

APPLICATION OF ADVANCED SEPARATION TECHNIQUES IN BIODIESEL PRODUCTION AND PURIFICATION

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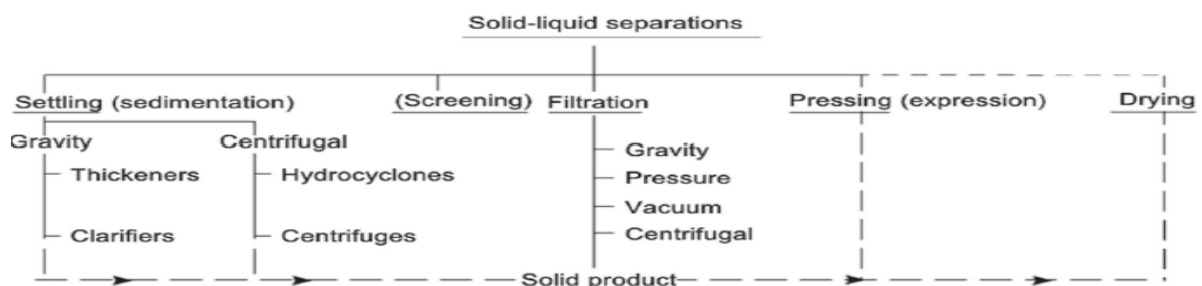
Abstract: Fossil fuel, especially crude oil and gas has dominated the global energy mix since World War II, and with it comes the challenges of global warming from greenhouse gases emissions, non-renewable and depleting resources, price hike of crude oil, and environmental pollution, all of which are key factors that have led to the quest for alternative energy sources. Some of the reliable alternative energy sources capable of replacing fuels include water, solar and wind energy, and biofuels, even though fossil fuel still constitutes about 86% of the total global energy consumed and close to a 100% utility in the transportation sector. In all these renewable sources, biodiesel has been identified as one of the most suitable replacement of fossil fuel in the transportation and power sectors. To achieve this energy transition, require efficient separation processes and techniques that will produce not only cost-effective fuels, but products that can also reduce the emission of greenhouse gases into the atmosphere. The paper noted that as environmental regulations become increasingly stringent, the costs associated with waste management are expected to rise, and therefore by reducing these costs, separation technologies can contribute to the competitiveness of any industrial economy. The paper further noted that less optimized separation processes are energy intensive coupled with creation of products that are hazardous to the environment and human health. Such systems are also very capital intensive and thus affect the redistribution of available resources to other growth sectors of the economy. This paper therefore reviewed the application of advanced separation techniques in biodiesel production and purification such as equilibrium based, affinity based, solid-liquid, and membrane based separation techniques, and noted that, the low energy intensive, but low quality membrane technology is preferred, and therefore has attracted further scientific and engineering investigation to improve its selectivity, throughput, capacity in order to provide the needed alternative systems to the high energy, high cost, but high quality distillation process, that currently handles fossil fuel used mostly in the transport system.

Keywords: Renewable Energy, Separation Processes and techniques, biofuel, membrane techniques, pollutants.

1. INTRODUCTION

Almost all materials, be it in elemental form or in a compound known to man is found naturally in an impure state such as a mixture of two or more substances, and this has made separation of materials as old as human history. Recorded history has thus shown that people have used various methods of separating and purifying substances in order to improve the quality of life, such as the extraction of metals from ores and of medicines from plants. Many industries now find separations indispensable: the petroleum industry separates crude oil into products used as fuels, lubricants, and chemical raw materials; the pharmaceutical industry separates and purifies natural and synthetic drugs to meet health needs; and the mining industry is based on the separation and purification of metals. Separation processes are thus carried out for two main reasons – first is to purify individual components by separating them from the mixture in order to produce higher quality versions. The second reason is to alter the composition of a sample so that one or more of the components can be

analyzed separately, and a typical example is the analysis of air pollutants to assess the quality of the air, since many of the pollutants are at a concentration too low for direct analysis, even with the most sensitive devices. (Karger, (2014). Separation is thus a process that changes the relative amounts of substances in a mixture, that may be completely homogeneous or sometimes heterogeneous as in solid plus liquid. In Heterogeneous mixtures, two or more phases intermingle, but remain physically separate such as in . (i) two liquids, (ii) a solid and a liquid, (iii) a liquid and a gas, or even (iv) a gas and a solid. Technically, a liquid/liquid mixture is referred to as emulsions, a solid/liquid mixture is suspension, a gas/liquid mixture is aerosol, while a gas/solid mixture is referred to as smoke. Homogeneous mixture on the other hand are indistinguishable, having merged into a single uniform phase, with its original parts undetectable even at very high magnification. Solutions have only one phase and the most common solutions are liquids, although there can be solutions of gases (air) and solids (alloys). At the concept level, separating a heterogeneous or a multiphase mixture, can be done physically by exploiting differences in density between the phase, as it cannot be accomplished on a molecular scale nor is it due to the differences among the various molecules. Technically, the separation will be accomplished using mechanical-physical forces and not molecular or chemical forces and diffusion. In the separation process, it is always important in terms of sequencing, to separate the different phases of a heterogeneous mixture before homogeneous separation, to take advantage of what already exists. On the other hand, separation of homogeneous mixtures is done either through the addition or creation of another phase within the system, during which the two phases are brought into more or less intimate contact with each other so that a solute or solutes can diffuse from one to the other. Consequently, in gas-liquid and vapour-liquid separation processes (e.g. absorption, distillation) the separation depends on molecules diffusing or vaporizing from one distinct phase to another phase, i.e. on mass transfer of the molecules, while for a liquid-liquid separation processes (e.g. extraction), where the two phases are chemically different, the separation is achieved on a molecular scale according to physical-chemical properties. In adsorption and membrane separation processes, the differences in the physical-chemical properties of the molecules lead to separation on a molecular scale. (Sorsamaki and Nappa, 2015). The specific separation design may vary depending on what chemicals are being separated, but the basic design principles for a given separation method are always the same. In addition to the obvious factors that influence the selection, design, and operation of separation processes, other factors such as the economics governing plant design, a renewed awareness of the impact of chemical processing on the environment, new products that require purity levels exceeding those typically encountered, a recognition of the hazards associated with production of dangerous materials, and a growing awareness of the importance of political and natural limitations on the availability of raw materials, are also critical as input to the design. Moreover, the methods by which processes of all types are conceived and designed have been altered substantially by the growth of computer hardware and software. (Ronald and Rousseau, 1987). According to Seader et al (2011) separation can either be at the laboratory levels by chemists or at the industrial levels by chemical engineers, and that while chemists use analytical separation methods, such as chromatography, to determine compositions of complex mixtures quantitatively, and small-scale preparative separation techniques, often similar to analytical separation methods, to recover and purify chemicals, chemical engineers are more concerned with the manufacture of chemicals using economical, large-scale separation methods, which may differ considerably from laboratory techniques. Separation processes can also be classified into simple and advanced separation based on the complexities of the process; those that require simple physical separation and those that would require rigorous processes guided by thermodynamics and chemical laws. Most of the simple separation processes involve heterogenous mixtures as shown in figure 1. The separation of heterogeneous mixtures is accomplished using mechanical-physical forces; these forces will be acting on particles, liquids, or mixtures of particles and liquids themselves and not necessarily on the individual molecules. The mechanical-physical forces include gravitational and centrifugal, actual mechanical and kinetic forces arising from flow



Generally, the principal method for the separation of heterogeneous liquid-liquid emulsions is decantation or hydrocyclones, while the principal types of equipment for gas-solid and gas-liquid separation (i.e. gas cleaning) can be classified according to the mechanism employed to separate the solid particles or liquid mists: gravity settling, impingement, centrifugal force, filtering, washing, and electrostatic precipitation. (Sorsamaki and Nappa, 2015). All of these can be classified as simple separation processes. However, advanced separation processes, which is the subject matter of this paper is involved with the exploitation of differences in molecular, thermodynamic, and transport properties of the species. The Molecular properties are molecular weight, polarizability, van der Waals volume, dielectric constant, van der Waals area Electric charge, molecular shape (acentric factor), radius of gyration, dipole moment, while the thermodynamic and transport properties include vapor pressure, adsorptivity, solubility, and diffusivity. (Seader et al (2011). The advances in research, technology and industrial practices and feedback, with the application of systems engineering toolboxes, have all helped in the design, scaling and controlled operations, and of a large number of separation processes. Such systems engineering toolboxes have also offered a fast-track simulation and investigation of the performances of separation systems. Also the combination of mass and energy balances, fluid phase equilibria, and rate processes offer a generic methodology, which can, in principle, be applied to any type of molecule in the feed mixture for a rational design. Separation processes, which is the main component of the chemical process industry (CPIs) produce around 10^5 different molecules at capacities ranging from less than one kilo to 300 million tons per year. The number of potential feed compositions to be treated by separation processes for industrial applications is thus enormous. (Favre, 2020). Consequently, Sholl and Lively, 2016 reported that separation processes such as distillation, account for 10–15% of the world's energy consumption, as refineries around the world process around 90 million barrels of crude oil — roughly 2 litres for every person on the planet, each day. Also, globally, high-pressure cryogenic distillation at temperatures as low as $-160\text{ }^\circ\text{C}$ is required in the separation of ethenes and propenes from hydrocarbons as intermediates for the manufacturing plastics such as polyethylene and polypropene. Globally, such process produces in excess of 200 million tonnes, about 30 kilograms annually of ethene and propene. Typically, purification of propene and ethene alone accounts for 0.3% of global energy use. Again, the supply chains of many polymers, plastics, fibres, solvents and fuel additives depend on benzene, a cyclic hydrocarbon, as well as on its derivatives such as toluene, ethylbenzene and the xylene isomers, which are all separated in distillation columns, with combined global energy costs of about 50 GW, enough to power roughly 40 million homes. Another major separation process of significant global impact according to Sholl and Lively, 2016, is the separation of rare-earth metals from ores, as the almost 15 lanthanide metals, or rare-earth elements, which are found in trace quantities in ores and are often mixed together because they are chemically similar. These rare-earth-metals are used in magnets, in renewable-energy technologies and as catalysts in petroleum refining. Compact fluorescent lamps use europium and terbium, for example, and catalytic convertors rely on cerium. These rare-earth-metals are thus produced through separation processes involving mechanical approaches (such as magnetic and electrostatic separation) and chemical processing (such as froth flotation). Now, regardless of the separation process, generally, the most effective separation process for a given target application can be identified through such efficiency indicators, as (i): the possibility of reaching the specifications imposed by the application (e.g., purity and recovery), (ii) the energy requirement, (iii) the productivity of the process, and (iv) the environmental and risk efficiencies (quantity of waste generated, explosion hazard, etc.). In all, the overall specific cost determines ultimate objective function for the process selection and design study. (Favre, 2020).

2. DESCRIPTION

Separation processes, or processes that use physical, chemical, or electrical forces to isolate or concentrate selected constituents of a mixture, are essential to the chemical, petroleum refining, and materials processing industries such as aluminium, steel, metal casting, glass, and the polymer-recycling sector of the chemical industry. This section therefore presents various separation processes and separation techniques commonly used in industrial processes.

2.1 Separation Processes:

Unlike mixing of chemicals that requires spontaneous chemical reactions accompanied by an increase in entropy or randomness, separation process is the reverse process, and therefore is not spontaneous, as it requires an expenditure of energy. (Seader et al (2011). Generally, all separation processes perform similar functions in all industries, whether if the materials streams are composed of homogeneous solids, liquids, gases, or supercritical fluids, or they may be composed of heterogeneous mixtures containing any combination of these phases. Separation processes generally remove impurities from raw materials, products, and by-products; the separation of recycle streams; and the removal of contaminants from air and water waste streams. For the chemical, petroleum refining, and materials processing industries as a group,

separation technologies are critical for reducing waste, improving energy efficiency, and increasing the efficiency of raw material use. For example, separation technologies have the potential to reduce waste and increase productivity by separating valuable materials that can be used or sold as by-products from waste streams. As environmental regulations become increasingly stringent, the costs associated with waste management are expected to rise. By reducing these costs, separation technologies can contribute to the competitiveness of any industrial economy. (National Research Council, 1998). Typically, a chemical or biochemical plant is operated either in a batchwise, continuous, or semicontinuous manner, and may also either be classified as key operations unique to chemical engineering because they involve changes in chemical composition, or as auxiliary operations, which are necessary to the success of the key operations but may be designed by mechanical engineers because the operations do not involve changes in chemical composition. The key operations are chemical reactions and separation of chemical mixtures, while the auxiliary operations include phase separation, heat addition or removal (heat exchangers), shaft work (pumps or compressors), mixing or dividing of streams, solids agglomeration, size reduction of solids, and separation of solids by size. Also, a typical separation process is represented by block-flow diagrams as shown in figure 2. They indicate, by square or rectangular blocks, chemical reaction, and separation steps and, by connecting lines, the process streams. (Seader et al (2011))

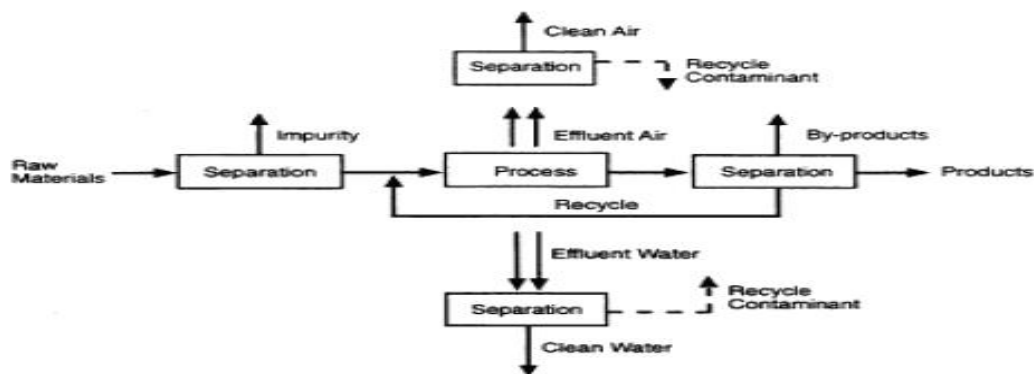


Figure 2: Separation in manufacturing processes; Source: National Research Council, 1998.

The block flow diagram also show auxiliary operations and utilize symbols that depict the type of equipment employed, as depicted in figure 3 for the manufacturing of hydrogen chloride gas from chlorine and hydrogen. Central to the process is a reactor, where the gas-phase combustion reaction, $H_2 + Cl_2 = 2HCl$, occurs. The auxiliary equipment required consists of pumps, compressors, and a heat exchanger to cool the product.

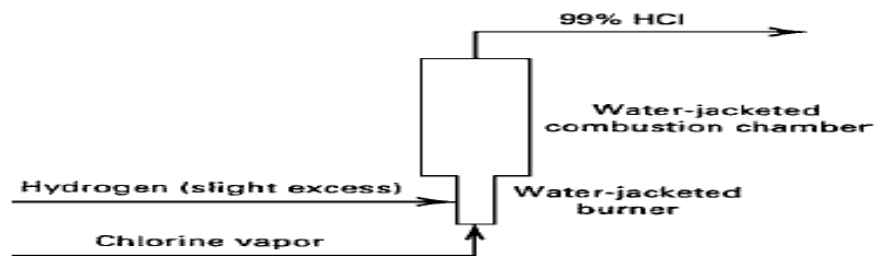


Figure 3: Process flow diagram for anhydrous HCl production; Source: (Seader et al (2011))

Many industrial chemical processes involve at least one chemical reactor, accompanied by one or more separation trains, and more than 95% of industrial chemical separation operations involve feed mixtures of organic chemicals from coal, natural gas, and petroleum, or effluents from chemical reactors processing these raw materials. The most common industrial technique involves the creation of a second phase (vapor, liquid, or solid) that is immiscible with the feed phase. The creation is accomplished by energy (heat and or shaft-work) transfer to or from the process or by pressure as inert carriers for other substances to cause separation. For all the techniques separations are achieved by enhancing the rate of mass transfer by diffusion of certain species relative to mass transfer of all species by bulk movement within a phase. The driving force and direction of mass transfer by diffusion is governed by thermodynamics, with the usual limitations of equilibrium. Thus, both transport and thermodynamic considerations are crucial in separation operations. The rate of separation is governed by mass transfer; while the extent of separation is limited by thermodynamic equilibrium. (Seader et al (2011))

2.2 Separation Techniques:

Separation techniques are classified based on the quantity of material to be processed, such as in chromatography that works best with a small amount of sample, while others such as distillation are more suited to large-scale operations. Another set of classification is based on the physical or chemical phenomena utilized to effect the separation, which are further subdivided into equilibrium and rate (kinetic) processes. Table 1 lists some separation methods based on equilibria, while table 1 indicates those methods based on rate phenomena.

Table 1: Separation Techniques based on Equilibria; source: Karger, 2014

Gas-Liquid	Gas-Solid	Liquid-Solid	Liquid-Liquid	Supercritical Fluid-Solid	Supercritical fluid-Liquid
Distillation	Absorption	Precipitation	Extraction	Supercritical fluid chromatography	Supercritical fluid extraction
Gas-liquid chromatography	Sublimation	Zone melting	Partition Chromatography		
Foam fractionation		Crystallization			
		Ion Exchange			
		Adsorption			
		Exclusion			
		Clathration			

Table 2: Separation Techniques based on Rates: Source, Karger, 2014

Barrier Separations	Field Separations
Membrane filtration	Electrophoresis
Dialysis	Ultracentrifugation
Ultrafiltration	Electrolysis
Electrodialysis	Field-Flow Fractionation
Reverse Osmosis	

The equilibrium stage concept is applicable when the process can be constructed as a series of discrete stages in which the two phases are contacted and then separated. The two separated phases are assumed to be in equilibrium with each other. For example, in distillation, a vapor and a liquid are commonly contacted on a metal plate with holes in it. Because of the intimate contact between the two phases, solute can transfer from one phase to another. Above the plate the vapor disengages from the liquid. Both liquid and vapor can be sent to additional stages for further separation. Assuming that the stages are equilibrium stages, the engineer can calculate concentrations and temperatures without detailed knowledge of flow patterns and heat and mass transfer rates. (Wankat, 2012). Mathematically, separation through the equilibrium method is effected by the differences in the equilibrium constants also termed as the distribution coefficients between two phases that are insoluble in one another. The distribution coefficient, k , is explained by mixing two immiscible liquids, benzene and water, where the water had coloured dye, that is also soluble in the benzene, such that the concentration of the dye continues to change in intensity across the two liquids until it attains equilibrium at the point where the concentration of the dye (as measured by the intensity of its colour) is constant in the two phases. Mathematically, distribution coefficient K is defined by the equation:

$$K = \frac{\text{concentration of dye in the benzene phase}}{\text{concentration of dye in the water phase}} \quad \text{Equation 1}$$

Separation happens due to different K values of the two substances. Now assuming two different dyes in the mixture, the ease of the separation will depend on the ratio of the two distribution coefficients, α , also sometimes called the separation factor, expressed as:

$$\alpha = \frac{K_2}{K_1} \quad \text{Equation 2}$$

On the other hand, rate separation processes are based on differences in the kinetic properties of the components of a mixture, such as the velocity of migration in a medium or of diffusion through semipermeable barriers. Similar to the equilibrium methods, the separation factor can be defined as the ratio of migration the velocities for the two substances:

$$\alpha = \frac{v_2}{v_1}$$

Equation 3

The extent of separation of the two substances depends on the different distances traversed by the two substances:

extent = $v_2t - v_1t$, where t is the time allowed for migration. Thus the extent of separation is directly proportional to the time of migration in the electric field.

Another rate separation methods as captured by Karger, 2014, is based on the diffusion of molecules through semipermeable barriers, where a porous membrane serves as a divide between a solution of different properties and pure water. Some of the substances diffuse freely through the membrane, while others with bigger molecules could not fit through the holes or pores. Still certain molecules could just squeeze through the pores and diffuse more slowly through the membrane, which in context indicates that the extent of separation greatly depends on the time allowed for diffusion to take place. Separations processes are also carried out at particles levels for one of two purposes: (1) to remove particles from gases or liquids, or (2) to separate particles of different sizes or properties. Separations to remove particles underlies many important applications such as in the electronics industry that requires dust-free “clean rooms” for assembly of very small components. Particles separations are very critical for such processes that use finely divided materials that require uniform sized particles. Some of the important particle separation methods are filtration, sedimentation, elutriation, centrifugation, particle electrophoresis, electrostatic precipitation, flotation, and screening, which are described in a later section. Separations can either be in single stage or multistage, and this is dependent on the separator factors, α , of the substances (Karger, 2014). Thus single stage separation processes occur when α lies between 100 and 1,000, a single equilibration in liquid-liquid extraction will be sufficient to separate at the level of 90 percent or higher. However, where the separation factor is smaller, it makes the entire separation process cumbersome, as more work would be required to achieve the desired separation, and this is where multistage separation comes in, by repeating the equilibration process many times. (Karger, 2014). In addition to the equilibrium and rate-based separation processes, another useful concept of separation is that of a unit operation. The idea here is that although the specific design may vary depending on what chemicals are being separated, the basic design principles for a given separation method are always the same. For example, the basic principles of distillation are always the same whether we are separating ethanol from water, separating several hydrocarbons, or separating liquid metals. Consequently, distillation is often called a unit operation, as are absorption, extraction, etc. A more general idea is that design methods for related unit operations are similar. Since distillation and absorption are both liquid-vapor contacting systems, the design is much the same for both. This similarity is useful because it allows us to apply a very few design tools to a variety of separation methods. (Wankat, 2012).

2.3 Description of basic separation techniques:

Section 2.2 highlighted the various separation techniques, however, for the purpose of this paper, we have limited it to 6 basic separation techniques as shown in figure 4 below

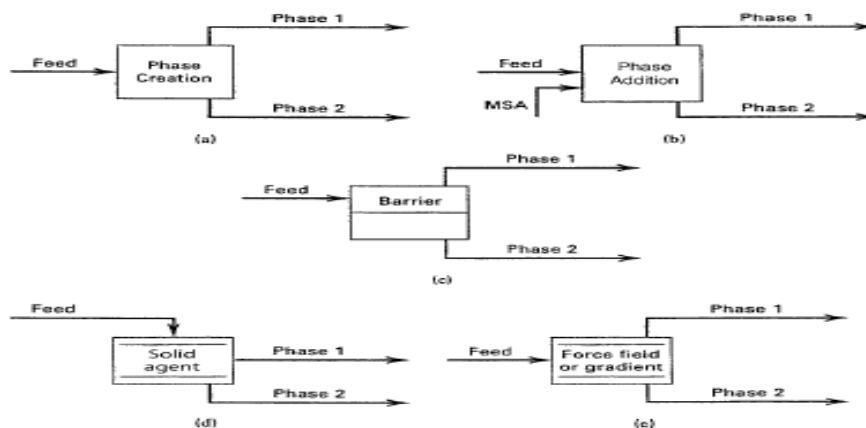


Figure 4: Basic separation techniques: (a) separation by phase creation; (b) separation by phase addition; (c) separation by barrier; (d) separation by solid agent; (e) separation by force field or gradient. Source: Sorsamaki and Nappa, 2015

And these are separation by phase creation, separation by phase addition, separation by barrier, separation by solid agents, and separation by force field or gradient. This section therefore presents brief description of examples of each of these separation techniques.

2.3.1 Separation by Phase Addition and Phase Creation:

Several separation processes operate by the phase addition or phase creation techniques, and some of these as listed by Sorsamaki and Nappa (2015) are partial condensation or partial vaporization, flash vaporization, distillation, extractive distillation, reboiled absorption, absorption, stripping, refluxed stripping, reboiled stripping, azeotropic distillation, liquid-liquid extraction, drying, evaporation, crystallization, desublimation, leaching, and foam fractionation. (Sorsamaki and Nappa, 2015). According to Seader et al, 2011, most of these processes operate either through the use of an energy separating agent (ESA) which involves heat transfer or transfer of shaft work, or through a mass separating agent, (MSA) which may be the constituent of the highest concentration within a partially immiscible mixture, or the miscible component within a liquid feed mixture, that may selectively alter the partitioning of species between liquid and vapor phases. This enhances the separation process if used in conjunction with an ESA, as in extractive distillation. The MSA have some shortcomings such as (1) the need for an additional separator to recover the MSA for recycle, (2) the need for MSA makeup, (3) possible MSA product contamination, and (4) more difficult design procedures. Seader et al, 2011, added that **partial condensation or partial vapourization** separation processes will become useful when the feed mixture includes species that differ widely in volatility, expressed as vapor-liquid equilibrium ratios (K-values). Due to their differences in volatility, separation is effected when a vapor feed is partially condensed by removing heat, and a liquid feed is partially vaporized by adding heat. Partial vaporization can be initiated by flash vaporization, by reducing the feed pressure with a valve or turbine. In both operations, the two phases are then separated by gravity. In the case where the species volatilities are not significantly different, the separation is effected by **distillation process**, which involves multiple contacts between counter currently flowing liquid and vapor phases, often made on horizontal trays arranged in a column. Each contact, called a stage, consists of mixing the phases to promote rapid partitioning of species by mass transfer, followed by phase separation. Now, in the case where the volatility difference between two species is so small as to necessitate more than about 100 trays, **extractive distillation**, where a miscible MSA, a least volatile species is introduced near the top of the column to act as a solvent, in order to increase the volatility difference among species in the feed, thereby reducing the number of trays. The MSA is recovered for recycling through a simple distillation process. Where it becomes difficult to condense the vapour leaving the top, a liquid MSA is fed into the top of the tray to act as an absorbent to absorb the vapor feed, and this process is **reboiled absorption**, however, where the feed is completely vapour, and the stripping section of the column is not needed, absorbers are introduced to dissolve the feed vapour in an absorption process that is dependent on the extent of their solubilities. **Stripping** on the other hand, which is the inverse of absorption, works where liquid mixtures are separated, at elevated temperature and ambient pressure, by contacting the feed with a vapor stripping agent. Another separation technique, **the azeotropes distillation** is used to separate minimum boiling azeotropes such as the mixture of n-butyl acetate, an MSA forms a two-liquid (heterogeneous), minimum-boiling azeotrope with water. The azeotrope is thus separated into into acetate and water layers, while the MSA is recirculated, and the distillate water layer and bottoms acetic acid are the products. **Evaporation separation** method uses heat transfer to create a volatile phase from a liquid, and is readily used in humidification, air conditioning, and concentration of aqueous solutions, while **Crystallization**, which is a purification process to cause the precipitation of a specie out of an organic or inorganic substance. Generally, for solution crystallization, the mixture, which includes a solvent, is either cooled and or evaporated, while for melt crystallization, two or more soluble species are separated by partial freezing. **Liquid-liquid extraction** on the other hand is used especially when the mixture to be separated is temperature sensitive, and normal distillation is impracticable. The process works by a solvent to selectively dissolve only one or a fraction of the components in the feed. Two-solvent extraction uses several counter currently arranged stages with each species having its specific selectivity for the feed components. **Supercritical-fluid extraction** operations occur where the extraction temperature and pressure slightly exceed the critical point of the solvent. This region is unstable as solute solubility can drastically change with small changes in temperature and pressure. **Liquid-solid extraction**, on the hand, also known as leaching, involves the removal of a soluble fraction (the solute or leachant) of a solid material by a liquid solvent. The solute diffuses from inside the solid into the surrounding solvent. Either the extracted solid fraction or the insoluble solids, or both, may be valuable products. Leaching is widely used in the metallurgical, natural product, and food industries. (Sorsamäki and Nappa, 2015). Another separation process is **drying**, which is required to dry wet substances to meet sales specification as dry products. It is deployed when the wetting liquid has higher partial pressure in the gas stream than the solid substance. Besides this, it is always a challenge using this method as solid, liquid, and vapor

phases coexist in drying, and therefore, it is important that the dryer design must consider such external conditions as temperature, humidity, air flow, and degree of solid subdivision on drying rate, the effects of internal diffusion conditions, capillary flow, equilibrium moisture content, and heat sensitivity. **Sublimation** is another separation process that involves the transfer of a species from the solid to the gaseous state without formation of an intermediate liquid phase, such as the use of dry ice as a refrigerant, and also in the separation of sulfur from impurities, purification of benzoic acid, and freeze-drying of foods. **Desublimation**, which is the reverse case is where gaseous effluent is transformed into a solid, such as in the recovery of phthalic anhydride from gaseous reactor effluent. Finally, foam fractionation is used to remove a solute from a substance by using a natural or chelate-induced surface activity to cause the solute to migrate to rising bubbles. (Seader et al, 2011).

2.3.2 Separation by Barrier:

Seader et al 2011, identified about 8 separation processes that utilize this technique, and these are Osmosis, Reverse Osmosis, Dialysis, Microfiltration, Ultrafiltration, Pervaporation, Gas permeation and Liquid membrane. All these processes utilizes one form of membrane, which can be either microporous or nonporous membranes that are semipermeable barriers that selectively allows the passage of some substances through them.

Separation Operation	Symbol ^a	Initial or Feed Phase	Separating Agent	Industrial Example ^b
Osmosis (1)		Liquid	Nonporous membrane	—
Reverse osmosis* (2)		Liquid	Nonporous membrane with pressure gradient	Desalination of sea water
Dialysis* (3)		Liquid	Porous membrane with pressure gradient	Recovery of caustic from hemicellulose
Microfiltration* (4)		Liquid	Microporous membrane with pressure gradient	Removal of bacteria from drinking water
Ultrafiltration* (5)		Liquid	Microporous membrane with pressure gradient	Separation of whey from cheese
Pervaporation* (6)		Liquid	Nonporous membrane with pressure gradient	Separation of azeotropic mixtures
Gas permeation* (7)		Vapor	Nonporous membrane with pressure gradient	Hydrogen enrichment
Liquid membrane (8)		Vapor and/or liquid	Liquid membrane with pressure gradient	Removal of hydrogen sulfide

Figure 5: Separation Processes by Barrier. Source: Seader et al, 2011

Microporous membranes effects separation by the rate of species diffusion through the pores, while nonporous membranes separation operates through differences in solubility in the membrane and rate of species diffusion. The most complex and selective membranes are found in the trillions of cells in the human body. Microporous membranes selectively pass only small solute molecules and/or solvents. Processes that utilize microporous membrane, include **Microfiltration** only retains molecules from 0.02 to 10 μm , while **Ultrafiltration** retains molecules that range from 1 to 20 μm . Other processes include **Dialysis**, which passes by concentration gradient small solute and diffusible molecules, sometimes called crystalloids, through a porous membrane. **Gas permeation** also uses porous membranes in the form of fluorocarbon barriers to separate $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$ using enormous amounts of electric power. Separation processes that utilize non porous membranes include hyperfiltration that retain molecules down to 0.1 μm . **Pervaporation** process also utilizes non porous membranes and uses heat of vapourization to evaporate the species that is transported through a nonporous membrane. It is mostly used to separate azeotropic mixtures. Nonporous polymer membranes are also employed to enrich mixtures containing H_2 , recover hydrocarbons from gas streams, and produce O_2 -enriched air in gas permeation. **Osmosis** and **reverse Osmosis** also uses non-porous membranes. Osmosis involves transfer, by a concentration gradient, of a solvent through a membrane into a mixture of solute and solvent, while reverse osmosis, transport solvent in the opposite direction by imposing a pressure, higher than the osmotic pressure, on the feed side. **Liquid membranes**, are formed from surfactant-containing mixtures at the interface between two fluid phases and can be used to separate aromatic/paraffinic hydrocarbons. Liquid membrane can also be formed by imbining the micropores with liquids doped with additives to facilitate transport of solutes such as CO_2 and H_2S .

2.3.3 Separations by Solid Agents:

Seader et al 2011, further identified about 3 separation processes that utilize this technique as shown in figure 6, and these are adsorption, chromatography, and ion exchange.

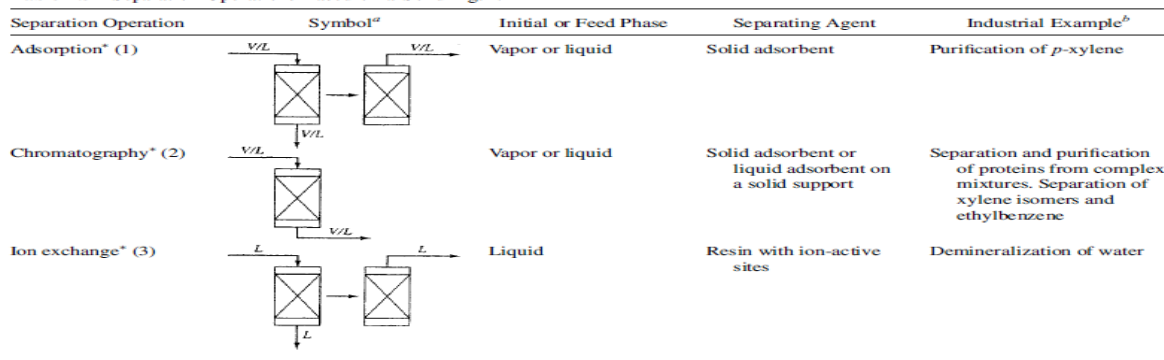


Figure 6: Separation processes by Solid Agents. Source: Seader et al, 2011

All the three processes utilize solids in granular forms or packings that work as adsorbents or in other cases as an inert support for a thin layer of adsorbent. Separation by **adsorption** occurs at the surface level, where the separating agent becomes saturated with the solute. Adsorption, is best utilized for species in low concentrations, so that the adsorbents can be regenerated by desorption through processes that utilize activated carbon, aluminum oxide, silica gel, and synthetic sodium or calcium aluminosilicate zeolites (molecular sieves). This is why adsorption processes utilizes two or more vessels one for desorption, while the other(s) for adsorption. Regeneration, which is desorption is a reverse adsorption process and can occur in one of four methods: (1) vaporization of the adsorbate with a hot purge gas (thermal-swing adsorption), (2) reduction of pressure to vaporize the adsorbate (pressure-swing adsorption), (3) inert purge stripping without change in temperature or pressure, and (4) displacement desorption by a fluid containing a more strongly adsorbed species. **Chromatography**, on the other hand utilizes packed beds either as solid particles (gas–solid chromatography or a solid–inert support coated with a viscous liquid (gas–liquid chromatography). It is used to separate gas or liquid mixtures by passing them through a packed bed. Because of selective adsorption on the solid surface, or absorption into liquid absorbents followed by desorption, components move through the bed at different rates, thus effecting the separation. **Affinity Chromatography** is where, a macromolecule (a ligate) is selectively adsorbed by a ligand such as an ammonia molecule in a coordination compound that is covalently bonded to a solid-support particle. Ligand–ligate pairs include inhibitors–enzymes, antigens–antibodies, and antibodies–proteins. Finally, **Ion exchange**, though like adsorption, involves a chemical reaction, where for instance in water softening, an organic or inorganic polymer in its sodium form is used to remove calcium ions by a calcium–sodium exchange.

2.3.4 Separations by external field or gradient:

Seader et al 2011, identified another 6 separation processes that utilize this technique as shown in figure 7.

Separation Operation	Initial or Feed Phase	Force Field or Gradient	Industrial Example ^a
Centrifugation (1)	Vapor or liquid	Centrifugal force field	Separation of uranium isotopes
Thermal diffusion (2)	Vapor or liquid	Thermal gradient	Separation of chlorine isotopes
Electrolysis (3)	Liquid	Electrical force field	Concentration of heavy water
Electrodialysis (4)	Liquid	Electrical force field and membrane	Desalinization of sea water
Electrophoresis (5)	Liquid	Electrical force field	Recovery of hemicelluloses
Field-flow fractionation (6)	Liquid	Laminar flow in force field	—

Figure 7: Separation processes by external field or gradient, Source: Seader et al, 2011

Separation by external fields take advantage of how molecules and ions respond differently when subjected to force fields. Separation by **centrifugation** occurs based on molecular weight differences of the component of a mixture under a pressure field, while thermal diffusion utilizes a temperature gradient applied to a homogeneous solution, to create a concentration gradient between the substances. Another process that utilize this separation technique is electrolysis, which operates by decomposing a mixture into its constituent parts, while electrodialysis, utilizes a cation- and anion-permeable membranes with a fixed charge that prevents the migration of species of like charge. This phenomenon is applied in seawater desalination. **Electrophoresis** exploits the different migration velocities of charged colloidal or suspended species in an electric field, where positively charged species, such as dyes, hydroxide sols, and colloids, migrate to the cathode, while most small, suspended, negatively charged particles go to the anode. Migration direction can change readily by changing from an acidic to a basic condition, and this is also why electrophoresis is such a versatile method for

separating biochemicals. Finally, **field-flow fractionation**, another separation technique for biochemicals and heterogeneous mixtures of micromolecular and colloidal materials utilizes an electrical or magnetic field or thermal gradient perpendicular to a laminar-flow field that causes components of the mixture to travel in the flow direction at different velocities. (Seader et al 2011).

3. GENERAL ANALYSIS

Separation operations are mostly driven by thermodynamic and mass transfer processes with occasional chemical reactions with the introduction of catalysts to facilitate the separation process. This section therefore presents the thermodynamic and mass transfer processes involved in separation operations.

3.1 Thermodynamics of Separation Operations:

Thermodynamic properties and equations play significant roles in separation operations, particularly with respect to energy requirements, phase equilibrium and sizing of equipment. The thermodynamic properties of interest include specific volume or density, enthalpy, entropy, availability, and fugacities and activities together with their coefficients, all functions of temperature, pressure, and phase composition. Estimating these properties thus requires formulating equations for energy balance, entropy and availability balances, and for determining phase densities and phase compositions at equilibrium. Since most separation processes utilize large quantities of energy in the form of heat and/or shaft work, any design for an efficient separation process would thus focus on the energy requirements and consumption during the process. This is where the thermodynamics laws become relevant. It is important, that all separation process must satisfy the energy balance in order to avoid inefficient separation processes that would require large transfers of heat and/or shaft work both into and out of the process; efficient processes require smaller levels of heat transfer and/or shaft work. (Colin, 2012).

3.1.1 Energy, Entropy, and Availability Balances:

Separation processes require a lot of energy in the form of heat and/or shaft work, however, the energy requirements differ from process to process. The processes with high energy requirements include distillation, evaporation and drying technologies all of which are thermally driven (based on the heats-of-vaporization of the components) and respectively account for 49%, 20%, and 11% of the industrial separations energy consumption. Others such as extraction, absorption, adsorption, membrane, crystallization and physical property-based operations, on the other hand, are low-energy separation processes. (BCS and Oak Ridge, 2005) Distillation separations alone account for about 3% of the total U.S. energy consumption, especially in the distillation of crude oil into its fractions which is very energy-intensive, and constitute about 40% of the total energy used in crude-oil refining. Therefore the energy requirement in separation process becomes critical in the design and operation of the process. Consider the continuous, steady-state flow system for a general separation process as shown in Figure 8. One or more feed streams flowing into the system are separated into two or more product streams that flow out of the system. Heat flows in or out of the system are denoted by Q , and shaft work crossing the boundary of the system is denoted by W_s . At steady state, if kinetic, potential, and surface energy changes are neglected, the first laws of thermodynamic (also referred to as the conservation of energy or the energy balance), states that the sum of all forms of energy flowing into the system equals the sum of the energy flows leaving the systems: n represents the molar flow rates z_i represents the component mole fractions T represents the temperature P represents the pressure h represents the molar enthalpies s represents the molar entropies b represents the molar availability

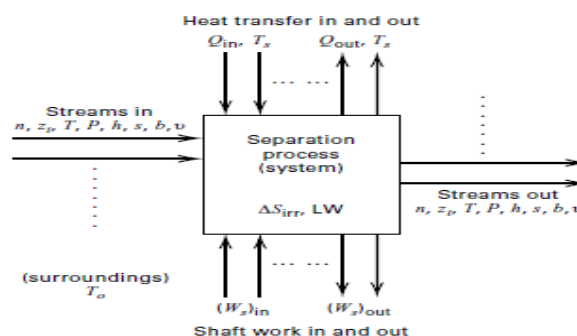


Figure 8: Models of separation process mathematically, under steady state flow gives the Energy, Entropy and Availability Balance equations. Source: Colins, 2012

Energy balance

$$\sum (\text{nh} + \text{Q} + \text{Ws})_{\text{Out of system}} - \sum (\text{nh} + \text{Q} + \text{Ws})_{\text{Into System}} = 0 \quad \text{Equation 4}$$

Entropy balance

$$\sum (\text{ns} + \text{Q}/\text{T}_s)_{\text{Out of system}} - \sum (\text{ns} + \text{Q}/\text{T}_s)_{\text{Into System}} = \Delta S_{\text{irr}} \quad \text{Equation 5}$$

Availability balance

$$\sum [\text{nb} + \text{Q}(1 - \text{T}_0/\text{T}_s) + \text{W}_s]_{\text{Into of system}} - \sum [\text{nb} + \text{Q}(1 - \text{T}_0/\text{T}_s) + \text{W}_s]_{\text{Out of System}} = \text{LW} \quad \text{Equation 6}$$

It should be noted that the first law of thermodynamics provides no information on energy efficiency, which is however, covered in the second law of thermodynamics (also referred to as the entropy balance). Technically, the entropy balance is unlike the energy balance, which states that energy is conserved, the entropy balance predicts the production of entropy, ΔS_{irr} , which is the irreversible increase in the entropy of the universe. This sum, which must be a positive quantity, is a quantitative measure of the thermodynamic inefficiency of a process. In the limit, as a reversible process is approached, ΔS_{irr} tends to zero. It should also be noted that the entropy balance contains no terms related to shaft work. Although ΔS_{irr} is a measure of energy inefficiency, it is difficult to relate to this measure because it does not have the units of energy/time (power). A more useful measure or process inefficiency is thus derived by combining the Energy and Entropy balance equations, to eliminate Q_0 to obtain a combined statement of the first and second laws of thermodynamics, which gives another equation referred to as an availability (or exergy) balance, where the term availability means “available for complete conversion to shaft work.” The stream availability function, b , as defined is a measure of the maximum amount of stream energy that can be converted into shaft work if the stream is taken to the reference state. It is similar to Gibbs free energy, $g = h - T_s$, but differs in that the infinite surrounding temperature, T_0 , appears in the equation instead of the stream temperature, T . It should also be noted that the terms in the availability balance equation containing Q are multiplied by $(1 - T_0/T_s)$ is the reversible Carnot heat-engine cycle efficiency, representing the maximum amount of shaft work that can be produced from Q at T_s , where the residual amount of energy ($Q - W_s$) is transferred as heat to sink at T_0 . Shaft work, W_s , remains at its full value in the availability equation, thus although Q and W_s have the same thermodynamic worth in the energy balance equation, heat transfer has less worth in the availability equation. This is because shaft work can be converted completely to heat (by friction), but heat cannot be converted completely to shaft work unless the heat is available at an infinite temperature. Availability, like entropy, is not conserved in a real, irreversible process. The total availability (i.e., ability to produce shaft work) passing into a system is always greater than the total availability leaving a process. Thus the availability equation is written with “into system” terms first. The difference is the lost work, LW , which is also called the loss of availability (or exergy), and as defined by Lost work is always a positive quantity. The greater its value, the greater is the energy inefficiency. In the lower limit, as a reversible process is approached, lost work tends to zero. (Colin, 2012). Unfortunately, in real terms, the first law condition cannot hold as there are reported inefficiencies due to the entropies within the system, which must be positive, and in the limit, as a reversible process is approached, ΔS_{irr} tends to zero. These inefficiencies expressed as lost work:

$$\eta = W_{\text{min}} / (LW + W_{\text{min}}), \text{ where} \quad \text{Equation 6}$$

$$W_{\text{min}} = \sum \text{nb}_{\text{Out of the system}} - \sum \text{nb}_{\text{Into the system}} \quad \text{Equation 7}$$

Where $b = h - T_0$ = availability function

$LW = T_0 - \Delta S_{\text{irr}}$ = Lost work

W_{min} = Minimum work of separation.

The lost work has the units of energy, thus making it easy to attach significance to its numerical value. To reduce lost work, driving forces for momentum, heat, and mass transfer; and chemical reaction must be reduced. Practical limits to reduction exist because, as driving forces decrease, equipment sizes increase, tending to infinity as driving forces approach zero. For a separation without chemical reaction, the summation of the stream availability functions leaving the process is usually greater than that for streams entering the process. (Seader et al, 2011).

3.1.2 Phase Equilibria:

Phase Equilibrium Analysis of separation equipment relies on Gibbs free energy, chemical potentials, fugacities, and activities. For each phase in a multiphase, multicomponent system, the total Gibbs free energy, G , is where N_i =moles of species, i . At equilibrium, the total G for all phase is a minimum, and methods for determining this minimum are referred to as free-energy minimization techniques. Gibbs free energy is also the starting point for the derivation of commonly used equations for expressing phase equilibrium. From classical thermodynamics, the total differential of G is given by where μ_i is the chemical potential or partial molar Gibbs free energy of species i . (Colin, 2012). Based on the Gibbs free energy, the chemical potential expressed as

$$dG = -SdT + VdP + \sum_{i=1}^c \mu_i dN_i \tag{Equation 8}$$

of each species in the multicomponent system is identical in all phases at equilibrium,

$$\mu_i^1 = \mu_i^2 = \mu_i^3 = \dots = \mu_i^N \tag{Equation 9}$$

However, because the chemical potential approaches an infinite negative value as pressure approaches zero, the chemical potential is not used in phase-equilibria calculations, but the fugacity, which is defined in terms of the partial fugacity of species i in a mixture in terms of the chemical potential by

$$f_i = C \exp(\mu_i/RT) \tag{Equation 10}$$

where C is a temperature-dependent constant. Regardless of the value of C , the chemical potential equilibrium can be replaced in fugacity terms $f_i^1 = f_i^2 = f_i^3 = \dots = f_i^N$

Thus, at equilibrium, a given species has the same partial fugacity in each phase. For a pure component, the partial fugacity, f_i , becomes the pure component fugacity, f_i . For a pure, ideal gas, fugacity equals the total pressure, and for a component in an ideal-gas mixture, the partial fugacity equals its partial pressure. Another useful thermodynamic property is the phase-equilibrium ratio, also known as the K -value defined as the ratio of mole fractions of a species present in two phases at equilibrium. For the vapor-liquid case, the constant is referred to as the K -value or vapor-liquid equilibrium ratio: For the liquid-liquid case, the constant is referred to as the distribution coefficient or liquid-liquid equilibrium ratio. These are expressed mathematically as captured in Seader et al 2011:

$$K = y_i/x_i \text{ for the vapor – liquid case, and} \tag{Equation 11}$$

$$K = x_i^1/x_i^2 \text{ for the liquid–liquid case.} \tag{Equation 12}$$

For equilibrium-stage calculations, separation factors, are defined by forming ratios of equilibrium ratios. For the vapor–liquid case, relative volatility $\alpha_{i,j}$ between components

i and j is given by

$$\alpha_{ij} \equiv \frac{K_i}{K_j} \tag{Equation 13}$$

Separations are easy for very large values of $\alpha_{i,j}$, but become impractical for values close to 1.00.

Similarly for the liquid–liquid case, the relative selectivity $\beta_{i,j}$ is

$$\beta \equiv \frac{K_{Di}/K_{Dj}}{\dots} \tag{Equation 14}$$

3.2 Mass Transfer:

Mass transfer is the movement of any identifiable species from one spatial location to another, which can be macroscopic in nature as in the flow of a fluid in a pipe or in the mechanical transport of solids by a conveyor belt. It can also be as a result of random molecular motion or random microscopic fluid motion in the presence of a composition gradient within a phase. (Kirvvan, 1987). Technically, mass transfer is the transport of one component from a region of higher concentration to that of a lower concentration, something that characterize many of our daily experiences such as the invigorating aroma of a cup of freshly brewed coffee and the sensuous scent of a delicate perfume from the source by diffusion through air. Also, a lump of sugar added to the cup of coffee eventually dissolves and then diffuses uniformly throughout the beverage, while laundry hanging under the sun during a breezy day dries fast because the moisture evaporates and diffuses easily into the relatively dry moving air. Besides the day to day experience in life, mass transfer is also the driver of most industrial processes, especially in operations that involve separating components of mixtures, which is based on the transfer of material from one homogeneous phase to another, with concentration gradient as the driving force for transfer in these operations, much as a temperature gradient provides the driving force for heat transfer. (Seader et al 2011). It should be noted that mass transfer is not bulk transfer movement as a result of pressure differentials as in pumping of a liquid through a pipe, but rather as a result of a concentration difference or gradient, with the diffusing substance moving from a place of high to one of low concentration. (Treybal, 1981). Since separation processes are based on the creation of composition differences within and between phases, a consideration of mass transfer principles is necessary to the analysis and design of such processes. It is the combination of mass transfer principles with phase-equilibrium relationships, energy considerations, and system geometry or configuration that permits the proper description of the separation processes.

3.2.1 Molecular Mass Transfer:

Mass transfer that drives the separation process is dependent mostly on the dynamics of that particular system, and has the following characteristics (1) it depends on concentration gradient of the species or phase differences, (2) the rate of mass transfer between two phases is proportional to their interfacial area and not to the volumes of the phases present. (3) mass transfer owing to microscopic fluid motion or mixing is much more rapid than that due to molecular motion (diffusion), (4) thermodynamics provides a limit to the concentration of a species within a phase and often governs the interfacial compositions during transfer, and finally, (5) temperature has only a modest influence on mass transfer rates under a given concentration driving force. Also, analysis of more complex mass transfer problems are based on three basic concepts namely, conservation laws, rate expressions and equilibrium thermodynamics, which have been treated under section 3.1. Mass can be transferred either by random molecular motion in quiescent fluids, or through a surface into a moving fluid, aided by the dynamic characteristics of the flow. These two distinct modes of transport are referred to as molecular mass transfer and convective mass transfer and are analogous to conduction heat transfer and convective heat transfer. (Kirvvan, 1987). Molecular mass transfer or molecular diffusion is the macroscopic transport of mass, independent of any convection effects within the system, and occurs in fluids that are stagnant, or in laminar or turbulent motion. The laws of mass transfer show the relation between the flux of the diffusing substance and the concentration gradient responsible for this mass transfer. Critical properties of mixture that facilitates mass transfer are the concentration of each species in the mixture, and the total mass concentration, and the velocity flux of the mixture. In a multicomponent mixture, the concentration of particular species, ρ_A can be defined as the mass of A per unit volume of the mixture. The total mass concentration, or density, ρ , is the total mass of the mixture contained in a unit volume; that is,

$$\rho = \sum_{i=1}^n \rho_i \tag{Equation 15}$$

where n is the number of species in the mixture. The mass fraction, ω_A is the mass concentration of species A divided by the total mass density,

$$\omega_A = \frac{\rho_A}{\rho} \tag{Equation 16}$$

The sum of the mass fractions, by definition, must be 1: consequently, the molar concentration of species A, c_A , is defined as the number of moles of A present per unit volume of the mixture. By definition, 1 mole of any species contains a mass equivalent to its molecular weight; therefore, the mass concentration and the molar concentration are related by

$$C_A = \frac{p_A}{M_A} \quad \text{Equation 17}$$

where M_A is the molecular weight of species **A**. When dealing with a gas phase under conditions in which the ideal gas law applies, the molar concentration is given by

$$C_A = \frac{p_A}{RT} \quad \text{Equation 18}$$

where p_A is the partial pressure of the species **A** in the mixture, T is the absolute temperature, and R is the gas constant. The total molar concentration, c , is the total moles of mixture contained in a unit volume; that is,

$$c = \sum_{i=1}^n c_i \quad \text{Equation 19}$$

The mole fraction for liquid or solid mixtures, x_A , and for gaseous mixtures, y_A , are the molar concentrations of species **A** divided by the total molar concentration:

$$x_A = \frac{c_A}{c} \quad \text{(liquids and solids)} \quad \text{Equation 20}$$

$$y_A = \frac{c_A}{c} \quad \text{(gases)} \quad \text{Equation 21}$$

The next set of properties are the velocities and fluxes of the species that define the molecular diffusion of the species in a multicomponent system. The molecular diffusion of the species which are dependent on the different velocities of the species, are better described in terms of the fluxes of a given species. This is the basis of Fick's first law, which states that a species can have a velocity relative to the mass or molar-average velocity (called diffusion velocity) only if gradients in the concentration exist. The molar fluxes are described as vector quantities that denote the amount of the particular species, in either mass or molar units, that passes per given unit time through a unit area normal to the vector. As a vector quantity, the flux may be defined with reference to coordinates that are fixed in space, or are moving with the mass-average velocity, or coordinates which are moving with the molar-average velocity. (Benitez, 2009). Seader et al 2011, showed that diffusion of species **A** with respect to **B** occurs due to the following driving forces: concentration gradients of species, (ordinary diffusion), pressure, temperature (thermal diffusion), and external force fields that act unequally on different species. Pressure diffusion requires a large gradient, which is achieved for gas mixtures with a centrifuge. Thermal diffusion columns can be employed to separate mixtures by establishing a temperature gradient. More widely applied is forced diffusion of ions in an electrical field. Fick's first law also features a proportionality between a flux and a gradient. For a mixture of **A** and **B**,

$$J_{Az} = -D_{AB} \frac{dc_A}{dz} \quad \text{Equation 22}$$

and

$$J_{Bz} = -D_{BA} \frac{dc_B}{dz} \quad \text{Equation 23}$$

where J_{Az} is the molar flux of **A** by ordinary molecular diffusion relative to the molar-average velocity of the mixture in the z -direction, D_{AB} is the mutual diffusion coefficient or diffusivity of **A** in **B**, c_A is the molar concentration of **A**, and dc_A/dz the concentration gradient of **A**, which is negative in the direction of diffusion. The fluxes of **A** and **B** are in opposite directions. If the medium through which diffusion occurs is isotropic, then values of k and D_{AB} are independent of direction. Non isotropic (anisotropic) materials include fibrous and composite solids as well as noncubic crystals.

(Seader et al 2011). Basmadjian, 2005, noted a third mode of diffusive transport, momentum that is induced by the molecular motion of the species. Momentum is the product of the mass of the molecular species and its velocity in a particular direction, for example, v_x .

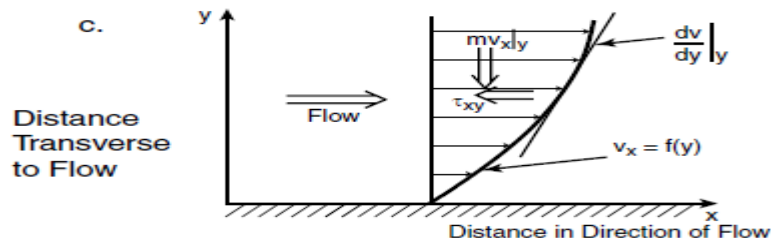


Figure 9: Momentum diffusion transport. Source: Basmadjian, 2005.

As in the case of the flow of mass and heat, the diffusive transport is driven the velocity gradient dv_x/dy transversing to the direction of flow as shown in figure 9. As the molecules enter a region of lower velocity, a braking force acts on them, so they relinquish part of their momentum to the slower particles in that region and are consequently slowed. The braking force is expressed in terms of a shear stress $F_x/A = \tau_{yx}$ pointing in a direction opposite to that of the flow. The first subscript on the shear stress denotes the direction in which it varies, and the second subscript refers to the direction of the equivalent momentum mv_x . The relation between the induced shear stress and the velocity gradient is attributable to Newton and is termed Newton's viscosity law. It is, like Fick's and Fourier's law, a linear negative relation and is given by

$$F_x / A = \tau_{yx} = -\mu \frac{dv_x}{dy} \quad \text{Equation 24}$$

and this can be rewritten to be

$$\tau_{yx} = -\frac{\mu}{\rho} \frac{d(\rho v_x)}{dy} = -\nu \frac{d(\rho v_x)}{dy} \quad \text{Equation 25}$$

where ν is termed the kinematic viscosity in units of m^2/s and the product of density ρ and velocity v_x can be regarded as a momentum concentration in units of $(kg \ m/s)/m^3$. This version of Newton's viscosity law brings it in line with the concentration-driven expressions for diffusive heat and mass transport, (Basmadjian, 2005).

3.2.2 Convective Mass Transfer:

Mass transfer by convection involves the transport of material between a boundary surface and a moving fluid, or between two relatively immiscible moving fluids, and depends strongly on the transport properties and dynamic characteristics of the flowing fluid. When a fluid flows across a solid surface under conditions that produces turbulence, molecular diffusion creates a laminar flow region close to the surface, while the fluid particles immediately adjacent to the solid boundary are at rest. This stagnant film of fluid creates resistance to convective mass transfer, however, under most convective conditions, this film is extremely thin and its thickness is virtually impossible to measure or predict theoretically under the concept of molecular diffusion alone. With increasing distance from the surface, the flow increasingly become turbulent to the point where the particles of fluid begin to flow in relatively large portions of the fluid, called eddies. These eddies, which are the sources of the mass transfer, move rapidly from one point to another with velocities in the direction perpendicular to the the surface. Because the eddy motion is rapid, mass transfer in the turbulent region is much more rapid than it would be under laminar flow conditions. This situation cannot be modeled in terms of Fick's law. Instead, it is explained in terms of a mass-transfer coefficient, an approximate engineering idea that simplifies the analysis of a very complex problem. (Benitez, 2009)

3.2.3 Mass Transfer Coefficients:

A large number of practical mass transfer applications involve transport between phases in complex flow situations: the turbulent flow of a fluid in a tubular membrane, the counter current flow of gas and liquid in a packed column gas absorber, or the dispersion of droplets in an agitated vessel. These flow conditions require conceptual models,

experimental observations, and correlative methods to obtain estimates useful for engineering analysis and design, and this is where the concept of mass transfer coefficient becomes relevant. Mass transfer coefficient is thus defined as the ratio of the molar (or mass) flux of a species across a particular surface to the composition difference causing the transfer of mass. (Kirvvan, 1987). Estimating the mass transfer coefficient will require knowledge of the flux, N_A under molecular diffusion, and can be approximated by using the kinetic theory model for molecular diffusion for gas. This is because of the difficulty in approximating the mechanism of the flow process involving the eddies in the turbulent region. The formula for the Flux under a Steady State Molecular Diffusion in fluids at rest and in laminar flow is given as

$$N_A = \frac{N_A}{N_A + N_B} \frac{D_{AB} \ln \frac{N_A / (N_A + N_B) - C_{A2} / C}{N_A / (N_A + N_B) - C_{A1} / C}}{Z} \quad \text{Equation 26}$$

Where N_A and N_B are the fluxes for components A and N, and D_{AB} is the diffusion coefficient of component A in Solution B, while C_A/C is the molar fraction concentration.

Therefore replacing D_{AB}/Z in the Molecular Diffusion equation with F , which is the Mass transfer coefficient gives;

$$N_A = \frac{N_A}{N_A + N_B} F \frac{\ln \frac{N_A / (N_A + N_B) - C_{A2} / C}{N_A / (N_A + N_B) - C_{A1} / C}}{1} \quad \text{Equation 27}$$

N_A is the flux at the phase interface or boundary where substance A with a mass transfer coefficient, F , enters or leaves the phase. The flux, N_A depends on the molar concentrations, c_{A1} and c_{A2} . Also, how these concentrations are defined will determine the value of the mass transfer coefficient, F , since the mass transfer coefficient is a local phenomenon, defined for a particular location, and can thus vary along the surface. This brings in an average value for F_{av} with constant C_{A1} and C_{A2} which takes into account these variations in F . The effect of variation in C_{A1} and C_{A2} on the flux must be accounted separately. (Treybal, 1981). According to Matar, 2014, the mass transfer coefficient in the liquid- liquid extraction experiment which is also called the distribution coefficient (KD), is the concentration of the solute in the extracting solvent / the concentration of the solute in the original solvent. The extracting solvent is good if $KD > 1$ & KD could be 1 (i.e. the solute is distributed evenly between the 2 solvents 50:50) or could be less than one. If $KD < 1$, it would mean that the extractive solvent is ineffective and require a replacement for a better extracting solvent for the solute.

3.2.4 The Film Theory of Mass Transfer:

The resistance to mass transfer in a given turbulent fluid phase is in a thin, relatively stagnant region at the interface, called a film, which is like the laminar sublayer that forms when a fluid flows in the turbulent regime parallel to a flat plate. (Seader etal, 2011). This film as was earlier pointed out in section 3.2.2 that when a fluid flows past a solid surface under conditions such that turbulence generally prevails, molecular diffusion creates a region close to the surface where the flow is predominantly laminar and the fluid particles immediately adjacent to the solid boundary are at rest. This stagnant film of fluid creates resistance to convective mass transfer, however, under most convective conditions, this film is extremely thin.

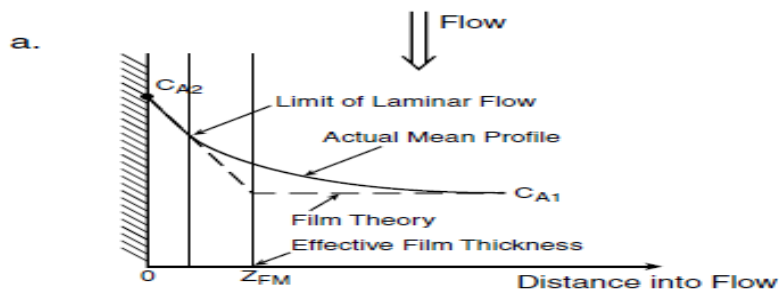


Figure 10: The effective film in the transport of mass. Source: Seader etal, 2011

Figure 10 thus depicts turbulent flow of either a gas or liquid past a liquid or solid boundary shown crosshatched on the left. That boundary can be the confining wall of a duct, or the interface separating two phases. Mass transfer is assumed to occur from a concentration C_{A2} of the boundary to a lower concentration C_{A1} in the bulk of the flowing fluid. This can come about if the boundary consists of a soluble substance or if a volatile liquid evaporates into a flowing gas stream. Mass transfer takes place initially through a laminar sublayer, or boundary layer, which is located immediately adjacent to

the interface. This layer is followed by a transition zone where the flow gradually changes to the turbulent conditions prevailing in the bulk of the fluid. However, in the main body of the fluid, macroscopic packets of fluid or eddies move rapidly from one position to another, including the direction toward and away from the boundary. Mass transfer in both the transition zone and the fully turbulent region is relatively rapid and contributes much less to the overall transport resistance than the laminar sublayer.

This increase in fluid velocity creates an attendant increase in the degree of turbulence which causes the eddies to penetrate more deeply into the transition and boundary layers, which also gradually wears out the boundary layer in thickness and the transport rate experiences a corresponding increase in magnitude. High mass transfer rate therefore occurs with a greater degree of turbulence. Now, because concentrations in the turbulent regime typically fluctuate around a mean value, making it difficult to quantify in order to fit into a rate law, the concentration profile is thus approximated as an equivalent linear concentration profile that extends from the boundary into the bulk fluid. This postulate forms part of the film theory, and the dimension of the film in question is termed the effective film thickness, denoted as z_{FM} . The film theory can be quantified into a rate law using Fick's law, and applying it to the constant gradient of film theory gives

$$N_A/N = \frac{D(C_{A2} - C_{A1})}{z_{FM}} = K_c(\Delta C_A) \quad \text{Equation 28}$$

The ratio of diffusivity to film thickness D/z_{FM} is coalesced into a single term called the mass transfer coefficient k_c .

3.2.5 The Two-Film Theory:

Gas-liquid and liquid-liquid separation processes involve two fluid phases in contact and require consideration of mass-transfer resistances in both phases. This led to the concept of two film theory by extending the film theory in series with each film presenting a resistance to mass transfer. This theory assumes that the concentrations in the two fluids at the interface are in phase equilibrium, such that there is no additional interfacial resistance to mass transfer. The challenge with this assumption is that though it is widely used, the assumption may not be valid when gradients of interfacial tension are established during mass transfer, as these gradients give rise to interfacial turbulence, resulting, most often, in considerably increased mass-transfer coefficients. This phenomenon is referred to as the Marangoni effect, and usually occurs at vapor-liquid and liquid-liquid interfaces, with the latter having received the most attention. However, by adding surfactants, which concentrate at the interface, the Marangoni effect is reduced because of interface stabilization, even to the extent that an interfacial mass-transfer resistance (which causes the mass-transfer coefficient to be reduced) results. (Seader et al, 2011).

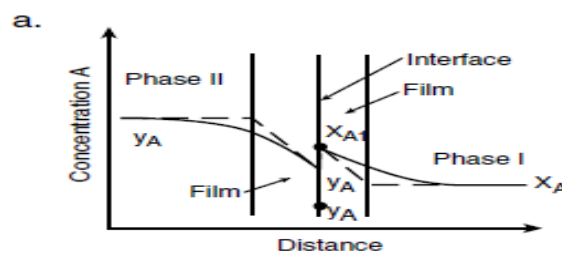


Figure 11: The two-film concept: mass transfer: Source, Seader et al, 2011

The two-film theory is explained in figure 11, where two phases, I and II are in turbulent flow and in contact with each other. Transport takes place in the first place, from a high concentration y_A through the effective film associated with Phase II to the interface. Here the Phase II concentration y_{Ai} is assumed to be in equilibrium with the Phase I interfacial concentration x_{Ai} , so that $y_{Ai} = m x_{Ai}$. Now for practical use, as neither of the interfacial concentrations x_{Ai} or y_{Ai} is generally known, an equivalent rate law is postulated below:

$$N_A/A = K_{oy}(y_A - y_A^*) \quad \text{Equation 29}$$

$$N_A/A = K_{ox}(x_A^* - x_A) \quad \text{Equation 30}$$

where K_{oy} and K_{ox} are termed overall mass transfer coefficients and the asterisked quantities are the concentrations in equilibrium with the bulk concentration of the neighboring phase.

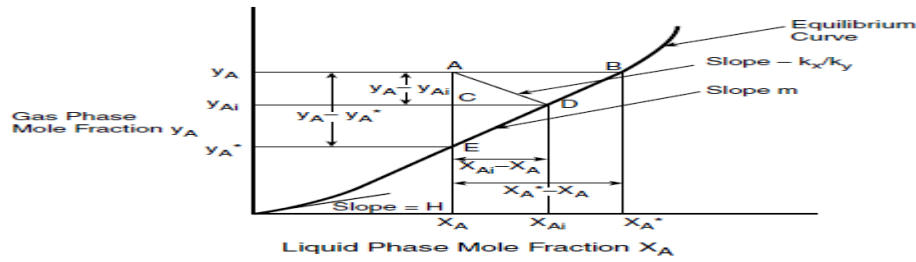


Figure 12: The driving forces in a two-film flow, Source: Basmadjian, 2005.

These overall coefficients are widely used to describe transport between two flowing phases in contact with each other and are usually determined experimentally and reported as lumped averages over the span of equilibrium constants m encountered in the operation. (Basmadjian, 2005).

4. ACTUALIZATION

This section presents the application of advanced separation processes in biodiesel production and purification.

Fossil fuel, especially crude oil and gas has dominated the global energy mix since World War II, and with it comes the challenges of global warming from greenhouse gases emissions, non-renewable and depleting resources, price hike of crude oil, and environmental pollution, all of which are key factors that have led to the quest for alternative energy sources. Some of the reliable alternative energy sources capable of replacing fuels include water, solar and wind energy, and biofuels, even though fossil fuel still constitutes about 86% of the total global energy consumed and close to a 100% utility in the transportation sector. (Atadashi et al, 2011). In all these renewable sources, biodiesel has been identified as one of the most suitable replacement of fossil fuel in the transportation and power sectors. Biodiesel, has been shown to have several advantages over the fossil fuel such as: it is safe, renewable, non-toxic, and biodegradable; it contains no sulphur; and it is a better lubricant. In addition, its use engenders numerous societal benefits: rural revitalization, creation of new jobs, and reduced global warming. (Aransiola et al, 2013). Biodiesel also known as fatty acid alkyl esters, as a substitute to diesel fuel, since they have hydrocarbon chains in the range of diesel fuel (C12-C18), is produced from renewable natural sources such non-edible vegetable oils, animal fats, as well as algae and waste oils, so that they do not cause any food vs fuel conflict, consist mainly of triglycerides and free fatty acids (FFAs). (Bateni et al, 2017). Besides being a renewable source, biodiesel is also carbon neutral, as biodiesel yielding plants such as jatropha curcas, rape plant and palm trees absorb carbon-dioxide to a greater extent than that contributed to the atmosphere when used as fuel in diesel engines. Also though biodiesel has similar physicochemical properties to that of fossil fuel diesel and can therefore be used directly to run existing diesel engines without major modifications or as a mixture with petroleum diesel and produces less harmful gas emission such as sulfur oxide, Atadashi et al, 2011 reported that the direct use of vegetable oils as fuel in compression ignition engines is problematic due to their high viscosity (about $11e^{17}$ times greater than diesel fuel) and low volatility. The high viscosity can be improved with transesterification reaction, a chemical reaction involving triglycerides and an alcohol of lower molecular weights using homogeneous or heterogeneous substances as catalyst to yield biodiesel and glycerol. However, the reaction has several drawbacks: it is energy intensive; recovery of glycerol is difficult; the catalyst has to be removed from the product; alkaline wastewater requires treatment and free fatty acids (FFA) and water interfere with the reaction. The presence of water lowers the activity of catalyst, while FFA react with the catalyst to produce saponified product, of which the produced soap can reduce the biodiesel yield and causes significant difficulty in product separation and purification. Thus, biodiesel and by product, glycerol must be refined by washing with hot deionized water two to three times, leading to high waste of time, energy and water. This is the major limiting factor to biomass use, the separation and purification technology and its transformation into biochemicals and biofuels. Bateni et al, 2011 also added that, ineffective biodiesel separation and purification causes severe diesel engines problems such as plugging of filters, coking on injectors, more carbon deposits, excessive engine wear, oil ring sticking, engine knocking, and thickening and gelling of lubricating oil. Biodiesel must therefore be profited to meet set down regional market specifications, and though density differences between biodiesel and glycerol are significant for gravitational and centrifugation separation, these will not purify the product to specifications. Further purification is required to remove impurities (i.e., remaining vegetable oil, alcohol, catalyst, soap, and FFAs) in order to meet the

standard specifications introduced in ASTM D6571 or EN14214. Such qualitative product that can meet market specification, according to Atadashi et al 2011, requires advanced separation and purification techniques that can effectively separate biodiesel from the glycol by-product. This is a more efficient technique than the conventional and simple separation techniques which are time and energy consuming, and less cost effective, such as gravitational settling, centrifugation, decantation, filtration and biodiesel purification such as water washing, acid washing, and washing with ether and absorbents. Other factors such as intense mixing, formation of emulsion, solubility of biodiesel in glycerol, and glycerol in biodiesel, would also not allow for such simple separation techniques to produce the desired quality of biodiesel.

4.1 Advanced Separation and Purification Processes of Biodiesel:

Biodiesel is a clean, biodegradable, and non-toxic diesel substitute produced via the transesterification of triglycerides with an alcohol in the presence of a proper catalyst. After initial separation of the by-product (glycerol), the crude biodiesel needs to be purified to meet the standard specifications prior to marketing. The presence of impurities in the biodiesel not only significantly affects its engine performance but also complicates its handling and storage. Also, the main adverse properties of biodiesel, namely moisture absorption, corrosiveness, and high viscosity, primarily arise from the presence of oxygen. Bateni et al (2017) classified biodiesel purification methods based on the nature of the process into equilibrium-based, affinity-based, membrane-based, reaction-based, and solid-liquid separation processes. This is shown in figure 13.

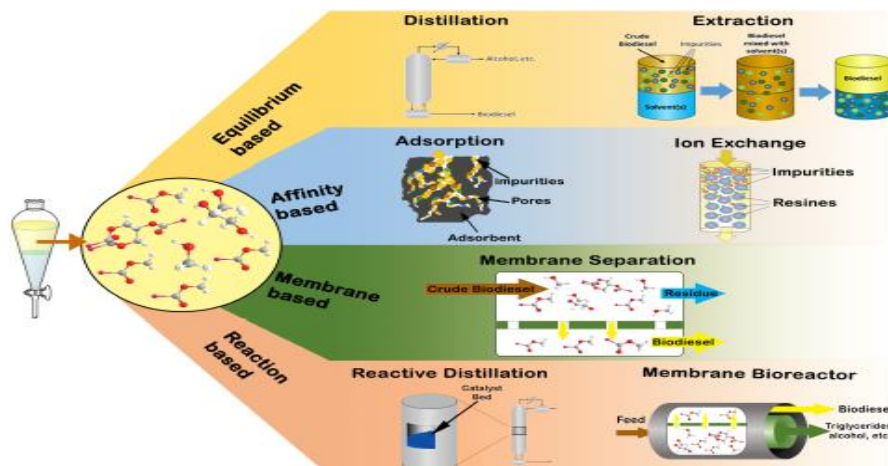


Figure 13: Classification of Biodiesel purification process. Source: Beteni et al 2017

4.1.1 Equilibrium-based separation processes:

Equilibrium based separation process includes absorption, distillation, as well as supercritical fluid extraction and liquid-liquid extraction (LLE). However, since absorption is commonly utilized for separating particles and impurities from a gaseous mixture, it does not have a major application in biodiesel separation. This paper only discussed distillation process under this category.

4.1.1.1 Distillation:

Distillation is the most common method for separation of more volatile compounds from heavier substances in a liquid mixture. There are different distillation techniques which are (Beteni et al 2017) conventional distillation (ordinary, vacuum, and steam distillation), azeotropic distillation, extractive distillation, and molecular distillation (MD). Conventional distillation and evaporation are perhaps by far the most common methods used in biodiesel purification to remove remaining alcohol or water from the crude biodiesel. Typically, the unreacted alcohol is separated from biodiesel prior to further purification. In molecular distillation, carried out under high-vacuum, the molecules' free path is longer than the evaporation and condenser surface distance; therefore, most of the evaporated molecules reach the condensing surface without being deflected on collision with foreign gas molecules, resulting in a higher separation yield. Besides removal of glycerol, Dhar and Kirtania,(2009) also identified the challenges with excess methanol in the biodiesel production that must be removed for better biodiesel quality. Methanol is widely used as primary alcohol in biodiesel production, and most biodiesel production process use excess methanol to get high yield, which must be removed to maintain the 0.2% methanol content of most biodiesel, since excess methanol in the biodiesel fuel is toxic and hazardous

to life and the environment. Excess methanol can also make the fuel flammable and more dangerous to handle and store. Though distillation can do the separation very efficiently, but it is high in energy consumption. So, a typical methanol recovery process consisting of two methanol recovery units is utilized as depicted by Dhar and Kirtania,(2009) in figure 14.

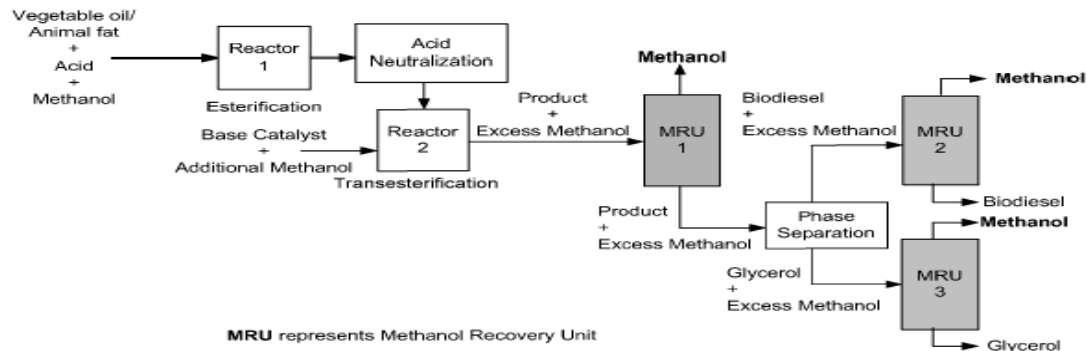


Figure 14: Process Flow Diagram of a Two Steps Biodiesel Production Process with possible Methanol Recovery units. Source: Dhar and Kirtania,(2009).

4.1.1.2 Liquid-liquid extraction:

This is the most common wet washing biodiesel purification method. Also known as solvent extraction, liquid-liquid extraction (LLE), is a well-established separation technique to extract desirable component(s) from a liquid feed to a specific solvent. Beteni et al, 2017 reported that while increasing water temperature and volume can significantly decrease glycerol content from 0.0933% to 0.09%, increasing the water temperature can result in higher water content in the final biodiesel, and may also result in the formation of emulsions and biodiesel losses. They further reported the use of acidified water followed by water wash to produce effective purification. However, the use of acidified water causes the hydrolysis of soap to FFAs which will subsequently decreases the tendency of emulsification and can also increase the acidity of the final product. Additionally, excess water must be removed from the biodiesel to achieve required specification. Beteni et al, 2017 also reported the use of ionic liquids (ILs) for biodiesel purification. Ionic liquids (ILs) are green solvents due to their non-flammable, non-volatile, and reusable properties, with additional properties of been able to dissolve different organic, inorganic, and organometallic materials. They are, however, relatively expensive compared to a cheaper Deep Eutectic Solvents (DES) with excellent solvent characterizations such as biodegradability, non-toxicity, and non-reactivity with water. Beteni et al 2017, reported that 51% glycerol removal was obtained when an eutectic mixture/biodiesel ratio of 1:1 was used for the eutectic mixture of choline chloride/glycerol (1:1). It was also reported that choline chloride combined with either ethylene glycol or 2,2,2-trifluoroacetamide was used as two series of DESs for biodiesel purification with effective results. Also, glycerol, KOH, mono- and diglycerides from the biodiesel could be effectively removed with the DES formed using methyltriphenylphosphonium bromide and ethylene glycol.

4.1.2 Affinity-based separation processes:

Two separation methods readily fall within this process, and these are adsorption and ion exchange, where an appropriate adsorbent is used to selectively adsorb certain impurities from the liquid phase onto its surface. Also known as dry-washing, Beteni et al 2017, stated that affinity based processes offer several advantages over wet washing, including ease of integration into an existing plant, shorter purification time, no water consumption and wastewater production, and smaller unit sizes. The absence of water in purification of biodiesel during dry washing produces biodiesel with acceptable water content (less than 500 ppm) based on ASTM D6751.

4.1.2.1 Adsorption:

Adsorption is the process by which atoms, ions, or molecules, known as adsorbates, from a substance (mostly liquid or gas) adhere to a solid surface, called the adsorbent. Adsorption differs from absorption; in absorption, the component penetrates or dissolves in the bulk of the adsorbent while surface adhesion occurs during adsorption. Adsorbents are natural or synthetic materials of amorphous or microcrystalline structures that with their basic and acidic adsorption sites can readily adsorb and filter out polar substances such as glycerol and methanol out of biodiesel. According to Beteni et al

2017, four types of adsorbents are known in biodiesel purification and these are Silica-based adsorbents (e.g., Magnesol and Trisyl), bio-based adsorbents such as (ligno) cellulosic substrates based and activated compounds, including AC, activated fiber, and activated clay. The choice of a particular adsorbent therefore depends on adsorption loading, selectivity, regenerability, kinetics, compatibility, and cost as the proper adsorbent can positively impact the process economy.

4.1.2. 1.1 Silica-based adsorbents:

Common adsorbents used in the industry include silica-gel, zeolites, and molecular sieves, with silica gel as the readily available. As an amorphous inorganic mesoporous adsorbent, silica gel is produced via polymerization of silicic acid, with a hydrophilic surface due to the presence of hydroxyl groups which gives it the property as an adsorbent for water, alcohol, and other polar molecules. Beteni et al 2017, reported that silica is highly effective even in the presence of small amounts of water and soaps as it removes glycerol, and monoglycerides from biodiesel synthesized from waste cooking oil. However, it was observed that the presence of methanol decreased the effective saturation capacity of glycerol by about half due to the affinity effect of methanol on silica surface and glycerol (in liquid phase). Silica also performed well in separating FFAs from the biodiesel produced from non-catalytic biodiesel production using supercritical methanol. Other types of silica according to Beteni et al 2017, that have shown promises in biodiesel purification include natural low silica content bentonite, Magnesol, an inorganic matrix of magnesium silicate and anhydrous sodium sulfate offering a great potential for selective adsorption of hydrophilic impurities of crude biodiesel.

4.1.2.1.2 Biomass-based adsorbent:

Biomass based adsorbents such as cellulosic and lignocellulosic substrates besides been inexpensive, in abundance, renewable, biocompatible, and non-toxic, have also been reported as effective adsorbents for biodiesel purification, especially in simple and small scale biodiesel plants. (Beteni et al 2017). Common biomass based adsorbent include corn starch and rice starch and potato. Regardless of the adsorbent type and content, it was found that the acidity index decreased, while the free glycerol content of the biodiesel, normally about 0.13% was completely removed after purification using 5% potato starch, 1-2% cassava starch, and 1% rice starch. Also, turbidity, showing the presence of impurities in the biodiesel, was significantly decreased in the case of using 5% potato starch or 1-2% cassava starch.

4.1.2.1.3 Activated compounds:

Activated compounds such as activated fiber (carbon fiber), and activated alumina are among the most common adsorbents in industrial applications due to their large porous volume and high surface area. Activated fiber are manufactured from any carbonaceous organics, e.g., sawdust, petroleum coke, wood, charcoal, peat, fruit nuts, bituminous coal, lignite, and coconut shells. According to Beteni et al 2017, the porous structure can be activated either through steam where the substrate is heated at 400-500 °C in an oxygen-free atmosphere to remove the volatile components (carbonization step), followed by oxidization using steam (or carbon dioxide) at 800-1000 °C. It can also be activated through chemical activation performed via impregnation of the substrate with a strong dehydration agent (e.g., phosphoric acid or zinc chloride), followed by heating to 500-800 °C, washing, drying, and grinding. Activated alumina on the other hand, are produced through thermal dehydration of hydrated alumina and recrystallization. Activated alumina has Lewis acid sites on its surface that makes it a suitable adsorbent for polar compounds and oxygenates such as alcohols, aldehydes, ketones, and carboxylic acids. Beteni et al 2017 reported that the use of activated compounds produced biodiesel with 91.50-93.75% purity with respect to water washed product (86-89%) on both feedstocks.

4.1.2.2 Ion exchange:

Ion exchange is the process of exchanging the ions between the solution and a proper solid phase (exchanger) due to a stronger affinity (electrostatic force) between the target species and the functional groups on the surface. Ion exchangers consist of a matrix with excess charges localized in specific sites of the structure. They are categorized based on the functionality and according to their strength (density of the charge) into strongly acidic cation-, weakly acidic cation-, strongly basic anion-, and weakly basic anion-exchange resins. The strong acid cation resins are the most common exchange resins such as T45BD and T45BDMP (Thermax) along with BD10 Dry (Dow Chemical) are used in industrial biodiesel purification. These resins showed great glycerol affinity through filtration, physical adsorption, ion exchange, and soap removal. Beteni et al, 2017, reported that resins showed a better performance for sodium soap removal compared with potassium soap and decreasing the particle size further improved the process in the case of sodium soaps. They further noted that the ion exchange resins can also effectively remove the metallic compounds leached out of a solid catalyst to the liquid phase (biodiesel) in the case of heterogeneous catalysis transesterification.

4.1.3. Solid-liquid separation processes:

This process is limited mostly to filtration after heterogenous transesterification or biodiesel purification by a dry washing method. As one of the main mechanism for soap removal, filtration method is more effective in the absence of methanol especially in the case of sodium soaps. It has been reported that, contrary to potassium soaps which are considered soft soaps, sodium soaps are hard soaps showing the tendency to solidify and make a gel-like layer at room temperature. Therefore, sodium soaps can be separated from biodiesel more effectively (Beteni et al, 2017).

4.1.4 Membrane-based separation techniques:

The goal of a membrane filtration system is to selectively permeate the fatty acid methyl esters (FAMES) component of a typical biodiesel product. It is thus a low or no-water alternative in the purification of crude biodiesel, and thus with its cost advantages due to the lack of wastewater, membrane technology prevents the formation of emulsion in the product, facilitating two-phase separation. (Beteni et al 2017). Atadashi et al 2015, indicated that the separation of solution components via membrane is achieved by restricting the passing of unwanted material via a semi-permeable barrier in a selective manner. The transportation using membrane is affected by diffusion of individual molecules, temperature or pressure gradient and concentration difference. Membranes are thus classified into organic and inorganic membranes. The organic membranes include polysulfone, polyamide, polycarbonate and a number of additional highly developed polymers, which are comprised of improved resistance to microbial degradation and chemical stability. Polyacrylonitrile (PAN) is an asymmetric and porous membrane which joins high permeation rate and high selectivity, while polymeric membranes may swell up, and result in either instant swelling or long-term pore-size changes, which can potentially lead to short life span. On the other hand, inorganic membranes such as ceramic membranes (Al₂O₃, TiO₂, ZrO₂, SiC) have great potentials toward aiding purification processes. The inorganic membranes have been tested to be superior to organic membranes in terms of increased resistance to fouling, long lifetime, narrower pore size distribution, mechanical, thermal, and chemical stability, resistance to microbial degradation, high flux, and high porosity. Atadashi et al, 2015 added that the common membrane separation technologies include reverse osmosis (RO), ultrafiltration (UF), and microfiltration (MF). Other membrane separation are mainly a size exclusion-based pressure-driven process, that is based on shapes and the sizes or weight of the particles. Separation by membrane is affected by interactions between membrane surface and components of the feed, velocity of flow, temperature, pressure, and membrane composition. Atadashi et al 2011, also added other benefits that membrane equipment has over the conventional separation processes such as eradication/minimization of higher capital cost and other related costs of production, plus the provision of high specific area of mass transfer.

4.1.4.1 Organic Membrane:

Glycerol as reported by Beteni et al, 2017, is difficult to separate from the final biodiesel product for the biodiesel to meet international standards, and this is where organic membranes becomes critical in the separation process. Generally, and based on its composition, glycerol forms droplets of varying sizes from 250 nm in pure FAME to more than 2500 nm in 0.06 wt.% water, making it necessary for the use of organic membrane with smaller pores than the glycerol droplets to facilitate the separation of these droplets. Beteni et al 2017, further reported that a modified hydrophilic polyacrylonitrile membrane at 100 kDa NMWCO was able to separate glycerol more easily with higher water contents – from 3% in pure FAME to 63% in 0.2 wt.% water after 180 min of time on stream. For a poly(ether-sulfone) membrane at 10 kDa NMWCO, small additions of water (up to 0.2 wt.% by mass) drastically improved glycerol removal, from 0.02% to 0.009% glycerol in the permeate. This glycerol/water miscibility directly contributes to a two-phase flow that is crucial for separation. However, soap and methanol, tend to complicate the mechanism of separation as they increase glycerol solubility. Beteni et al, 2017, also noted that these organic membranes showed varying degree of successes depending on their hydrophilicity or corresponding hydrophobicity. A hydrophilic membrane is less susceptible to fouling from a variety of biorefinery feeds due to the water content but is more susceptible to deformation due to pH and temperature swings, while a hydrophobic material is more useful for the separation of oils. Also, They in addition to the high purity (97.5%) biodiesel, the membrane extraction method had an additional advantage in successfully decreasing ester losses that endemic to water and acid washing methods. The report showed that 10.1 wt.% esters were lost even at the optimum temperature of 50 °C with distilled water due to emulsification. The polysulfone and polyacrylonitrile membranes, by contrast, were able to purify biodiesel with only 8.1 wt.% and 10.3 wt.% ester losses. However, the polyacrylonitrile membrane could tolerate higher water content in the final biodiesel product than any other methods, making it perhaps unsuitable for biodiesel refining. The polysulfone membrane additionally led to the highest purity of biodiesel at roughly 99% without additional steps.

4.1.4.2 Inorganic Membrane:

Inorganic membranes have an alpha-alumina support structure with titanium oxide or zirconium oxide that have far more positive qualities over organic membranes, such as increased fouling, temperature and pH fluctuation resistance, and a longer time-on-stream. These qualities, according to Beteni et al 2017, gives inorganic membranes the added property to effectively work with the base catalysts used in transesterification reactions that is endemic to biodiesel production. Also, its increased resistances have helped unhindered separation of a FAME-rich permeate flow from an unreacted retentate during transesterification along the length of a membrane bioreactor. According to Atadashi et al, 2011, the development of membrane reactor technology in the production of biodiesel has reasonably reduced the complicated separation and purification of crude biodiesel. This technology has led to the successful separation of the unreacted emulsified oil from the transesterified products which is a key factor in the production of biodiesel. There has been further attempts to also purify crude biodiesel without the use of water washing process, even though water washing process proved critical to the production of economically viable biodiesel. Atadashi et al 2011 further reported the excellent performance of ceramic membranes in the biodiesel refining process. Using different membrane sizes of 0.1 mm, 0.2 mm and 0.6 mm, temperatures of 30, 40, 50, 60, and 70 degC, and transmembrane pressures of 0.05 and 0.2 MPa, the results of the content of potassium, sodium, calcium, magnesium and free glycerol recorded were far better than those obtained when water washing was employed.

In his further work on biodiesel purification, Atadashi 2015 showed that ceramic membrane technique using micro- and ultrafiltration effectively removes glycerol from biodiesel. The microfiltration was deployed with tubular Al₂O₃/TiO₂ ceramic membranes, with average pore size of 0.2, 0.4, and 0.8 μm, and filtration area of 0.005 m². The biodiesel samples were microfiltered at a temperature of 60 C, and transmembrane pressures of 1.0, 2.0, and 3.0 bar, and using a feed solution with 5% ethanol, this technique, which is highly efficient, produced lowest flux decline rate and 99.6% glycerol retention, as well as minimizing energy usage. In order to achieve biodiesel fuel that meets ASTM D6751 standard specifications, a ceramic membrane with a pore size of 0.02 μm, under best operating conditions at temperature of 40 C, flow rate, 150 L/min and transmembrane pressure, 2 bar were used. The results show permeate flux of 9.08 (kg/m² h), with corresponding potassium value of 0.297 mg/L and free glycerol value of 0.007 wt.%; which are quite lower than those specified by ASTM D6751 standard specifications, while physical properties of the biodiesel are also comparable to those of ASTM D6751 and EN 14214 standards.

4.2 Role of Membranes in Sustainable Energy:

According to Roy and Ragnath (2018), membrane technologies are increasingly adopted in many industries because of their low energy requirements. This separation technique is supporting the alternative energy industry through the application of membrane technologies in Proton-exchange membrane fuel cells (PEMFCs) commonly used in automotive applications for their rapid start-up and shutdown capabilities. These membranes are also capable of withstanding thermal shock and high temperature corrosion. There is also significant progress in the design and process conditioning in enhancing the stability and performance of the anion exchange membrane fuel cell (AEMFC). The applications of PEMFCs have been increasing in transportation, and portable and stationary power generation systems. In transportation, PEMFCs have replaced internal combustion engine units in many lightweight vehicles, utility vehicles and regular domestic vehicles, which range from 20 kW to 250 kW, due to their higher efficiency and lower greenhouse gas emissions

5. DISCUSSIONS

This section presents some of the progresses in separation technology, the challenges inherent in some of them, and the innovations and other developments that proffer optimal separation processes.

Separation process has grown to become a major global economic driver representing 60 to 80% of the CAPEX (equipment) and OPEX (energy requirement) of production costs in Chemical Process Industry (CPI) plants since world war II. Chemical process industry now produces about 105 different molecules at capacities ranging from less than one kilo to 300 million tons per year. With this growth, separation processes if they must meet both current and future demands, requires a series of efficiency indicators, such as the possibility of reaching the specifications imposed by the application (e.g., purity and recovery), the energy requirement, the productivity of the process, and the environmental and risk efficiencies (quantity of waste generated, explosion hazard, etc.) to measure their progress and performance. (Favre, 2020). It is important therefore to design separation processes to create high selectivity, capacity, and throughput and that

are robust over time, all of which may be dependent on the selection of appropriate materials. This would no longer require designers to rely on the current fundamental knowledge of the static and dynamic properties of interfaces, and how matter interacts in complex environments. Rather, separation scientists now use many concepts such as reversible-reaction chemistry, enthalpic attractions between molecules, and differing diffusivities based on molecular size in order to appropriately design a separation system that are more selective, with higher capacity and higher throughput, and that can be effective for more complex mixtures and in more challenging environments. (National Academies of Sciences, Engineering, and Medicine 2019). One of such remarkable evolution is the commercial adoption of membrane-based separation technique for water desalination through reverse-osmosis technology, to replace the traditional energy intensive evaporation method to remove salt from water. With the low energy intensity, reverse-osmosis technology has now become a dominant technology in all new commercial desalination installations, with the prospects of providing access to clean and portable water for hundreds of millions of people. One point of note is that modern reverse osmosis membranes require about twice the thermodynamic minimum energy, which can adversely affect the membrane longevity in regard to fouling, pre-treatment, and post-treatment condition. More improvements are thus required to remedy these challenges. A second example of commodity-scale separations in which nonthermal methods are becoming widespread is the use of adsorption or membranes for separating oxygen or nitrogen from air. (National Academies of Sciences, Engineering, and Medicine 2019).

5.1 Challenges with Separation Processes:

One other major challenge is the high-energy intensity processes of some of the key industrial separation process such as distillation, evaporation and drying technologies that are thermally driven (based on the heats-of-vaporization of the components) and which respectively account for 49%, 20%, and 11% of the industrial separations energy consumption. On the other hand, extraction, absorption, adsorption, membrane, crystallization and physical property-based operations utilize much less energy in their separation processes. Figure 15 is a chart showing the relative energy consumption of each separation process.

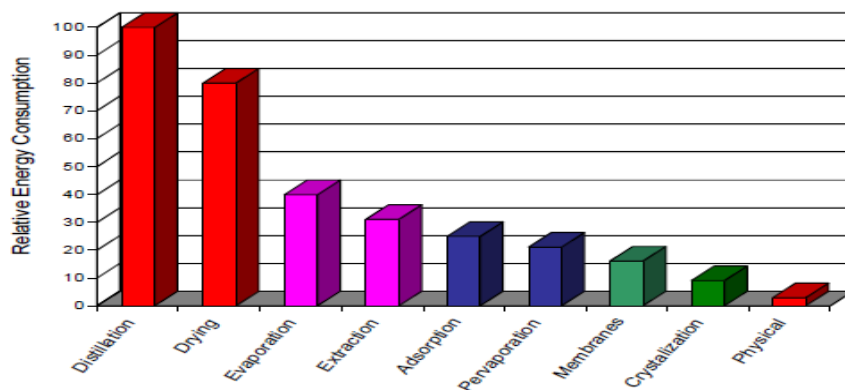


Figure 15: Relative energy consumption of various separation process: Source: (BCS and Oak Ridge, 2005)

It is obvious from the chart that moving separation processes towards the low energy intensity techniques, especially in the United States can potentially save an estimated \$4 billion in energy costs a year. Besides the challenges with high energy intensity processes, some chemical industries also discharge pollutants into the environment with adverse effects on human health and the environment. As part of the drive for sustainability of the chemical enterprise, a practical solution is to reduce the use of solvents, and also use more sustainable solvents in the separation process, and to also to remove heavy metals and other contaminants from wastewater before discharge. One other separation difficulty is the separation of compounds that are similar in size as in the separation of carbon dioxide from a gas mixture or potentially separation of oxygen from air for use in oxyfuel combustion. This process is the most energy-intensive and capital-intensive part of carbon sequestration process, and can be resolved through the use of membrane separation technology, that has potential of reducing carbon dioxide emissions by 100 million tons a year. This will in turn further reduce carbon emissions relative to climate-change initiatives. Finally, improving the processes in separation of rare-earth metals from ores or used electronic components could lead to more efficient recovery more useful materials and reduce waste generation and unwanted products. Rare earth metals are important resources that are used regularly in magnets, in renewable-energy technologies, and as catalysts in petroleum refining. (National Academies of Sciences, Engineering, and Medicine 2019).

5.1.1 Challenges with Through-Put and Capacity:

Through-put of a separation process is the rate at which a given flow or input stream is processed, and therefore a critical measure that determines whether a separation concept can advance to practical applications. The throughput of membrane system, and hence the net rate of separation, and the overall productivity of the system, is measured by the continuous running, and the flux of the species (the rate at which it passes) through the membrane. On the other hand, the main determinant of throughput in a batch operation, such as chromatography, is the capacity of the column. This notwithstanding, what determines the overall efficiency of the system is the overall cycle processing time (the time it takes to process all the species). One of the factors that has adversely affected throughput, especially in membrane process is fouling, especially during the early use of synthetic-membrane filtration for biotechnology, food and beverage production (such as cheese, beer, and wine production), and protein production and purification. Technically, fouling leads to a rapid decline in membrane performance, such as decreased permeation rates and adverse changes in selectivity. Ofcourse these limitations are being resolved through the redesigning of membrane modules with short path lengths, the use of polar instead of nonpolar membrane surfaces and improvements in mass transfer and fluid mechanics. Also, many membranes today are coated with regenerated cellulose to reduce fouling and prevent target proteins from denaturing. These solutions, have popularized the use of membrane technology in variety of applications such as such as in the production of monoclonal antibodies (major protein products in the biotechnology industry), in the use of filters for buffer, and in conjunction with chromatography for product purification and concentration. (National Academies of Sciences, Engineering, and Medicine 2019).

5.2 Advances and Improvements in Separation Processes:

Separation science has evolved over the years with solutions to some of the inherent challenges and limitations facing the industry, with ever increasing spending in research and development for more pragmatic and optimal solutions. One of such improvements is in the area of energy efficiency, through the use of reverse-osmosis membranes for desalination, which has significantly reduced power consumption of the reverse osmosis from over 15 kWh/m in 1970 to less than 2 kWh/m³ in 2008 making reverse osmosis a clear choice over evaporation. (National Academies of Sciences, Engineering, and Medicine 2019). One of the greatest benefits in ensuring energy efficiency comes from re-engineering and improving the distillation process which is widely used throughout the chemical and petroleum refining industries as shown in table 3. Distillation operations in the chemicals and petroleum refining industries alone account for almost 53% of the total separation energy used, while petroleum refining, consumes 1,460 TBtu/yr in separations energy, and is one of the most separation energy-intensive industries globally. According a report by BCS, 2005, distillation process operate at thermal efficiencies as low as 6%, which of course implies a huge potential for significant process improvements in energy and environmental performance. However, the majority of distillation in refining provides thermal (heat of vaporization) “cuts” indicating that low-energy intensity alternatives to distillation that use different separation mechanisms and would not yield the same products. Membranes and adsorbents could potentially replace distillation for relatively “clean” chemical separations such as gas recovery and yield 10 TBtu/yr in savings.

Table 3: Energy consumption of various distillation processes: (BCS and Oak Ridge, 2005)

Feed	Typical Components Light/Heavy Key	Distillation Energy Consumption
Petroleum	gasoline/naptha	26%
Crude oil	light naptha/heavy naptha/light distillate	22%
Liquefied petroleum gas (LPG)	ethane/propane/butane	11%
Olefins	ethylene/ethane, propylene/propane	6%
Miscellaneous hydrocarbons	cumene/phenol, acetone/acrylonitrile	5%
Water—oxygenated hydrocarbons	methanol/water, water/acetic acid	5%
Aromatics	ethylbenzene/styrene, benzene/toluene	4%
Water—inorganics	ammonia/water	3%
Air	nitrogen/oxygen	1%
Water—hydrocarbons	p-xylene/water	1%
Other		16%

Source: Humphrey and Keller, Separation Process Technology, McGraw-Hill, 1997, page 292

According to Bravo, 2019, there has been remarkable advancements in distillation processes in the past three decades in the areas of : thermodynamics and thermodynamic efficiency, process configurations, process simulations, process control, column internal design, column peripherals (e.g., heat transfer), reliability and availability, operation in harsh environments and in diagnostics. This is shown in table 4. Bravo 2019, further reported significant development in the area of tray technology : multiple-downcomer trays, minivalves (fixed and movable), truncated-downcomer trays, push valves, non-chordal downcomers, small sieve holes, umbrella downcomers, dynamically sealed downcomers, fast-installation

designs, fouling-resistant designs, and centrifugal aids. According to Bravo 2019, these improvements offer better performance at a reasonable cost without requiring complex fabrication, as in the case of truncated-downcomer trays which increase vapor capacity due to its more useable bubbling area, while fouling-resistant designs keep distillation columns in service for longer period. Other areas with significant improvements in the distillation technology as reported by Bravo, 2019, include: enhancement of heat transfer in boilers and condensers systems, through the retrofitting older shell-and-tube heat exchangers with new tubes. This has also reduced capital expenditure; extractive distillation for use with higher-boiling-point solvents; reactive distillation, which adds a reactant and/or catalyst to cause a reversible and selective reaction with one of the feed components; homogeneous azeotropic distillation, which includes an entrainer to form a minimum- or maximum-boiling-point azeotrope with one or more of the feed compounds; heterogeneous azeotropic distillation, which uses an entrainer to form a minimum-boiling-point heterogeneous azeotrope; pressure-swing distillation for pressure-sensitive azeotropes and at distillation boundaries; steam distillation, which adds steam to reduce the temperature of the distilling organic mixture and finally salt distillation, which dissolves a soluble ionic salt into the reflux to alter the relative volatilities of the feed. Additional areas of major improvement in distillation technology is in process intensification, which focuses on smaller, cleaner, safer, and more energy-efficient processes, and one of such area is reactive distillation, in which chemical reactions take place in the distillation column. Reactive distillation is now commonly used in fuel-ether and chemical-ester production in which the reactions depend on equilibrium conditions. There is also catalytic distillation process, in which the heterogeneous catalyst is packed in the distillation column and used for some hydrogenation processes to recover products efficiently and selectively. One other area of the intensification process is in divided-wall columns, which effectively combine multiple distillation columns into a single column, that has the capability of isolating multiple product streams from one unit. There is also the hybrid separation systems, which is an alternative to complex distillation schemes, that combines older and newer technologies to create a cost-effective upgrades that improve manufacturing process rates and capacities. This is seen in the combination of novel membrane separation with conventional distillation for the separation of olefins and paraffin. This hybrid system combines the low energy of membrane and the high purity of distillation process to produce a better product at lower energy consumption. (National Academies of Sciences, Engineering, and Medicine 2019.) Other areas of innovation that can increase both throughput, such as in pressure swing adsorption, where structured contactors can allow cycle times that are far shorter or driving forces that are much smaller than are possible with more traditional packed bed. Advances in separation technology have also helped in the handling of more complex substances by increasing the speed and capacity of the separation system. This was noted when Ultrapformance liquid chromatography with particles that are typically less than 2 μm in diameter is subjected to a column inlet pressures as high as 15,000 psi, in the presence of superficially porous packing materials. The result is an ultrafast separation within minutes and sometimes in less than a second with high efficiency, typically by a factor of 8 to 10 compared with 5- μm particles. Other examples of high-throughput systems that can separate complex mixtures are multidimensional analytical separation systems, such as comprehensive gas chromatography (GC \times GC) and comprehensive liquid chromatography (LC \times LC). GC \times GC includes an initial separation in one column and then fast transfer to a second column with different selectivity. It is used in petroleum characterization, odorant separations, and metabolomics. Hundreds or even thousands of compounds can be separated with this method, and better separation can be achieved with a multidimensional approach for very complex volatile or semi volatile mixtures. (National Academies of Sciences, Engineering, and Medicine 2019. Finally, there is an ongoing investigation in the modelling of the separation process to shift from fossil fuel feedstock to renewable raw materials (e.g., starch, cellulose, lipids, or proteins extracted from plants or trees), through the biorefinery concept. According to Favre, 2020, this will significantly change the distillation processes as it will handle more aqueous feed mixtures rather than the organic feed for classical, oil-based refineries. Besides biorefineries, more advanced concepts, such as e-refineries based on electricity as the energy vector and CO₂ as the carbon source, are also currently being investigated.

6. GENERAL RECOMMENDATIONS

Separation technology is a constantly evolving system in view of the dominant roles it now play in the global energy and overall economic wellbeing of everybody. While there are enormous benefits in the use of separation processes, there is also increasing need to continuously progress towards more advanced and sustainable systems to combine its benefits with the environment and health of the users. Specifically, while the world is moving towards renewable energy, fossil fuel, such as oil and gas still dominate the power and transportation industry, both of which are dependent on the high energy intensive distillation process. There are concerted efforts at reducing the energy consumption of distillation process, however, according to Sholl and Lively, 2016, finding an alternative to distillation poses some challenges since crude oil contains many complex molecules, some with high viscosities, and myriad contaminants, including sulfur

compounds and metals such as mercury and nickel. While it is feasible in principle to separate hydrocarbons according to their molecular properties, such as chemical affinity or molecular size, there is need for further investigation on how to create a hybrid separation of the low energy membrane based separation methods, and the high quality distillation system to make this huge energy savings of 100% fully distillation process. Sholl and Lively, 2016, further opined that, establishing a sustainable and efficient separation system requires huge capital expenditure and this is where the economics and sustainability of any separation technology need to be evaluated in the context of a whole chemical process. It is critical that performance metrics such as cost per kilogram of product and energy use per kilogram, and the lifetime and replacement costs of components such as membrane modules or sorbent materials be factored in the entire economic modelling of the separation process. Given its long term benefit and cost component, achieving the global benefits of a new separation technology would also require long term planning involving all stakeholders, which will amongst other things include physical infrastructure such as academic and industrially operated test beds that will translate the new technologies from the lab to pilot scales so that any perceived risk can be reduced. The critical stakeholders include the academia, government agencies and industry partners. Finally, it will also require continuous training and reskilling of the workforce, especially, chemical engineers and chemists in current and innovative separations technologies and processes, not only in the traditional distillation system, but also in such as adsorption, crystallization and membranes .

7. CONCLUSION

The purpose of a chemical separation process is generally to enrich a product stream in one or more of the components of the original mixture, and to also divide the mixture fully into its pure components. At the simplest level, separation can be physical using centrifuge and or decanters or by simple chemical separation through boiling and condensing water to eliminate salts or preferentially evaporating a more volatile component from a mixture. However, more advanced separation processes are required at sustainable industrial scales such as distillation columns or the use of specialized membrane that interacts with specific constituents to affect their permeabilities and thus separates them. No doubt separation processes are vital to numerous industries, including the oil and gas industry, chemical and pharmaceutical manufacturing, biotechnology, food production, water desalination and purification, and waste management and treatment. They are critical for providing clean water and air to the world's population, extracting natural resources for energy storage and use, and delivering effective and affordable health care. (National Academies of Sciences, Engineering, and Medicine 2019). While it has enormous benefits, less optimized separation process are energy intensive coupled with creation of products that are hazardous to the environment and human health. Such systems also are very capital intensive and thus affect the redistribution of available resources to other growth sectors of the economy. However, because of its ever increasing application in many industrial sectors, there has also been concerted efforts at research and development in the field of separation science and technology in order to create more energy efficient with better selectivity, through put, and capacity systems, with less and less pollutants into the environment. In all of these innovations, the low energy intensive membrane technology but with low quality system is been investigated to improve its selectivity, throughput, capacity in order to provide alternative systems for the high energy, high cost, but high quality distillation process, which the process that currently handles fossil fuel that is used predominantly in the transport system. Investigations are also on how to efficiently utilize renewable feedstock in biorefinery system as the next transportation and power fuel. Finally, because this is an evolving technology with a long term vision, creating a sustainable and efficient and cost effective separation system will require the collaborations of all stakeholders from the industry to government and the academia, in order for an early development of any model.

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