revealed the high stability of zeolite A for vanadium removal.

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Nomenclature

C_o: Concentrations of vanadium at initial, (mg/ L)
C_e: Concentrations of vanadium at equilibrium, (mg/ L)
V: Volume of the heavy oil used, (ml)
W: Mass of zeolite A used, (gm)
q_m: Maxima quantity of metal V adsorbed per unit mass of zeolite, (mg/ gm)
q_e: Concentricity of V at equilibrium, (mg/ L)
K_L: Langmuir constant, (L/ mg)
K_F: Freundlich constant (mg/ gm) (L/ mg)$^{-n}$

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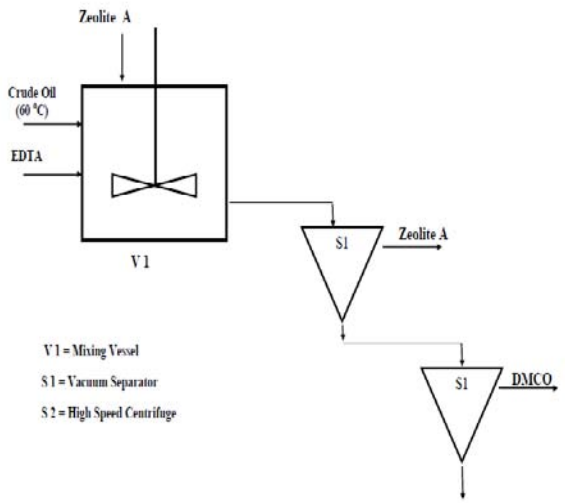

Fig. 1: Schematic of the experimental setup

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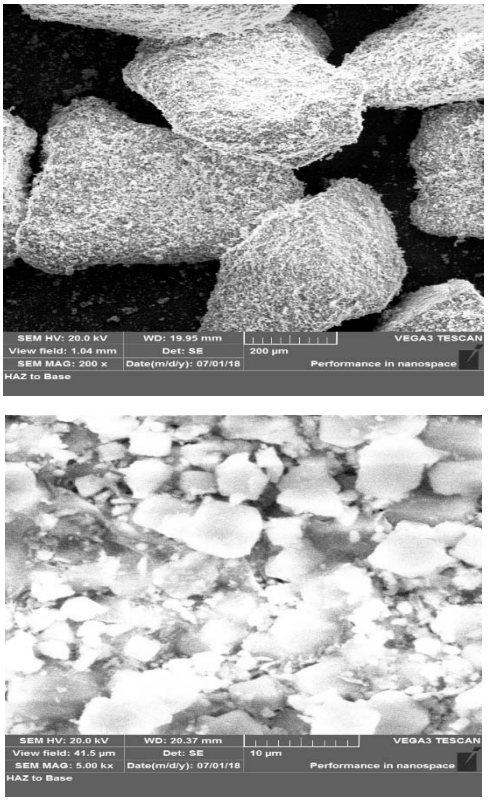


Fig. 2: Electron Imageof zeolite A particles (top) before grounded and after grounded (bottom)

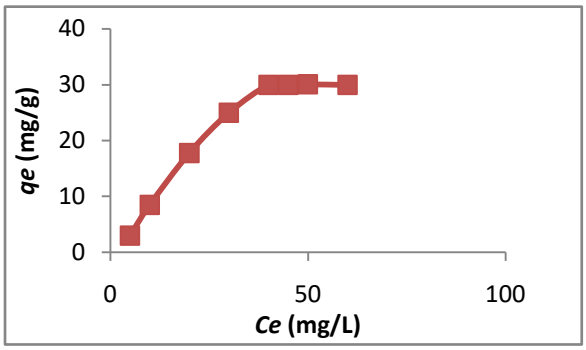
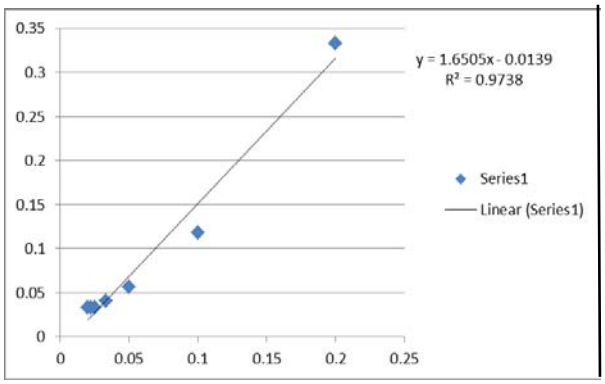


Fig. 3: Experimental results of adsorption of vanadium at equilibrium on Zeolite A

4a



4b

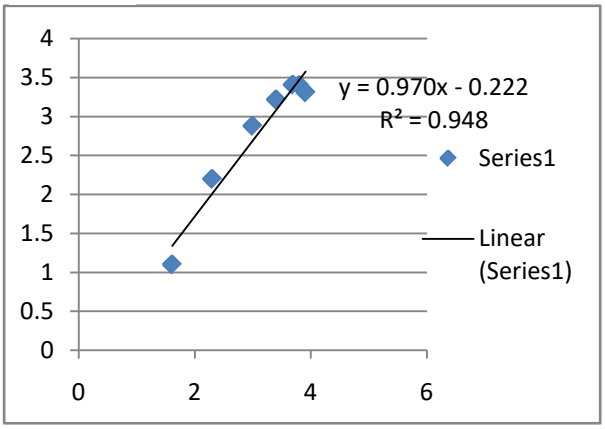


Fig. 4: Linearization plots of Langmuir isotherm model (4a) and Freundlich isotherm model (4b) for vanadium adsorption on Zeolite A.

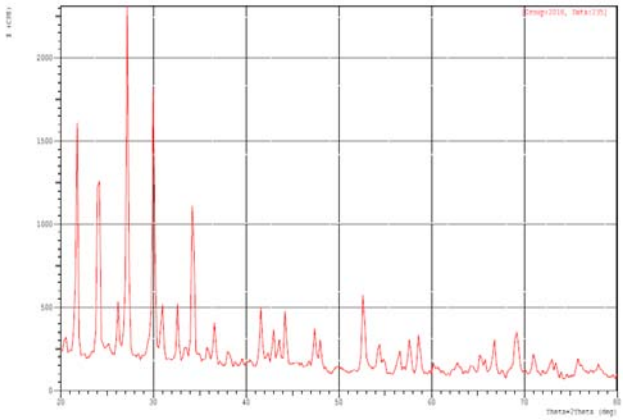


Fig. 5a: XRD image of zeolite A before vanadium uptake

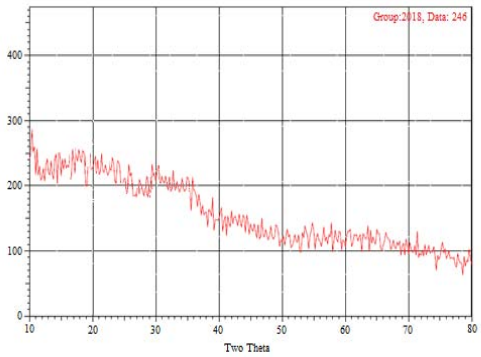


Fig. 5b: XRD image of zeolite A after vanadium

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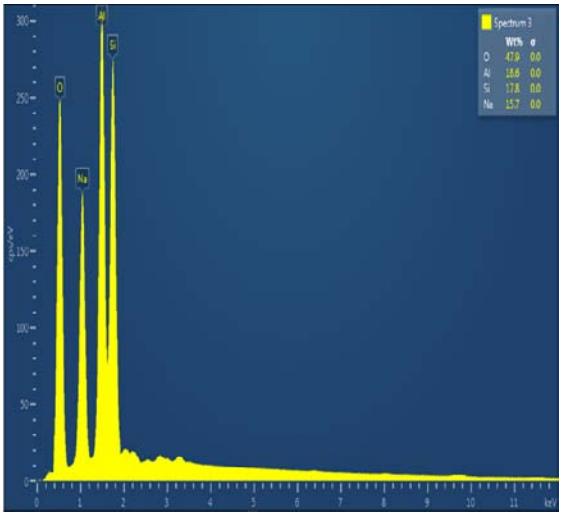

Fig. 6a: EDX image of zeolite before vanadium uptake

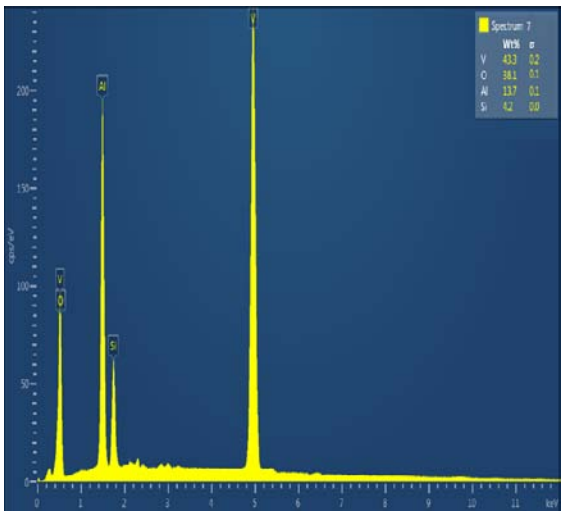

Fig. 6b: EDX image of zeolite after vanadium uptake

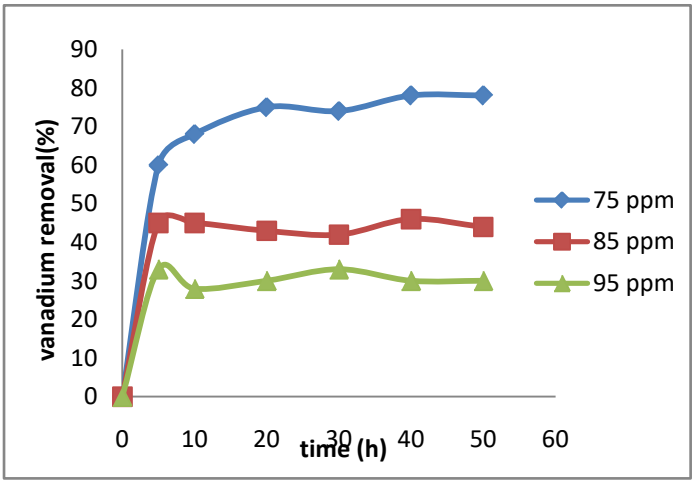

Fig. 7: Vanadium removal efficiency from crude oil as a function of operating time at zeolite loading 1 g/100ml oil

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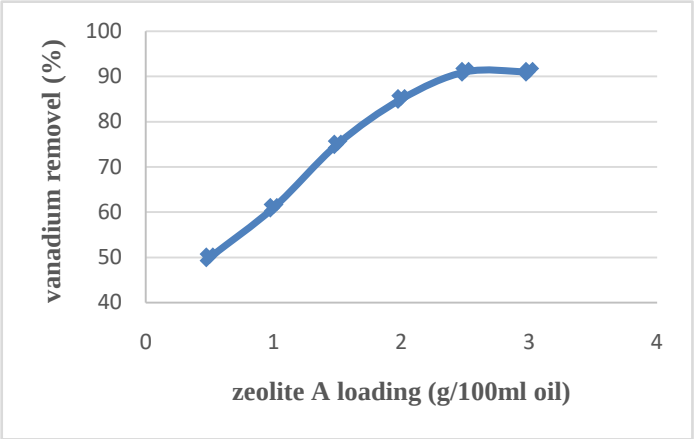

Fig. 8: Vanadium removal (%) as a function of zeolite A loading (g/100ml oil) at vanadium loading = 75 ppm and operating time=5 h

Table 1: Physicochemical properties of crude oil of east Baghdad field [15]

Item	Property	Value
1	Density @ 15 ^{o}C g/cm^{3}	0.932
2	Sulfur content %wt	3.998
3	Vanadium, ppm	75.970
4	Nickel, ppm	25.340
5	Aluminum, ppm	2.684
6	Asphaltenes %wt	6.412

Table 2: Percentage weight of elements before and after vanadium uptake

Elements	O		Na		Al		Si		Si/Al		V	
%weight	before	after	before	after	before	after	before	after	before	after	before	after
	47.9	38.1	15.7	0.0	18.6	13.7	17.8	4.2	0.957	0.306	0.0	43.3

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Non-Linear Mathematical Modelling of Nylon-6 Polymerization Reactors

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Abstract- Investigations on Nylon-6 polymerization reactors such as VK (Vereinfacht Kontinuierliches Rohr) tube (vertical column) reactors have been explored to a very limited extent owing to their complex internal structure, which leads to uncertain velocity profile of the reactants inside the reactor. However, usually a flat velocity profile (plug flow profile) of reaction mixture is assumed inside the reactor leading to large errors in prediction of final properties of the product. In the current study, a modified simulation model has been developed for the Nylon-6 polymerization using mono acid stabilizers (acetic acid) in an industrial VK tube reactor. The variation of the velocity profile, which may result in axial changes of concentrations of different reactants along the length of the reactor has been accounted for by considering a small value non-linear time dependent decaying function. The model fetched significantly better results than the earlier model with plug flow profile of the reactants.

Keywords: *Nylon-6 polymerization, VK tube reactors, modelling and simulation, optimization.*

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Non-Linear Mathematical Modelling of Nylon-6 Polymerization Reactors

Devika P.D [α] Ashwini K. Agrawal [σ] Dinesh P.A [ρ] & Rama Krishna Prasad [ω]

Abstract- Investigations on nylon-6 polymerization reactors such as VK (Vereinfacht Kontinuierliches Rohr) tube (vertical column) reactors have been explored to a very limited extent owing to their complex internal structure, which leads to uncertain velocity profile of the reactants inside the reactor. However, usually a flat velocity profile (plug flow profile) of reaction mixture is assumed inside the reactor leading to large errors in prediction of final properties of the product. In the current study, a modified simulation model has been developed for the Nylon-6 polymerization using mono acid stabilizers (acetic acid) in an industrial VK tube reactor. The variation of the velocity profile, which may result in axial changes of concentrations of different reactants along the length of the reactor has been accounted for by considering a small value non-linear time dependent decaying function. The model fetched significantly better results than the earlier model with plug flow profile of the reactants[24]. The pattern of the concentration profiles of conversion, molecular weight and the end groups were found to be similar in the two cases, however, the results on end-group concentrations and the molecular weight of the final polymer were predicted to be much closer to the actual industrial data for the simulated reactor. This model can be very useful in the process optimization and in the designing of new VK tubes for increased productivity.

Keywords: Nylon-6 polymerization, VK tube reactors, modelling and simulation, optimization.

I. Introduction

VK (Vereinfacht Kontinuierliches Rohr) column reactor is one among the most well known reactors used for the hydrolytic polymerization of ε-caprolactam. Vertical tube reactors are designed using the internal gratings to achieve the equal heating and close uniform flow (i.e. flat velocity profile). In literature[24], raw materials, viz., ε-caprolactam, water and acetic acid are passed freely at the reactor entrance.

The velocity profile of the feed seems to be one more important parameter in controlling the rate of reactions in the model in addition to the pressure, temperature, and water concentration. Work on modelling and simulation of such reactors is scanty due to their complicated reactor configuration and lack of industrial data.

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Many models were developed to study of the significance of H_2O elimination in the polymer mixture in a tubular reactor by different authors[5,11,16-19]. Recently, we reported[24] the result of hydrostatic pressure within the reacting system using a plug flow velocity profile. The model predicted M_n, NH_2 and COOH concentrations with higher accuracy compared to the other models reported in the literature. However, the non-linear time dependent effects of induced velocity profile due to the internal structure of the reactor could not be incorporated in this model. The industrial VK tube reactors used for nylon-6 polymerization are very complex and it is extremely difficult to include actual velocity profiles of the reactants inside the reactors.

In the current study, a simulation model has been developed for Nylon-6 polymerization with mono acid stabilizers in a VK tube reactor. The axial changes of concentrations of various reaction components down the length of the reactor have been simulated by considering the non-linear time dependent decaying factor for each reactant species.

II. Model of Vk Tube Reactor With Correction for Velocity Profile

The VK tube reactor that was modelled has five independent portions . The temperatures in the reaction mixture were measured by the thermocouple wells at six places. Figure 1A represents the schematic representation of the VK tube reactor. Input consisting of molten caprolactam, mono functional acid and water was passed to the entrance of the VK tube under a nitrogen cover. A water seal was kept above the reactor to allow the purged nitrogen to escape. The heat exchanger 1 (HE-1) heated the reaction mixture in zone-1 as it passes through HE-1. The melt in zone-3 upper and lower was heated by the heating jackets and the exothermic reactions. The temperature of the polymer mixture slowly increased from the top layer to the centre portion until the temperature reached the maximum point. Another heat exchanger was used to decrease and stabilize the temperature towards the bottom of the reactor. The end products such as unreacted caprolactam and the polymer were collected from the bottom of reactor.

In our earlier work[24], feed to the VK tube reactors were considered to be flowing normally (that is with no velocity profile), which might not be realistic.

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However, in the present work, the flow of reactants was assumed to have a mild and possibly an irregular velocity profile caused by the shear forces exerted in the reactor walls and gratings in the upward direction and the gravitational force in the downward direction. Therefore, our earlier model[24] was modified to incorporate non-linear time dependent effect on the reaction mixture (monomer (m), W, P, and acetic acid (P_{1x})). Considering the geometry of the reactor to be symmetrical, an empirical non-linear time dependent exponential quantity given by equation (1) has been included in the mass balance equations of the reaction components. These modified mass balance equations which are of first order non-linear ordinary differential equations type (Table 2) have been solved by using the fourth order Runge-Kutta numerical method for the concentrations of all the species in the reaction scheme.

Quantity of reaction species changed due to the faster or slower velocity of the species 'i' compared to the average velocity profile of the reaction mixture is given as

$$= \alpha_i \exp(\beta_i t) \text{ moles/kg/h.} \quad (1)$$

where α_i and β_i are the parameters to be fitted for each species 'i' so that the output polymer properties match well with the industrial data.

a) Determination of water concentration

As mentioned in our previous work[24] the following vapour liquid equilibrium equation which is selected after testing several vapor liquid equilibrium equations[11,20,21] was used in the model to find the water quantity in the polymer mass in the vaporizing zone of the reactor.

$$[W] = 10^{-2} P_T \exp(8220/T - 24.36) \quad (2)$$

The given relation was used to determine the amount of water that was retained in the reaction mixture at each point in the reactor in the vaporizing zone. For the modified model with pressure effect and the non-linear time dependent adjustment of the concentration, the above equation was modified as given below.

$$[W] = 10^{-2} P_T \exp(8220/T - 24.24) + \alpha_4 \exp(\beta_2 t) \quad (3)$$

Where P_T is the total pressure in pascals given by

$$P_T = P_A + 9.81 (\rho_W H_W + \rho_M H_P) \quad (4)$$

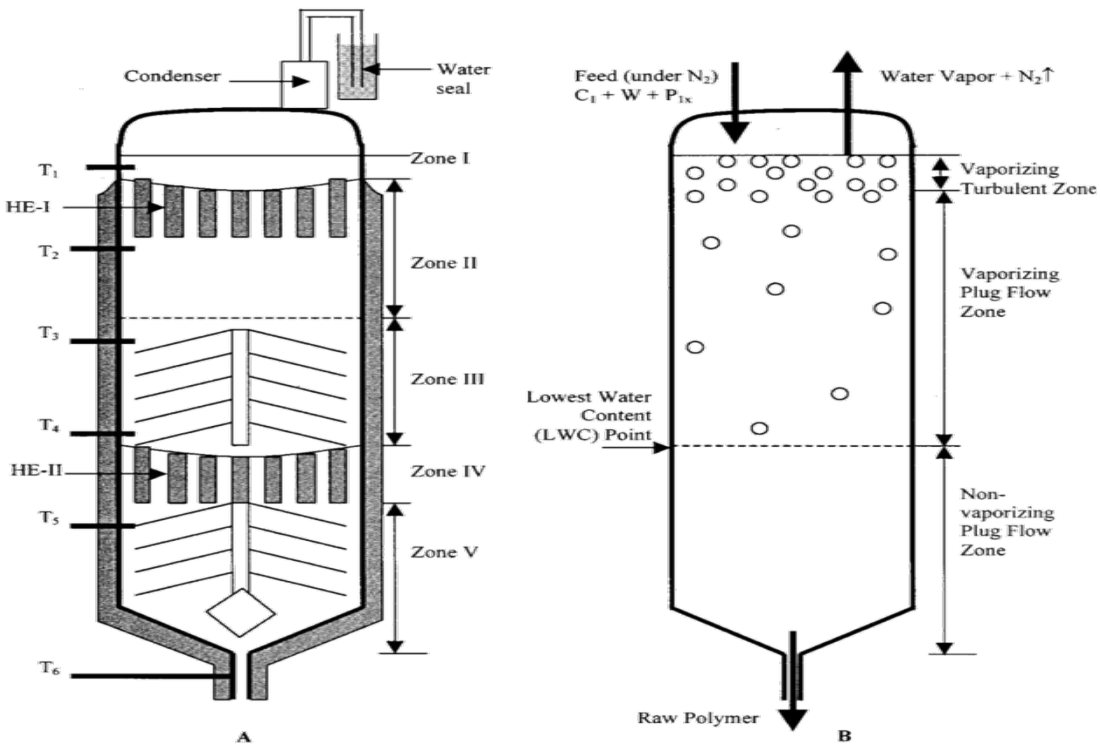

Figure 1: VK Tube Reactor

Where P_A is the atmospheric pressure given by 1.013×10^5 Pa. The original atmospheric pressure (P_A) at the industrial place was 2% lower than P_A and hence the change from 24.36 to 24.24 in Equation (2). α_4 and β_2 are the factors to be adjusted to fit the industrial results and to get the quantity of water consumed/produced in moles/kg/h, representing the non-linear time dependent influence of the velocity on the water concentration. The value of [W] was calculated using Equation (3) at all the points in the top portion of the tube. In the non vaporizing zone, i.e, from the LWC point downward, the total water in the reaction mass and in the product was assumed to be a constant. Therefore the value of [W] is calculated using a mass balance equation.

$$[W] + [P] = [W_{CP}] + [P_{CP}] \quad (5)$$

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where [P] is moles/kg of Nylon-6 near the interested point and [W_{CP}] and [P_{CP}] are moles/kg of H_2O and Nylon-6 at the lowest water content location.

Table 1: Kinetic Scheme for Nylon 6 Polymerization -

1. Ring-Opening

$$C_1 + W \xrightarrow[k_1' - k_1/K_1]{k_1} P_1$$

2. Polycondensation

$$P_n + P_m \xrightarrow[k_2' - k_2/K_2]{k_2} P_{n+m} + W, \quad n, m = 1, 2, 3, \ldots$$

3. Polyaddition

$$P_n + C_1 \xrightarrow[k_3' - k_3/K_3]{k_3} P_{n+1}, \quad n = 1, 2, 3, \ldots$$

4. Ring Opening of Cyclic Dimer

$$C_2 + W \xrightarrow[k_4' - k_4/K_4]{k_4} P_2$$

5. Polyaddition of Cyclic Dimer

$$P_n + C_2 \xrightarrow[k_5' - k_5/K_5]{k_5} P_{n+2}, \quad n = 1, 2, 3, \ldots$$

6. Reaction with Monofunctional Acid

$$P_n + P_{mx} \xrightarrow[k_2' - k_2/K_2]{k_2} P_{n+mx} + W, \quad n, m = 1, 2, 3, \ldots$$

Table 2: Mass Balance Equations with Induced Input to the Top of the Reactor

$$\frac{dm}{dt} = -k_1 m w + k_1' p - k_3 m \lambda_0 + k_3' (\lambda_0 - p) + \alpha_1 \exp(\beta_1 t)$$

$$\frac{dp}{dt} = \begin{cases} k_1 m w - k_1' p - 2k_2 p \lambda_0 + 2 k_2' m w (\lambda_0 - p) - k_3 p m + k_3' p - k_2 \lambda_{0x} p + \\ k_2' w (\lambda_{0x} - p_{1x}) - k_5 p c_2 + k_5' p + \alpha_2 \exp(\beta_1 t) \end{cases}$$

$$\frac{d\lambda_0}{dt} = k_1 m w - k_1' p - k_2 \lambda_0^2 + k_2' w (\lambda_1 - \lambda_0) - k_2 \lambda_0 \lambda_{0x} + k_2' w (\lambda_{1x} - \lambda_{0x}) + k_4 w c_2 - k_4' p$$

$$\frac{d\lambda_1}{dt} = \begin{cases} k_1 m w - k_1' p + k_3 m \lambda_0 - k_3' (\lambda_0 - p) - k_2 \lambda_{0x} \lambda_1 - k_2' w (\lambda_{1x} - \lambda_{2x})/2 + \\ 2 k_5 c_2 \lambda_0 - 2 k_5' (\lambda_0 - 2p) + 2 k_4 w c_2 - 2 k_4' p \end{cases}$$

$$\frac{d\lambda_2}{dt} = \begin{cases} k_1 m w - k_1' p + 2 k_2 \lambda_1^2 + k_2' w (\lambda_1 - \lambda_3)/3 + k_3 m (\lambda_0 + 2\lambda_1) + \\ k_3' (\lambda_0 - 2\lambda_1 + p) - k_2 \lambda_2 \lambda_{0x} + k_2' w (2\lambda_{3x} - 3\lambda_{2x} + \lambda_{1x})/6 + 4 k_5 c_2 (\lambda_1 + \lambda_0) + \\ 4 k_5' (\lambda_0 - \lambda_1 + p) + 4 k_4 w c_2 - 4 k_4' p \end{cases}$$

$$\frac{dc_2}{dt} = - k_4 c_2 w - k_4' p - k_5 c_2 \lambda_0 + k_5' (\lambda_0 - 2p)$$

$$\frac{d\lambda_{1x}}{dt} = k_2 \lambda_1 \lambda_{0x} - k_2' w (\lambda_{2x} - \lambda_{1x})/2$$

$$\frac{d\lambda_{2x}}{dt} = = k_2 (2 \lambda_1 \lambda_{1x} + \lambda_2 \lambda_{0x}) - k_2' w (4\lambda_{3x} - 3\lambda_{2x} - \lambda_{1x})/6$$

$$\frac{dp_{1x}}{dt} = -k_2 p_{1x} \lambda_0 + k_2' w (\lambda_{0x} - p_{1x}) + + \alpha_3 \exp(\beta t)$$

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Table 3: Polynomial Expressions for the Constants (Magnitudes & Amplitudes) Used in the Non Linear Time Dependent Functions Incorporated in the Mass Balance Equations of the Various Reaction Species

Expressions For The Magnitudes And Amplitudes Terms*	Best Fit Values In The Present Model		
	Data 1 T=11.71 Hrs	Data 2 T=14.5 Hrs	Data 3 T=15.17 Hrs
$A_1 = 0.00197T^2 - 0.058397T + 0.433939$	0.02	0.001	0.001
$A_2 = -0.002485T^2 + 0.06476T - 0.42068$	-0.003	-0.004	-0.01
$A_3 = 0.0001T^2 + 0.0001T + 0.01$	0.01	0.01	0.01
$A_4 = -0.000207T^2 + 0.00615T - 0.05057$	-0.007	-0.005	-0.005
$B_1 = 0.0001T^2 + 0.0001T - 0.001$	-0.001	-0.001	-0.001
$B_2 = 0.0001T^2 + 0.0001T + 0.001$	+0.001	+0.001	+0.001

* *T = total polymerization time*

b) kinetic model

The reaction model of nylon-6 polymerization has been presented in Table 1. The previous model rate equations[21] for different species were modified to incorporate the non-linear time dependent factor for the various species and are presented in Table 2. The major reactions included in the reaction model in nylon-6 polymerization were ring opening, poly-condensation and poly-addition. The production of cyclic oligomers were accounted by the ring opening and poly-addition reactions of cyclic dimer (C_2) in the process. Higher order cyclic oligomers were neglected to make the analysis easy. The kinetic scheme includes the reactions involving a mono functional acid such as acetic acid and the reactions were catalysed by the carboxyl end groups of the mono functional acid. The rate constants for all the reactions were estimated by the values of kinetic data determined from experimental work[2,3,5].

The constants, α and β,, which are magnitudes and amplitudes of the nonlinear time dependent functions incorporated in the mass balance equations of the reactive species are expressed by the second order polynomial equations as a function of total polymerization time (T) in Table 3. Since the velocity profile of the reaction mass is expected to be highly dependent on the total reaction time (obtained from total volume of reactor/feed velocity), it is reasonable to relate the two using empirical relations given in the table. The best fit values of constants obtained for the three experimental cases are also given in the table. Even though the three data sets have different termperature profiles in the zones, the changes in values from one data set to another data set are insignificant in most cases. The equations given in the table can be used to predict the constants for an unknown set of reaction conditions.

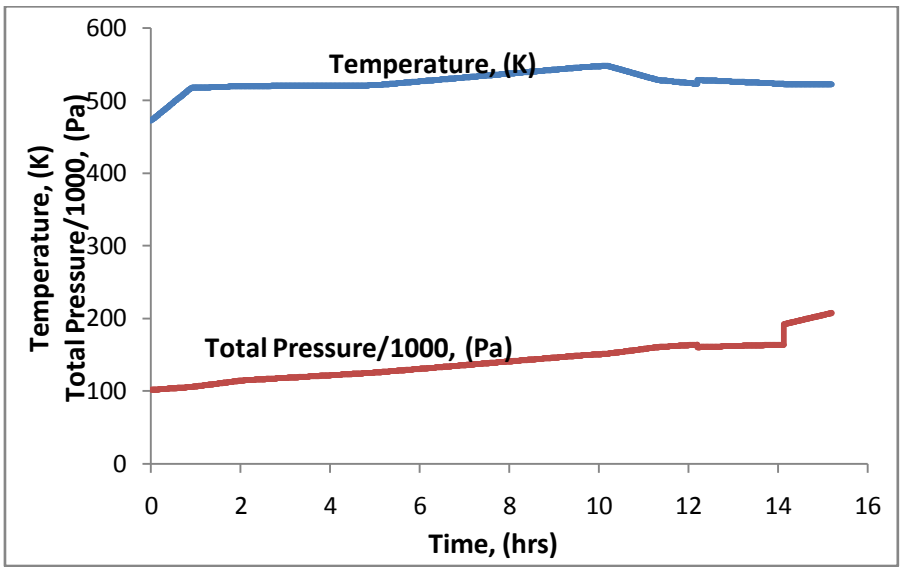

Figure 2: Graph of Polymer Mass Temperature (Measured) and Total Pressure (Predicted) Down the Length of VK Tube with Respect to Time for Data 3

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c) Temperature and Pressure Estimation

Three sets of experimental data measured from a nylon-6 polymerization VK tube were used for the modelling and simulation of the process. At any point of time, the total pressure in the reactor was calculated by using water seal length above the reactor, the atmospheric pressure and the pressure exerted by the mass of polymer above the interested point in the reactor. The reactor design parameters were used to determine the time of the reactions and the hydrostatic pressures of the polymer mass at any point along the length of the reactor. The temperatures of the polymer mixture were measured at different poin ts in the reactor . Straight line assumption has been used to interpolate the temperature values between any two closely measured points. The temperatures and the properties of the polymer mixture have been listed in Table 3 in all the zones for three sets of experimental data

d) Starting parameters used in the simulation of the model

The modified mathematical model represented by the set of non- linear ordinary differential equations were solved simultaneously by using Runge- Kutta IV order method, with an iteration step size of 0.01h. To break the hierarchy of equations closure conditions[21] were used. The starting parameters for all the three data sets were as follows:

$[m_0] = 8.837$ mol/kg; $[P_1] = 0.0$ mol/kg; $\lambda_0 = \lambda_1 = \lambda_2 = 0.0$; $[C_2] = 0.0$ mol/kg; $\lambda_{0x} = \lambda_{1x} = \lambda_{2x} = [P_{1X}]$; Water fed = [W] = 1.3889 mol/kg of mass = 2.5 wt% of input caprolactam Starting value of temperature = 473 K (considered)

Table 4: Experimental Nylon-6 Polymerization Reactor Data Collected for Three Different Sets of Data

Property[a]	Data 1		Data 2		Data 3	
Reaction Time(H)	11.71		14.5		15.17	
Acetic Acid Fed, (Wt%) (Mol/Kg)	0.07 0.0117		0.07 0.0117		0.06 0.0100	
	Melt[b] Temp (K)	Dow[c] Temp (K)	Melt[b] Temp (K)	Dow[c] Temp (K)	Melt[b] Temp (K)	Dow[c] Temp (K)
T_1(Zone I)	517	-	518	-	521	-
T_2(Zone II)	521	546	520.5	538	521	550
T_3(Zone III Upper)	524	555	522	549	527	550
T_4(Zone III Lower)	548	555	546.5	549	547	550
T_5(Zone IV)	531.5	497	529	501.5	531	504
T_6(Zone V)	526.5	496	523.5	501.5	527	505
Extractables(%)	10.56		9.62		9.66	
M_n (G/Mol)	17084		16.484		16.384	
[COOH](Mol/Kg)	0.0517		0.0548		0.0590	
$[NH_2]$(Mol/Kg)	0.0460		0.0452		0.0480	

[a, b, c] *as defined elsewhere*[24]

The properties of polymer such as number-average molecular weight (M_n), [COOH], $[NH_2]$, polydispersity index (excluding the effect of caprolactam and cyclic dimers) and the quantity of extractables have been determined.

III. Data from Industrial Observations

The change in pressure down the length of the reactor and the temperature of the polymer mixture in various zones were measured by finding the average of 10-12 values, found after every two hours and are presented in Table 4. The resident time of polymer mass in each zone was measured by using the mechanical dimensions and the internal structure of the tube. The polymer properties were measured from the polymer samples collected at the bottom of the reactor in the raw form before the monomer was extracted at every two hours. The relative viscosity was calculated by the methods given in literature[22] and the average values were listed in Table 3. The following equations were used to find M_n, relative viscosity (RV_C) and extractables wt% (E) from the experimental raw chips and were

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presented in Table 3.Intrinsic viscosity

$$[\eta]\ (dL/g) = \{[1 + 4k_H(RV_C - 1)]^{1/2} - 1\}/2K_H(1 - 0.01E) \quad (6)$$

Relative viscosity (extracted chips)

$$RV_1 = 1 + [\eta] + K_H[\eta]^2 \quad (7)$$

Number-average molecular weight

$$M_n\ (g/mol) = 113.16F(RV_1 - 1) \quad (8)$$

where k_H is the Huggins constant (0.286 for nylon-6 polymer) and F is an empirical relation constant[23] determined for the industrial reactor (95.7). The refractive index was measured by an immersion refractometer. The percent of extractables can be measured by refluxing 15.0g of raw chips for 8 hours in 80ml of distilled water. The refractive indices calibration table was used for various concentrations of caprolactam to obtain the percentage of extractables.

IV. Results and Discussion

a) Water concentration, temperature and total pressure calculation down the reactor

Total pressure and temperature along the length of the reactor were calculated using the procedure explained elsewhere[24]. The pressure of the polymer melt varies from 1.023×10^5 Pa to 2.081×10^5 Pa down the length of the reactor. Moreover, the viscous polymer mixture flowing down the VK tube decreases the pressure. However these changes are very small to be neglected. The temperature at any point was measured by linearly interpolating the two measured points. The temperature and pressure profiles along the length of the system were plotted in Figure 2 for data 3. The volumes of the various portions and the mass flow rate into the VK tube were used to calculate the reaction times. The temperature and pressure values were shown with respect to the estimated polymerization time at all points from the top to the bottom of the reactor.

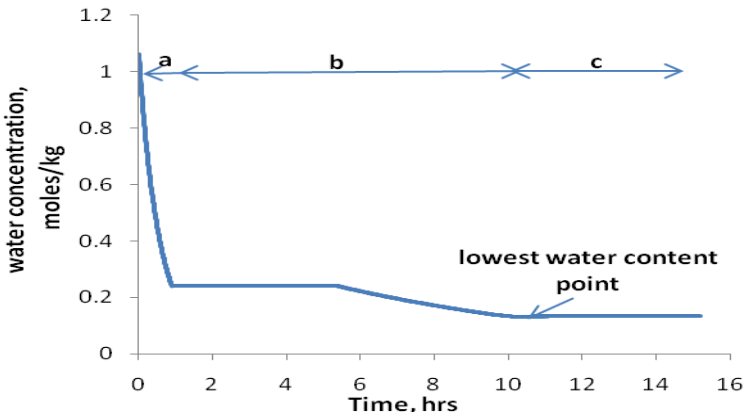

Figure 3: Water Profile Down the Length of the Vk Tube Versus Polymerization Time for Data 3: (A), (B), and (C) As Explained Elsewhere [24].

Table 5: Comparison Between Predicted Results of Polymer Properties with Experimental Values for the Three Data Sets

Property	$[NH_2]^b$ (mol/kg)	M_n^c (g/mol)	Extractable (%)	C_1 (wt%)	$C_1+P_1+C_2$ (wt%)	$[COOH]^b$ (mol/kg)
Actual – Industrial data	0.0460	17084				0.0517
Data I : Old model						
f=0.65	0.0466	16750		9.00	9.02	0.0542
f=0.75	0.0460	16564		8.99	9.01	0.0548
Error (%)	1.0	2.0	10.56	14.8	14.6	4.6
	0.0	3.0		14.9	14.7	6.0
Data I : Present Model						
f=0.65	0.0459	17356		9.34	9.35	0.0534
f=0.75	0.0453	17161		9.32	9.34	0.0541
Error (%)	0.2	1.6		11.6	11.5	3.2
	1.5	0.4		11.7	11.6	4.6

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Actual – Industrial data	0.0452	16484				0.0548
Data II: Old Model						
f=1.0	0.0451	16096		8.41	8.43	0.0567
Error (%)	0.2	2.4	9.62	12.6	12.4	3.5
Data II : Present Model						
f=1.0	0.0448	16358		8.40	8.42	0.0564
Error (%)	0.8	0.8		12.7	12.5	2.9
Actual – Industrial data	0.0480	16384				0.0590
Data III : Old Model						
f=0.8	0.0467	16703		8.33	8.35	0.0547
Error (%)	2.7	1.9	9.66	13.8	13.6	7.2
Data III : Present Model						
f=0.8	0.0484	16379		8.19	8.21	0.0564
Error (%)	0.8	0.03		15.21	15.01	4.0

b) VK tube reactor model

The assumed constant flow profile of the feed to the top of the reactor and down the length of the VK tube reactor as per our earlier work was modified in the present model to include the non linear time dependent factors (due to deviation from plug flow profile).

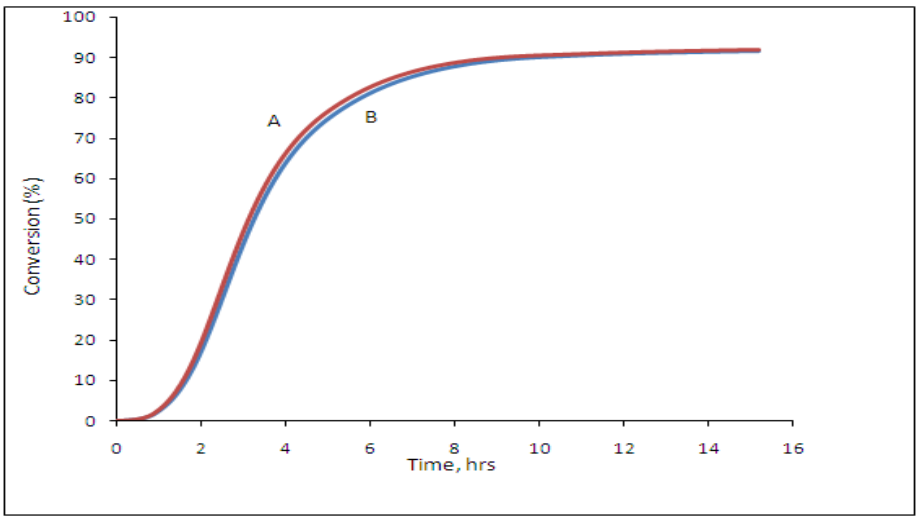

Figure 4: Predicted Conversions Comparison for Case 3: (A) Old Model, (B) Present Model

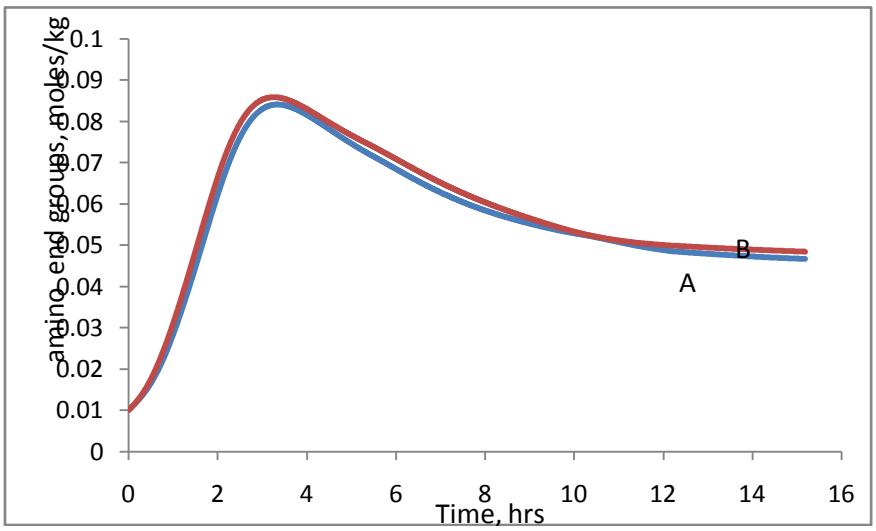

Figure 5: Predicted Amino end Groups Comparison fot Case 3: (A) Old Model, (B) Present Model

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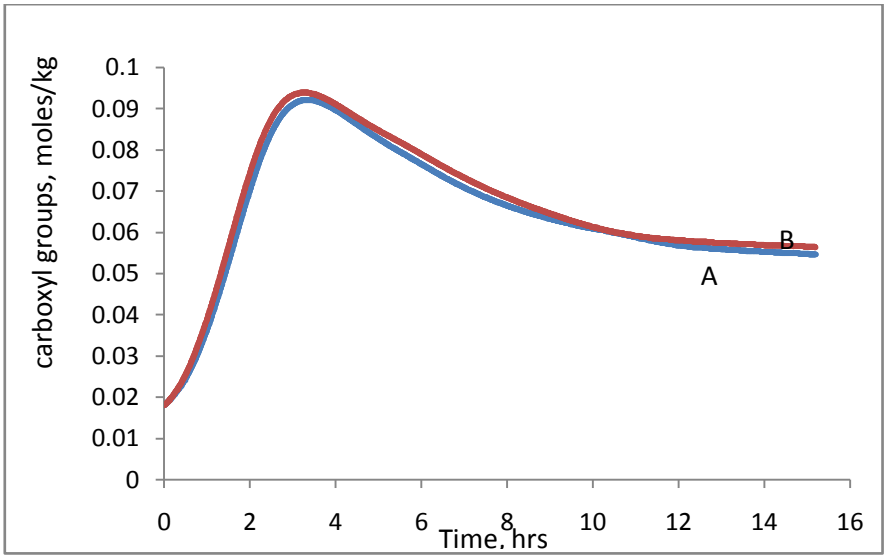

Figure 6: Predicted Carboxyl end Groups Comparison for Case 3: (A) Old Model and (B) Present Model

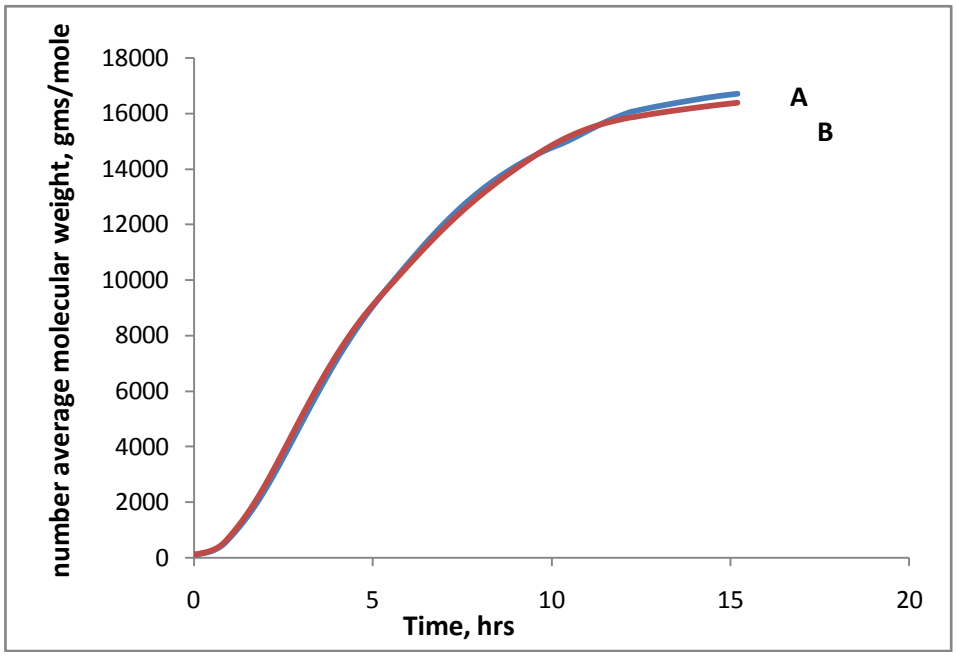

Figure 7: Predicted M_n Values Comparison for Case 3: (A) Old Model (B) Present Model

c) Comparison of predicted polymer properties with the experimental results.

The conversion of caprolactam plotted versus polymerization time (Figure 4) revealed increased faster conversion in the first 3-8 hours and attained equilibrium thereafter. The rates of the conversion in the present model are slower than in the previous model because of the slightly controlled vaporization of water in the top zone of the reactor. The present model determined a monomer (m) concentration of approximately 8.2 % when polymerization was completed. The result has been compared with the experimental extractables concentration of 9.66% in Table 3. The difference is about 14%. For the other two data sets also similar results were obtained. The estimation was not so good because the experimental extractables contained around 15-20 wt% of cyclic and linear oligomers along with the remaining monomer (m).

d) Similar results were obtained in the earlier model[4] as well.

This is because both the models are not capable of calculating the concentrations of higher oligomers and hence a better comparison could not be made. Figures 5-7 depict the comparison between the predicted values for [NH_2] end groups, [COOH] end

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groups and number average molecular weight for old model[24] and present model. The comparison has also been presented in Table 3. In the present model, the end group concentrations increase in the middle zone and in the bottom zone of the reactor better than the old model because of more water retained due to the controlled vaporization by the induced velocity.However in the bottom zone M_n values decrease in the present model because of the increased quantity of water due to the controlled vaporization in the top and the middle zones. This happens because of the assumed non plug velocity profile where water moves down the reactor at a faster rate than when there is flat velocity profile for the flow of the reactants. The error percentages reduced considerably for the carboxylic end groups and the M_n values. The predicted values for the present model incorporating the non-linear time dependent effect for the various species namely, caprolactam, polymer, water and acetic acid gives the better comparison for carboxylic end groups and M_n values with the experimental values. The errors in amino end groups were also improved considerably in some cases. The improved results are due to adjustment of concentrations of various species induced due to non-flat velocity profile, which controls the reaction rates of the polymerization process in the top zone and in the middle zone thereby maintaining the required quantity of water concentration for better results. This helps to control the end polymer properties and the M_n value of the end polymer.

e) Validation of the present model in predicting the effects of pressure and temperature down the VK tube reactor

In Figure 8, the influence of head pressure,that is the pressure caused by the water seal at the top of the reactor can also be observed to affect the M_n value of polymer. For instance, when the water seal length is increased from 0.1 - 5m, rates of reactions improve significantly because of the retention of huge quantity of water inside the reactor. However M_n decreases by about 10.7 % (Figure 8) because of the higher quantity of water at equilibrium. Similar results were obtained in the old model[24]. As discussed in the previous section, down pressure in the reactor was observed to be a controlling parameter. This is observed from Figures 9-12 as the discrepancies between the experimental values and the predicted model values were significant. Therefore, the reaction rates and the end product values at the bottom of the reactor can be controlled using the pressure in the reactor.

f) Similar performance was obtained using the earlier model[24] as well

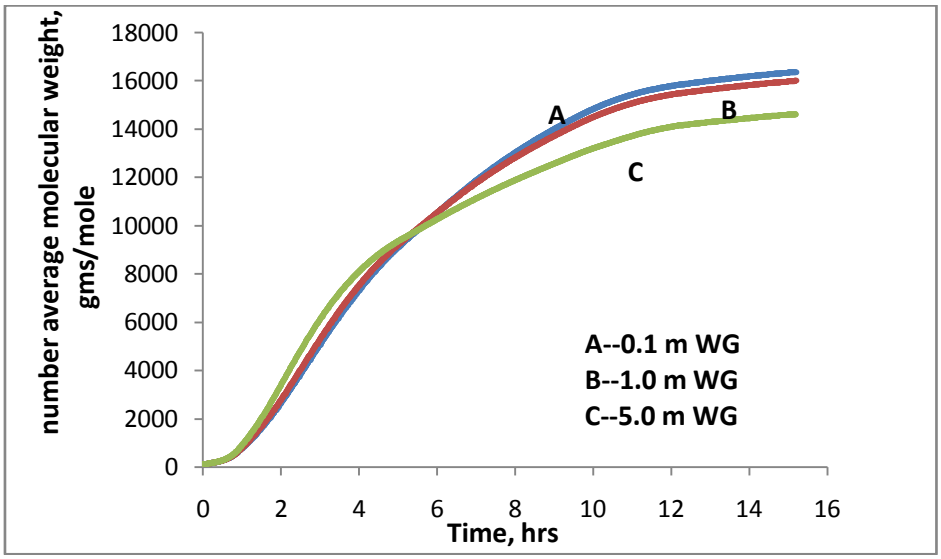

Figure 8: Influence of Water Seal Length on M_n for Data 3

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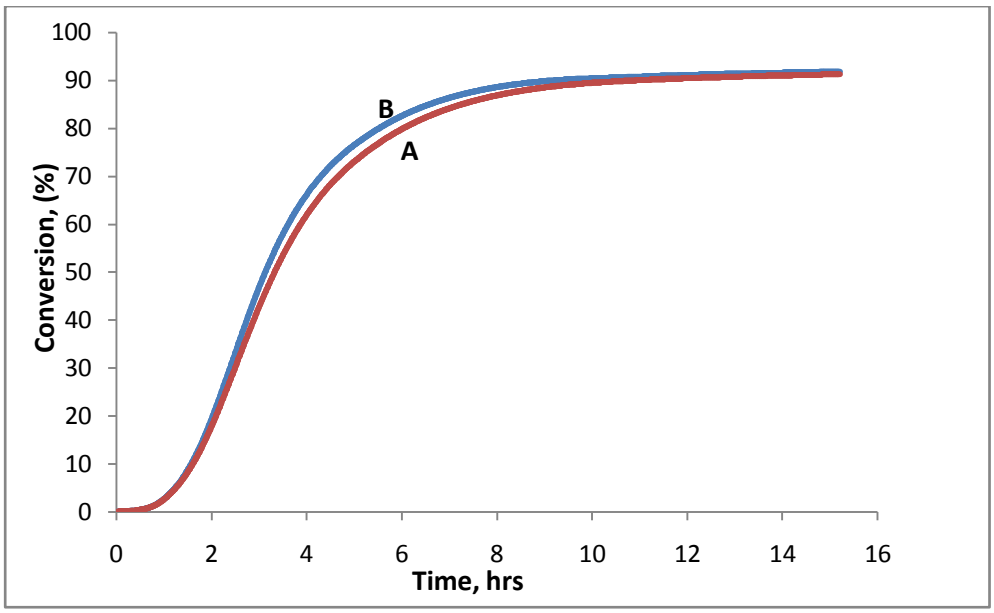

Figure 9: Predicted Conversions Comparison for Data 3 With the Present Model: (A) With Hydrostatic Pressure Variation in the Vk Tube and (B) At Normal at mospheric Pressure

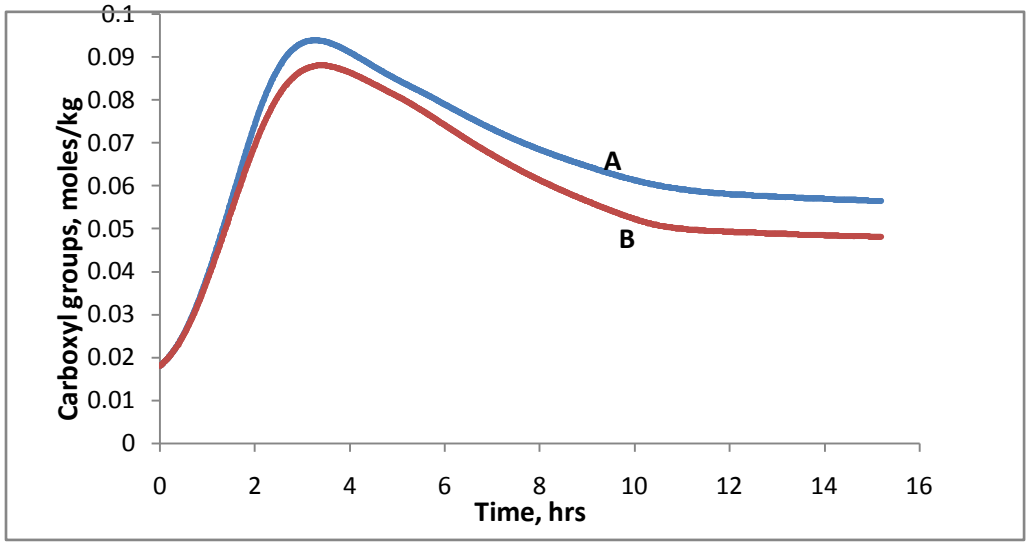

Figure 10: Predicted [Cooh] Concentrations Comparison for Data 3 Using the Present Model: (A) with Hydrostatic Pressure Variation in the Vk Tube and (B) At Normal At mospheric Pressure

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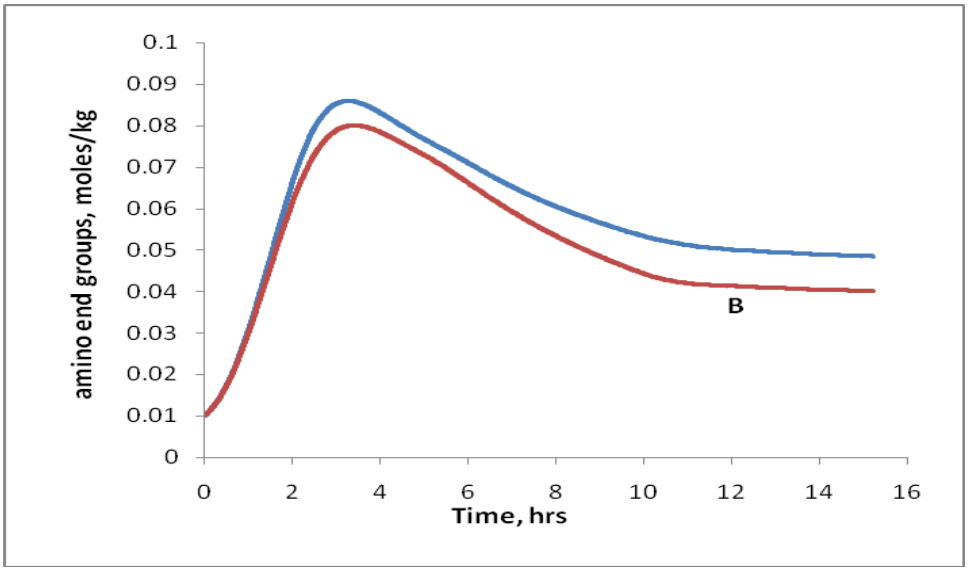

Figure 11: Predicted [Nh_2] Concentrations Comparison for Data 3 Using the Present Model: (A) with Hydrostatic Pressure Variation in the Vk Tube and (B) At Normal Atmospheric Pressure

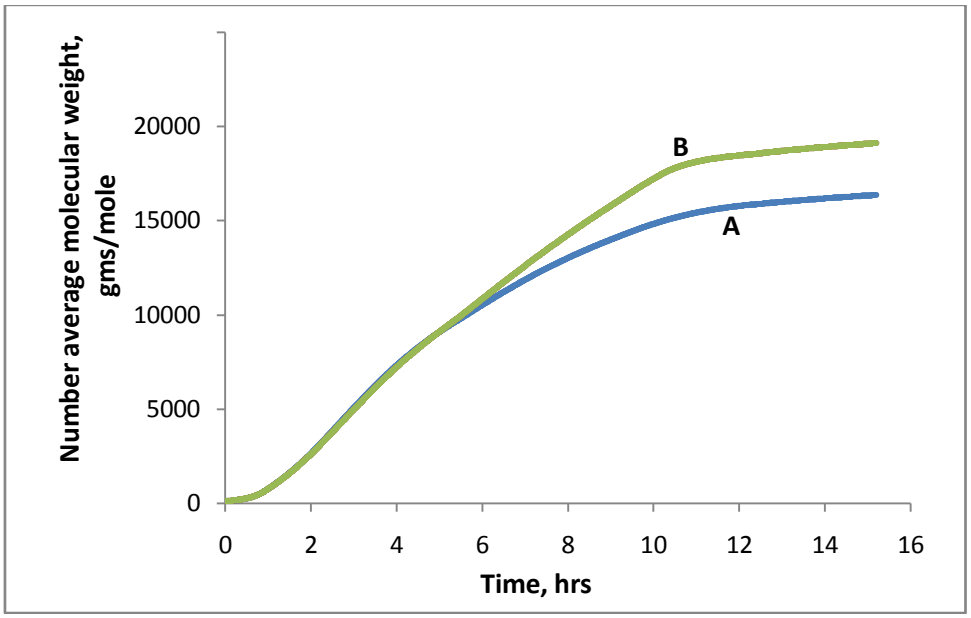

Figure 12: predicted m_n values comparison for data 3 using the present model: (a) with hydrostatic pressure variation in the vk tube and (b) at normal atmospheric pressure

VK tube reactor's performance can be optimized by another important parameter, the polymer melt temperature profile down the reactor. To get the proper initiation of the reactions water should be retained at the beginning by slowly increasing the temperature to the highest temperature point. Thereafter, water should be allowed to evaporate to the required quantity at the maximum temperature and then reduced to the expected equilibrium value. The properties of the polymer at the end of the reaction are determined by the water content at the highest temperature point. If the highest temperature point is increased there will be a decrease in [W] in the non-vaporizing zone. This will increase the average molecular weight as shown in Figure 13. Therefore, the temperature at the maximum temperature position (T_h) affects the final polymer properties. When the maximum temperature (T_h) has been changed nominally by a few degrees (10K), M_n changes by about 21.6%. Similar behaviour was observed in the previous model[24].

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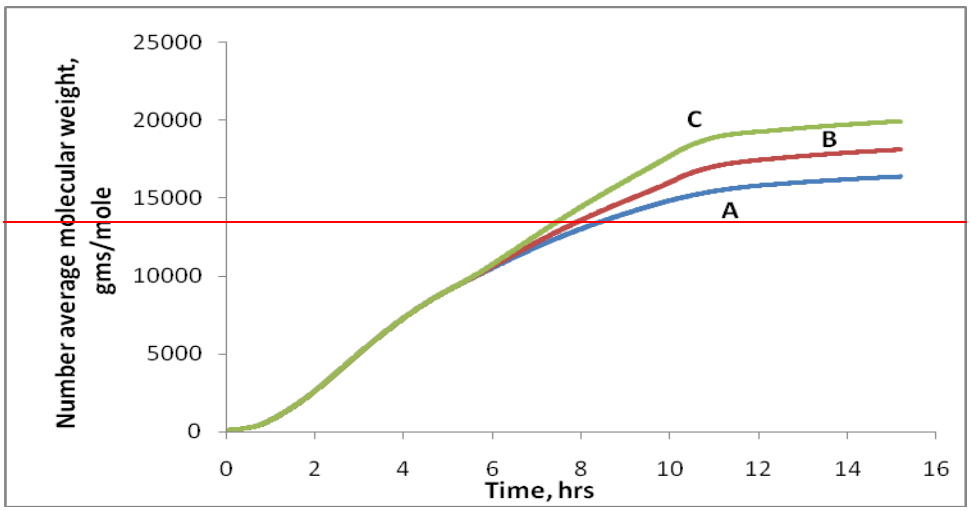

Figure 13: Highest Temperature (T_h) Influence on M_n For Data 3: A-548 K, B-558 K, C-568 K

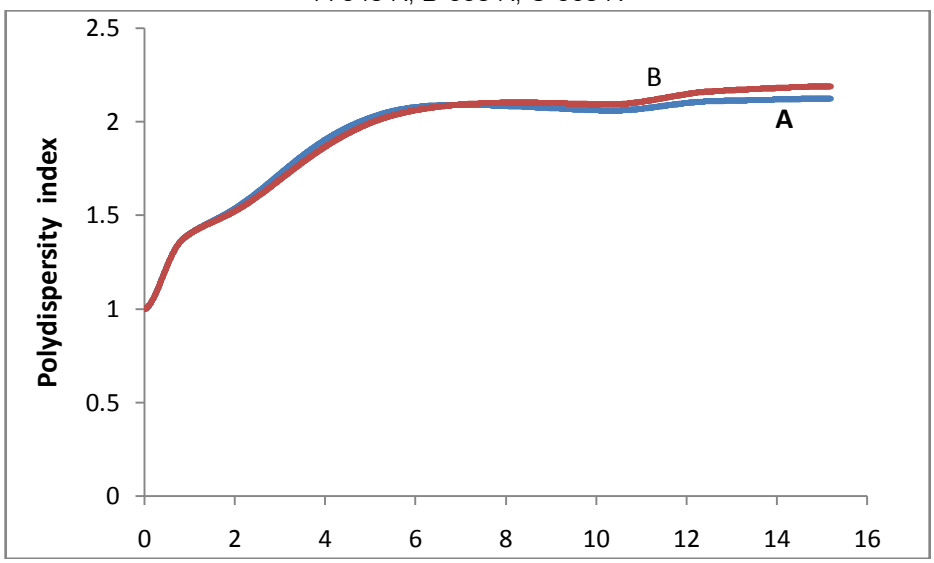

Figure 14: Predicted Polydispersity Index Values Comparison For Data 3: (A) With The Influence Of Pressure Variation In The Vk Tube And (B) At Normal Atmospheric Pressure

Table 5: Listed Polydispersity Index Values With Respect To Polymerization Time For Data 3

Time(H)	M_w/M_n
0.0	1.0003
1.0	1.4014
2.0	1.5364
3.0	1.7220
4.0	1.9035
5.0	2.0215
6.0	2.0782
7.0	2.0907
8.0	2.0851
9.0	2.0735
10.0	2.0615
11.0	2.0696
12.0	2.1002
13.0	2.1130
14.0	2.1192
15.0	2.1232

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The predicted net reaction values and the equilibrium values of the three major reactions have been depicted in Figures 15 and 16. The pattern and the performance are similar to those of earlier model [24]

- Hence it can be concluded that the present non-linear explicit time dependent simulation model is useful in estimating the nylon-6 end group results in a VK tube reactor accurately, in improving the system operation and provides insights for the improvement of such reactor designs.

V. Conclusions

Following conclusions could be drawn from the present work:

- The Nylon-6 polymerization was simulated in an industrial VK tube reactor using a modified non-linear model incorporating a time dependent modification function, T.
- Non-linear time dependent decay functions were introduced in mass balance equations for calculating the concentrations of various species at any position in the reactor to account for the change in concentration of the species due to non-flat velocity profile. This reduces the errors compared to models that use a strict plug flow model for a VK Tube. Since the internal design of the VK Tube is not ideally suited to achieve a flat velocity profile, the incorporated functions tries to accommodate small differences from the ideal condition of plug flow.
- A modified empirical VLE relation was used in the vaporizing zone to predict the water profile inside the reactor incorporating the non-linear time dependent functions as mentioned above.
- A lowest water content (LWC) point was noted, which defined the end of the vaporizing zone, due to the changing temperature and pressure down the axis of the reactor. The location and $[H_2O]$ at the LWC point were observed to be very important in determining the end product results.
- The non-flat velocity profiles of the various reactants in the VK tube reactor controlled the reaction rates, controlled the vaporization of water to the required Quantity in the vaporizing zone and in the non-vaporizing zone that favoured simulation of polymer properties with exceptional accuracy.
- The calculated values of M_n for data 3 by the present model evaluates the industrial data with an error of 0.03, as compared to the previous model with an error of 1.9%.
- Amino end group concentrations were predicted by the present model for data 3 with an error of 0.8% as against the prediction error of 2.7% in the earlier model.
- Carboxyl end groups predicted by the present model for data 3 match with the industrial data with an error of 4% over the error of 7.2% in the previous model.
- The present model was found to be in conformity with the experimental values, superior over the earlier model[24], where the reactants were assumed to flow in a perfect flat velocity profile.

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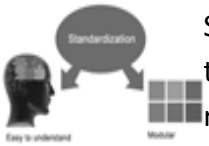

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AUXILIARY MEMBERSHIPS

Institutional Fellow of Open Association of Research Society (USA)-OARS (USA)

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The "FARSC" is a dignified title which is accorded to a person's name viz. Dr. John E. Hall, Ph.D., FARSC or William Walldroff, M.S., FARSC.

The IFOARS institution is entitled to form a Board comprised of one Chairperson and three to five board members preferably from different streams. The Board will be recognized as "Institutional Board of Open Association of Research Society"-(IBOARS).

The Institute will be entitled to following benefits:

The IBOARS can initially review research papers of their institute and recommend them to publish with respective journal of Global Journals. It can also review the papers of other institutions after obtaining our consent. The second review will be done by peer reviewer of Global Journals Incorporation (USA) The Board is at liberty to appoint a peer reviewer with the approval of chairperson after consulting us.

The author fees of such paper may be waived off up to 40%.

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The board members can also join us as Individual Fellow with 40% discount on total fees applicable to Individual Fellow. They will be entitled to avail all the benefits as declared. Please visit Individual Fellow-sub menu of GlobalJournals.org to have more relevant details.

We shall provide you intimation regarding launching of e-version of journal of your stream time to time. This may be utilized in your library for the enrichment of knowledge of your students as well as it can also be helpful for the concerned faculty members.

After nomination of your institution as "Institutional Fellow" and constantly functioning successfully for one year, we can consider giving recognition to your institute to function as Regional/Zonal office on our behalf.
The board can also take up the additional allied activities for betterment after our consultation.

The following entitlements are applicable to individual Fellows:

Open Association of Research Society, U.S.A (OARS) By-laws states that an individual Fellow may use the designations as applicable, or the corresponding initials. The Credentials of individual Fellow and Associate designations signify that the individual has gained knowledge of the fundamental concepts. One is magnanimous and proficient in an expertise course covering the professional code of conduct, and follows recognized standards of practice.

Open Association of Research Society (US)/ Global Journals Incorporation (USA), as described in Corporate Statements, are educational, research publishing and professional membership organizations. Achieving our individual Fellow or Associate status is based mainly on meeting stated educational research requirements.

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- The professional accredited with Fellow honor, is entitled to various benefits viz. name, fame, honor, regular flow of income, secured bright future, social status etc.

- In addition to above, if one is single author, then entitled to 40% discount on publishing research paper and can get 10%discount if one is co-author or main author among group of authors.
- The Fellow can organize symposium/seminar/conference on behalf of Global Journals Incorporation (USA) and he/she can also attend the same organized by other institutes on behalf of Global Journals.
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- • This individual has learned the basic methods of applying those concepts and techniques to common challenging situations. This individual has further demonstrated an in–depth understanding of the application of suitable techniques to a particular area of research practice.

Note :

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- In future, if the board feels the necessity to change any board member, the same can be done with the consent of the chairperson along with anyone board member without our approval.
- In case, the chairperson needs to be replaced then consent of 2/3rd board members are required and they are also required to jointly pass the resolution copy of which should be sent to us. In such case, it will be compulsory to obtain our approval before replacement.
- In case of "Difference of Opinion [if any]" among the Board members, our decision will be final and binding to everyone.

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Unless specified in the notification, the Editorial Board's decision on publication of the paper is final and cannot be appealed before making the major change in the manuscript.

Acknowledgments

Contributors to the research other than authors credited should be mentioned in Acknowledgments. The source of funding for the research can be included. Suppliers of resources may be mentioned along with their addresses.

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The following is the official style and template developed for publication of a research paper. Authors are not required to follow this style during the submission of the paper. It is just for reference purposes.

Manuscript Style Instruction (Optional)

- Microsoft Word Document Setting Instructions.
- Font type of all text should be Swis721 Lt BT.
- Page size: 8.27" x 11'", left margin: 0.65, right margin: 0.65, bottom margin: 0.75.
- Paper title should be in one column of font size 24.
- Author name in font size of 11 in one column.
- Abstract: font size 9 with the word "Abstract" in bold italics.
- Main text: font size 10 with two justified columns.
- Two columns with equal column width of 3.38 and spacing of 0.2.
- First character must be three lines drop-capped.
- The paragraph before spacing of 1 pt and after of 0 pt.
- Line spacing of 1 pt.
- Large images must be in one column.
- The names of first main headings (Heading 1) must be in Roman font, capital letters, and font size of 10.
- The names of second main headings (Heading 2) must not include numbers and must be in italics with a font size of 10.

Structure and Format of Manuscript

The recommended size of an original research paper is under 15,000 words and review papers under 7,000 words. Research articles should be less than 10,000 words. Research papers are usually longer than review papers. Review papers are reports of significant research (typically less than 7,000 words, including tables, figures, and references)

A research paper must include:

a) A title which should be relevant to the theme of the paper.
b) A summary, known as an abstract (less than 150 words), containing the major results and conclusions.
c) Up to 10 keywords that precisely identify the paper's subject, purpose, and focus.
d) An introduction, giving fundamental background objectives.
e) Resources and techniques with sufficient complete experimental details (wherever possible by reference) to permit repetition, sources of information must be given, and numerical methods must be specified by reference.
f) Results which should be presented concisely by well-designed tables and figures.
g) Suitable statistical data should also be given.
h) All data must have been gathered with attention to numerical detail in the planning stage.

Design has been recognized to be essential to experiments for a considerable time, and the editor has decided that any paper that appears not to have adequate numerical treatments of the data will be returned unrefereed.

i) Discussion should cover implications and consequences and not just recapitulate the results; conclusions should also be summarized.
j) There should be brief acknowledgments.
k) There ought to be references in the conventional format. Global Journals recommends APA format.

Authors should carefully consider the preparation of papers to ensure that they communicate effectively. Papers are much more likely to be accepted if they are carefully designed and laid out, contain few or no errors, are summarizing, and follow instructions. They will also be published with much fewer delays than those that require much technical and editorial correction.

The Editorial Board reserves the right to make literary corrections and suggestions to improve brevity.

Format Structure

It is necessary that authors take care in submitting a manuscript that is written in simple language and adheres to published guidelines.

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The title page must carry an informative title that reflects the content, a running title (less than 45 characters together with spaces), names of the authors and co-authors, and the place(s) where the work was carried out.

Author details

The full postal address of any related author(s) must be specified.

Abstract

The abstract is the foundation of the research paper. It should be clear and concise and must contain the objective of the paper and inferences drawn. It is advised to not include big mathematical equations or complicated jargon.

Many researchers searching for information online will use search engines such as Google, Yahoo or others. By optimizing your paper for search engines, you will amplify the chance of someone finding it. In turn, this will make it more likely to be viewed and cited in further works. Global Journals has compiled these guidelines to facilitate you to maximize the web-friendliness of the most public part of your paper.

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A major lynchpin of research work for the writing of research papers is the keyword search, which one will employ to find both library and internet resources. Up to eleven keywords or very brief phrases have to be given to help data retrieval, mining, and indexing.

One must be persistent and creative in using keywords. An effective keyword search requires a strategy: planning of a list of possible keywords and phrases to try.

Choice of the main keywords is the first tool of writing a research paper. Research paper writing is an art. Keyword search should be as strategic as possible.

One should start brainstorming lists of potential keywords before even beginning searching. Think about the most important concepts related to research work. Ask, “What words would a source have to include to be truly valuable in a research paper?” Then consider synonyms for the important words.

It may take the discovery of only one important paper to steer in the right keyword direction because, in most databases, the keywords under which a research paper is abstracted are listed with the paper.

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Numerical methods used should be transparent and, where appropriate, supported by references.

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Authors must list all the abbreviations used in the paper at the end of the paper or in a separate table before using them.

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Authors are advised to submit any mathematical equation using either MathJax, KaTeX, or LaTeX, or in a very high-quality image.

Tables, Figures, and Figure Legends

Tables: Tables should be cautiously designed, uncrowned, and include only essential data. Each must have an Arabic number, e.g., Table 4, a self-explanatory caption, and be on a separate sheet. Authors must submit tables in an editable format and not as images. References to these tables (if any) must be mentioned accurately.

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Figures are supposed to be submitted as separate files. Always include a citation in the text for each figure using Arabic numbers, e.g., Fig. 4. Artwork must be submitted online in vector electronic form or by emailing it.

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Although low-quality images are sufficient for review purposes, print publication requires high-quality images to prevent the final product being blurred or fuzzy. Submit (possibly by e-mail) EPS (line art) or TIFF (halftone/ photographs) files only. MS PowerPoint and Word Graphics are unsuitable for printed pictures. Avoid using pixel-oriented software. Scans (TIFF only) should have a resolution of at least 350 dpi (halftone) or 700 to 1100 dpi (line drawings). Please give the data for figures in black and white or submit a Color Work Agreement form. EPS files must be saved with fonts embedded (and with a TIFF preview, if possible).

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1. Choosing the topic: In most cases, the topic is selected by the interests of the author, but it can also be suggested by the guides. You can have several topics, and then judge which you are most comfortable with. This may be done by asking several questions of yourself, like "Will I be able to carry out a search in this area? Will I find all necessary resources to accomplish the search? Will I be able to find all information in this field area?" If the answer to this type of question is "yes," then you ought to choose that topic. In most cases, you may have to conduct surveys and visit several places. Also, you might have to do a lot of work to find all the rises and falls of the various data on that subject. Sometimes, detailed information plays a vital role, instead of short information. Evaluators are human: The first thing to remember is that evaluators are also human beings. They are not only meant for rejecting a paper. They are here to evaluate your paper. So present your best aspect.

2. Think like evaluators: If you are in confusion or getting demotivated because your paper may not be accepted by the evaluators, then think, and try to evaluate your paper like an evaluator. Try to understand what an evaluator wants in your research paper, and you will automatically have your answer. Make blueprints of paper: The outline is the plan or framework that will help you to arrange your thoughts. It will make your paper logical. But remember that all points of your outline must be related to the topic you have chosen.

3. Ask your guides: If you are having any difficulty with your research, then do not hesitate to share your difficulty with your guide (if you have one). They will surely help you out and resolve your doubts. If you can't clarify what exactly you require for your work, then ask your supervisor to help you with an alternative. He or she might also provide you with a list of essential readings.

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10. Use proper verb tense: Use proper verb tenses in your paper. Use past tense to present those events that have happened. Use present tense to indicate events that are going on. Use future tense to indicate events that will happen in the future. Use of wrong tenses will confuse the evaluator. Avoid sentences that are incomplete.

11. Pick a good study spot: Always try to pick a spot for your research which is quiet. Not every spot is good for studying.

12. Know what you know: Always try to know what you know by making objectives, otherwise you will be confused and unable to achieve your target.

13. Use good grammar: Always use good grammar and words that will have a positive impact on the evaluator; use of good vocabulary does not mean using tough words which the evaluator has to find in a dictionary. Do not fragment sentences. Eliminate one-word sentences. Do not ever use a big word when a smaller one would suffice.

Verbs have to be in agreement with their subjects. In a research paper, do not start sentences with conjunctions or finish them with prepositions. When writing formally, it is advisable to never split an infinitive because someone will (wrongly) complain. Avoid clichés like a disease. Always shun irritating alliteration. Use language which is simple and straightforward. Put together a neat summary.

14. Arrangement of information: Each section of the main body should start with an opening sentence, and there should be a changeover at the end of the section. Give only valid and powerful arguments for your topic. You may also maintain your arguments with records.

15. Never start at the last minute: Always allow enough time for research work. Leaving everything to the last minute will degrade your paper and spoil your work.

16. Multitasking in research is not good: Doing several things at the same time is a bad habit in the case of research activity. Research is an area where everything has a particular time slot. Divide your research work into parts, and do a particular part in a particular time slot.

17. Never copy others' work: Never copy others' work and give it your name because if the evaluator has seen it anywhere, you will be in trouble. Take proper rest and food: No matter how many hours you spend on your research activity, if you are not taking care of your health, then all your efforts will have been in vain. For quality research, take proper rest and food.

18. Go to seminars: Attend seminars if the topic is relevant to your research area. Utilize all your resources.

19. Refresh your mind after intervals: Try to give your mind a rest by listening to soft music or sleeping in intervals. This will also improve your memory. Acquire colleagues: Always try to acquire colleagues. No matter how sharp you are, if you acquire colleagues, they can give you ideas which will be helpful to your research.

20. Think technically: Always think technically. If anything happens, search for its reasons, benefits, and demerits. Think and then print: When you go to print your paper, check that tables are not split, headings are not detached from their descriptions, and page sequence is maintained.

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22. Report concluded results: Use concluded results. From raw data, filter the results, and then conclude your studies based on measurements and observations taken. An appropriate number of decimal places should be used. Parenthetical remarks are prohibited here. Proofread carefully at the final stage. At the end, give an outline to your arguments. Spot perspectives of further study of the subject. Justify your conclusion at the bottom sufficiently, which will probably include examples.

23. Upon conclusion: Once you have concluded your research, the next most important step is to present your findings. Presentation is extremely important as it is the definite medium though which your research is going to be in print for the rest of the crowd. Care should be taken to categorize your thoughts well and present them in a logical and neat manner. A good quality research paper format is essential because it serves to highlight your research paper and bring to light all necessary aspects of your research.

Informal Guidelines of Research Paper Writing

Key points to remember:

- Submit all work in its final form.
- Write your paper in the form which is presented in the guidelines using the template.
- Please note the criteria peer reviewers will use for grading the final paper.

Final points:

One purpose of organizing a research paper is to let people interpret your efforts selectively. The journal requires the following sections, submitted in the order listed, with each section starting on a new page:

The introduction: This will be compiled from reference matter and reflect the design processes or outline of basis that directed you to make a study. As you carry out the process of study, the method and process section will be constructed like that. The results segment will show related statistics in nearly sequential order and direct reviewers to similar intellectual paths throughout the data that you gathered to carry out your study.

The discussion section:

This will provide understanding of the data and projections as to the implications of the results. The use of good quality references throughout the paper will give the effort trustworthiness by representing an alertness to prior workings.

Writing a research paper is not an easy job, no matter how trouble-free the actual research or concept. Practice, excellent preparation, and controlled record-keeping are the only means to make straightforward progression.

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Specific editorial column necessities for compliance of a manuscript will always take over from directions in these general guidelines.

To make a paper clear: Adhere to recommended page limits.

Mistakes to avoid:

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- Separating a table, chart, or figure—confine each to a single page.
- Submitting a manuscript with pages out of sequence.
- In every section of your document, use standard writing style, including articles ("a" and "the").
- Keep paying attention to the topic of the paper.

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- Use paragraphs to split each significant point (excluding the abstract).
- Align the primary line of each section.
- Present your points in sound order.
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- Use past tense to describe specific results.
- Do not use familiar wording; don't address the reviewer directly. Don't use slang or superlatives.
- Avoid use of extra pictures—include only those figures essential to presenting results.

Title page:

Choose a revealing title. It should be short and include the name(s) and address(es) of all authors. It should not have acronyms or abbreviations or exceed two printed lines.

Abstract: This summary should be two hundred words or less. It should clearly and briefly explain the key findings reported in the manuscript and must have precise statistics. It should not have acronyms or abbreviations. It should be logical in itself. Do not cite references at this point.

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Reason for writing the article—theory, overall issue, purpose.

- Fundamental goal.
- To-the-point depiction of the research.
- Consequences, including definite statistics—if the consequences are quantitative in nature, account for this; results of any numerical analysis should be reported. Significant conclusions or questions that emerge from the research.

Approach:

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- An outline of the job done is always written in past tense.
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- Present a justification. State your particular theory(-ies) or aim(s), and describe the logic that led you to choose them.
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Approach:

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Approach:

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The page length of this segment is set by the sum and types of data to be reported. Use statistics and tables, if suitable, to present consequences most efficiently.

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Content:

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Discussion	Well organized, meaningful specification, sound conclusion, logical and concise explanation, highly structured paragraph reference cited	Wordy, unclear conclusion, spurious	Conclusion is not cited, unorganized, difficult to comprehend
References	Complete and correct format, well organized	Beside the point, Incomplete	Wrong format and structuring

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