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Simulated Moving Bed Technology: Overview and Use in Biorefineries

Deepak Sharma

Abstract

Synthesis of chemical compounds oftentimes produce a mixture of desired and undesired components. The ease of purification and recovery of the desired component more often than not determines the viability of the production technology. Simulated Moving Bed (SMB) technology is a continuous purification and separation technique with better performance (less solvent consumption and higher throughput) than traditional batch chromatography. SMB is a continuous separation technology which can be used to achieve the desired product purity with considerably lower power and raw material consumption. A lot of research and development is undergoing in the SMB technology which is enabling the search for more economical and carbon neutral ways of producing industrial chemicals. SMB has proven to be of great assistance in extracting products produced in biorefinery fermentation processes in an economical and energy efficient fashion. This chapter outlines the various processes the author has developed using SMB technology, its use in biorefineries, and prospective use in the future.

Keywords: Simulated Moving Bed, Chromatography, Adsorption, SMB, Purification, Separation, Unit operation, Manufacturing, Adsorbent, Desorbent, Extract, Raffinate, Biorefinery

1. Introduction

Simulated Moving Bed (SMB) technology is an improvement over the traditional batch chromatography to a continuous chromatography process. SMB allows scale-up of lab chromatography process for high production outputs needed in the chemical industry. Most chemical reactions also produce many byproducts along with the desired product. Therefore, many purification steps are needed in order to achieve the desired purity of the final product. Synthesis of products have traditionally been given more importance in the chemical industry. The recovery and purification of desired product is often more time consuming and costly in comparison to the synthesis reaction. There are several widely employed purification techniques, such as distillation, crystallization, filtration etc. Almost every chemical manufacturing operation requires the use of purification process to achieve the desired product purity. Oftentimes the choice and efficiency of the selected purification technology determines the quality and cost of the product. Liquid-phase adsorption has traditionally been used in the industry to remove specific by-products produced

during synthesis of industrial chemicals. Batch chromatography used for purification of feed streams use principles such as adsorption, size exclusion, complexation, ion-exchange, hydrogen bonds or a combination of these mechanism. SMB chromatographic technique was first used in the petrochemical industry in the 1940s [1]. In this chapter the author focuses on use of SMB in the energy, pharmaceutical, and nutraceutical industry and how the use of this technology enables the development of greener and sustainable process.

2. Background

Batch chromatography has been used in the industry for several years, however, the technology has suffered from low yield, high solvent consumption, poor column utilization and high product dilution. SMB technology was developed to overcome the limitations of batch chromatography and convert it into continuous process. The very nascent form of SMB technology dates all the way back to the 1840s where fixed beds and moving ports to simulate a counter current movement of liquids and solids was first used in Shank's system for leaching [2]. A family of SMB processes were developed by UOP LLC (Des Plaines, Illinois, U.S.) for the petrochemical industry. Some of the processes industrialized by UOP were Parex for the recovery of para-xylene, Molex for the separation of linear paraffins, Ebex for the separation of ethyl benzene from a mixture of C8 aromatic isomers, Olex for the separation of paraffins and olefins. Until 1970 most of the processes for SMB technology were in the petrochemical industry. The sugar industry started seeing SMB process development around 1980s when UOP developed the Sarex sugar purification process [3, 4]. In 1990s the use of SMB technology in pharmaceutical industry caught speed. Several processes were developed using chiral stationary phase [5–7]. SMB technology has found its use in almost all chemical industries including pharmaceutical, petrochemical, waste removal, enzyme separation, organic acid separation, purification of fine chemicals. Traditionally SMB technology has only been used for binary separations i.e. two component or at most three components. Most recently there has been developments in SMB technology to separate multiple components from a complex feed stream. The author has developed several complex SMB processes that are outlined in this chapter.

3. Separation principles for batch chromatography and SMB

In batch chromatography a column is packed with adsorbent material which is called the stationary phase or sorbent. The stationary phase is determined based on the characteristics of the feed stream. Typical stationary phase used are carbon, silica gel, alumina, modified silica etc. Once the column is packed it is flushed with a mobile phase. Mobile phase is a single solvent or a mixture of solvents that are decided based on the solute solvent interactions. Similar to analytical chromatography the feed solution is injected into the column and then eluted with the mobile phase called desorbent. Mobile phase and desorbent will be interchangeably used in this chapter. The components of the feed that have higher affinity for the sorbent are referred to have a higher partition coefficient. Having a higher partition coefficient means that the component is strongly bound to the sorbent so has a higher concentration on the sorbent than in the mobile phase. Since only the components in the mobile phase migrate with the desorbent a higher affinity feed component migrates slower than a low affinity feed component thereby creating a concentration gradient in the column resulting in separation of the various feed components.

Batch chromatography can be used to separate such components by collecting the desired product in one vessel and reject byproducts to a separate vessel. In most industrial applications there are components in the feed that either have a higher affinity or lower affinity than the desired product. A higher degree of separation is desired from the two undesired components to achieve a pure product. In an ideal world one would assume that one can easily achieve this in a single column with a reasonable column length. In practice this is not feasible as the short column length does not give enough run length to the components, as a result of which both purity and yield is compromised. To overcome this drawback of single column separation, SMB technology was developed to provide the much-desired solution.

SMB technology overcomes most of the shortcomings of batch chromatography. In a SMB several identical columns are connected in series. **Figure 1** shows eight columns connected in series such that the outlet from one column is connected to the inlet of the next column. In this figure the desorbent enters the first column and feed enters the fifth column. The feed in this illustration contains two components A and B. The fast-moving component A is removed in the raffinate stream which comes out from the bottom of column # 7. The component B, which is strongly adsorbed on to the stationary phase, is tapped from the bottom of column # 3, labeled as extract. The inlet and outlet ports divide the eight-column setup connected in series into four zones. Each zone in a SMB has different flow rate. The ports move periodically along the loop to follow the migrating solute bands. On every switch of SMB port, the desorbent and feed move one column downstream to the inlets of column 2 and column 7 respectively. Even the extract and raffinate port move one column downstream and are drawn from column 3 and column 8 respectively.

The inlet and outlet streams determine the various zones in the SMB. The zone between the desorbent inlet and extract outlet is zone I which is called the desorption zone. The zone between the extract and feed port is zone II which is called the

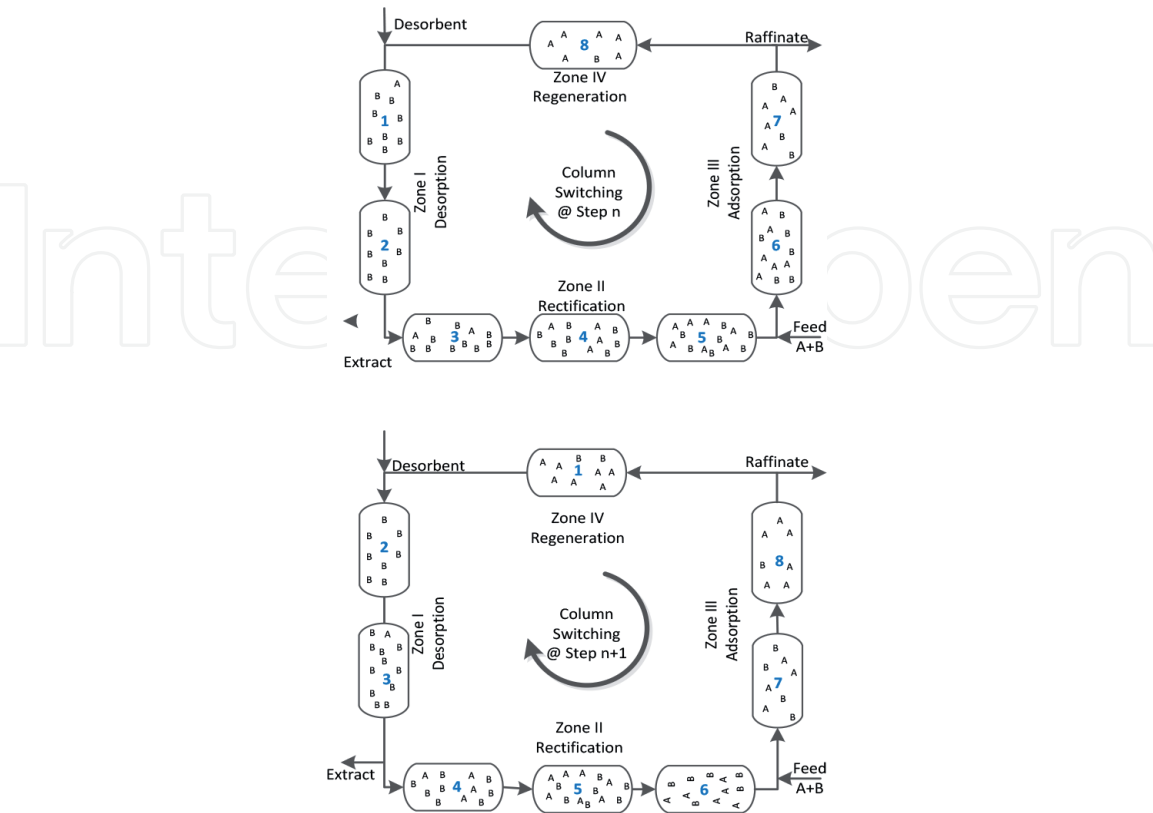


Figure 1.
SMB setup with column switch illustration.

rectification zone. The zone between the feed port and the raffinate port is zone III which is called the adsorption zone. The zone between the raffinate and desorbent is zone IV which is called the regeneration zone. The column switch time is determined carefully such that the slow-moving feed component B never reaches the raffinate port and the fast-moving component A never reaches the extract port. Fine tuning the switching time ensures the fast-moving component A only come out from the raffinate port and the slow-moving feed component B only comes out of the extract port. The setup can be optimized to achieve the desired product purity and yield. This periodic port switching achieves a simulated counter current movement of the solid phase with respect to the mobile phase. This enables a continuous process where the desired product can be continuously produced.

4. Advantages of SMB technology

There are several advantages of using SMB over batch chromatography or any other industrial purification technologies. One of the advantages of SMB is the continuous purification of feed components achieved at high product purity and yield. SMB also considerably reduces the amount of desorbent usage over batch chromatography. The continuous regeneration of the adsorbent in a single setup also reduces the usage of adsorbents considerably thereby increasing the overall adsorbent utilization. The reduced consumption of desorbent [8] and adsorbent makes this a greener process as it enables in reducing the carbon footprint of achieving the same purification with higher efficiency. These improvements also lend its advantage to cost savings not only in operating cost but also in capital cost by requiring a smaller footprint, equipment size, and manpower. More importantly, SMB technology is particularly useful in biorefineries as it is naturally favorable for the low concentration product stream from biorefineries. Fermentation reactors are typically limited by the concentration of product one can achieve in the fermenter before the producing organisms get deactivated. The low concentration is favorable for adsorption, making SBM the preferred technology to achieve economic purification of the products.

Biorefineries particularly face a huge challenge in isolating the desired products from the reaction mixer. The cost of separation and purification account for a large portion of costs in biorefineries. SMB provides the much-required cost effective solution which makes biorefinery production feasible and competitive to traditional synthetic production techniques.

5. Shortcomings of SMB technology

In the past decade a lot of technological development has happened in the field of SMB technology. The author has enabled the commercialization of some of the purification processes. An SMB process involves a complex design which requires a lot of inputs. A typical 4 zone SMB requires research on multiple lab-scale experiments to determine the flow rate of feed, desorbent, extract, and raffinate. Along with that the frequency of switching the columns need to be determined, the zone length for each of the four zones, and the operating temperature. A total of ten design parameters need to be identified for the successful run of SMB setup.

During startup of SMB processes all the ten parameters need to be developed using experimental setups and scaled up to parameters for the manufacturing unit. Every run of the SMB setup involves optimization which leads to production of off spec product. Even slight variation in any parameter can easily disturb the

equilibrium of the entire process. Moreover, some parameters drift and are heavily dependent on accuracy of pump flow rate and varying pressure drop in the different columns.

6. SMB operation

In this setup the author will compare SMB process with a hypothetical moving-bed system shown in **Figure 2**. In the schematic the desorbent D moves from the top to bottom counter current to the adsorbent which moves from bottom to top. The desorbent chosen is a solute which has a lower boiling point than the feed components. This setup explains separation of a binary mixture A and B. Component A is the faster moving component and does not interact with the adsorbent as much as B does. Component B is adsorbed selectively on to the adsorbent. As shown in the **Figure 2** feed enters the column at a particular point on the column. The desorbent moves the faster moving component A which has little interaction with the adsorbent with it and comes out with the desorbent from the raffinate which is right below the feed point. The adsorbent moves the component B due to increased interaction with the adsorbent and come out at the extract port right above the feed.

The inlet and outlet of streams split the entire column into 4 zones:

Zone 1: This is the desorption zone. The zone between extract and desorbent is called the desorption zone. In this zone component B is removed from the adsorbent (solid).

Zone 2: This is this rectification zone. The zone between the feed and extract is called the rectification zone. In this zone component B is selectively enriched on the adsorbent over component A.

Zone 3: This is the adsorption zone. The zone between the raffinate and feed is called the adsorption zone. In this zone component B is adsorbed on the adsorbent (solid).

Zone 4: This is the regeneration zone. The zone between the desorbent and raffinate is called the regeneration zone. This zone acts as a buffer to prevent component B from reaching the raffinate port.

In practice there are two types of continuous chromatography operations prevalent in the industry. Moving bed operation [9] where the actual adsorbent bed

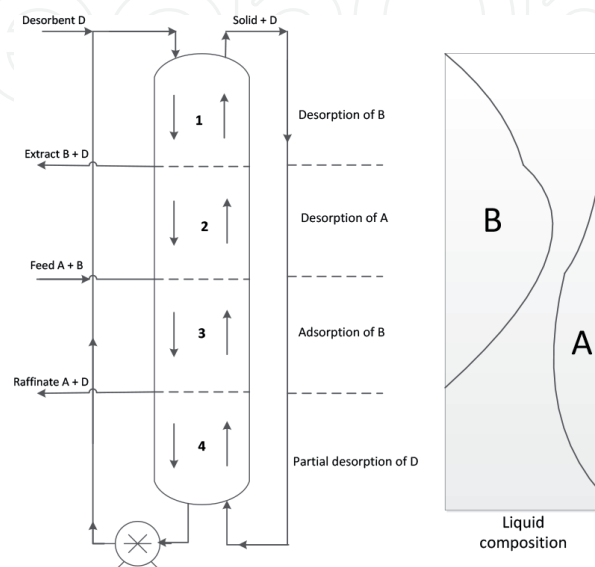


Figure 2.
Illustrating SMB as a distillation column.

moves and another one is a simulated moving bed [10] where the movement of the beds is simulated by series of valves [11, 12].

7. SMB parameters

7.1 Adsorbate-adsorbent interaction

Selection of separation technology employed for any particular application is determined by the phase relation that can be developed using various separative agents. Adsorption is a complex phenomenon compared to any other form of separation technique employed in the industry. Adsorption is typically used as a last resort when none of the other separation techniques are practically feasible.

Interaction of components that are intended to be purified need to have selectivity for the adsorbent that is chosen for purification. Moreover, there needs to be enough selectivity between components to achieve a higher purity and yield of the components. There is not much literature on adsorbate-adsorbent interaction. The only literature available is covered in patents [13–21]. With the little that has been established it has been concluded that the selection of adsorbent is more of an art than science.

7.2 Adsorbents used in the industry

The choice of an adsorbent for any adsorption process is primarily governed by four parameters; mass transfer rate, capacity, long-term stability, and selectivity. Adsorbents traditionally used in the industry are silica, activated alumina, and activated carbon due to their large micropore volume and surface area.

As a rule of thumb silica and alumina are used for polar components. Equilibrium data published in the literature [13–20] can be used to identify a suitable adsorbent. The order of affinity of various chemical species is; saturated hydrocarbons, aromatic hydrocarbon, halogenated hydrocarbons, ethers, esters, ketones, amines, alcohols, carboxylic acids [10]. For non-polar components the widely used adsorbent is activated carbon or modified silica. Equilibrium data is available in the literature for activated carbon [13, 14, 18–20]. Polymeric resins are mostly used in the pharmaceutical and food industry. Polymeric resins have ionic properties which have shown selectivity for cation-anion exchangers and sugar separations [21]. Resins are primarily used in aqueous phase separations.

7.3 Normal phase

Normal phase adsorbents are primarily adsorbents that are polar in nature. Polar adsorbents can either have a solid base or the solid base can be modified by chemically bonding a polar molecule to a solid base. Separations using normal phase chromatography typically use non-polar solvents or solvent mixtures with somewhat lower polarity than the adsorbent. Separations using normal phase chromatography separates molecules in order of increasing polarity. For products that are generated in biorefineries in a non-polar medium, one can use normal phase adsorbent to achieve the desired separation.

7.4 Reverse-phase

In reverse phase chromatography the adsorbent is non-polar and the solvent used is polar. Like the name suggests separation using reverse phase

chromatography separates molecules in reverse order of polarity. Most commonly used adsorbents for reverse phase chromatography are silica base adsorbent bonded with trimethyl, octadecyl, cyano, butyl, octyl ligands. Reverse-phase chromatography packings find its application as both physically adsorbed-phase and bonded-phase materials, application of bonded-phase packaging have dominated the industry since the early 1980's. Fermentation products that generate products in polar medium can use reverse-phase stationary phase to achieve the separation.

7.5 Ion-exchange

As the name suggests ion-exchange separates solute molecules based on their ionic interaction with the adsorbent. Adsorbents used for ion exchange are composed of a base material like silica or a cross linked polymer primarily with a pore diameter range of 10 to 100 nm derivatized with negatively or positively charged ligands. The ligands chosen determine if the adsorbent would be a weak or strong ion-exchange resin based on the pH range they are operated in. In addition to extraction of Tagatose from a mixture of glucose and galactose from a biorefinery discussed in Section 9.1, Ion exchange has been used in biorefineries to remove inhibitors from biomass hydrolysate (acid, salts), carboxylic acid, impurities in biodiesel (glycerol, methanol, soap etc.), purification of succinic acid and many other.

7.6 Size exclusion

Size exclusion chromatography is used to separate molecules based on their molecular size. Another name for size exclusion chromatography is gel permeation chromatography. Pore size of the adsorbent determines the size of molecule the adsorbent can separate. Operating pressure of the apparatus is very critical when using size exclusion chromatography. Adsorbents used for size exclusion chromatography are carbohydrates (soft gels) or carbohydrates cross linked with agarose or acrylamides or silica 5–10 micron in diameter possessing a controlled pore size distribution.

Recently there have been several advances in the development of new sorbent materials. New adsorbents like acrylamide gels and microscopic rods of silica are being developed for chromatography application.

7.7 Desorbent selection

Selection of desorbent is equally important to the selection of adsorbent. Even though the desorbent is an inert solvent that is not a desired product, particular attention needs to be paid to the selection of the desorbent to ensure it does not compete for the adsorption sites and reduce the active sites available for the components to be separated. Another factor to consider is the boiling point of the desorbent should be somewhat different than the components to be separated so that the separated products can be easily recovered. Lower boiling point of the desorbent also favors the economics of the process. A sweet balance between safety and stripping cost should be given due consideration while selecting a desorbent. Low boiling solvents can cause a flammability hazard mitigating which can turn out to be costly for operation.

8. Lab experiments for scale-up of SMB

Every process that is commercialized and produced in the industry goes through a discovery phase. Like any other unit operation even SMB process has unique

experimental setup's that can be used to determine parameters required to scale up and run industrial scale SMB setup. The author has conducted extensive research in identifying experimental setups that can be used by anyone assessing the use of SMB technology for separation of a mixture of compounds. Some of the experimental setup's that provide insight on the feasibility of the technology is outlined in this section. Every separation is unique, based on the properties of the product and medium in which the product is produced one can perform sequential experiments to identify the right adsorbent and mobile phase to achieve the separation.

8.1 Adsorbent capacity determination

The selection of adsorbent to be used for a particular separation depends on the capacity and selectivity of the adsorbent for the component in question. The capacity of the adsorbent can be determined by using the setup shown in **Figure 3**.

A column with a length of 250 mm and internal diameter 10 mm is packed with dried adsorbent for which the adsorption capacity needs to be determined. Before packing the column with the adsorbent the initial weight of the column is recorded and after filling the adsorbent with the adsorbent in consideration the final weight of the column is measured. The difference between the initial and final weight tells you the weight of adsorbent added to the column.

In order to determine the capacity of the adsorbent for a particular component, isolated pure components can be purchased from any vendor (example Sigma Aldrich) for the study. It is important that pure component is used for the study as the presence of impurity in the component can interact with the active sites of the adsorbent thereby giving a false adsorbent capacity. A 1–5% solution of the component is prepared in the mobile phase. Say if it is desired to study the adsorption capacity of ethanol on activated carbon then a 1% solution of ethanol can be prepared in water and passed through a column packed with activated carbon. To determine the adsorption of the component, the solution is passed through the column using a pump at a fixed flow rate say anywhere between 1 and 5 gpm. The effluent from the column is collected in vials. Sterilized 50 ml vials are available from several vendors for laboratory experiments. Since we do not know the capacity of the adsorbent, it is best to collect 10 ml samples of the effluent. If a rough estimate needs to be determined for the exact point of the breakthrough then the effluent from the column can be directly connected to an IR detector to determine when the peak happens. Based on the rough breakthrough volume one can decide the volume of sample required. The effluent samples collected are injected in a high-pressure liquid chromatogram to determine when the sample collected contains the

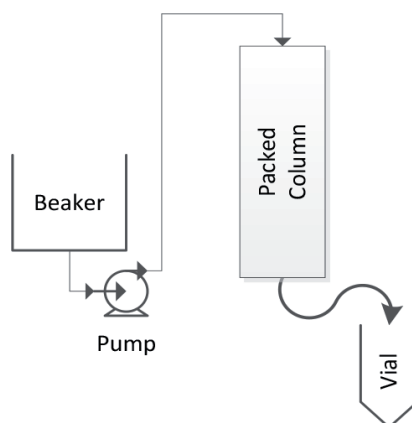


Figure 3.
Adsorption test setup.

component adsorbed on the adsorbent. It will be seen that the first few vials only contain the mobile phase in which the component is dissolved. Since the adsorbent will keep adsorbing the component till it has capacity, once the adsorbent is saturated the component will break through at which point no more adsorbent will get adsorbed on the adsorbent. The first vial which matches the composition of the feed solution marks the breakthrough point and can be called the breakthrough vial. Calculate the cumulative volume of all the vials before the breakthrough vial. Based on the cumulative volume identified one can calculate the mass of the component adsorbed on the adsorbent. Dividing the mass of component adsorbed by the mass of the adsorbent gives the adsorption capacity of the adsorbent.

$$\text{Adsorption capacity of adsorbent} = \frac{\text{Mass of component adsorbed}}{\text{Mass of adsorbent in the column}} \times 100 \quad (1)$$

$$\text{Mass of component adsorbed} = \text{wt\% of component in the feed} \times \text{Cumulative volume before breakthrough} \quad (2)$$

8.2 Pulse test

Pulse test is primarily done to identify the residence time of various components as they pass through a column packed with the adsorbent used for achieving the separation in an SMB.

If one wants to conduct a quick pulse test using a lab scale SMB column (250x10mm), one can connect the discharge of the column directly to IR detector or UV detector based on the characteristics of components to be identified as shown in **Figure 4**. One can first inject a blank injection to know the void volume of the column. Blank injection can include any component that does not interact with the adsorbent and hence comes out at the void volume. For activated carbon one can use salt solution like NaCl. In the next step one can inject a solution of the component to find the residence time of the component in the IR or UV detector. Knowing the residence time of the various adsorbents can give a rough idea of starting condition of a SMB which can then be optimized.

Several applications of SMB require separation of multiple components from a feed stream. Some feed streams can contain 20–30 components that fight for the adsorbent sites. For such feed components one might need to run multiple SMB runs to get the desired component. As an example, the author has developed a process for isolating alpha-tocotrienol from palm oil [22]. Palm oil contains several

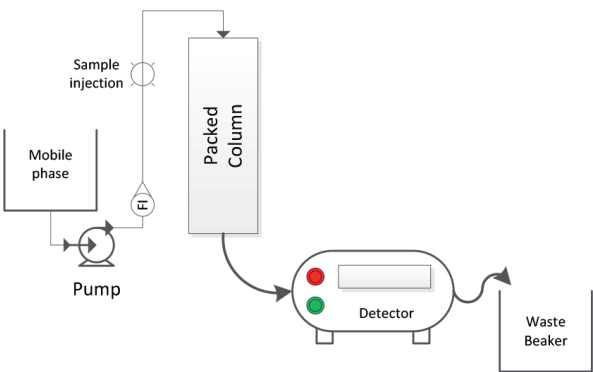


Figure 4.
Residence time detection.

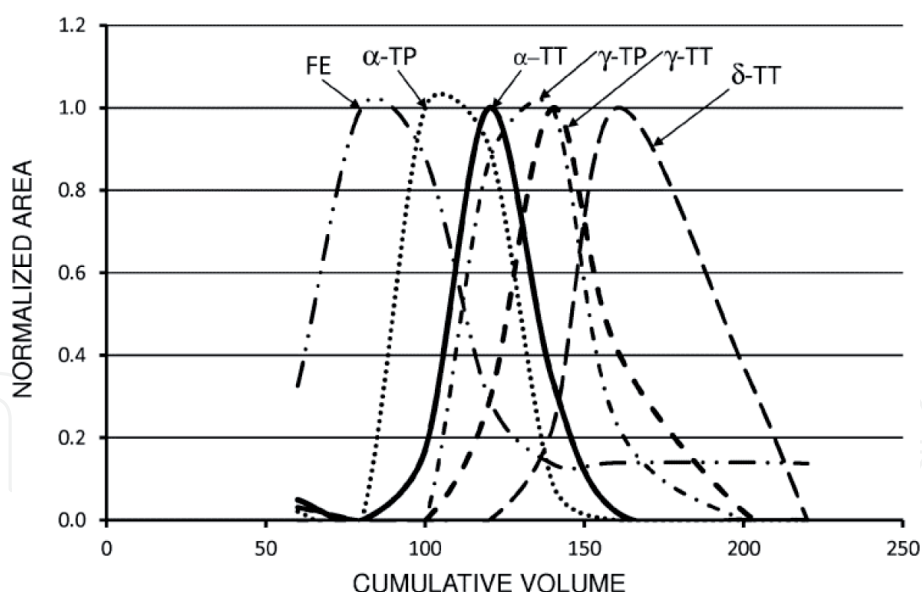


Figure 5.
Shows the results of a pulse test conducted for the palm oil extract feed. Source [22].

components like alpha-tocopherol and tocotrienol; beta-tocopherol and tocotrienol; gamma-tocopherol and tocotrienol; delta-tocopherol and tocotrienol; and several other backend and frontend components.

A detailed pulse test is required to get a good idea of residence time of various components and identify the effect of the presence of one component on other components.

In order to conduct a pulse test a stainless steel column is packed with the desired adsorbent. Tare weight of the column is registered before filling the column with the adsorbent to know the exact weight of adsorbent added to the column. Once filled the column is kept in a water bath and maintained at the operating temperature desired for the SMB run. In order to equilibrate the column the desorbent chosen for the separation is passed through the column for 30 minutes. Once the column is equilibrated a known amount of feed dissolved in the desorbent is fed to the top of the column preferably 5 ml solution of 5% feed dissolved in the mobile phase. Once the feed is injected it is then eluted with the desorbent at a desired flow rate preferably 1–5 ml/min. The effluent from the column is directed to a RI detector or a UV detector based on the constituents of the feed to get a rough estimate of the elution of the components. For detailed analysis the effluent is also collected in 10 ml vials. The vials collected are then injected in a high-pressure liquid chromatograph to know the exact composition of the effluent stream. The results of the chromatograms are plotted on a graph to study the separation profile of the various components. **Figure 5** shows results of a pulse test conducted by the author to identify the elution profile of α -Tocotrienol and other feed components in palm oil extract feed.

9. Application of SMB in the industry

The first industrial scale SMB process was commercialized by UOP (United Oil Products check) for the separation of n-paraffins from branched paraffins, and aromatics. The first plant was started in 1960 and was used for the manufacture of biodegradable detergents. Traditionally p-xylene was purified using crystallization, however the SMB technology showed a big improvement over the crystallization process. After being successful in hydrocarbon separations there has been several novel processes that were developed for fatty chemicals, pharmaceuticals,

carbohydrates, and biochemicals [10, 23–42]. Recently, a lot of process developments happened at Orochem Technologies with which the author was directly involved either in the R&D phase [22, 43–45] or in the commercialization phase [46–50].

9.1 Ion-exclusion SMB process

The extraction of sucrose from molasses have been researched extensively in the industry, in 1953, Dow Chemical company invented [51] an ion-exclusion process to separate the ionic and nonionic constituents of molasses. It was identified that under equilibrium conditions certain non-ionic components of molasses could be separated from the ionic components of molasses using SMB technology with high throughput and yield. This SMB technology can also be used for extracting sugar or related products from other biorefineries in addition to the one discussed in this section.

In 2012, the author was involved in developing a process using SMB technology to separate d-Tagatose from a mixture of d-Galactose and d-Tagatose produced in a biorefinery [43]. The process uses a strong acid cation exchange resin to provide a pure d-Tagatose product from a mixture of d-Tagatose, d-Galactose, glucose, and calcium salt. **Figure 6** shows a bench scale lab SMB that was run to find conditions to run the commercial scale SMB. In the lab scale setup, a 2–3–3 column configuration was established for the columns in a simulated SMB setup where a plethora of solenoid valves simulated the movement of the columns. Desorbent entered from top of 1st column and feed entered from top of 6th column. Extract was drawn from the bottom of 2nd column and raffinate was drawn from the bottom of 8th column. Column 1–2 are in desorption zone. Column 3–5 are in rectification zone and column 6–8 are in adsorption zone. After determining the flow conditions the flow rates were scaled up to run a commercial unit in Italy.

At industrial scale a continuous moving SMB was used for this process and a pilot unit was run to illustrate this process in Italy. The continuous SMB consisted of 30 ports to which 30 columns were connected. The 30 columns were separated into 3 sets of 10 columns each. **Figure 7** shows a schematic of the SMB process for separating d-Tagatose from d-Galactose using the continuous SMB. The desorbent which is water enters the 1st column as shown in **Figure 7**. The feed which is a mixture of d-Tagatose, d-Galactose, and salt enters from top of 5th column. Since the adsorbent has selectivity for d-Tagatose it gets preferentially adsorbed on the adsorbent and moves with it to come out from the bottom of 2nd column, this

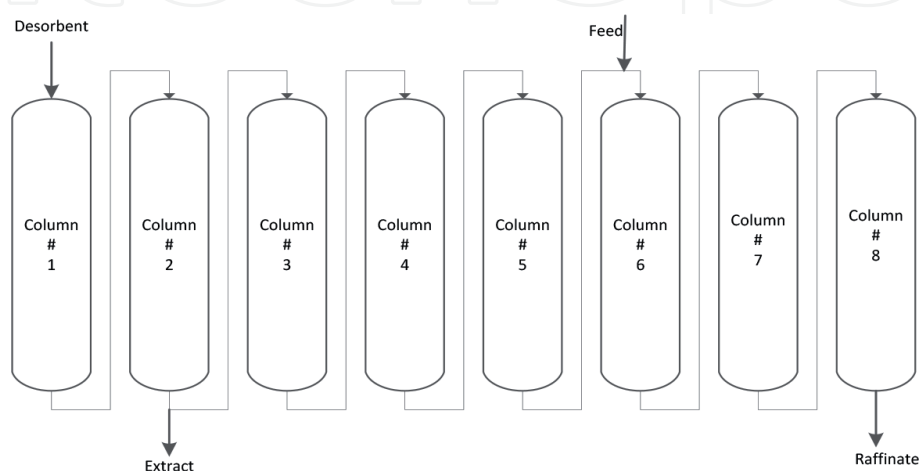


Figure 6.
 Lab scale SMB process for separation of d-tagatose from d-galactose.

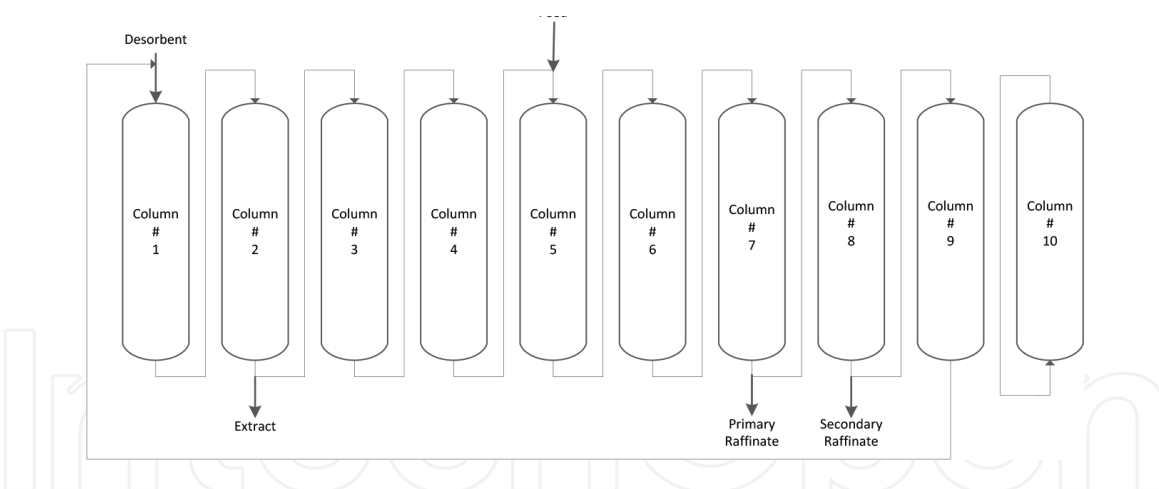


Figure 7.
Industrial scale SMB setup to separate *d*-tagatose from *d*-galactose.

stream is called extract and consists of pure *d*-Tagatose. *D*-Galactose the faster moving component comes out from the bottom of 7th column and is called the raffinate stream. In the continuous SMB a 2–3–2–1 column setup was employed to concentrate the raffinate stream and recycle part of desorbent making it a greener and more efficient process. Using SMB to concentrate streams saved considerably in energy cost by reducing the load on evaporators. This setup illustrates that not only can SMB be used to achieve an efficient separation with high purity and yield. The technology can also be used to build a greener process where process intensification can be used to integrate concentration steps to reduce the load on other unit operations such as evaporation.

9.2 SMB process to extract oxygenates from dilute fermentation stream

The author was involved in developing a novel process for extracting ethanol and other oxygenates produced in dilute fermentation processes in a biorefinery. Bio fermentation processes have extensively been used to produce products such as ethanol, non-condensable gases such as methane, oxygenated organic compounds such as 2,3 Butanediol (2,3-BDO). Oxygenated organic compounds have traditionally been produced from sugar sources such as corn, sugarcane, molasses, etc. The author has worked in collaboration with Lanzatech for isolating ethanol and other oxygenates produced in dilute fermentation broth. The process developed by Lanzatech uses unique microbes to convert carbon monoxide and other flue gases from power plant exhausts to useful chemicals such as ethanol, 2,3BDO. The Lanzatech process uses microbial gas fermentation to convert carbon monoxide containing gases produced by industries such as steel manufacturing, chemical production, and oil refineries as well as gases generated by gasification of forestry and agricultural residues, municipal waste, and coal into valuable fuel and chemical products to produce ethanol and other oxygenates such as 2,3-BDO [52, 53]. This process can also be used for extraction of products from other biorefineries working towards producing other products.

Since the ethanol and associated oxygenates such as isopropanol, 2,3-butanediol, and other diols are produced in very dilute concentrations in aqueous fermentation solutions, recovery of these constituents by traditional means such as distillation and crystallization is largely hindered by the energy requirements. The energy requirement for separating ethanol from a dilute mixture of ethanol and water is about 30,000 BTU/gal of ethanol produced. The author has developed a SMB process which can achieve the same separation with 75% less energy consumption [44].

9.2.1 Experiment for identifying capacity of adsorbent

A bench scale setup is used by the author to calculate the capacity of the adsorbent [44]. In the setup a column with a length of 250 mm and diameter of 10 mm is packed with the desired adsorbent. In this experiment the adsorbents chosen for comparison are activated carbon (E-325 Orochem adsorbent) and fluorinated activated carbon (E-325 an Orochem Technology proprietary product). A 1% solution of ethanol in demineralized water is passed through the columns with different adsorbents to find out the capacity of the adsorbents. The results of the adsorbent studies are shown in **Table 1**.

Another adsorbent studied for the SMB process was silica bonded with C-18. Since the performance of the fluorinated carbon was better than C-18 silica further analysis of the C-18 is not discussed in this chapter, more information can be found in the patent application [52].

9.2.2 Desorbent analysis

Once the adsorbent was finalized for the SMB process a solvent analysis was performed. The solvent selected should be selectively able to remove the adsorbed components without compromising the relative selectivity desired to achieve the separation. Solvents studied for this analysis were methanol, ethanol, propanol, methyl tertiary butyl ether (MTBE). In order to test the viability of the desorbent it was passed through a column saturated with the feed and eluted with the desorbent. 10 ml samples of the eluent was tested using a high-pressure liquid chromatogram to see if the desorbent was completely able to regenerate the column. Once regenerated the adsorption capacity of the adsorbent was calculated to understand if the regeneration was successful.

9.2.3 SMB setup

Lab scale SMB for extracting ethanol and butanediol from dilute fermentation broth was developed by the author. The SMB setup shown in **Figure 8** illustrates an 8-column setup where each column was packed with fluorinated carbon. The columns were connected in series to a bench scale SMB from Semba. Methanol was used as the desorbent. Synthetic feed solution containing 6% ethanol and 2% 2,3-butanediol was prepared and pumped to the top of column # 6. The complex SMB valve system facilitated switching of the inlet and outlet ports of the columns at regular intervals. The interval after which the inlet and outlet of the columns were switched is called the cycle time. The SMB setup is a continuous process where the desorbent and feed enters the columns and extract and raffinate are drawn out of the columns as designated in **Figure 8**. The switching of the SMB valve simulates a continuous counter current movement of the adsorbent and mobile phase. In the

	Exp#1	Exp#2	Exp#3	Exp#4
Organic @1% in water	Ethanol	2,3-Butanediol	Ethanol	2,3-Butanediol
Adsorbent	E-325	E-325	FC-5	FC-5
Breakthrough Volume (ml)	68	108	106	188
EtOH adsorbed(gm)	0.68	1.08	1.06	1.88
Adsorption ratio (W/W)	6.07	9.64	9.46	16.7

Table 1.
Below are the results of the adsorption capacity of the various adsorbents.

lab setup it was demonstrated that the extract stream did not have any water and the raffinate stream contained pure water. In order to achieve pure water at the raffinate stream the column had to be purged with nitrogen at 140°C to eliminate the methanol filled in the column. Since there was no way to establish the purging and heating of the column in the SMB setup the column was physically removed and replaced with a fresh column already purged with nitrogen at 140°C to simulate the concept. In the 2–3–3 SMB setup 2 columns between the desorbent and extract are in desorption zone, 3 columns between the extract and feed ports are in the rectification zone, and 3 columns between the feed and raffinate port are in the adsorption zone.

The lab scale setup explained in **Figure 8** was scaled up to as a 10 column SMB setup for industrial scale. **Figure 9** shows the 10 column SMB setup. The desorbent which was chosen to be ethanol as shown in **Figure 9** moves from left to right and the adsorbent beds switch from right to left simulating the counter current movement of the adsorbent and desorbent. During the next valve switch the column marked as column#1 moves to the position of column marked as column #10 and each column moves one position to the left. In the setup shown in **Figure 9** two columns are in an isolated regeneration mode. Column # 1 has steam passing

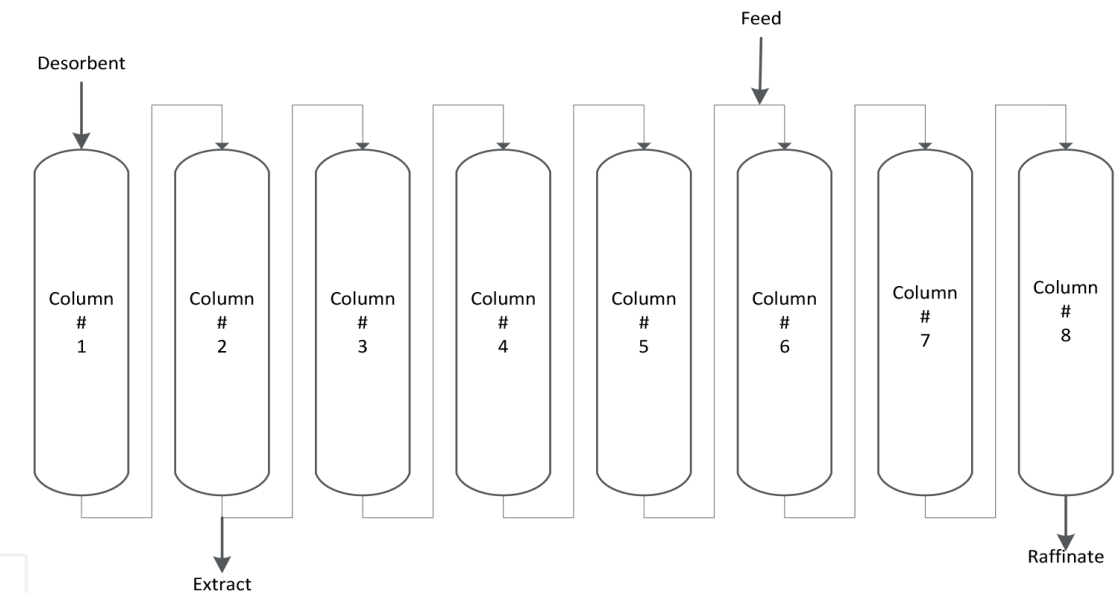


Figure 8.
Lab SMB setup for extracting ethanol and 2,3-BDO from dilute fermentation stream.

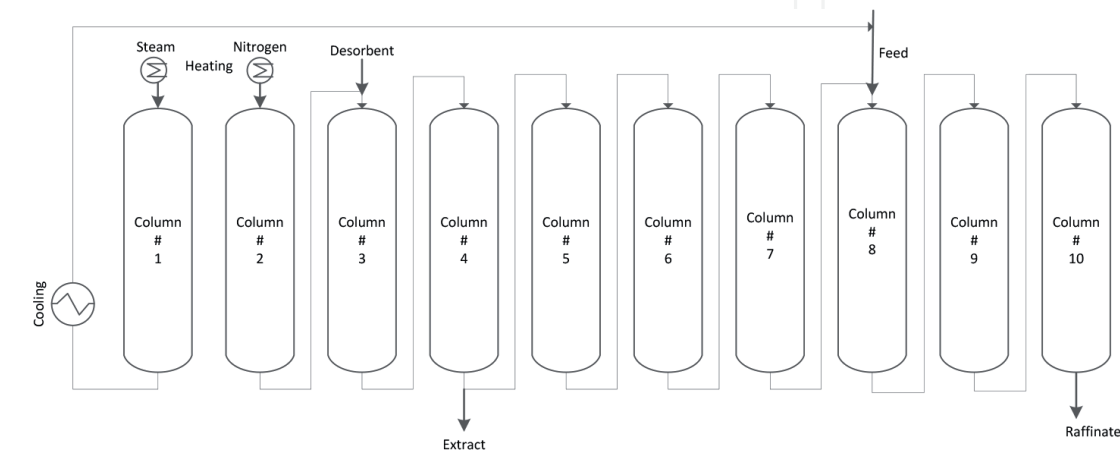


Figure 9.
Industrial setup to extract ethanol and 2,3-BDO from dilute fermentation stream.

through it at 100–120°C to eliminate any residues of ethanol – the ethanol water mixture derived from column # 1 is mixed with the feed entering the top of column # 8. Column # 2 has nitrogen heated to 80–120°C entering the column to strip as much ethanol as possible and mix with the desorbent which is ethanol. In the setup shown in **Figure 9** the raffinate contains only water which comes out from the bottom of column # 10. The 2,3-BDO contained in the feed comes out in the extract as a mixture of 2,3-BDO and ethanol.

The SMB processes explained in this section are an improvement over the traditional distillation or crystallization processes as the SMB process excessively reduces the amount of energy required to achieve higher purity and yield of the oxygenates produced in the fermentation process. Further optimization of the SMB process has been achieved by the author for several processes where the desorbent consumption can be reduced to achieve higher purity and yield of the feed components versus using any other separation technology.

In a further optimization of the SMB process for extracting ethanol and 2,3-BDO from dilute fermentation stream the author has developed a schematic depicted in **Figure 10**. In this SMB setup the same stationary phase can be used either fluorinated carbon or C-18 bonded silica [45]. For commercial scale a 15 column SMB setup is recommended where 5 columns can be dedicated to an improved and separate regeneration step from the rest of the 10 columns that perform the actual separation of the feed components. As depicted in **Figure 10** desorbent which is chosen to be ethanol is passed through the first column. Each subsequent column from 1 to 10 are connected in series like other SMB setup's such that the outlet of first column is connected to the inlet of the next column. A portion of the outlet stream from column # 3 is drawn as extract. The extract contains ethanol, 2,3-Butanediol and < 0.5% water. Feed enters the top of column # 7. Raffinate which is the water contained in the feed stream comes out of column # 9 and 10. In the improved SMB setup 5 columns are dedicated for improved regeneration. In the improved regeneration the columns are heated using superheated ethanol. As the columns step through the various zones once the column comes in the regeneration zone it is heated using superheated ethanol. The adsorbent bed is heated in 4 steps and eventually purged using nitrogen to remove the interstitial ethanol in the adsorbent bed. The columns are heated to about 110°C. Before the purged column must enter the adsorption zone it needs to be cooled to achieve the desired separation. The cooling is achieved by passing water coming out of the raffinate stream through the column to cool it to room temperature. The columns from 1 through 10 follow the same separation mechanism identified in **Figure 9**.

In order to heat the columns in the regeneration step superheated steam is passed through the columns, since the effluent from the columns would be hot it can be

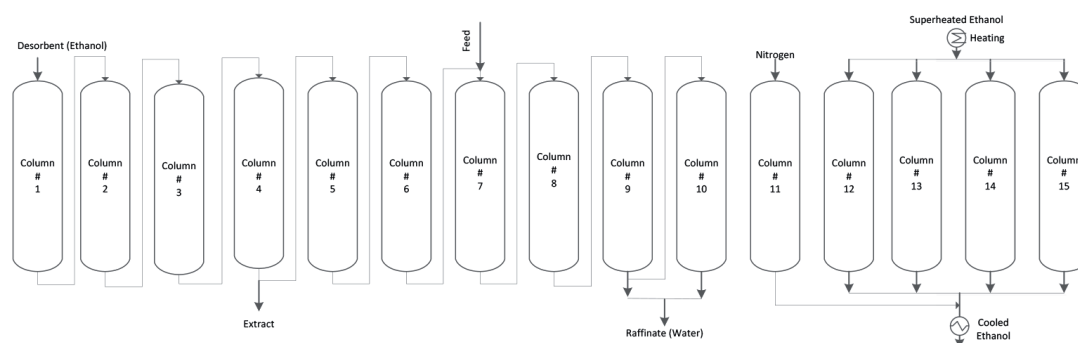


Figure 10.
 Improved SMB setup for extracting oxygenates from fermentation broth.

cooled down using coolers and be used as the desorbent. The optimized SMB setup shown in **Figure 10** has removed the need to recycle a dilute ethanol stream from the SMB back to the feed stream as shown in **Figure 10**. If other desorbents like methanol, propanol, or MTBE were used for the separation then streams containing a mixture of desorbent and water would be created that would need to be distilled separately. More details on the different regeneration setups can be found in the work published by the author [44, 45].

9.3 Use of SMB for extracting biorefinery products

Most biorefineries produce products in dilute aqueous mixtures. For most cases the amount of energy required to separate the chemicals by traditional separation means is cost prohibitive, thereby making industrial scale production of biorefinery products impractical. The simulated moving bed technology provides the much-required unit operation for extracting biorefinery products at a fraction of the cost for traditional separation means. The author was involved in the extraction of fermentation products created in a bioreactor using SMB technology. If conventional distillation techniques were employed to separate the fermentation chemicals the technology would not have been feasible as the amount of energy required to separate the products using distillation was much more than the fuel value of the chemicals. The chemicals produced in the technology were ethanol and butanediol in a 6% and 2% concentration in the fermentation broth. Specifics of the technology can be found in Section 9.2. Until recently, most of the chemicals were produced by fossil fuel-based resources that are now depleting and are not sustainable. The depleting fossil fuels have catalyzed the use of biotechnology techniques for generating chemicals to meet the growing population. SMB technology has proven to be very successful in aqueous product streams. Moreover, the lower concentration of the product streams is favorable to SMB technology as it works on the principles of adsorption. In the examples outlined in this chapter SMB technology has demonstrated feasibility for extraction of biorefinery chemicals such as ethanol, lactic acid, sugars (Tagatose, Galactose, Glucose), butanediol etc. As new processes are developed SMB technology can be applied to several biorefineries using techniques explained in this chapter to produce many other biorefinery products.

9.4 SMB in pharmaceutical industry

The use of SMB is not only limited to the petroleum, energy, biorefinery, or sugar industry. Recently there has been a lot of development in isolating active pharmaceutical ingredients using SMB technology. The author has developed a novel SMB process for isolating α -tocotrienol from palm oil extract [22]. In all the SMB processes we discussed the stationary phase used was non-polar and a polar solvent was used as desorbent. In the SMB setup for isolating α -tocotrienol [22] from palm oil extract the adsorbent used is either silica or alumina (polar adsorbent) and the mobile phase is a non-polar solvent. In this SMB setup α -tocotrienol needs to be isolated from the rest of the components in palm oil extract like β -tocopherol/tocotrienol, μ -tocopherol/tocotrienol, δ -tocopherol/tocotrienol, front end and back end carotenoids. The SMB process developed creates a novel and green process due to the reduced amount of solvent required to achieve higher purity and yield of α -tocotrienol which would not have been possible using any other separation technology. The author has also contributed to the commercialization of the use of SMB technology for purification of highly pure EPA/ DHA from fish oil. The technology for purification of fish oil is documented

in patents [46–50]. In addition to developing processes for achieving purification using SMB technology the author has worked on several other optimization projects for several other industries specifics of which can be found in publications referenced [54–56]. The author has also delivered several talks on safety topics with one of the topics on pump safety being published in CEP magazine [57]. The polar stationary phase SMB setup developed by the author can also be used to extract biorefinery products that are non-polar. Pharmaceutical products that are produced via fermentation can use SMB technology to achieve a cost effective separation with high throughput.

10. Future research directions

The use of SMB in biorefineries is gaining traction. With the growing population the need to conduct further research on using SMB for isolating biorefinery, pharmaceutical, and other biological products sustainably is imperative. The pharmaceutical, neurocritical, and biologics industry has primarily used batch processes which are limiting by capacity throughputs. The use of a continuous technology will create new opportunities in these industries and enable large scale production of products required to meet the growing demand of the world.

11. Conclusion

Adsorption processes have successfully been demonstrated for purification of commercial products. For those processes SMB technology has shown great advantage over batch chromatography. One can achieve higher yield and purity using SMB technology. Various process developments in using SMB for multi component feed streams have been successfully commercialized. Process Intensification can be achieved using this novel technology in biorefineries. Fermentation products that are produced in dilute streams have found an efficient way of extraction using the SMB technology. Higher throughput processes in the pharmaceutical and bio-fermentation industry will enable the use of SMB technology. The successful implementation of SMB will enable increased capital investment for R&D related to this technology.

Several processes have been developed using SMB technology to achieve separation in biorefineries: e.g. purification of glycerol from biodiesel production (using the Ambersep BD50 resin, or gel-type acidic ion-exchange resin beads) where the raffinate stream contains salts and organic impurities including free fatty acids, purification of oligosaccharides (made up of xylose and arabinose units), isolation of lactic acid from acetic acid, separation of sugars (glucose and xylose) [58] to name a few. The SMB technology has shown immense promise in achieving a sustainable, cost effective, and safe product isolation technology for various industries with equivalent promise for biorefineries. Future research in the field has a bright future for developing industries such as biorefineries.

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