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APPLICATION OF PROCESS INTENSIFICATION METHODOLOGY TO PROPIONIC ACID RECOVERY

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ABSTRACT

Increasing competition among the different industries made chemical industry to look for alternative processes or techniques which could provide a low cost and environmentally friendly production which have had not been provided by the existing setups. This could be the only alternative to survive the competition of other industries like software etc. With this view, fermentation and recovery of propionic acid was taken for discussion. Process intensification methodology was applied to the existing process. The shortcomings in the existing setup were removed by introduction of PI technology (reactive extraction). The high productivity, improved propionate yield, highly concentrated and purified product and stable and consistent performance of the reactive extraction process, proposed it to as a suitable process for recovery of propionic acid.

KEYWORDS:

Process intensification, Methodology, Reactive extraction, Propionic acid.

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1. INTRODUCTION

Process intensification is a key strategy that the chemical industry is adopting to increase energy efficiency and profitability. It is a highly innovative concept in the design of chemical process plants. It opens the prospects of smaller, safer, cheaper, environment friendly operation in comparison to existing one. In other words process intensification consists of the development of novel equipments and techniques, as compared to the present state-of-art, to bring dramatic improvements in manufacturing and processing, substantially decrease in equipment size/production-capacity ratio, energy consumption, or waste production.

Process intensification is a revolutionary approach to process and plant design, development and implementation. Process intensification aims to drastic improvement of performance of a process, by rethinking the process as a whole. Alternative routes may be thinked off, which till now have not been employed because of safety and control reasons. Process intensification has came out of the laboratory and is making an impact on design philosophy of process plant for more efficient and cleaner production. Process intensification is simply equivalent to process improvement and is defined by Ramshaw [1] as devising an exceedingly compact plant which reduces both the main plant items and the installation cost. According to Heggs [2], PI is concerned with order of magnitude reduction in both the process plant and equipment. Douglas [3], interpreted Process intensification as the novel equipment, processing techniques and process development methods that compared to the conventional ones, offers a substantial improvements in chemical manufacturing and processing. Process intensification is an interdisciplinary field of research that needs an integrated approach. In growing number of areas, the limitations of traditional batch processing are being overcome by moving to continuous process through the application of intensification techniques. To sum-up, process intensification is a rapidly developing field inspiring ideas of modeling and new equipment designing and operating modes, which's potential are still to be explored.

There are two ways by which process intensification can bring a drastic improvement in the existing chemical plant/process: Employing PI equipments (micro reactors, SDR, micro channel heat exchanger etc) or process intensifying methods (reactive separations, hybrid separations and alternative form and sources of energy) (**Figure 1 and 2**). Combination of multiple tasks such as reaction and separation into a single unit is an important PI method (**Figure 2a**). The basic philosophy is to choose the task in a manner such that their combination leads to better overall performance. Since any chemical process involves unit operations for reaction and separation, most of such task combinations fall under the umbrella of reactive separation processes. The combination of reaction and separation is effective when either the reaction substantially improves separation through enhanced mass transfer rates or the separation drives the reaction to higher conversions or both. The fusion of reaction and separation as one combined operation is also prized for its simplicity and novelty the approach brings to the process flow sheet. These operations are also coveted for the investment and operating cast savings garnered on successful scale up to commercial operations.

In recent years, reactive extraction processes are gaining lot of importance in response of extreme economic pressure posed by industries as the result of emergence of new industries and decline of existing industries, demand of high purity products with low cost and environmentally safe. However commercialization of reactive separation processes is desired, which can be achieved by the mutual working of chemists and engineers. Reactive extraction links chemical sources and sinks to enhance reaction rates, conversions and selectivies. Since most of chemical processes are equilibrium driven, removal of product as soon as it is produced would lead to enhanced reaction rates and increased feed conversions reduce reaction severity and provide operation under milder conditions. Mass transfer and reaction coupling improves catalyst life since high mass transfer forces leads to better catalyst irrigation and surface renewals with transport of catalyst inhibitors away from catalyst surfaces. Further in reaction and separation operations, the duo would lead to high local driving forces for separation leading to reduction in equipment size, elimination of recyclable streams and reductions in utility costs. Reactive separators also lead to safer equipments since it reduces the working inventory of reactive chemicals in the equipment. Lower the hazardous chemical lower will be the chance of its leakage, spills and environmental release. Coupling of reaction and separation also leads to suppression of byproduct reactions which are likely to exhibit runaway behavior; the reactive separator design will increase the inherent safety in the unit against severe process upsets. The combination also provides low cost equipment through the consolidation of multiple pieces of process equipment into single piece and/or through the elimination of process recycles streams.

In view of the numerous advantages of reactive separation methods, it has been decided to apply the PI methodology to the recovery of propionic acid produced by fermentation process. Results show that process intensification is a vital tool to realize an improved process.

2. METHODOLOGY

The step by step implication of process intensification is called as methodology and constitutes a number of steps (**Figure.3**):

In first step the whole process including its chemistry and unit operations and appreciating how each aspect affects the other was studied. The chemistry includes explanation of the synthesis route and catalyst/solvent choice and the potential of alternative solvents/catalysts are also looked. Lab scale experiments are conducted to get the information about chemistry and kinetics. Process performance in measure of yield, selectivity or other measurable factors is related to product quality. In unit operations, the existing plant is examined to determine the operating capabilities of each unit. Mass and heat transfer capabilities and the reason of the choice of particular equipment are discussed.

In second step the drivers: business drivers, which are economic and social considerations relating to profitability; and process drivers, which involves optimizing factors such as heat transfer and mass transfer within the system are identified. The proper driver's selections would improve plant performance and reduce costs. This

will make the process more efficient and possibly reduce downstream costs eg. problems like poor conversion and safety problems from byproducts [4]. The drivers will show where attention has to be focused in the plant.

In third stage, from the analysis of equipment and chemistry, the rate limiting step is identified. The kinetics of synthesis and the capabilities of plant are compared and the plot of working condition in the process performance and mixing effectiveness is made to generate conditions for improved plant.

In the next stage, ideas are collected to intensify the process within the boundaries of goal of the study. Well balanced team of engineers, R&D, process technologist and chemical experts undergo a brain storming session to suggest an optimal operating condition. The database of various process intensification equipments is made and a design of a draft of new process alternatives is made by drawing a flow sheet. The idea behind the choice of database is to fit the requirement of process and drivers. There are certain keywords on which the session is based upon. (**Table.1**)

In stage five, based on the results of analysis, most suitable equipment for the task is selected. If a particular approach cannot be decide upon, options were made. The choices available are compared in detailed construction and costing.

In stage six, to justify the choice, the selected equipment/s is/are compared with the conventional and concern is mainly made of performance and economics. This also includes safety and environmental factors. Finally with open mind process intensification is introduced in the plant.

3. PROPIONIC ACID RECOVERY

Propionic acid is one of the important carboxylic acid used in the food industries, pharmaceuticals and chemical industries. Propionic acid and its salts are used in numerous processes such as in the production of cellulose plastics (used in textiles, filters, reverse osmosis membranes, lacquer formulations and molding plastics), herbicides, in the manufacture of ester solvents, fruit flavors, perfumes bases and butyl rubber to improve processability and scorching resistance. Industrially, propionic acid is produced by petrochemical route [5]. With the rising cost of the petrochemical products, research is now focused on the production through the fermentation technology. Production of propionic acid by fermentation is gaining importance. The propionic acid produced need to be recovered from the fermentation broth. Energy budget studies and economic analysis have indicated that product separation is the most energy-intensive and expensive stage in fermentation processes for manufacture of bulk chemicals and liquid fuels. Since the fermentation occurs at a about neutral pH while the recovery occur at a low pH, reduction in pH at around pK_a values of acids is necessary before sufficient concentrations of free unionized acids are generated. The conventional method of propionic acid recovery is by precipitation of calcium carboxylate with calcium hydroxide. In this recovery scheme, calcium carboxylate is precipitated, recovered by filtration, and converted to propionic acid by the addition of sulfuric acid. The dilute propionic acid product is then sequentially purified using activated carbon, evaporation, and crystallization.

These separation and final purification stages account for up to 50% of the production costs. Thus, this method of recovery is expensive and unfriendly to the environment because it consumes lime and sulfuric acid and also produces a large quantity of calcium sulfate sludge as solid waste. Because of the detrimental effect of low pH, reactor productivities are low and the products are obtained in a dilute form. The effects of end-product inhibition can be reduced by in situ removal of propionic acid from fermentation broth by several methods. It is, therefore, reasonable to look for other methods of recovery for propionic acid.

4. IMPLEMENTATION OF PI METHODOLOGY

4.1 Overview whole process: *Chemistry and equipment*

The reaction in the fermentation broth for propionic acid production is represented as:

$$\text{Glucose source} \longrightarrow \text{Propionic acid} + CO_2 + H_20$$

The reaction has theoretical maximum yield of 54.8 % w/w propionic acid. Bacteria used for the reaction is *propionibacterium* species. The conventional fermentation suffers from disadvantages of low reactor production, low product yield (<50 % w/w) and low product concentration (< 40 g/l) [6]. The main reason of this being the accumulation of acid, which destroys bacteria responsible for growth, and hence lower the production rate.

Conventionally separation is carried out by calcium hydroxide precipitation method. This involves the addition of calcium hydroxide to the fermentation mass, producing calcium propionate. Upon that sulphuric acid is added to product propionic acid and calcium sulphate. In the next step the acid is esterified to produce methyl propionate. On hydrolysis of methyl propionate, purified propionic acid was produced. To make higher grades of product the liquor was cooled, crystallized, and washed. The mother liquor and wash water were also cooled, crystallized, and washed. The crystals were redissolved and similarly recycled as in earlier steps to create pure grades. Acids of different purity were made from the different grades of crystals by dissolution in water, acidification, evaporation, carbon treatment, and heavy metals precipitation.

4.2. Drivers:

In second step the drivers are defined. The drivers' shows where attention has to be focused in the plant. There are two types of drivers: business drivers and process drivers. Business drivers for the propionic acid fermentation involves: desire to increase reactor productivity and production rate, lower energy consumption, and reduce expenses in purification and separation of product acid. On the other hand the process drivers includes: low product yield, requirement of efficient product purification, prevention of product accumulation, and the use of high concentrated substrate as process feed to reduce process wastes and production costs.

4.3. Identify Rate Limiting Steps:

After the drivers are defined, the rate limiting step is defined. The subsequent removal of product acid, end product inhabitation of the acids and separation of the heterogeneous system can be thought of as the rate limiting steps.

4.4 Generate Design Concepts:

In the next step, the design concepts are generated. The step is the outcome of a brain storming session of technologists, scientists, researchers and persons having deep knowledge of the subject. Removal of inhibitory acid product from reactor, requirement of purer and concentrated product and saving in the down streaming recovery and purification costs were proposed to be the requirement of the process.

4.5. Analyze the Design Concepts:

Based on the requirements proposed above, the database of various process intensification equipments is made and a design of a draft of new process alternatives is made by drawing a flow sheet (**Figure 4**). Reactive extraction process for propionic acid recovery was proposed. The process provides a number of advantages like: feed concentration in the bioreactor outlet stream was found to decrease, thus more substrate was fermented; concentration of propionic acid in bioreactor was reduced, thus pH fall was prevented; propionic acid concentration in recycle stream was found to be < 1 g/l; solvent extraction removes a small fraction of acetic acid produced and most acetic acid remained in recycle stream; purer product was obtained and the production was found to increase [6,7].

4.6. Comparison with conventional process and making final decision

The high productivity, improved acid yield, highly concentrated and purified product and stable and consistent performance of the reactive extraction process, proposed it to as a suitable process for recovery of propionic acid.

CONCLUSION

Process intensification methodology was applied to the recovery of propionic acid from fermentation broth. A conventional separation technique was proved to be environmentally unfriendly, since lot of waste sludge was generated. This inspired the search of an alternative separation method. Reactive extraction with its lot of advantaged was chosen to be a bright alternative. Step by step application PI methodology was conducted to the present process and reactive extraction was compared to the conventional fermentation and separation and the sure advantages of reactive extraction prove it to be better technology. Thus PI can be introduced with open mind.

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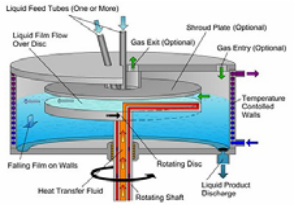
Table 1. Keywords for brain storming session

Keywords	Example
Intensify	Make the process smaller
Segment	Divide into independent parts
Use a different aid	A different solvent, temporary shielding agent
Change conditions	Change pressure or temperature
Combine	Combine unit operations
Fix	Fix one phase to prevent separation problem
Add or remove	Quickly remove or add a product or reactant
Periodic action	Change a continuous system into periodic actions

Figure. 1 PROCESS INTENSIFICATION EQUIPMENTS
(Reactors and equipment for non reactive operations)

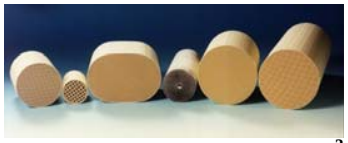


Spinning disk reactor[1] (HiGee Technology)

- Rotating bed with centrifugal force
- For fast or very fast liquid liquid reactions
- Very short residence time(≈0.1s)
- HT rate= 10,000 W/m^{2}K
- Heat is efficiently removed

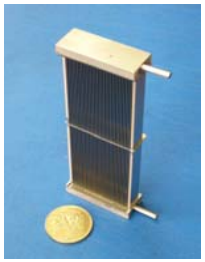
Micro Reactors[2]

- Higher value of HT coeff. upto 20000 W/m^{2}K
- Extremely small in dimensions
- Sandwich like structure with number of layers that perform mixing, reaction , heat exchange and separation operations.
- Very low reaction to Surface area ration. Adv: to carry out explosive and poisonous reactions



Monolithic catalysts[3]

- To intensify heterogeneous catalytic processes
- Metallic or non metallic
- Straight channels of defined uniform cross section
- Inner wall of the monolith channel covered with thin layer of wash coat to ensure porosity and enhance catalytically active surface.
- Adv: low P drop, higher geometrical area per unit volume, very high catalytic efficency.



Microchannel heat exchanger[4]

- Channel size ≈ < 1 mm
- HT coeff. 10000-35000 W/m^{2}K
- Fabricated by micromachining, deep lithography etc.

Static mixer[5]

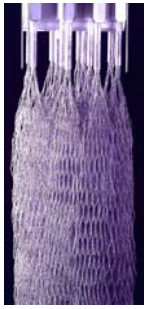
- More size and energy efficient mixing
- Mixing elements are made of heat transfer tubes which provide simultaneous mixing and intensive heat removal

HEX Reactor[6]

- For highly exothermic reactions
- HT coeff. 3500-7500 W/m^{2}K and HT area= 2200 m^2/m^3

Open cross flow structure catalysts[7]

- Mixing coupled with solid catalyzed reaction
- Eg KATAPAK- good mixing and act as support for catalyst particles.
- Application: Catalytic distillation, gas phase exothermic oxidation process(adv good HT)



Super X- Pack[8]

- For nonreaction distillation
- Wire based packing
- Reduced the height of distillation column by a factor of 5 compared to the conventional tray design

Ir

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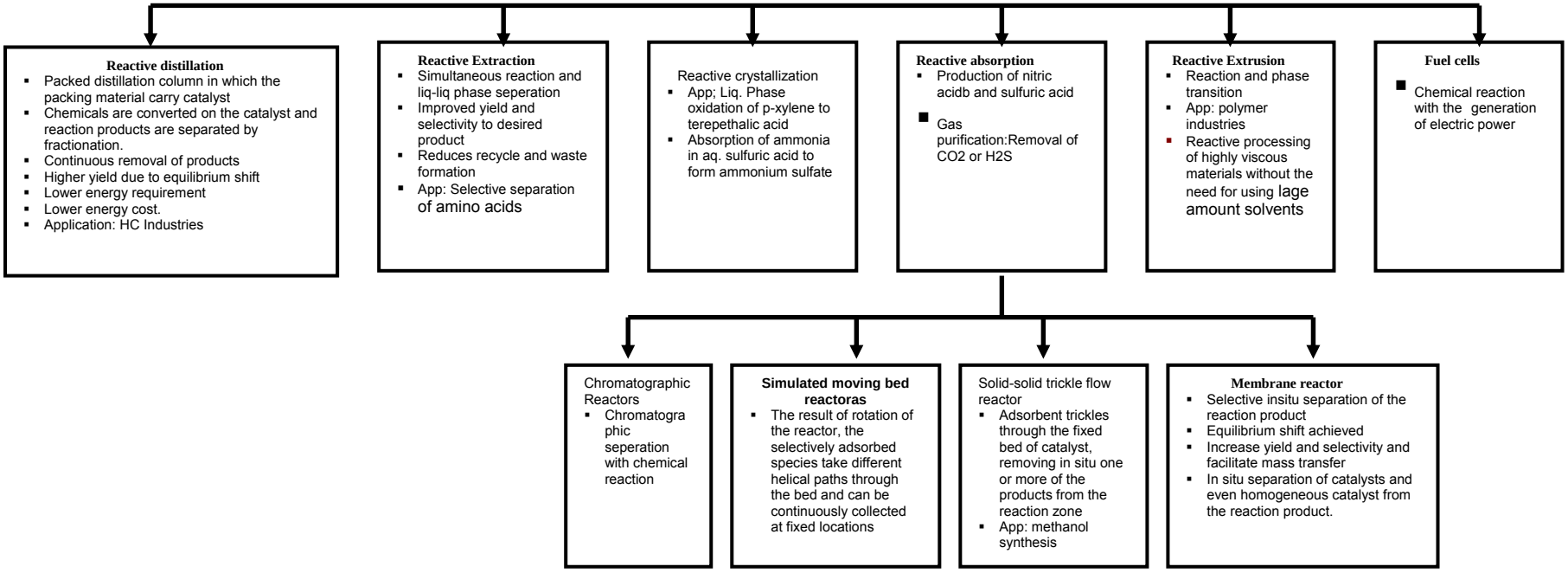
Reactive Separation



b) Hybrid Separations

Membrane absorption and stripping
- Membrane is used as a permeable barrier bet the gas and liq. phases.
- Large MT area are created.
- Compact equip.
- Operation ind. Of gas and liquid flow rates
- No entrainment, flooding, channeling or foaming

Membrane distillation
- Two liquid held at different temperature are mechanically separated by hydrophobic membrane
- Vapour transported via the membrane from hot solution to cold one
- Applications: water desalination and water decontamination, removal of water from azeotropic mixtures

Membrane chromatography
- Microporous/ macroiporous membrane contain functional ligands attached to their inner pore structure which act as adsorbent
- Applications: separations of biomolecules such as proteins, nucleic acids etc.

Adsorptive distillation
- Selective adsorbent is added to a distillation mixture
- Increased separation ability- attractive in separations of azeotropes
- Applications: removal of trace impurities in the manufacturing of fine chemicals

c) Alternative forms and Sources of Energy

Centrifugal field
Centrifugal forces are used instead of gravitational ones

Ultrasound waves
- Formation of microbubbles in the liquid reaction medium
- Cavities act as high energy micro reactors- when they collapse they release very high local energy (T= 5000K and P = 10000 bar)- can cause hemolytic bond breakage with free radical formation, in situ catalyst cleaning/ rejuvenation

Solar energy
Applications: water treatment plants, cyclo addition of a carbonyl compound to an olefin carried out in a solar furnance reactor.

Microwave dielectric heating
Enebles some organic synthesis reactions to proceed up to 1240 times faster than by conventional techniques.

Electric field
Application ; paint spraying, crop spraying and coating processes, bioseperations. Electrically charged droplets exhibits much better adision properties Enhances processes involving liq/liq mixtures- eg in liq-liq extraction, rate enhancement of 200-

300% were reported.

Gliding arch technology
- Use of plasma generated by the formation of gliding electric discharges
- Offer lower energy alternative for conventional high enrgy consuming high temp. processes.
- Applications: methane transformation to acetylene, destruction of NO2 etc.

Super critical fluids
High diffusion coefficen t

Cryogenic techniques
Production of industrial gases

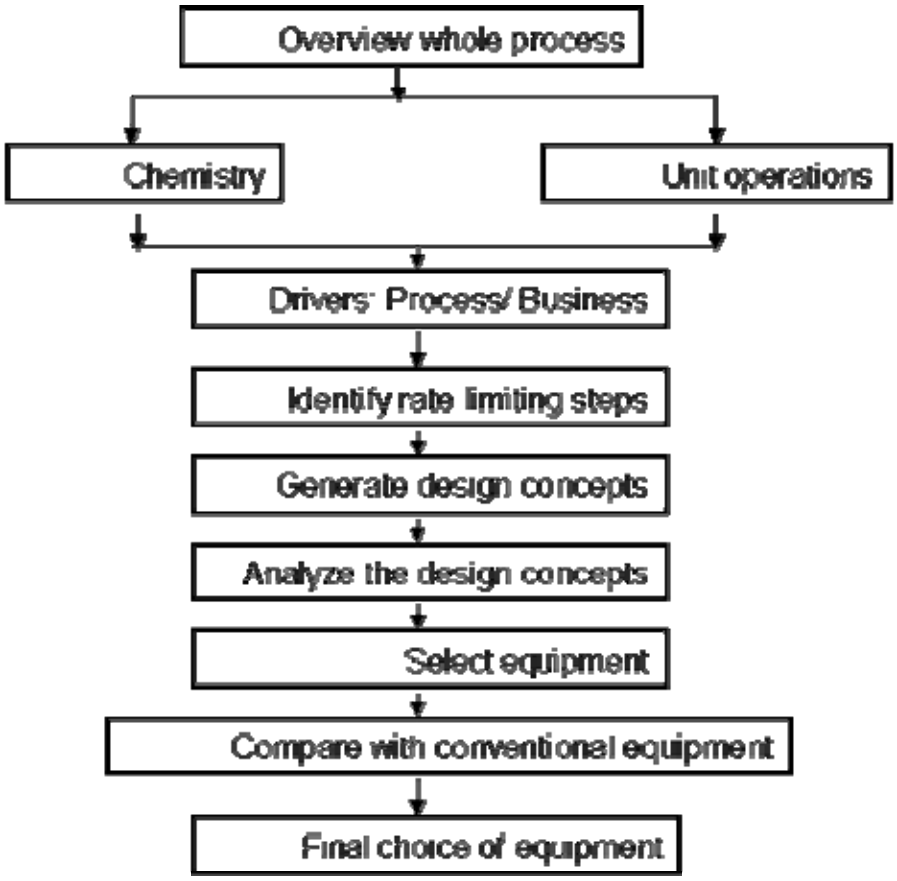


Figure 3. Process intensification methodology

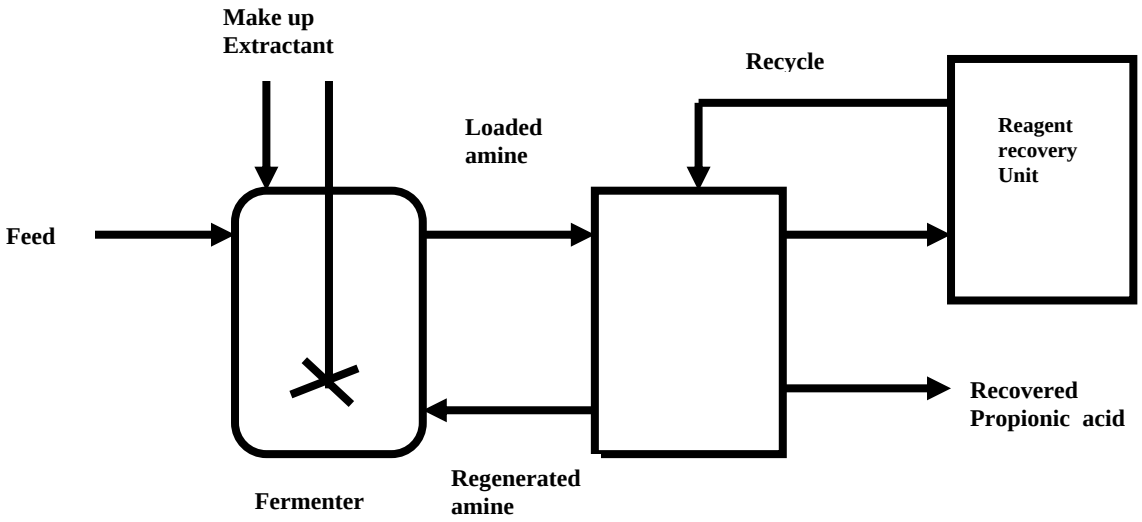


Figure 4. Reactive extraction for recovery of propionic acid.