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DESIGN METHODOLOGY FOR INTEGRATED DOWNSTREAM SEPARATION SYSTEMS IN AN ETHANOL BIOREFINERY

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ÉCOLE POLYTECHNIQUE DE MONTRÉAL

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DESIGN METHODOLOGY FOR INTEGRATED DOWNSTREAM SEPARATION SYSTEMS IN AN ETHANOL BIOREFINERY

présenté par : MOHAMMADZADEH ROHANI Navid

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RÉSUMÉ

Les enjeux de sécurité d'approvisionnement énergétique et de protection de l'environnement ont mené à une augmentation significative de production de biocarburants. La réussite de ce choix stratégique dépend, entre autres, de la rentabilité et de la viabilité à long terme des unités de production. Les biocarburants de seconde génération, par exemple l'éthanol, sont souvent produits à partir de matière ligno-cellulosique. Ils sont plus difficiles à produire que ceux de première génération car (1) des étapes coûteuses supplémentaires sont nécessaires pour la séparation des différents constituants de la biomasse avant fermentation, (2) et la concentration en produit quittant le réacteur de fermentation est plus faible, ce qui augmente les difficultés pour la purification.

Dans une bio-raffinerie produisant de l'éthanol, les coûts relatifs à la purification du produit quittant le réacteur de fermentation sont significatifs. L'opération classique de purification inclut un ensemble de colonnes de distillation. Cependant, la nature non-idéale du mélange eau-éthanol, qui forme un azéotrope à 95 % en poids d'éthanol, complique cette opération. Une étape additionnelle de déshydratation est ainsi nécessaire afin d'obtenir de l'éthanol pur à 99.5 % en poids. Plusieurs techniques ont été proposées afin de résoudre les difficultés inhérentes aux équilibres liquide-vapeur des mélanges éthanol-eau. Ces techniques, telles que l'utilisation de membranes ou l'extraction par solvant organique, visent non seulement à obtenir de l'éthanol pur mais aussi à réduire la consommation d'énergie.

Réduire la consommation d'énergie lors de la production est de première importance pour la viabilité de l'industrie des biocarburants. L'intégration de procédé, telle que définie par Ressources Naturelles Canada, est une approche système pour l'analyse et la synthèse de procédés afin de minimiser la consommation en énergie, eau et matières premières. L'utilisation de cet outil peut permettre aux bio-raffineries d'économiser de l'énergie et augmenter leur rentabilité. Les techniques d'intégration de procédé ont été adoptées avec succès par plusieurs industries ; elles sont basées sur l'utilisation optimale des sources en énergie, eau et matières premières disponibles dans le procédé afin de satisfaire les demandes et ainsi réduire la consommation externe.

Du point de vue de l'industrie papetière, qui doit faire face à une demande en produit déclinant avec le temps, à une compétition globale et à des prix de vente peu élevés, l'intégration de

technologies de bio-raffinage dans des usines de production de pâte kraft peut être une option intéressante, leur permettant de diversifier le portfolio de produits et d'entrer sur de nouveaux marchés. Les systèmes d'utilités existants, le savoir-faire en génie et en gestion de la chaîne logistique, ainsi que des opportunités d'intégration énergie et matière entre une usine de pâte et une unité de bio-raffinage peuvent offrir des avantages compétitifs et améliorer la performance économique de l'industrie papetière. Par conséquent, l'intégration énergie est une possibilité qui doit être considérée par l'industrie du bio-raffinage forestier.

L'objectif de ce travail est de développer une méthodologie pour la conception de systèmes de purification du produit de bio-raffinage et de la tester sur une étude de cas, une unité de bio-raffinage produisant de l'éthanol. Plusieurs techniques de purification ont été évaluées selon trois scenarii : (1) sans intégration énergie, (2) avec intégration énergie à l'intérieur du système de purification et (3) avec intégration énergie entre le système de purification et une usine de pâte kraft. Les consommations en énergie, les coûts d'investissement ainsi que les performances économiques ont été évalués pour chaque technique de purification et chaque scénario d'intégration. La meilleure des options a finalement été identifiée selon des critères technico-économiques.

Les possibilités d'intégrations ont été identifiées avec la méthode de pincement pour le deuxième scénario, et avec la méthode pontale pour le troisième scénario car ce dernier requiert une analyse pour la rétro-installation du réseau d'échangeur de chaleur du procédé kraft.

Les résultats révèlent l'importance de l'intégration énergie pour réduire la consommation énergétique et améliorer la performance des unités de production de bio-raffinage. Ils montrent également que le système classique de purification d'éthanol conduit à de meilleurs résultats après intégration énergie que les autres techniques de purification. Les techniques alternatives peuvent impliquer des risques technologiques supplémentaires et ne mènent à aucun avantage de consommation énergétique lorsque l'intégration interne ou externe avec une usine de pâte kraft est incorporée dans le modèle d'affaires.

Il est important de souligner que la méthodologie développée dans le cadre de cette maîtrise peut être étendue pour évaluer les performances énergétiques et économiques de l'ensemble d'un procédé de bio-raffinage.

ABSTRACT

Energy security and environmental concerns have been the main drivers for a historic shift to biofuel production in transportation fuel industry. Biofuels should not only offer environmental advantages over the petroleum fuels they replace but also should be economically sustainable and viable. The so-called second generation biofuels such as ethanol which is the most produced biofuel are mostly derived from lignocellulosic biomasses. These biofuels are more difficult to produce than the first generation ones mainly due to recalcitrance of the feedstocks in extracting their sugar contents. Costly pre-treatment and fractionation stages are required to break down lignocellulosic feedstocks into their constituent elements. On the other hand the mixture produced in fermentation step in a biorefinery contains very low amount of product which makes the subsequent separation step more difficult and more energy consuming.

In an ethanol biorefinery, the dilute fermentation broth requires huge operating cost in downstream separation for recovery of the product in a conventional distillation technique. Moreover, the non-ideal nature of ethanol-water mixture which forms an iseotrope at almost 95 wt%, hinders the attainment of the fuel grade ethanol (99.5 wt%). Therefore, an additional dehydration stage is necessary to purify the ethanol from its azeotropic composition to fuel-grade purity.

In order to overcome the constraint pertaining to vapor-liquid equilibrium of ethanol-water separation, several techniques have been investigated and proposed in the industry. These techniques such as membrane-based technologies, extraction and etc. have not only sought to produce a pure fuel-grade ethanol but have also aimed at decreasing the energy consumption of this energy-intensive separation. Decreasing the energy consumption of an ethanol biorefinery is of paramount importance in improving its overall economics and in facilitating the way to displacing petroleum transportation fuel and obtaining energy security.

On the other hand, Process Integration (PI) as defined by Natural Resource Canada as the combination of activities which aim at improving process systems, their unit operations and their interactions in order to maximize the efficiency of using water, energy and raw materials can also help biorefineries lower their energy consumptions and improve their economics. Energy integration techniques such as pinch analysis adopted by different industries over the years have

ensured using heat sources within a plant to supply the demand internally and decrease the external utility consumption.

Furthermore, from the stand-point of a pulp and paper mill and considering the declining demand, volatile price, high energy cost and fierce global competition, it looks as a promising option to integrate a biorefinery technology with the core business in order to diversify the product portfolio and enter new markets. Existing utility systems, engineering know-how and feedstock supply network as well as mass and energy integration potentials between mills and new processes foster competitive advantage for pulp and paper mills to adopt implementing biorefineries to improve their economic performances.

Therefore, adopting energy integration can be one of the ways biorefinery technology owners can consider in their process development as well as their business model in order to improve their overall economics.

The objective of this thesis is to propose a methodology for designing integrated downstream separation in a biorefinery. This methodology is tested in an ethanol biorefinery case study. Several alternative separation techniques are evaluated in their energy consumption and economics in three different scenarios; stand-alone without energy integration, stand-alone with internal energy integration and integrated-with Kraft. The energy consumptions and capital costs of separation techniques are assessed in each scenario and the cost and benefit of integration are determined and finally the best alternative is found through techno-economic metrics. Another advantage of this methodology is the use of a graphical tool which provides insights on decreasing energy consumption by modifying the process condition.

The pivot point of this work is the use of a novel energy integration method called Bridge analysis. This systematic method which originally is intended for retrofit situation is used here for integration with Kraft process. Integration potentials are identified through this method and savings are presented for each design. In stand-alone with internal integration scenario, the conventional pinch method is used for energy analysis.

The results reveal the importance of energy integration in reducing energy consumption. They also show that in an ethanol biorefinery, by adopting energy integration in the conventional distillation separation, we can achieve greater energy saving compared to other alternative techniques. This in turn suggests that new alternative technologies which imply big risks for the

company might not be an option for reducing the energy consumption as long as an internal and external integration is incorporated in the business model of an ethanol biorefinery. It is also noteworthy that the methodology developed in this work can be extended as a future work to include a whole biorefinery system.

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LIST OF ABBREVIATIONS

A	Annuity factor
BC	Beer column
CCC	Cold composite curve
ET	Enterprise transformation
ETD	Energy transfer diagram
EG	Ethylene glycol
FBR	Forest biorefinery
GCC	Grand composite curve
GHG	Greenhouse gas
HCC	Hot composite curve
HEN	Heat exchanger network
IFBR	Integrated forest products biorefinery
IRR	Internal rate of return
MER	Maximum energy recovery
MINLP	Mixed integer linear programming
P&P	Pulp and paper
PI	Process integration
ROI	Return on investment
TAC	Total annualized cost
VLE	Vapor-liquid equilibrium

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INTRODUCTION

Background

Despite the rapid growth of biofuel production all around the world, serious issues regarding the sustainability of this production has required the industry to rethink its pathway and seek new type of feedstocks. The concerns over sustainability enumerated by IEA(2010) as competition with food chain, effects on the environment and climate change which are mostly caused by using food crop feedstocks have led to the production of so-called second generation biofuels.

Second-generation feedstocks such as forest biomass, forest residues, agricultural waste etc. contain sugar molecules which can be subsequently converted to transportation fuels and at the same time address the sustainability concerns. Programs such as RFS which was initially enacted in 2005 in the US, mandates production of 36 billion gallons of second-generation biofuels by 2022 which emit fewer greenhouse gases than the petroleum fuels they replace.

Research-and-development activities on second-generation biofuels so far have been mostly limited to a number of developed countries and in some large emerging economies like Brazil, China and India. Second-generation biofuels are not yet widely produced commercially, but a considerable number of pilot and demonstration plants have been set up in recent years, and research activities are being undertaken mainly in North America, Europe and a few emerging countries. Production of second generation ethanol from sugars contained in the lignocellulosic feedstocks has been investigated in many academic works. Different approaches have been sought to make this type of feedstock more amenable for ethanol production. Fractionation of lignocellulosic materials and separation of its sugar contents have proven a difficult and capital intensive procedure in contrast with the first-generation feedstocks. Moreover, the dilute nature of produced fermentation broth has made the purification stage of the second-generation ethanol an energy intensive step.

The aforementioned problems and in particular the energy intensity of purification of the second-generation bio ethanol requires new techniques as well as a comprehensive engineering approach to resolve the problems.

Problem statement

Recovering ethanol from fermentation broth and purifying it to fuel grade is difficult and energy intensive because of the dilute nature of the fermentation broth and the constrained water/ethanol vapor liquid equilibrium (VLE) with an azeotrope at about 95 wt% ethanol. Simple distillation is not able to recover ethanol above the azeotropic composition.

The ethanol concentration in the fermentation mixture ranges around 15 wt% ethanol from corn (Côté, Noël et al. 2010) compared to about 3 to 6 wt% for cellulosic ethanol. Recovering and purifying ethanol from fermentation broth in corn-ethanol requires about 70 % of the total steam generated in the dry milling plant. While the separation energy demand for corn-ethanol is high, the separation energy demand for cellulosic ethanol is even higher due to the huge increase in the distillation energy demand with the decrease in the concentration of ethanol in the fermentation broth. Consequently downstream separation could represent the whole energy consumption of a biorefinery.

In practice, the conventional technology used in the fuel ethanol industry to produce fuel ethanol is distillation close to the azeotropic composition followed by dehydration in a molecular sieve-based adsorption unit. Molecular sieves are not a popular separation choice due to their cyclic nature of sorption-regeneration process, inefficiency in high flow rates and additional energy requirement which they inflict to the system and high capital cost.

The difficulty and energy intensity of this separation has led to several R&D research and academic investigations in the hope of finding more cost-effective techniques to accomplish this task.

Among the researched techniques are found Azeotropic distillation, membrane, Pressure swing, Liquid-liquid extraction, etc. Technologies such as membrane, extractive distillation and steam stripping have been reported to achieve acceptable reduction in energy consumption as an alternative for ethanol-water conventional separation system.

On the other hand, second-generation biorefineries have a lot in common with pulp and paper industry. The type of feedstock, pre-treatment methods and supply chain similarities as well as synergies for energy integration offer an outstanding opportunity for a biorefinery to be built in proximity of a pulp and paper facility. From energy standpoint, there are several heat sources in a

biorefinery and pulp and paper facility which can potentially exchange heat and reduce the need for an external utility consumption.

Furthermore from economic perspective, integration with existing pulp and paper facilities could potentially generate competitive advantage for lignocellulosic ethanol production. This synergy is furthered by the growing interest from pulp and paper industry to expanding their product portfolio in the face of recent economic crisis which has plagued this sector and the decline in demand of pulp and paper products(Moshkelani, Marinova et al. 2013).

Objective

The problem statement calls for the development of a systematic design methodology to reduce the energy consumption of a bio-ethanol downstream separation by identifying the potentials for energy integration and selecting the best alternative among the separation options.

This general objective could be divided into following sub-objectives:

- To identify potential process modifications in process units by using energy transfer diagram (ETD)
- To identify the opportunities for energy integration with Kraft process through sets of bridges identified in heat exchanger network
- To conduct an overall techno-economic analysis and explore the trade-off between energy reduction savings and capital investment

Hypothesis

The energy consumption of the downstream separation system of an ethanol biorefinery could be significantly reduced by applying energy integration approaches and this will prove economical.

This general hypothesis could be divided into following sub-hypotheses.

- Using a new retrofit approach in integration with Kraft process will identify the heat recovery potentials and will reduce energy consumption
- The energy reduction achieved in the conventional separation is superior to an alternative technology
- A systematic approach in designing integrated downstream separation systems can identify heat recovery potentials and increase the integration opportunities

Thesis organization

This thesis is organized as follows: In chapter 1, the relevant literature is reviewed in order to identify the gaps in the body of knowledge. Chapter 2 presents the project methodology and the steps taken in order to achieve the objective of this thesis. Chapter 3 introduces the case studies and presents the results and final methodology developed in this work. In chapter 4, a general discussion and recommendations are presented. Appendices A and B present the economic and simulation data respectively.

CHAPTER 1 LITERATURE REVIEW

1.1 Lignocellulosic Ethanol - drivers and demand

The industry of converting abundant lignocellulosic biomass to biofuels as transportation fuel is undergoing a fast expansion driven by policy, environmental concerns, economic profit, and energy security. Over the past decades, governments have been seeking renewable energy technologies in order to reduce their dependency on volatile fossil fuel market. Converting biomass to biofuels is one of the most studied processes because of the necessity of finding alternative renewable fuels.

Developed regions such as United States, Canada, and the European Union have been pursuing support policies in biofuel development. Brazil, China, India, South Africa, Thailand, and others have also adopted support policies for biofuels (Eisentraut 2010).

According to Renewable Fuel Association (RFA) (2010), the U.S daily fuel ethanol demand has increased from 350 to 695 barrels from 2006 to 2009. The average monthly demand of fuel ethanol was approximately 900 million gallons in the US in 2009(2010) .

Another reason to use bioethanol is its contribution in the reduction of greenhouse gases (GHG). Reports from United Nations Environment Programme (UNEP) in 2009 and also IEA in 2010 indicate that more than 70% GHG reduction is estimated for bioethanol produced from biomass(Eisentraut 2010), (Group and Management 2009).

The life cycle energy analysis report from different feedstocks were evaluated by the National Renewable Energy Laboratory (Spatari, Bagley et al. 2010) .Their results show that ethanol from forest residues can bring about 94% energy reduction in fossil and 72% in petroleum consumption and also ethanol from corn can foster a 43% reduction in energy input in fossil and 88% in petroleum.

The first generation fuel ethanol is mainly produced from corn in the US ,sugar cane in Brazil and rapeseed in the EU (Eisentraut 2010) . Similar to corn ethanol, fermentation can be used to produce fuel ethanol from cellulosic feedstock (Cardona Alzate and Sánchez Toro 2006),(Meredith 2003).

The IEA (2010) in their report summarized the main drivers for second-generation biofuels development (See Figure 2.1). As can be seen in this Figure, support policies are at the core of developing second generation biofuels.

Key messages

- Biofuel support policies are a key driver for the promotion of biofuels and have been adopted in several OECD countries, as well as developing and emerging countries. Of the countries studied, Brazil, China, India, South Africa and Thailand have adopted respective policies and blending quotas for biofuels. However, these countries are not yet directly addressing second-generation biofuels in their policies.
- R&D activities in OECD countries are supported by governmental funding (*e.g.* more than USD 1 billion in the US, USD 430 million in Canada and USD 12 million in Australia), whereas financing possibilities in developing countries are more limited and often depend on foreign investment. This is one of the reasons why only a few second-generation biofuel projects have yet been set up outside the OECD (*e.g.* in Brazil, China, India and Thailand).
- One of the main drivers for second-generation biofuel production in the next years will be the US Renewable Fuels Standard (RFS), due to its steadily increasing blending mandate for cellulosic ethanol. The EU Renewable Energy Directive (RED) does not set a specific quota for second-generation biofuels. It fosters their use only indirectly by counting their contribution twice toward mitigation targets; hence, its impact on the development of this industry is less certain compared to that of the US RFS.
- For emerging countries, trade opportunities of second-generation biofuels with the EU and the US are likely to grow, since production in these regions is expected to fall short of domestic demand. In particular, countries like Brazil and China that are already developing second-generation biofuels and can provide good export infrastructure and skilled labour are likely able to profit from the growing demand for second-generation biofuels.
- Feedstock trade could be an option for countries that currently cannot provide suitable framework conditions for a domestic second-generation biofuel industry. This might only bring limited economic benefits, but could be a possibility for less-developed countries to profit from the growing demand for second-generation biofuels globally.

Figure 1-1 : Drivers for second-generation biofuel development (Eisentraut 2010)

1.1.1 Ethanol production - history

Contrary to popular belief, ethanol is an old transportation fuel. In the beginning of automotive history certain type of cars could run on ethanol. During the First World War, demand for fuel increased thus ethanol production continued to grow. However after Second World War there was a shift towards gasoline as the main choice of transportation fuel. Ethanol was still used as octane booster in this era. After discovery of tetraethyl lead, this lead-enhanced gasoline was shown to be cheaper than ethanol to produce amid persistent concerns over its health impacts. When tetraethyl lead was phased out in the U.S in the mid-80, the use of MTBE as an octane booster and volume extender grew increasingly. In the early 21 century there was a boom in ethanol production in the U.S. due the ban of MTBE in several states and the requirement of Energy Policy Act (2006) in adding oxygenated molecules such as ethanol to gasoline (Solomon, Barnes et al. 2007).

In Brazil in almost the beginning of 20th century, a mandatory blend of 5% was enacted in order to reduce dependence on foreign imported fuels and also to use excess of ethanol production from sugar industry. In the 90's the rate of blend which had enjoyed an increase in prior years fell from 20% to 10% as government withdrew its subsidy policies. In 2003 and after introduction of flex-fuel cars into Brazilian automotive market, Ethanol gained even more interest and the demand increased higher (Nogueira, Seabra et al. 2008).

In order to meet the expected demand of ethanol in the future, many new plants are needed and, in turn, new feedstocks are required. Almost 50% of the total biomass found on earth is lignocellulosic biomass and in order to meet the growing demand for sustainable ethanol, a shift from 1st generation feedstock to 2nd generation one is necessary. The main challenge identified in producing ethanol from 2nd generation feedstock is the difficulty of breaking down the lignocellulosic biomass to its constituting sugars (Galbe, Sassner et al. 2007).

1.1.2 Ethanol production process

As opposed to ethanol from first generation feedstocks which are rich in sugar, lignocellulosic feedstocks require more complex steps to turn into ethanol. At first step lignocellulosic biomass should be broken down and its polysaccharide contents should be liberated. Next these polymeric

sugars are hydrolysed to monomeric ones. Two different pathways are shown in Figure 1.2 for hydrolysis namely acid or enzymatic. If enzymatic pathway is adopted, the feedstock needs to undergo a pre-treatment step in order to make polysaccharides ready for the enzymes. In acid hydrolysis such step is not necessary. Monomeric sugars are fermented to ethanol afterwards. Ethanol is subsequently recovered and purified up to the desired purity.

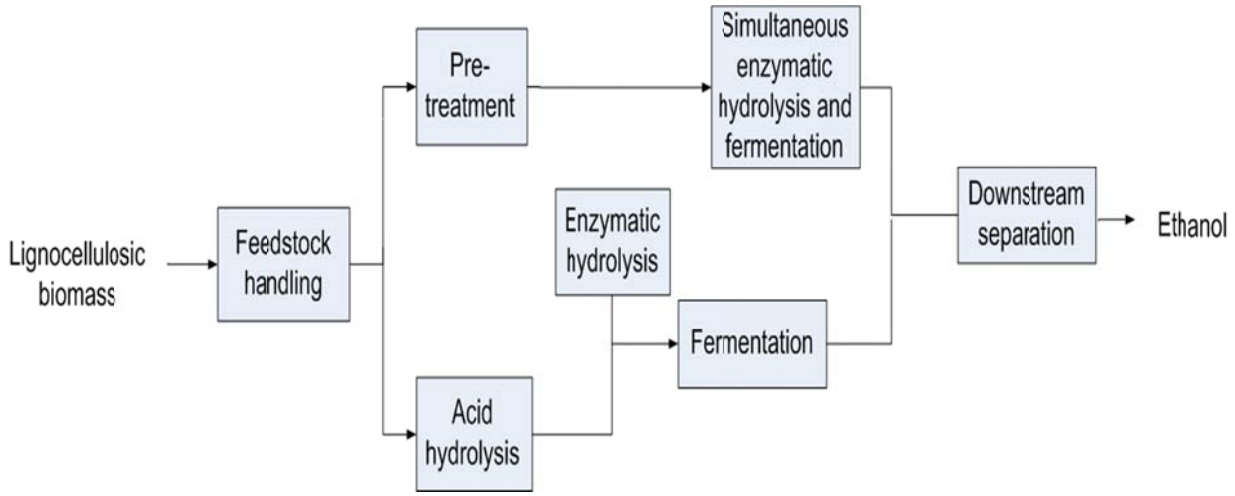

Figure 1-2 : Block diagram of different lignocellulosic ethanol pathway

- **Pre-treatment and hydrolysis**

  The common acid used in hydrolysis is sulphuric acid. Acid could be used at high or low concentration. At low concentration, higher temperatures will be needed which could be detrimental to sugars while at higher concentration which results in high yields, lower temperatures could be applied but recovering acid and corrosion are the main downsides (Wooley 1999) .

  The yield of sugars in enzymatic hydrolysis is higher than the acid hydrolysis due to lower temperature and performance of enzymes. Other pre-treatment methods such as acid, neutral and alkaline have been introduced and used for enzymatic pathway (Galbe and Zacchi 2002).

- **Fermentation**

  If the hydrolysis and fermentation are done separately, optimal conditions can be achieved for both of them; however the product inhibition is a big issue for enzymatic hydrolysis. This challenge could be partly alleviated in simultaneous fermentation and hydrolysis (SSF) but recycling the yeasts used in fermentation is a disadvantage. In second generation ethanol compared to 1st generation, the solid content is lower and this has a negative impact on the purification step.(Wooley 1999)

- **Ethanol purification**

  Ethanol and water forms an azeotrope at around 96 wt% ethanol at atmospheric pressure. There are different ways to break up an azeotropic mixture such as changing the pressure or adding a solvent to the mixture. The more common way in industry is to use a molecular sieve to dehydrate ethanol to the desired purity. After fermentation step a sequence of distillation columns are used to purify the ethanol up to azeotropic composition. This chain of distillation normally includes two or three columns. In the first which is called beer column, ethanol is removed from bulk water, solid residues and unfermented materials and in the following columns which is called rectifier is purified up to azeotropic concentration.(Vane 2008)

1.1.3 Energy efficiency and downstream separation

IEA (2010) defines energy efficiency as “delivering more services for the same energy input or the same services for less energy input”. Energy efficiency is a way of managing and limiting the growth in energy consumption which offers a powerful and cost-effective tool for achieving a sustainable energy future.

Improvements in energy efficiency can reduce the need for investment in energy infrastructure, cut energy bills, improve health, increase competitiveness and improve consumer welfare. Environmental benefits can also be achieved by the reduction of greenhouse gases emissions and local air pollution. Energy security can also profit from improved energy efficiency by decreasing the reliance on imported fossil fuels.

IPCC (2007) in their synthesis report of 2007, evaluated four different measures for mitigating greenhouse gas emissions which aimed at stabilizing carbon dioxide emission concentration at 650 ppm (See Figure 1.3).

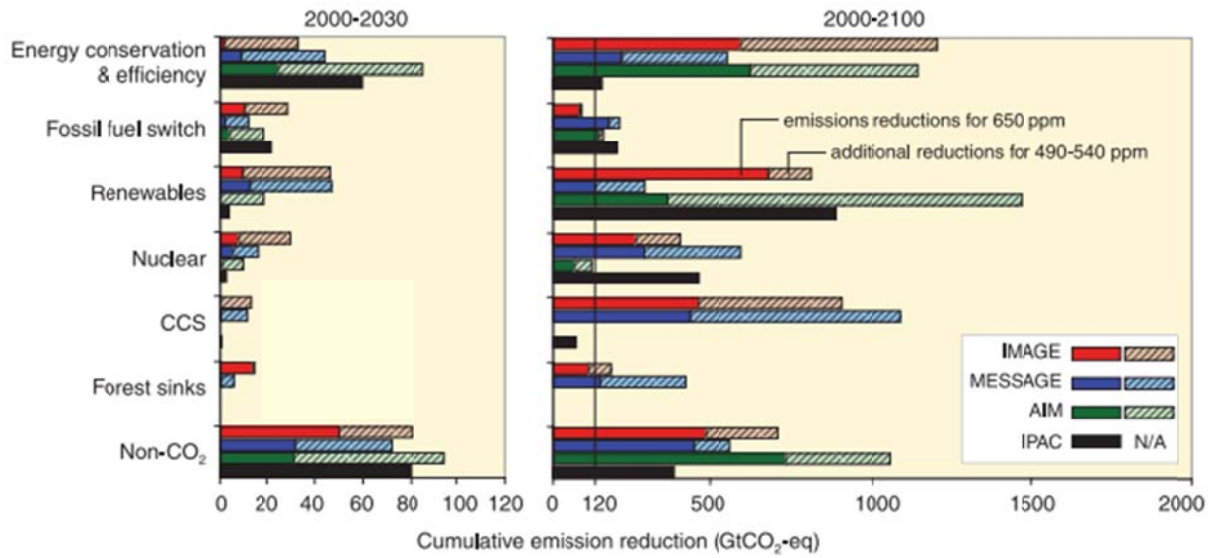

Figure 1-3 Cumulative emission reduction according to 4 mitigation models (Pachauri and Reisinger 2007)

As can be seen in Figure 1.3, improving energy efficiency can play an important role in reducing greenhouse gas emissions and achieving sustainability.

IEA in an update report (2010), recommended 25 energy policy recommendation in different sectors which if implemented, could save as much as 7.6 gigatonnes (Gt) CO2/year by 2030 – almost 1.5 times current US annual CO2 emissions. As figure 1.4 suggests, by applying energy efficiency measures, up to 32% carbon dioxide saving could be achieved in industry sector.

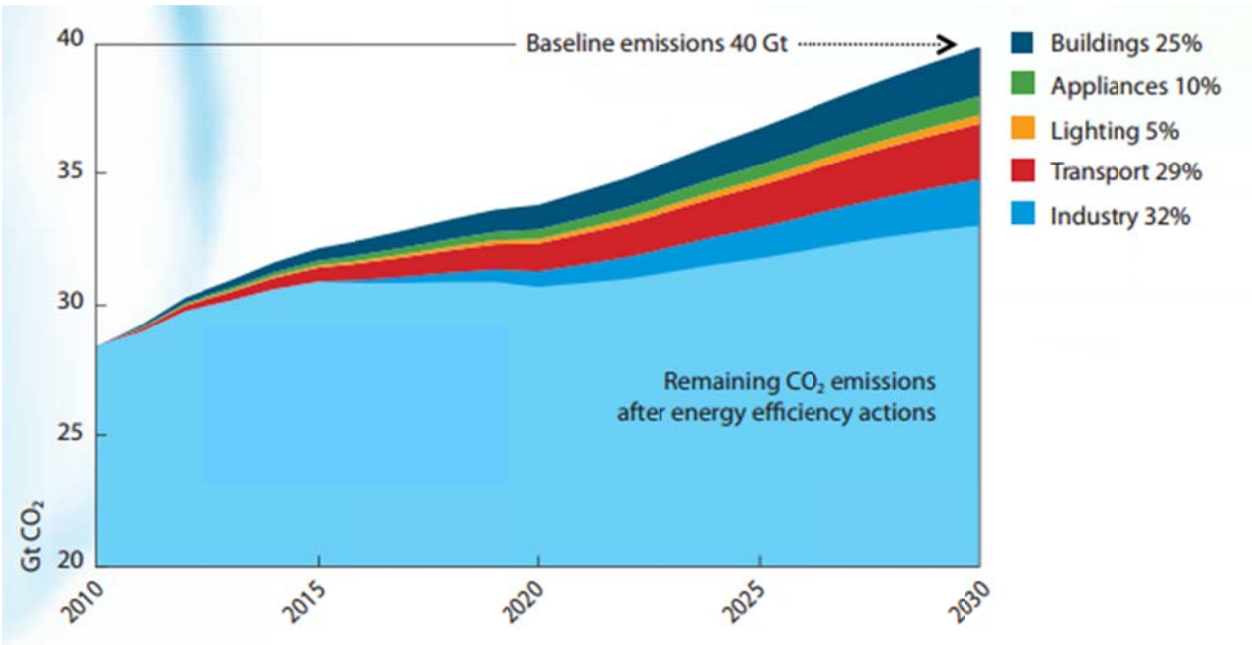

Figure 1-4 : CO2 saving potential from energy efficiency measures (Jollands, Waide et al. 2010)

In an Ethanol biorefinery, recovering ethanol from fermentation broth and purifying it to fuel grade is difficult and energy intensive because of the dilute nature of the fermentation broth and the challenging water-ethanol vapor liquid equilibrium (VLE) with an azeotrope at about 96 wt% ethanol (see Figure 1.5).

Simple distillation cannot be used to distill ethanol above the azeotropic composition. The conventional technology used in the fuel ethanol industry to produce fuel ethanol is distillation close to the azeotropic composition followed by dehydration in a molecular sieve-based adsorption unit (Vane 2008).

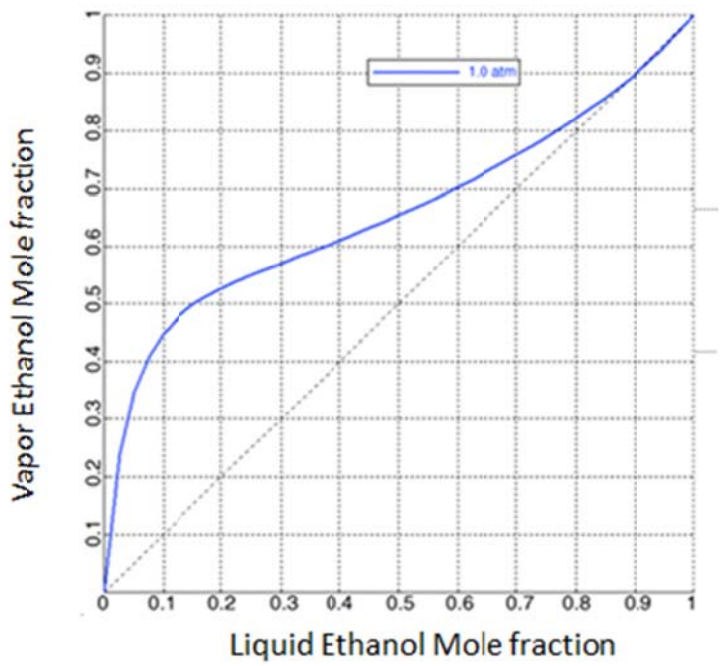

Figure 1-5 : Ethanol-Water equilibrium curve

The ethanol concentration in the fermentation mixture varies from about 10 to 15 wt% for corn ethanol (Côté, Noël et al. 2010) compared to about 3 to 6 wt% for cellulosic ethanol (Cardona Alzate and Sánchez Toro 2006),(Meredith 2003) .

Meredith (2003) estimates that recovering and purifying ethanol from fermentation mixture in case of corn from ethanol needs about 70 % of the steam generated in the dry milling plant. While the separation energy demand for corn from ethanol is high, the separation energy requirement for cellulosic ethanol is even higher due to the huge increase in the distillation energy demand which in turn is the result of low ethanol concentration in the fermentation broth (Côté, Noël et al. 2010).

In practice as mentioned before, for the production of fuel-grade ethanol, the azeotropic ethanol from distillation is dried to fuel ethanol by adsorption with hydrophilic molecular sieve. Unlike distillation columns ,molecular sieves are not a popular separation choice due to their cyclic nature of sorption-regeneration process , additional energy requirement which they inflict to the system and high capital cost (Vane 2008). Figure 1.6 schematically illustrates the general

configuration of ethanol-water separation system. In some cases an optional side stripper in rectifier can be added to the system (Summers 2006), (Kwiatkowski, McAloon et al. 2006)

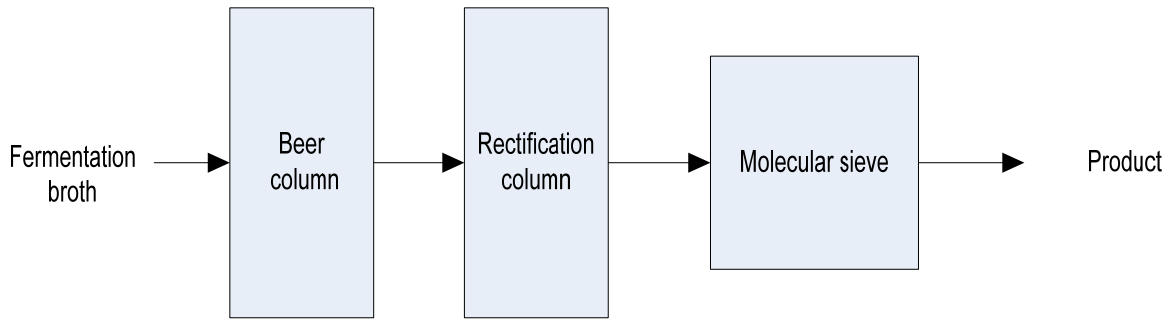

Figure 1-6 : Schematic diagram of the downstream separation of an ethanol biorefinery

Distillation is a common separation technique in biofuel industry. Advantages such as high alcohol recovery, scalability, adequate energy efficiency at moderate concentration (i.e >10 wt%) make distillation an attractive option (Vane 2008).

On the other hand disadvantages such as Azeotrope formation which prevents the achievement of final desired dryness and high- energy requirement in alcohol concentration of less than 5 wt%, have pointed to the need for techniques that can overcome the azeotrope constraint and being simultaneously less energy-intensive. In lignocellulosic ethanol where ethanol concentration in the fermentation broth is low (<5 wt%), product inhibition is not an important issue thus end-of-pipe alcohol recovery techniques can be used to recover and dehydrate ethanol. If inhibition becomes an important issue like in the case of butanol or higher concentrated ethanol, an integrated fermentation and separation technique known as slip-stream recovery is required to remove the product before it reaches the inhibitory concentration which is lethal to micro-organism (Vane 2008). Figure 1.7 illustrates the recovery modes in enzymatic pathway.

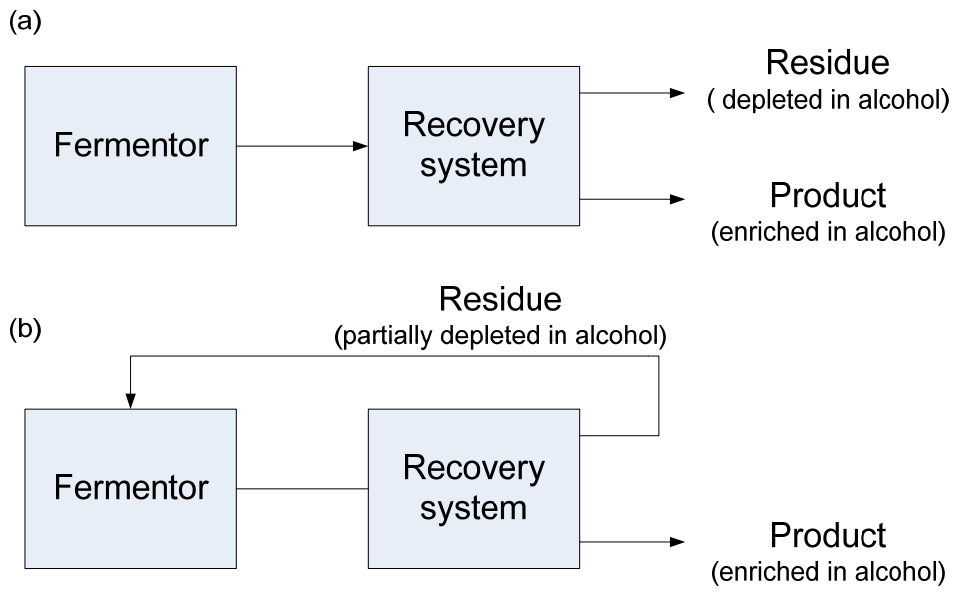

Figure 1-7 : Recovery mode in alcohol production from enzymatic pathway a) End-of-pipe b) Slip-stream

1.2 Alternative separation techniques

The most often considered end-of-pipe alternative techniques to replace the conventional practice of ethanol-water separation generally fall into 4 general groups. These groups consists of techniques that include alteration to standard distillation, distillation-like techniques, membrane-based approaches and Liquid-Liquid extraction

- **Alteration to standard distillation**

Several modifications can be made to a standard distillation unit to avoid azeotrope formation and improve VLE pattern of ethanol-water mixture. These include addition of solvents or salts to alter the VLE behavior of the mixture. Examples of solvents include ethylene glycol (EG), benzene and cyclohexane.

Heterogeneous azeotropic, extractive and pressure swing distillation fall into this group of alternatives. In Heterogeneous azeotropic distillation, an entrainer is added to the system which forms a low-boiling heterogeneous azeotrope allowing a relatively easy separation through two distillation columns and a decanter (Henley, Seader et al. 2011) .

In extractive distillation, a high-boiling solvent is added to the azeotropic mixture in the extractive column which, alters the VLE and is later retrieved in the recovery column. Key components are recovered in the overhead of extractive and recovery columns (Zaretskii, Rusak et al. 2010).

In pressure swing distillation which does not involve an entrainer, two columns operating at different pressures are used. Pressure selection for columns depends on VLE behavior of the components and the choice of cooling system in the condenser (Henley, Seader et al. 2011).

Figure 1.8 schematically shows pressure swing distillation in a minimum-boiling azeotropic mixture. The total feed F1 to column 1 which operates at lower pressure (P1) is the sum of the fresh feed F and the recycled distillate D2 at mole fraction close to azeotropic mole fraction of high pressure curve. The mole fraction of the total feed F1 (xF1) is richer in A than the azeotropic mole fraction at pressure P1. The bottoms of column 1 is almost pure A. The distillate leaving column 1 is at the mole fraction xD1 and is richer in A than the azeotropic mole fraction at low pressure (P1), but less rich in A than the azeotrope mole fraction at high pressure (P2). Distillate D1 is sent to column 2. Almost pure B is obtained from bottom of column 2, and the distillate D2 is recycled to Column 1.

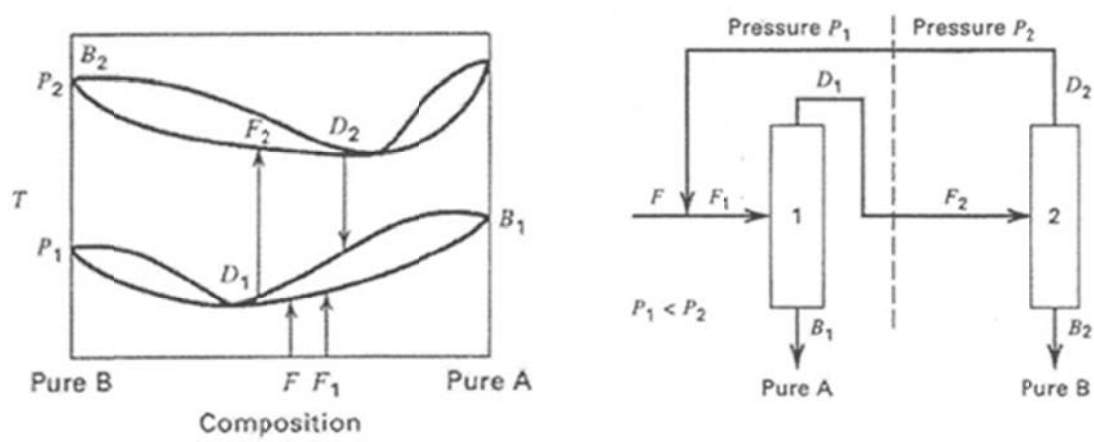

Figure 1-8 :Pressure swing distillation schematic in a low-boiling azeotrope (Mazzotti 2005)

Luyben et al. (2013) compared extractive distillation and pressure swing distillation for separation of an azeotropic mixture. Through a techno-economic analysis extractive distillation

was identified as the superior option. However their analysis did not include the energy consumption and costs related to the beer column.

Marquardt et al. (2008) also evaluated several azeotropic distillation for the separation of ethanol and water in a systematic design framework. This framework proposes a three-step approach in which firstly different flow sheets are generated , next through shortcut methods which have been developed in their group, the flow sheets are evaluated and screened and in the final step and after a MINLP optimization the best alternative is identified. The proposed optimization program being the final step after two previous eliminatory steps has been reported to be quite straight-forward. Among several alternatives such as pressure swing, heterogeneous azeotropic distillation, pervaporation-distillation and extractive distillation, they found extractive distillation as the most energy-efficient option.

Bastidas et al.(2010) compared three dehydration techniques namely extractive distillation, heterogeneous azeotropic distillation and molecular sieve for the production of fuel-grade ethanol. Through an Aspen simulation and after calculating the operating and capital costs of each alternative, they identified extractive distillation to be the best option among all.

In other types of study, Errico et al. (2012) examined extractive distillation as the base case for dehydration of ethanol from fermentation and proposed a systematic method for the generation of new distillation sequences by employing the successful thermally coupling technique for ideal mixtures. They identified several variations of column sequences and concluded that operating and capital cost reductions are feasible through these new configurations.

In a similar study to the work of Errico, Van duc et al. (2013) retrofitted an extractive distillation to thermally coupled columns for an azeotropic mixture. Significant reduction in energy consumption was observed as a result of this modification.

- **Distillation-like techniques**

Gas and steam stripping has been proposed for recovering alcohol from fermentation broth. Transferring the alcohol from a mixture to a gas stream is a relatively simple process.

In gas stripping, an inert gas or the carbon dioxide produced in the fermentor can be introduced to stripping column for removal of the alcohol. In a condensation stage after the stripper, the alcohol is recovered. It is obvious that stripping stage cannot remove the whole water and consequently

other separation steps are needed to fully dehydrate the alcohol. The advantage of gas or steam stripping is its ability to work at temperatures similar to those of fermentors. This finds importance in situations where toxicity inhibits higher yield like in butanol fermentation or ethanol at higher concentrations (> 10 wt%).

Taylor et al. (1995) after conducting a cost analysis has shown that the fermentor/stripper is possibly a lower-cost alternative to conventional fermentation and distillation for ethanol-water separation.

In another work Taylor et al.(2000) have reported a savings of $0.03 per gallon of ethanol produced by the stripping process. Steam stripping operates similar to gas stripping with the difference of feeding steam as the stripping agent. Figure 1.9 depicts the general configuration of steam stripping for recovering alcohol.

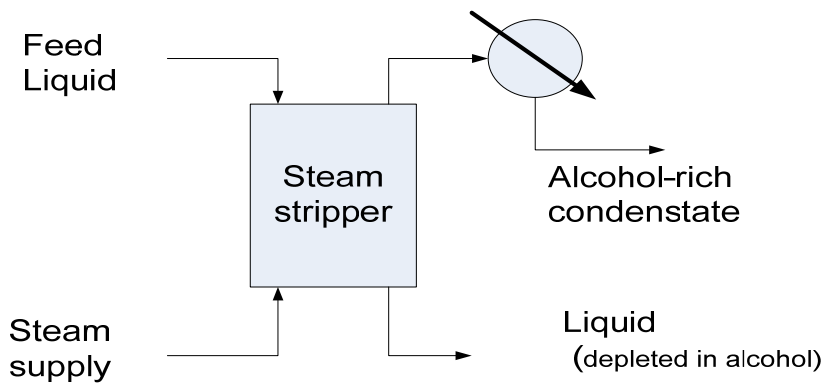

Figure 1-9 Steam stripping process for recovering alcohol

Vane (2008) breaks down the energy demand in a gas stripper and compares it with steam stripping for separation of fermentation broth. Due to non-existence of incondensable inert gas in steam stripping, the condensation of vapor stream can be done in higher temperatures resulting in lower condensation duty relative to gas stripping.

- **Membrane-based techniques**

Membrane-based technologies have gained a substantial position in biofuel industry for recovery and dehydration of alcohol fuels from fermentation broth. The parameters based on which

membrane-based processes operate fall into two distinct categories; size and chemical potential. Processes which operate based on size include Ultra filtration, Micro filtration etc. Processes which function based on chemical differences between the components and membrane material includes Pervaporation and vapor permeation (Vane 2013).

The selective permeation of one of the key components in the mixture circumvents the vapor-liquid equilibrium (VLE) constraint. In pervaporation process, a liquid feed stream is brought to contact with one side of a non-porous membrane. A vacuum or a sweeping gas on the other side of the membrane creates the permeate vapor stream. Components of the feed due to difference in their sorption and diffusion behavior, selectively partition into the membrane, diffuse through it and evaporate into vapor permeate side. Vapor permeation follows the same principal with the exception that the feed to the membrane is a vapor (Henley, Seader et al. 2011). Figure 1.10 depicts pervaporation and vapor permeation processes and their differences. In vapor permeation process in contrast with Pervaporation, feed side temperature and pressure drop are insignificant since the feed is a pressurized vapor and goes through no phase change. This property of vapor permeation provided that the required driving force for separation is generated makes this process more energy efficient than other membrane systems like pervaporation (Fontalvo, Cuellar et al. 2005)

Organic and inorganic compounds are used to build membrane materials. Polymers such as PDMS (silicone rubber) are used to selectively pass inorganic material through the membrane in a water-inorganic solvent mixture. PDMS membranes are categorized as hydrophobic membranes. On the other hand polymers like PVA(polyvinyl alcohol) is used in dehydration step to selectively separates water from the mixture and are classified as hydrophilic membranes (Vane 2013).

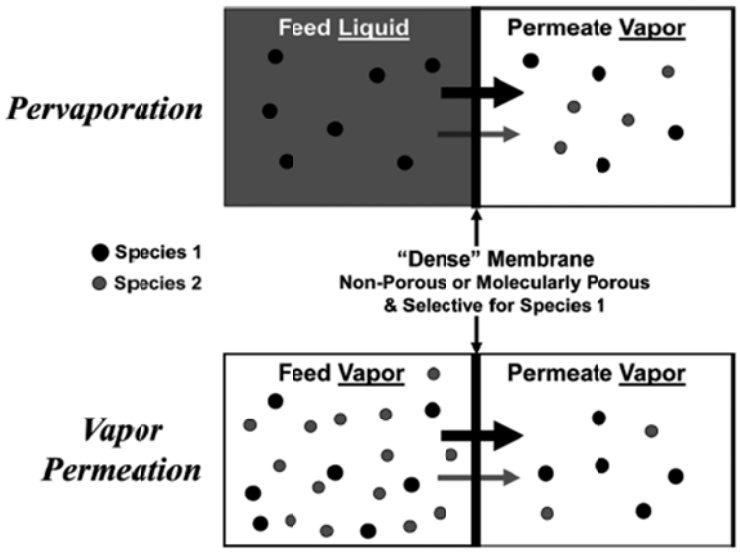

Figure 1-10 : Membrane pervaporation and vapor permeation systems (Vane 2013)

Many scientists have investigated the role of membrane-based technologies in biorefining and particularly in downstream separation.

Yi He et al. (2012) have examined the latest advancements in membrane technology for biorefinening. They have identified several potentials for using membrane in variety of applications in a biorefining context. Low energy requirement and membrane fouling are among the main advantages and disadvantages of membrane reported by them. Application of membranes in dehydration step of fermentation broth has received significant attention over the past years.

Sander et.al (1988) have examined the energy consumption of producing fuel-grade ethanol from azeotropic mixture in a PVA based membrane system. In their paper they described the development of a special plate -type membrane module and an integrated permeate condenser combined in one compact unit. They examined the specific design criteria as well as the operational performance of the first commercial-scale pervaporation plant.

Sandet et al. (1991) in another work compared energy consumption of membrane-based processes and molecular sieve in dehydration of ethanol from azetrope composition (~ 95 wt%) to fuel-grade ethanol(~99.5 wt%) and reported a superior performance for membrane processes.

However the molecular sieve in their study was regenerated by external steam supply rather being regenerated by purified ethanol.

Tsuyumoto et al. (1997) have reported a fuel-equivalent energy usage of 0.71 MJ per kilogram of ethanol in their hollow fiber-type membrane for dehydration of azeotropic mixture. However in their report they made no energy comparison with the conventional methods.

Kunnakorn et.al (2013) have compared azeotropic distillation of an ethanol-water mixture with a hybrid distillation-pervaporation process and shown that membrane option outperforms the azeotropic distillation in operating and capital costs.

Most energy and cost comparisons in alcohol dehydration have been made between hybrid distillation-membrane processes and ternary azeotropic distillation and in most of the cases membrane process have been reported to be more energy efficient.(Lipnizki, Field et al. 1999), (Humphrey and Siebert 1992), (Drioli and Romano 2001), (Noble and Stern 1995), (Kunnakorn, Rirksomboon et al. 2013).

- **Liquid-Liquid Extraction**

Liquid-liquid extraction and perstraction have been investigated in several works mostly for in-situ removal of butanol from fermentation in order to decrease micro-organism inhibition (Groot, Van der Lans et al. 1992),(Ezeji, Qureshi et al. 2004), (Qureshi and Maddox 2005).

In liquid-liquid extraction, a liquid extractant is added to the fermentation broth and the alcohol as well as the water is transferred into the extractant. This contact could be done directly via a mixing device or through a packed-column contactor or indirectly via a porous membrane which the latter is often referred to as “Perstraction” (Henley, Seader et al. 2011).

In order to reuse the extractant, the absorbed compound should be removed in a following regeneration unit. Figure 1.11 schematically shows Liquid-Liquid extraction process.

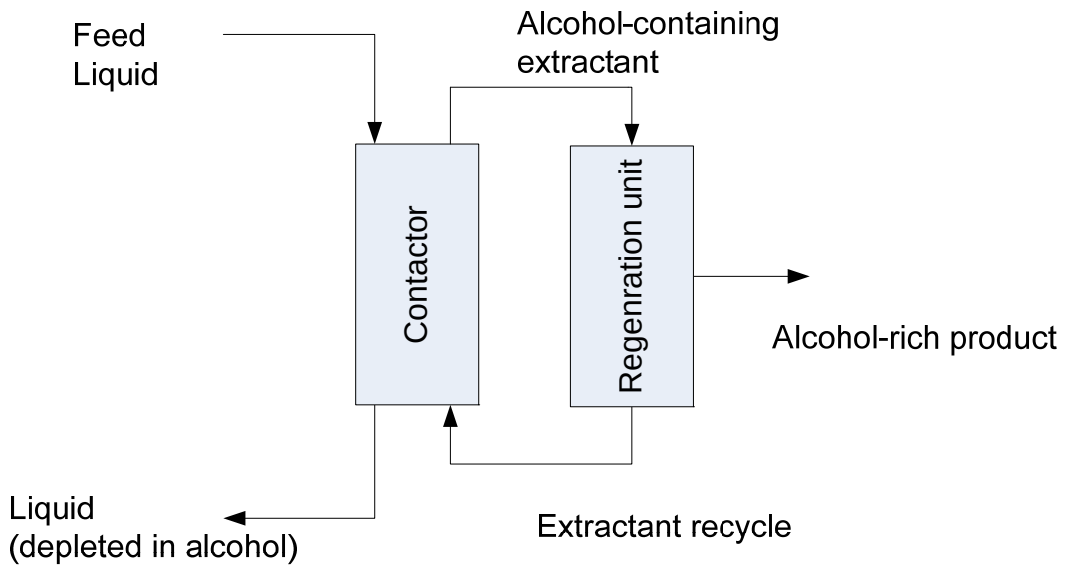

Figure 1-11 : Liquid-Liquid extraction process

The choice of solvent selection has significant influence on the performance of liquid-liquid separation as well as on the energy efficiency of subsequent separation steps to recover the solvent and the product. The most commonly investigated extractants include long alkanes, long-chain alcohols, fatty acids and silicone oils. The concentration of alcohol after regeneration unit depends on the selectivity of the extractant for the alcohol. The alcohol after this step needs another purification level to reach fuel-grade purity (Vane 2008).

Ionic liquids have recently attracted attentions and shown superiority over solvent extraction (Fadeev and Meagher 2001).

1.3 Integration

In order to provide the energy demand of a new biorefinery, a new utility system including a cooling tower and a steam boiler must be built in a stand-alone design. From energy stand point it will be much more cost-effective if a biorefinery is set up in the proximity of a pulp and paper facility in order to use the existing equipment for satisfying its demand. Furthermore from economic perspective, the competitiveness of lignocellulosic ethanol production could potentially be improved if they were integrated with existing facilities. This synergy is furthered by the growing interest from pulp and paper industry to expanding their product portfolio (Moshkelani,

Marinova et al. 2013) . There are great opportunities in integrating a biorefinery with a pulp and paper facility which can provide a competitive advantage for the biorefinery. The examples of integration opportunities include using existing infrastructure and unit operations, recovering heat and employing existing skilled personnel (Moshkelani, Marinova et al. 2013), (Lundberg, Axelsson et al. 2012), (Fornell and Berntsson 2012).

1.3.1 Energy efficiency studies in downstream separation of lignocellulosic ethanol biorefineries

Several studies over the past years have investigated the importance of energy efficiency in lignocellulosic ethanol production. Colura et al. (1988) investigated a few modified designs in evaporation and distillation of an ethanol facility to minimize energy consumption. Internal heat integration in distillation and in evaporation using heat pump and external heat integration between distillation and evaporation were considered. They concluded that heat pumping due to decreasing operating cost was a favorable option.

The energy efficiency of an ethanol production was reported to improve by using heat pump in distillation and evaporation units and also by optimizing the heat exchanger network of distillation train in the work of Ficarela et al (1999).

Several integration aspects were examined in the work of Galbe et al. (2002) including integration of distillation and multi-effect evaporation. They concluded that reducing energy demand creates opportunities for by-product sales and is vital for the economics of the process.

The advantages of using a structured packing in the rectification column of an ethanol production facility was investigated in the work of Summers (2006). Lower pressure drop and thus lower temperature difference as the result of using this structure creates more opportunities for internal and external heat integration.

Integration with a district heating system which fostered more energy efficiency and reduced the operating cost was examined in the work of Sassner et al. (2007).

Haelssige et al. (2008) conducted a techno-economic analysis on 6 different fermentation-distillation strategies. One and 2-column distillation series were considered with inclusion of heat pump in two of the schemes. They reported that 2 heat integrated columns and one column using a heat pump were the most favorable schemes.

1.3.2 New opportunities for Kraft mills

As mentioned earlier due to increasing competition in pulp and paper sector and simultaneous decline in the demand, a growing focus has been placed on utilizing different wood constituents to produce new products in order to diversify the product portfolio and improve the economics.

In North American context, Van Heiningen (2006) stated the importance of producing bioenergy and biomaterial alongside the traditional pulp and paper products to remain competitive. He presented the concept of Integrated Forest Product Biorefinery (IFBR) which aims at producing value-added products such as biofuels, carbon fiber and biopolymers to generate more revenues for the core business.

The U.S Department of Energy (2007) published a report identifying building block chemicals which could be co-produced from wood constituents. They reported power, fuel and syngas production as the main potentials for lignin in near terms and micro-molecules and aromatics as longer-term applications of this substance.

Extracting hemi-cellulose prior to pulping and hydrolyzing in order to produce ethanol was investigated by Frederick et al. (2008). They concluded that their small scale process model resulted in high capital cost and that the price of raw material has a large impact on the economics of the process.

In another study retrofitting a pulp mill to produce ethanol instead of pulp was examined by Phillips et al. (2008). They concluded that this could be an interesting way to produce ethanol as they identified the potentials for using existing infrastructure and reducing capital cost.

In another study by U.S Department of Energy (2006), the possibility of producing biofuels from spent liquor in thermo-chemical pathway was investigated. The study identified a potential opportunity from this pathway if the technology is commercialized.

Chambost et al. (2008) identified several challenges such as key technological, financial, cultural and enterprise transformation (ET) risks related to implementation of forest biorefinery at existing pulp and paper mills. They proposed a three-phase implementation strategy which fosters cost reduction with fossil fuel replacement, revenue increase with production of new products and margin optimization through knowledge-based production. Product design and foundation concepts with regard to ET were also discussed in their study.

Wising et al. (2006) in their work highlighted the importance of process integration in identifying possible products which can be economically produced in a pulp and paper mill. They concluded that specifying possible products with regards to market demand, product margins, production flexibility and the supply chain in conjunction with examining and modelling the process and using cost accounting models for the mill should be strategically taken into account before embarking on a biorefinery pathway.

Another opportunity for pulp and paper facilities which is a corollary of integrating a biorefinery is reduction in energy consumption.

Axelsson et al. (2006) identified opportunities for saving 52-56 MW of steam through pinch analysis of a model mill. The same measures could be used in designing or retrofitting a biorefinery plant.

Schenck et al. (2007) evaluated the possibilities for heat integration in an ethanol process. The excess heat could be mutually used in a pulp and paper facility in an integrated plant or could decrease the utility consumption of the biorefinery in a stand-alone project.

Lundberg et al. in (2012) explored the integration of semi-neutral hemicellulose extraction in a Kraft pulp mill and have shown that it is possible to eliminate the need for additional steam through a rigorous heat integration with Kraft process. Finally they concluded that the success of biorefinery concepts is materialized by implementation of intensive energy integration and optimization measures.

Fornell et al. (2009) by applying conventional as well as process integration measures analyzed the energy efficiency of a pulp mill converted to an ethanol production plant and reported steam reduction of 36-42% as a result of integration.

1.4 Energy efficiency methods

The most common and widely-used method for energy integration in a plant is the famous pinch analysis developed by Linnhoff et al. (1982). Since its introduction until today, the pinch methodology has been used in a wide variety of processes and industries.

In this method hot and cold composite curves (HCC, CCC) which combine all the hot and cold streams of a plant are constructed, the potentials for heat saving are identified and minimum energy consumption is obtained. The heat saving is proportional to the minimum temperature difference between the hot and cold streams. Grand composite curve which is resulted from HCC and CCC represents the net heat flow in the system relative to temperature. GCC is used to determine the temperature level of utilities and also is used to evaluate the position of a process unit against the background process (Split GCC). The concept of pinch method has been schematically shown in Figure 1.12.

Pinch methodology over its lifetime has evolved into new areas of applications such as efficient use of water and hydrogen proposed by Klemes et al. (2011).

Hackle et al. (2011) and Klemes et al. (1997) studied the concept of "Total site heat integration" which examines the integration of several processes at an industrial site via pinch analysis.

A challenging issue which faces industrial processes in energy optimization projects is retrofitting their current heat exchanger network. Another application of pinch analysis in addressing retrofit cases is to solve pinch violation and proposes and identify a new topology after the modifications correcting pinch violations are applied (Tjoe and Linnhoff 1986).

Mathematical approaches have also been investigated and implemented in addressing the retrofit problem of existing heat exchanger networks. Ciric et al. (1989) proposed optimization-based approaches in addressing this issue. Asante et al. (1997) proposed an automated and interactive approach for a practical retrofitting of an existing heat exchanger network. Their proposed method has so far been the most used and implemented approach in retrofit issues.

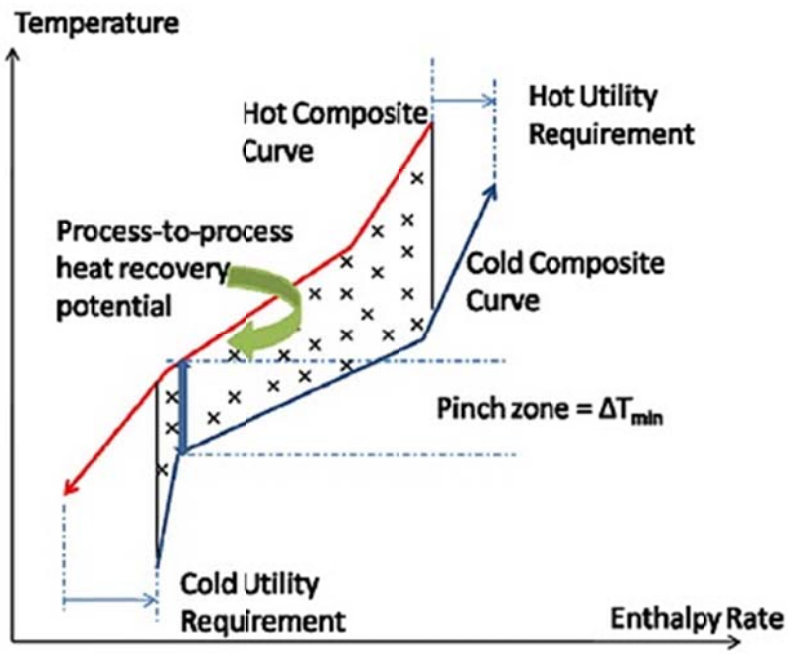

Figure 1-12 : Hot and composite curves (Dornfeld 2010)

Although pinch-based methods have been successful in addressing the retrofit problem of existing heat exchanger network but issues like complexity and local optima in mathematical approaches and use of heuristics in others, have somewhat hindered finding an optimal solution.

Bonhivers et al. (2014) in their study discuss that the difficulties of existing approaches in addressing retrofit situation are due to lack of understanding on how heat is transferred and degraded from hot utility to environment. In his work he has introduced a graphical method called Energy Transfer Diagram (ETD) whereby heat saving opportunities in a given process operation are identified. The heat saving opportunities requires modification to the existing HEN. These heat saving modifications imply bridging heat outlets to hot utility users. Through energy transfer diagram these modifications are identified via a set of "bridges" through which heat outlets are linked to hot utility sources.

In this method, the flow rate of heat transferred as a function of temperature through unit operations and heat exchangers are depicted by Energy transfer curves.

Figure 1.13 shows the actual flow rate of heat in heat exchanger and process operations in a hypothetical plant.

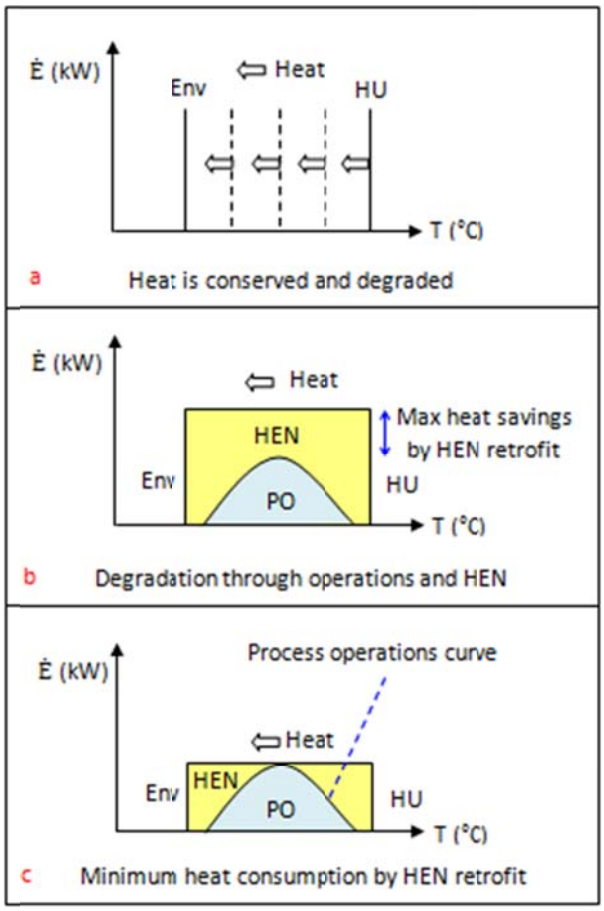

Figure 1-13 : Energy transfer diagram concept a- Heat is conserved and degraded in process operations b- Heat saving in HEN is equal to maximum of process operation c- Situation after HEN retrofit (Bonhivers, Korbel et al. 2014)

The shape of a process diagram is normally in the form of a rectangle if heat is not converted to another form. In this given system as Figure 1.13 suggests, the minimum heat consumption that can be achieved by HEN retrofit is equal to the maximum of the global process curve. The global process curve lies between the process area including the operations, and the HEN which includes the heat exchangers. In order to achieve heat savings, a set of HEN modifications that reduces the flow rate of heat transferred between the heating utility and environment is required. The minimum heat consumption after retrofitting the heat exchanger network is equal to the maximum of the global process curve. Another implication of constructing the ETD of a process operation is obtaining a global view of the energy transferred in unit operation with respect to the temperature. In that sense energy transfer diagram can provide designers with insights on how to modify the process condition in order to reduce the energy consumption.

1.5 Gaps in the body of knowledge

Based on the literature review the following gaps in the body of knowledge were identified:

- **A systematic methodology:** It is imperative to develop a systematic approach that can analyze the downstream separation of a bio process for the purpose of energy reduction. Such methodology by employing systematic tools can identify process modifications and heat recovery potentials and also through techno-economic metrics can select the best separation alternative. This methodology in particular should :
    - **Employ novel insight-based method for identifying heat recovery opportunities:** Designing grass-root heat exchanger network with pinch analysis results in maximum energy recovery network and is a straight-forward task. In retrofit situations, on the other hand, obtaining the maximum recovery is not as easy, which not always leads to optimum solution.. Thus employing a method that can easily identify the integration opportunities and enhance the recovery is much needed.
    - **Identify necessary modifications to process operation for energy reduction:** Commonly, the main focus of energy reduction studies is placed on modifying existing heat exchanger network and potentials for energy reduction through systematic analysis of process modification has not systematically been addressed. Therefore, utilizing a tool that can map the underlying process units in a global energy-temperature curve, which shows the heat flows in the process operation, is necessary. This tool should identify the modifications which can potentially lead to energy reduction.

CHAPTER 2 METHODOLOGY

In order to put the hypotheses assumed in this work to the test and develop a methodology for early-stage design decision making, the following steps presented in Figure 2.1, have been employed. The major steps of this project methodology are as follows:

- **System definition**
  Dilute fermentation broth (5 wt%) is purified and dehydrated to fuel-grade ethanol (99.5 wt%) as the product.
- **Identification of separation strategies**
  Separation strategies are identified based on their separation performance to achieve the objective of the system definition step. Systematic frameworks have been proposed by different scientist such as Marquardt et al. (2008) to select the best choices of separation systems.
- **Stand-alone non-integrated design**
  The selected separation systems are simulated and designed to achieve the goal of the system definition step. After performing a mass and energy balance and data extraction, the designs are evaluated based on their operating and capital costs. The final metric of total annualized cost (TAC) is calculated for each design.
- **Stand-alone internally-integrated design**
  In order to design a heat-integrated flow sheet, the stream data extracted from mass and energy balance in stand-alone design is employed in order to be analyzed for energy targeting via pinch analysis. In order to further analyse the designed flow sheets, the energy transfer diagram (ETD) of each flow sheet is constructed and possible process modifications to improve energy efficiency are identified. After these steps, the heat exchanger network of the new designs is constructed according to pinch method. Finally the designs are evaluated in their operating and capital costs.
- **Integrated-with Kraft design**
  In order to design an integrated separation system, the data from energy analysis and the heat exchanger network of the internally-integrated design are used to identify possible heat integration with a Kraft pulp mill. The energy integration opportunities are identified through Bridge analysis.

After identification of the bridges, the energy savings and their associated capital cost are evaluated.

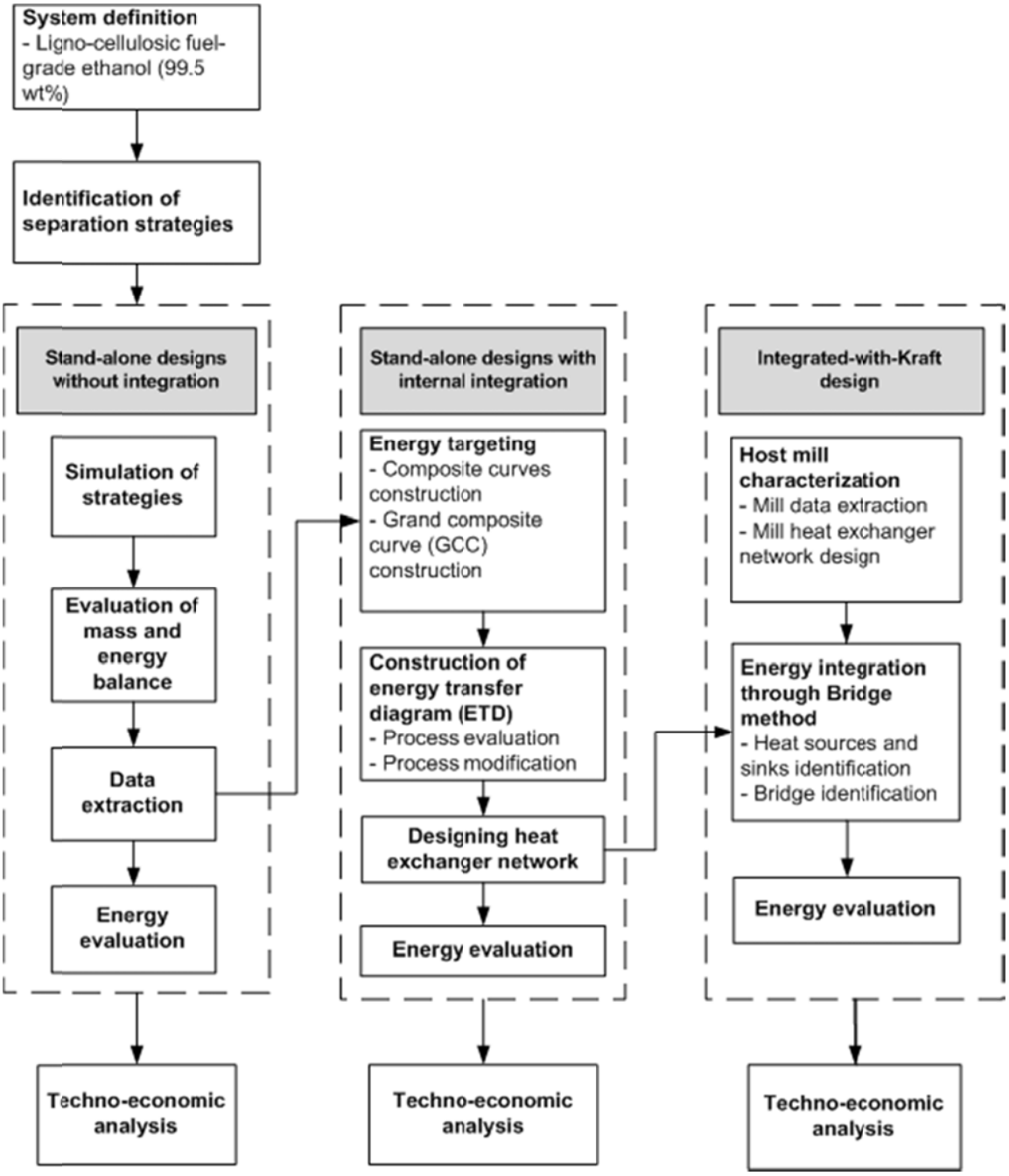

Figure 2-1 : Step-wise project methodology

2.1 Process simulation

A multitude of commercial flow sheeting softwares such as Aspen plus, Hysys, ProII ,etc. are used to do the calculations related to phase change in multi-component mixtures. Most of these programs use similar approaches for solving the problems. Several empirical thermodynamic equations , activity coefficients and binary interaction parameters for different compounds are included in the database of these programs. In this study Hysys and Aspen plus have been used for estimating mass and energy balances. Selection of thermodynamic property method is of paramount importance since it can have a big impact on the final result. The thermodynamic model adopted for this study is NRTL which perfectly predicts the non-ideality of azeotropic mixtures and is in accordance with several studies such as Luyben (2013). The number of stages and feed stage was set to obtain a minimum reboiling duty or minimum reflux ratio. In vapor permeation system the necessary process data were obtained from Pervatech company (www.pervatech.com). Details of simulation results and stream data are presented in Appendix c.

2.2 Pinch analysis

The thermal analysis used in this study is the conventional pinch analysis described by Linnhoff et al. (1982). Stream data associated with hot and cold streams were combined to construct the respective Hot Composite Curve (HCC) and Cold Composite Curve (CCC). A minimum temperature difference of 10 $^{\circ}$C between hot and cold streams was considered. The Grand Composite Curve (GCC) which shows the net heat flow was constructed to obtain the minimum hot and cold utility requirement. Excel spreadsheet was used to perform the pinch analysis and construct the composite curves.

2.3 Energy transfer diagram (ETD)

Energy transfer diagram was constructed as proposed by Bonhivers et al. (2014). In ETD the vertical axis represents the flow rate of energy transferred (E$^{\circ}$) and the horizontal axis represents the temperature range between the heating utilities and the environment. In this study ETD is used to present the transfer of energy vis-à-vis the temperature through process operations and provide a tool for holistic analysis of the designs. The application of energy transfer diagram for process modification for energy saving is schematically shown in Figure 2.2. As this Figure

suggests, altering the pressure of a distillation column can reduce the minimum heat consumption in a plant. The insights obtained from ETD for process modification is just the first-stage screening; meaning that implementing them requires more thorough investigation in next stages for their feasibility. In this study, the opportunities for process change are identified and discussed as a first-stage screening procedure.

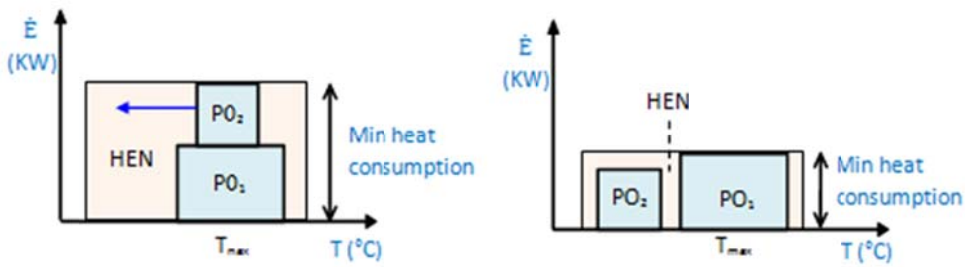

Figure 2-2: Process modification through ETD. Decreasing minimum heat consumption by altering the pressure of distillation column PO2 (Bonhivers, Korbel et al. 2014)

2.4 Heat exchanger network design

The grass root heat exchanger network for separation strategies have been designed according to Linnhoff et al.(1982). The networks have been designed to achieve the Maximum Energy Recovery (MER) for a relevant minimum temperature difference (10 ˚C). Excel spread sheet was employed for designing the networks. Detailed costs for piping and pressure drop have not been accounted for since the processes are conceptual. However, in integration with a Kraft mill, an additional cost was assumed for piping between the biorefinery and the Kraft mill, which is explored in economic data in Appendix B.

2.5 Integration through Bridge method

A bridge is a set of matches which links a heat outlet (${C_X}^S$) to a heater receptor (${h_Z}^r$). In this method as elaborated by Bonhivers et.al (2014), Process heat sources are broken down into suppliers of process heat exchanger (${e_y}^S$) and suppliers of cooler (${C_X}^S$) in the existing HEN. Process heat demands on the other hand are broken down into receptors of process heat

exchanger ($e_y{}^r$) and receptor of heater ($h_z{}^r$) in the existing network. A match is a connection between supplier and receptor and a set of matches linking heat outlets with hot utility users is called a Bridge. The bridges can be identified with an algorithm, a grid diagram, an energy transfer diagram or a network table. In this study grid diagrams (HEN) have been used to identify the bridges for external heat integration with Kraft process.

2.6 Capital cost estimation (CAPEX)

In this study the estimated purchased capital costs have been obtained from reference investment cost data from other studies or through industrial quotation from manufacturers. The equipment have been sized and actualized in cost according to conventional equation stated by Peters et al. (2003). The purchased costs have been actualized considering the CE index of April 2013 which is **569.5.**

The total capital cost is the sum of direct and indirect cost applying the method for capital estimation based on purchased equipment cost proposed by Peters et al. (2003). More details have been presented in Appendix B.

2.7 Operating cost estimation (OPEX)

Costs related to the operation of each design were calculated by obtaining the energy consumption of the designs from mass and energy balances. The cost of energy which includes steam and electricity were obtained assuming steam price of 4.1 $/GJ and electricity of 0.05 $/Kwh. The details of economic calculations have been presented in Appendix B.

2.8 Economic analysis

Different designs in this project have been evaluated using the annuity method also known as Total Annualized Cost (TAC) considering a project period of 10 years. The investment cost was annualized by using the annuity factor as shown below and is defined as the share of the loan for an investment that needs to be paid annually throughout the lifetime of the investment (n) in order to pay off the investment and the interest (i). The interest rate assumed for this work is 10%.

$$A = \frac{i(1+i)^n}{(1+i)^n - 1} \quad , \quad TAC = OPEX + A*CAPEX$$

These tools are standard tools for economic evaluations in techno-economic studies which have been used in similar works (Wang, Pan et al. 2012), (Olsson 2009).

The details of economic analyses are found in Appendix B.

CHAPTER 3 RESULTS

3.1 Results

The main results of the work obtained in this study, in order to address the proposed methodology are presented in this section. In the following sections, first the design cases are introduced and evaluated in three different scenarios and secondly an economic comparison of all scenarios is presented.

3.1.1 Design cases

In this section the base case design which is the conventional separation practice for recovery and dehydration of ethanol is presented. The alternatives separation designs namely, double-effect extractive distillation, steam stripping and hybrid distillation-vapor permeation which will replace the base case are introduced and their capital and operating costs are evaluated. Designs are numbered according to their order of appearance in this work; meaning that the base case=1, extractive distillation=2, steam stripping=3 and vapor permeation=4.

The design cases are simulated in ASPEN-HYSYS softwares. After performing mass and energy balances, the energy consumption of each design in terms of heat demand and electricity demand is obtained. The details of simulation data is found in Appendix C. An economic evaluation and comparison among all the options are presented afterwards.

3.2 Stand-alone designs without integration

In this section the design flow sheets in stand-alone basis are presented. The base case design is the downstream separation of a biorefinery which produces fuel-grade ethanol (99.5 wt%) at the production rate of 21.6 Mt/h which corresponds to a 59 MM gal/yr ethanol facility. The lignocellulosic biomass is processed in an enzymatic pathway and after fermentation, a very dilute broth which contains 5 wt% Ethanol is obtained. The fermentation broth is subsequently sent to downstream separation to be dehydrated into fuel-grade Ethanol (Wooley 1999).

Ethanol traditionally is recovered through a series of distillation columns and is dehydrated in a final dehydration step in a molecular sieve (Vane 2008). Fermentation broth with an ethanol concentration of about 5 wt% is preheated and fed to the beer column which its main task is to

remove the dissolved carbon dioxide and solids and to produce a vapor distillate with an ethanol concentration of about 37 wt%. The bottoms of the beer column is an aqueous stream (stillage), consisting of water, dissolved matter, unfermented solids, proteins, and trace amounts of ethanol.

The vapor distillate from the beer column is sent to a rectifier column, which produces an enriched overhead azeotropic product of about 92 wt% ethanol and a bottoms with trace amounts of ethanol. The vapor distillate from the rectifier is superheated and is fed to the adsorption cycle of a molecular sieve unit. The overhead is dehydrated to fuel- grade ethanol by the selective adsorption of water, while in the desorption cycle, the molecular sieve is regenerated with purged dry ethanol vapors. The regeneration stream from the molecular sieve which contains

72 wt% ethanol is recycled to the rectifier.

This process has been shown schematically in Figure 3.1.

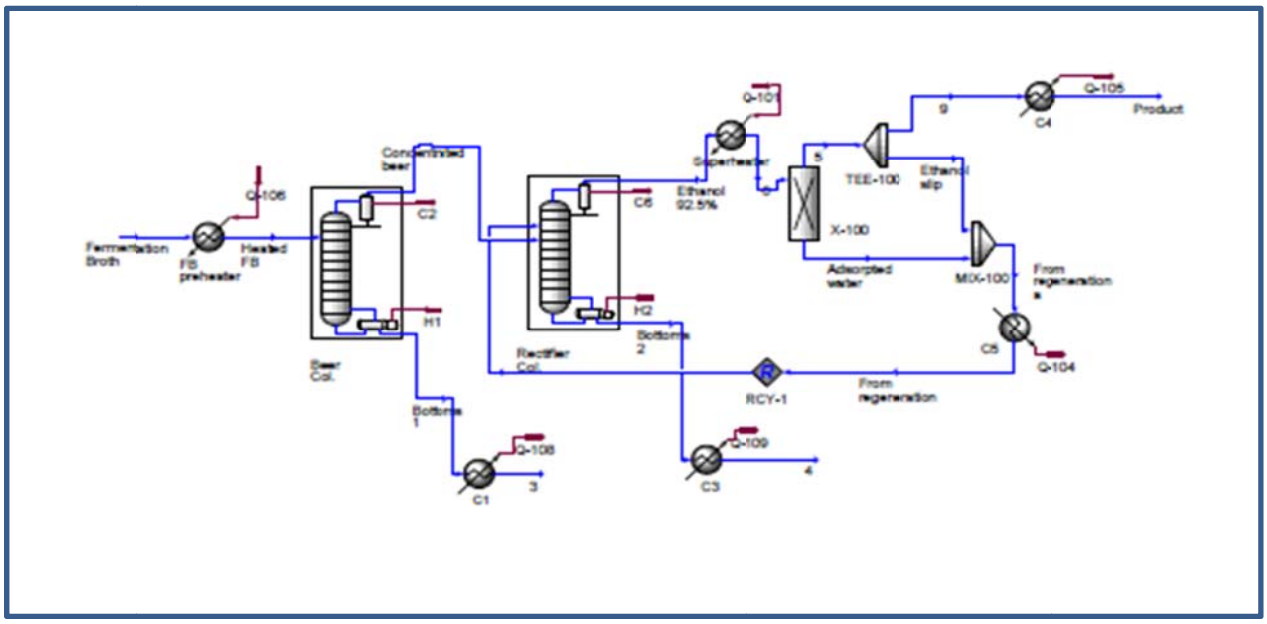

Figure 3-1 : Flow diagram of Ethanol-Water downstream separation (the base case)

A summary of operating conditions of this design is presented in Table 3.1.

Table 3.1 : The operating condition of the base case

Base case specification	
Beer column	
Number of stages	30
Operating pressure (Kpa)	189
Distillate Ethanol concentration (wt%)	37
Steam(MW)	46
Reflux ratio	0.3
Feed stage	5
Rectifier	
Number of stages	60
Operating pressure (Kpa)	150
Distillate Ethanol concentration (wt%)	92.5
Reflux ratio	5
Feed stage	15(from beer),44(from regeneration)
Molecular sieve	
Operating temperature (° C)	116
Purge Ethanol concentration	72
Fuel Ethanol concentration (wt%)	99.5
Energy	
Heat demand (MW)	85
Electricity demand (MW)	Small

3.2.1 Double-effect extractive distillation

One of the ways to overcome the vapor-liquid equilibrium(VLE) constraint and break up the azeotrope, is by adding to the mixture a high-boiling ,non-volatile solvent which is miscible with the mixture and doesn't form any azeotrope with the constituent components. Due to the difference between the affinity of the solvent with the components of the mixture, a change is caused in their relative volatilities and consequently the resulting mixture could be separated in a normal distillation column. The solvent due to its high boiling point is easily recoverable in a secondary column (Van Duc Long and Lee 2013) . Ethylene glycol has been studied in several works as the solvent for ethanol-water mixture (Hernández 2008), (Errico and Rong 2012) . The

efficient recovery and re-use of ethylene glycol is of paramount importance from the perspective of energy demand, cost and process requirements.

In this design first the fermentation broth is stripped, producing a distillate free of solids for subsequent purification in an extractive column to fuel grade ethanol. A double-effect distillation with split feed is used to reduce the huge energy demand needed for removing ethanol from the fermentation mixture. After initial preheating, the fermentation mixture stream is divided into two streams and fed to two beer columns (BC 1 and BC 2) which are in parallel. Overhead vapor distillate from BC 2 is condensed and will provide the required duty of BC 1. In order to balance the duty of the reboiler of BC 1 with the duty of the condenser of BC 2 and also provide enough driving force (ΔT=10 °C) in the reboiler and condenser, the operating pressures of BC 1 and BC 2, and the feed split ratio between them has to be adjusted. Then, the overheads from BC 1 and BC 2 are purified in the extractive column to fuel grade ethanol. Ethylene glycol is recovered in the bottoms of the recovery column and is recycled back to the extractive column. Figure 3.2 shows the extractive design schematically.

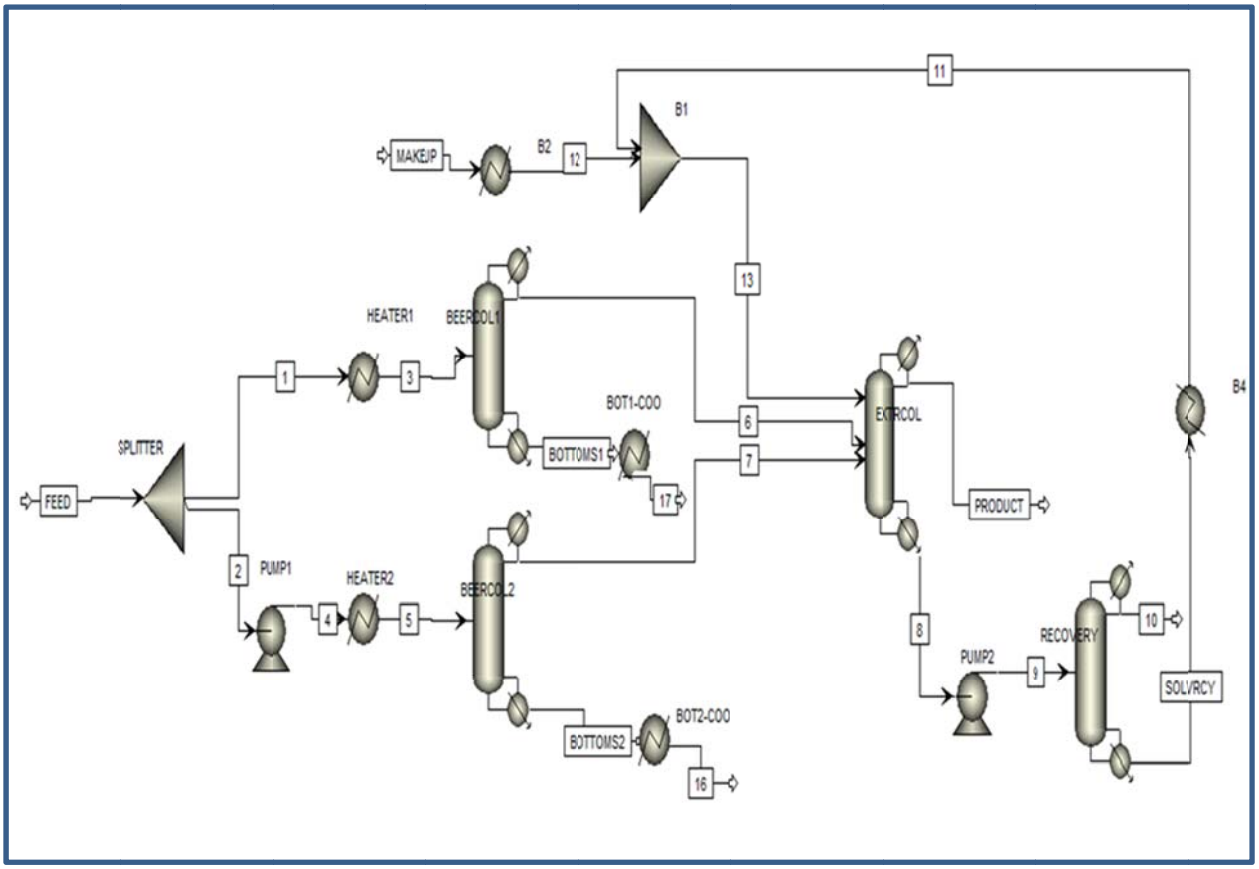

Figure 3-2 Flow diagram of double-effect extractive distillation

Process specifications of this design are listed in Table 3.2.

Table 3.2 : Operating conditions of double-effect extractive distillation

Double-effect extractive distillation specification		
	Feed splitter	
Stream 1	51.5% (mass)	
Stream 2	48.5% (mass)	
	Beer column 1	**Beer column 2**
Number of stages	40	40
Operating pressure (Kpa)	101.3	303.3
Distillate Ethanol (wt%)	92	92
Feed stage	20	18
Reflux ratio	3	4
	Extractive column	**Recovery column**
Number of stages	30	12
Operating pressure (Kpa)	101.3	101.3
Ethylene glycol (Kg)	16,488	99.9 wt% recovered from bottoms
Distillate Ethanol (wt%)	99.5	-
Feed stage	11(BC1 dis.) ,12 (Solvent)	3
Solvent stage	3	-
Reflux ratio	0.9	0.3
	Solvent makeup	
Ethylene glycol (Kg/h)	72	
Solvent-to-feed ratio	0.7	
Total Energy demand		
Heat demand (MW)	78	
Electricity demand (MW)	Small	

3.2.2 Steam stripping

Steam stripping is a common technology in chemical process industries as well as in the treatments of liquid containing volatile components. In this design steam stripper column has substituted for the beer column in the base case. Liquid feed is fed to the top of the column and the steam is fed at the bottoms. The feed and the steam interact counter-currently and as a result ethanol is recovered in the overhead vapor and the liquid water goes into the bottoms.
Stripping factor ratio in a stripping column is defined as S= KV/L.
According to this equation, in which K represent the K-value, V is the amount of required vapor and L is the amount of liquid feed, a higher K-value will increase the stripping factor of the system. Generally in strippers in order to obtain a high K-value, a lower than atmospheric pressure is applied to foster a better performance of the system (Henley, Seader et al. 2011). Another advantage of employing low pressure is that the steam required in the stripper will be at low temperature and this heat demand could easily be satisfied by available sources at low temperature (Ortiz-Del Castillo, Guerrero-Medina et al. 2000).The optimum operating pressure designed for this column is 10 Kpa which correlates to 45 tonne of saturated steam at atmospheric pressure. This low pressure creates a low temperature throughout the system and the corresponding low temperature demands could be satisfied via available sources later on.
The resulting vapor in the stripper overhead contains 42 wt% ethanol. This stream is fed to a rectification column for further purification up to azeotropic composition (~ 94 wt% Ethanol). A partial condenser in the rectifier generates vapor at very low pressure (10 Kpa). The compressor after this stage increases the pressure and thus the temperature of the stream to atmospheric pressure (at 169 °C). Unlike the base case at this temperature this stream needs no superheating for being processed in the molecular sieve since the minimum recommended temperature for Molecular sieve is 116 ˚C. Fuel-grade ethanol is produced in the molecular sieve unit.
Similar to the base case, pure ethanol is used to regenerate the molecular sieve in a cyclic manner. 16% of ethanol product is withdrawn and used for the regeneration. The resulting stream after regeneration contains 72 wt% ethanol and is subsequently recycled back to the rectifier.
This design although more energy efficient than the base case in terms of heat demand but due to low pressure requirement in the stripping column consumes a lot of electricity in the vacuum pump . The schematic of this design is shown in Figure 3.3 and the corresponding operating condition in Table 3.3 .

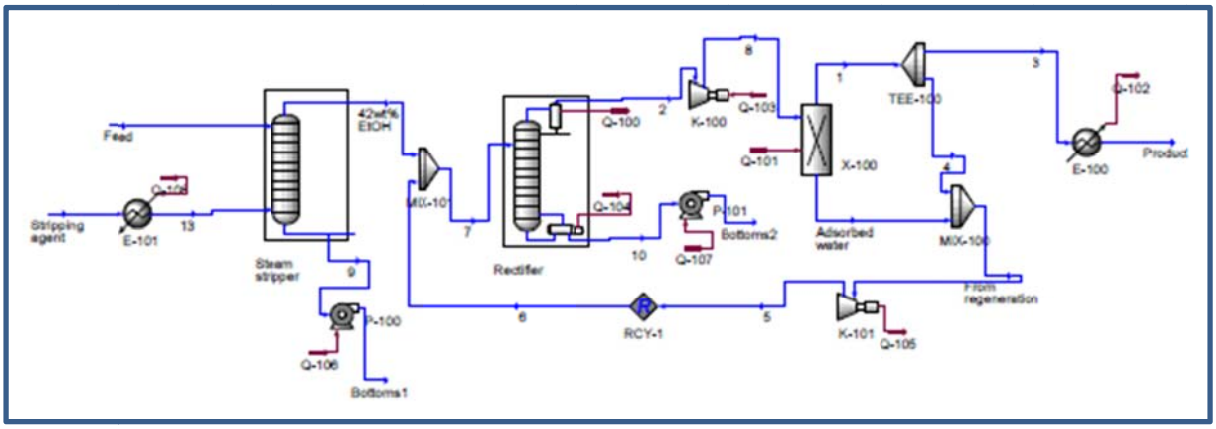

Figure 3-3 : Flow diagram of steam stripping design

Table 3.3 : Operating conditions of steam stripping

Steam stripping specification	
Steam stripper	
Pressure (Kpa)	10
Number of stages	18
Rectification column	
Number of stages	30
Operating pressure (Kpa)	10
Distillate Ethanol concentration (wt%)	93
Reflux ratio	4
Feed stage	28
Molecular sieve	
Operating temperature (° C)	160
Purge Ethanol concentration	72
Fuel Ethanol concentration (wt%)	99.5

Table 3.3: Operating condition of steam stripping (Continued)

Steam stripping specification	
Liquid ring pump	
ΔP (Kpa)	91
Total Energy demand	
Heat demand (MW)	43
Electricity demand (MW)	7.5

3.2.3 Hybrid distillation-vapor permeation

Separation through membrane systems offers several advantages compared to the traditional thermal separation. As stated before, the difference in chemical activity is the main driving force in membrane separation which circumvents the VLE azeotrop constraint (Vane 2013). Lower energy consumption, continuous operation compared to molecular sieve and no needing for entrainers in contrast with extractive distillation is among other advantages of membrane systems.

In Vapor permeation a vapor feed is brought into contact with a non-porous or molecularly porous membrane (Vane 2013). A vacuum or a gas sweep is applied on the other side of the membrane to generate the needed driving force. Water in the vapor feed selectively partition into the hydrophilic membrane, diffuse through it and goes to the permeate vapor side. Consequently, the membrane separates water from the ethanol in the permeate and ethanol goes into the retantate stream.

Fig 3.4 presents the hybrid distillation- vapor permeation design. This design is very similar to the base case with the difference being the substitution of vapor permeation for the molecular sieve unit.

Fermentation broth after being processed in beer and rectifier columns reaches its azeotropic composition. In order to prevent the azeotropic vapor from being condensed in the membrane, its pressure is increased in an adiabatic compressor to 200 Kpa (2 bar) before entering the vapor permeation unit. The membrane is a tubular hydrophilic ceramic membrane which is used for

dehydration of organic materials. The specification of the membrane which is a production of Pervatech BV Company is presented in table 3.4.

Ceramic membranes enjoy a unique thermal, chemical and mechanical properties which gives them a longer working-life and lower maintenance cost (Sondhi, Bhave et al. 2003).

A vacuum level of 1-2 Kpa (10-20 mbar) is applied on the permeate side to generate the driving force for water to pass through the membrane. Vapor Ethanol is retrieved and then condensed in the retantate. In this study, it is assumed that the module operates isothermally and pressure loss is negligible.

Due to vacuum pump and internal circulation in vapor permeation systems an amount of 1 MW of electricity is needed for this design. Table 3.4 summarizes the specification of this design.

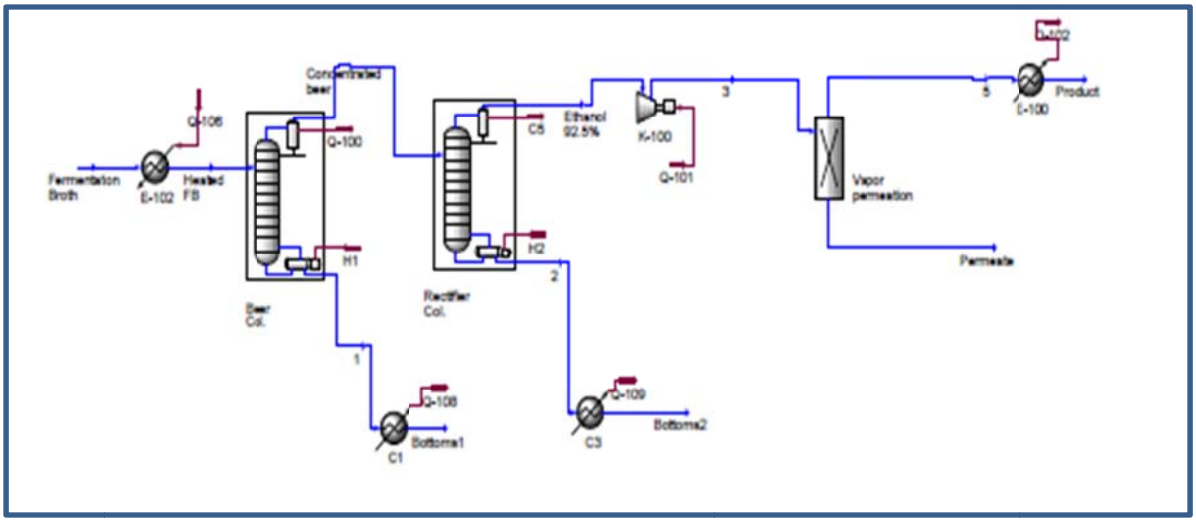

Figure 3-4 : Flow diagram of hybrid distillation-vapor permeation

Table 3.4 : Operating conditions of hybrid distillation-vapor permeation design

Hybrid distillation vapor permeation spec.	
Beer column	
Number of stages	30
Operating pressure (Kpa)	189
Distillate Ethanol concentration (wt%)	37
Reflux ratio	0.3
Feed stage	5
Rectifier column	
Number of stages	60
Operating pressure (Kpa)	150
Distillate Ethanol concentration (wt%)	92.5
Reflux ratio	4
Feed stage	37
Compressor K-100	
ΔP(bar)	0.5
Vapor permeation unit	
Membrane surface (m2)	1200
Operating pressure(bar)	2
Permeate pressure (mbar)	20
Separation factor	20
Flux(Kg/m2.hr)	4
Retantate Ethanol concentration(wt%)	99.5
Total Energy demand	
Heating demand (MW)	85
Electricity demand (MW)	1

3.2.4 Energy analysis in stand-alone without integration

The result of energy consumption obtained from simulation is presented in Figure 3.5. The energy consumption is expressed in MJ-fuel/Kg-EtOH. In order to be able to sum the heat demand and electricity demand and express it in one single unit, a boiler efficiency of 90% and a fuel-to-delivered electricity efficiency of 33% have been assumed. This conversion is important when comparing technologies with different combinations of heat energy and electrical power.

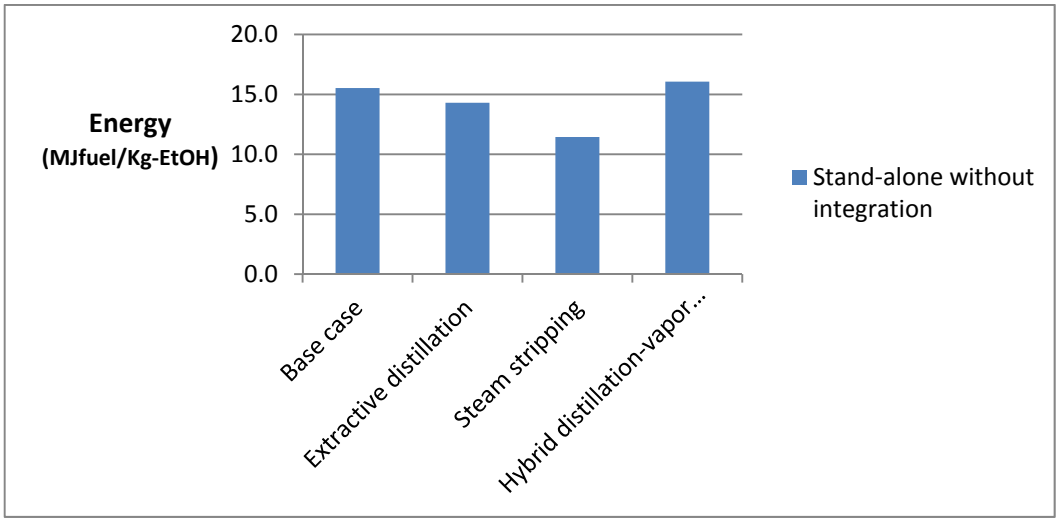

Figure 3-5: Energy consumption comparison diagram in stand-alone without integration

As Figure 3.5 suggests, extractive distillation and steam stripping consumes less energy comparing to the base case. Hybrid distillation-vapor permeation although marginally is less heat consuming than the base case but due to its higher power consumption is rendered more energy intensive. The results in stand-alone design show that employing hydrophilic membrane in place of molecular sieve will not decrease the overall energy consumption of the separation system. Nowadays where molecular sieves are regenerated internally with pure ethanol purge rather than by external use of steam, the energy consumption of this dehydration stage is significantly reduced. Thus as figure 3.5 shows, using hydrophilic membrane in place of molecular sieve will not bring a change in overall energy consumption.

3.2.5 Economic analysis in stand-alone without integration

The result of techno-economic analysis of the base case as well as that of each alternative is presented in Figure 3.6. For each design, the annualized capital cost (CAPEX) and the operating cost (OPEX) have been calculated. In terms of capital cost, in the base case, the most capital intensive equipment is the molecular sieve which accounts for half of the total purchase cost (see Appendix B). Among alternative options, the double-effect extractive distillation design cost less comparing to other alternatives whereas the steam stripping which needs the least amount of heating utility among all the alternatives, requires a large capital cost investment. This large capital cost is mostly due to low pressure generation and the cost of vacuum pumps. Vapor permeation which uses a ceramic membrane system for dehydration shows similar capital cost as the base case; however it costs is higher due to higher purchase cost of the membrane system. In terms of operating cost (see Appendix C), beer column in the base case consumes the highest amount of energy and contribute the most to the total energy consumption. The operating cost in double-effect extractive distillation is the sum of energy consumption and the cost associated with ethylene glycol make-up in the extractive column. Although double-effect extractive design is less heat consuming than the base case but as Figure 3.6 shows, its overall OPEX is almost at parity with the base case which is due to high operating cost associated with solvent make-up. In steam stripping, power consumption which is the result of low pressure compression and circulation pumps (see table 3.3) is the most contributor to its overall operating cost. In hybrid distillation-vapor permeation, the operating cost is similar to the base case and the increase observed in the overall OPEX is due to the power consumption in membrane unit. The total annualized cost (TAC) depicted in Figure 3.6 reconciles the operating and capital cost in one single unit and suggests that double-effect extractive distillation is the alternative of choice among all the stand-alone non-integrated designs.

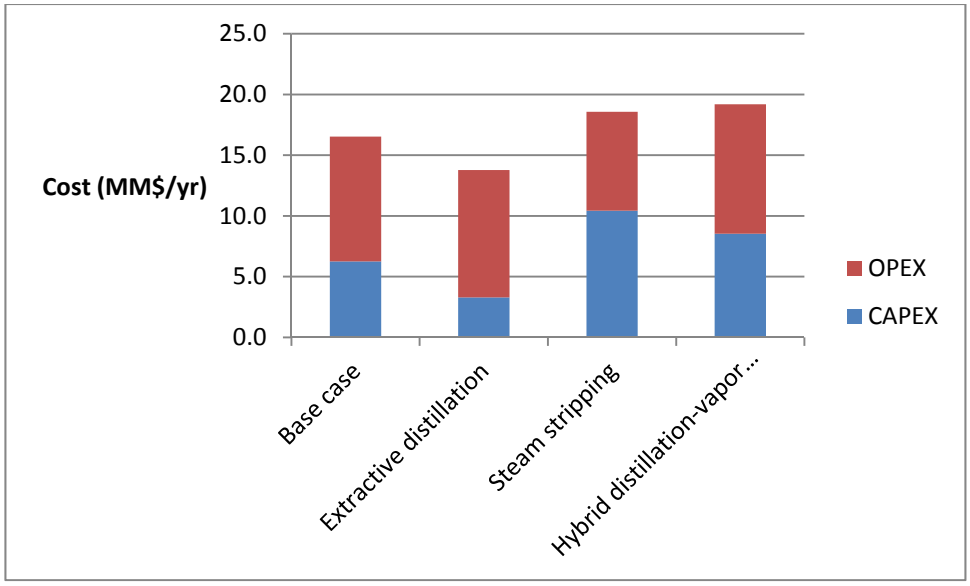

Figure 3-6 :Total annualized cost in stand-alone without integration

3.3 Stand-alone designs with internal integration

In this part, designs with internal heat recovery are presented. As explained in the methodology, an energy efficiency analysis is performed on the generated flow sheets from previous section. Through Pinch method, the minimum utility consumption of each flow sheet is identified and their related heat exchanger network (HEN) is designed after being evaluated by energy diagram tool for the possible process modifications.

3.3.1 Base case

In order to assess the potential of the base case for heat recovery, the data regarding the hot and cold streams are extracted from the mass and energy balance and shown in Table 3.5 and 3.6. Subsequently the composite curves of this design are constructed and presented in Figure 3.7.

Table 3.5 : Hot streams in the base case

Stream	Cp (KJ/kg-c)	Flow rate(Kg/h)	Ts	Tt	Duty (KJ/h)	Duty (MW)
Beer-cond	4.13E+02	7.27E+04	113	112	3.00E+07	8
Rec-cond.	7.13E+02	1.20E+05	88	87	8.6E+07	24
Product cooler	1.14E+01	2.16E+04	111	30	2.00E+07	6.3
From regeneration	29.70	8.10E+03	115	70	1.1E+07	3
Bottoms 1	4.23E+00	3.75E+05	122	30	1.46E+08	41
Bottoms 2	4.21E+00	3.70E+04	111	30	1.26E+07	4
Total					**3.05E+08**	**85**

Table 3.6 : Cold streams in the base case

Stream	Cp (KJ/kg-c)	Flow rate (Kg/h)	Ts	Tt	Duty(KJ/h)	Duty (MW)
Beer_reb	2.19E+03	7.59E+04	122	123	1.7E+08	46
Rec_reb	2.22E+03	5.85E+03	111	112	1.30E+07	4
Feed preheater	4.17	4.34E+05	30	100	1.27E+08	35
Molecular sieve super heater	1.67	3.00E+04	88	116	1.40E+06	0.4
Total					**3.07E+08**	**85**

The composite curves which are based on a minimum $\Delta T = 10$ °C between hot and cold streams, shows the theoretical minimum heating demand of this process as 49 MW. The pinch point happens at 116 °C shifted temperature. This in turn suggests that there exists a potential for heat recovery of 36 MW (85 -49) which is equivalent to 42% reduction in heat consumption

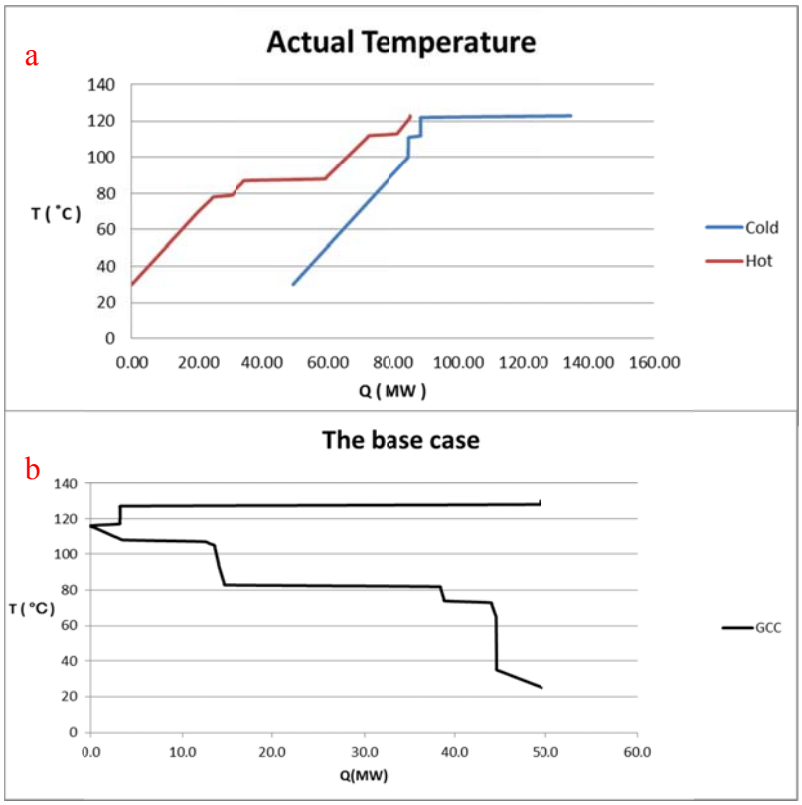

Figure 3-7 : Base case composite curves a- Actual temperature b- the grand composite curve

3.3.1.1 Energy transfer diagram (ETD)

Energy transfer diagram of the base case is shown in Figure 3.8. This diagram shows how heat is cascaded and degraded from hot utility to environment. As can be seen in Figure 3.8, the heat demand in beer column in the reboiler is at 122 ˚C and the cooling demand in its condenser is at 112 ˚C. As this figure depicts, the heat continues to flow in the rectifier column and ultimately is released to the environment. Molecular sieve shows a little energy degradation and low heat consumption and thus is not visible in the diagram. This diagram is equivalent of grand composite curve with the exception that the net heat flow is visible in each process unit. However no minimum temperature difference has been taken into account for constructing ETD and this is why the minimum energy consumption read from this diagram is lower than that of GCC. Figure 3.8 also suggests that by increasing the pressure of the beer column or decreasing that of rectifier, the condenser of the beer column could be coupled with the reboiler of the rectifier which can enhance the heat integration potential for this system.

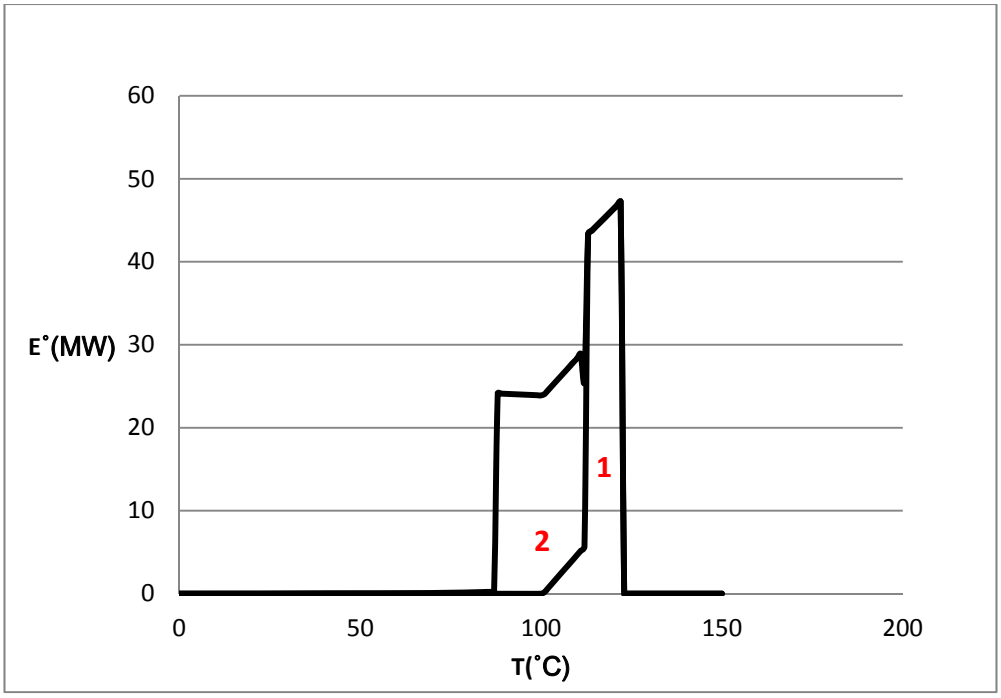

Figure 3-8: Energy transfer diagram of the base case; 1- Beer column 2- Rectifier column

3.3.1.2 The grid diagram of the base case

The grassroots heat exchanger network of this design is shown in Figure 3.9. In this figure, coolers, heaters and exchangers are distinguished from by two subscripts. The left subscript represents the number of design case (1) and the right one represents the number of equipment in the grid.

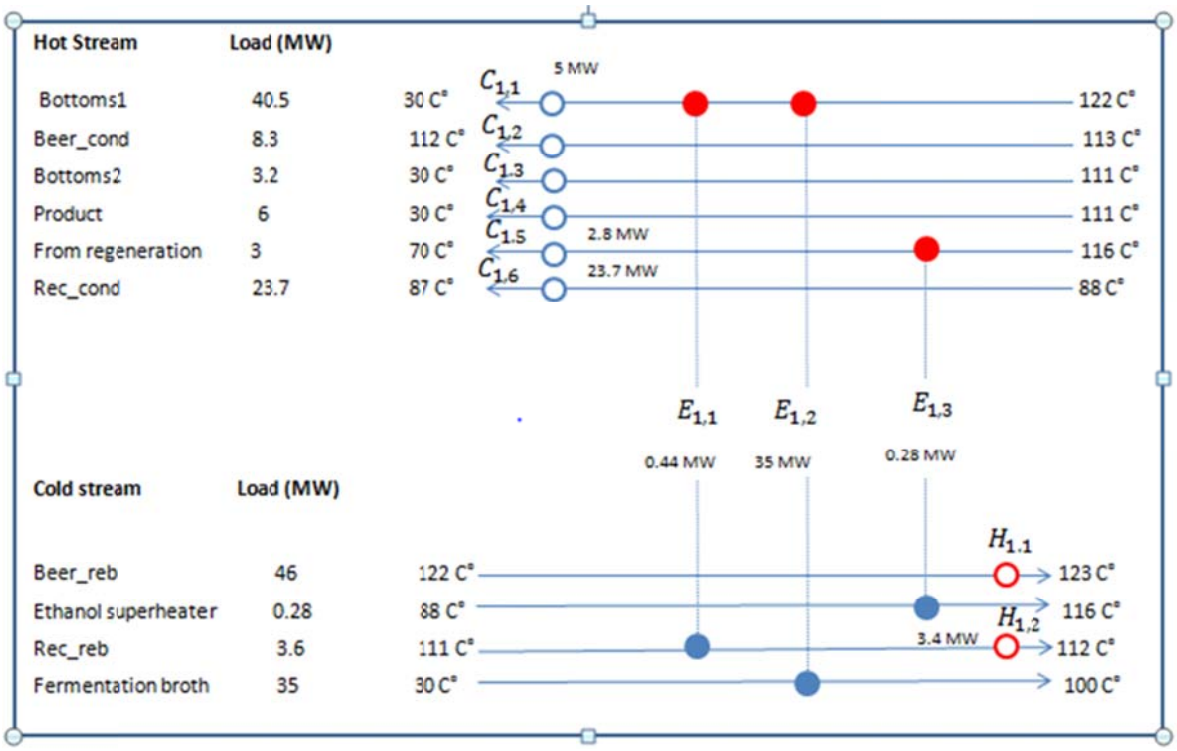

Figure 3-9 : Heat exchanger network of the base case design

3.3.2 Double-effect extractive distillation

Data extraction for extractive distillation is summarized in tables 3.7 and 3.8. Similar to the base case, composite curves are constructed based on minimum temperature difference of 10 ˚C and presented in Figure 3.10. As described in previous section, the design objective of double-effect beer column is to couple the reboiler of first beer column with the condenser of second beer column. This key design element is reflected in composite curves where large amount of energy can potentially be recovered.

Similar to the base case, the GCC of this design is constructed and shown in Figure 3.10. This figure shows the pinch point is at 89 °C and the minimum heating demand for this design is almost 40 MW if internal heat integration is applied.

Table 3.7: Extractive distillation hot streams

Stream	Cp(KJ/kg-c)	Flow rate(Kg/h)	Ts	Tt	Duty(KJ/h)	Duty (MW)
Beercol1_cond	9.65E+02	8.50E+04	78	77	8.20E+07	22.8
Bottoms1	4.17E+00	2.10E+05	98	30	6.0E+07	16.5
Beercol2_cond	9.35E+02	9.30E+04	109	108	8.7E+07	24.2
Bottoms2	4.17E+00	1.98E+05	134	30	8.6E+07	23.9
Extrac-cond	8.49E+02	4.12E+04	77	76	3.5E+07	9.7
Recov_cond	2.21E+03	2.53E+03	94	93	5.6E+06	1.6
Product	3.54E+00	2.18E+04	76	30	3.55E+06	1.0
solvent recyle	3.40E+00	1.67E+04	175	60	6.52E+06	1.81E+00
Total					**3.65E+08**	**101.41**

Table 3.8 : Extractive distillation cold streams

Stream	Cp(KJ/kg-c)	Flow rate(Kg/h)	Ts	Tt	Duty(KJ/h)	Duty (MW)
Feed preheater 2	4.17E+00	2.10E+05	30	127	8.49E+07	23.6
Feed preheater 1	4.17E+00	2.20E+05	30	94	5.87E+07	16.3
Beercol1_reb	2.26E+03	3.80E+04	98	99	8.6E+07	23.9
Beercol2_reb	2.16E+03	4.30E+04	134	135	9.3E+07	25.8
Extract_reb	2.07E+03	1.79E+04	130	131	3.7E+07	10.3
Recovery_reb	1.51E+03	5.03E+03	175	176	7.6E+06	2.1
Solvent preheater	8.09E+00	1.65E+04	30	60	4.0E+06	1
Total					**3.71E+08**	**103.13**

This heat consumption is inferior to the consumption of the base case which shows that double-effect extractive distillation is relatively an energy- efficient design.

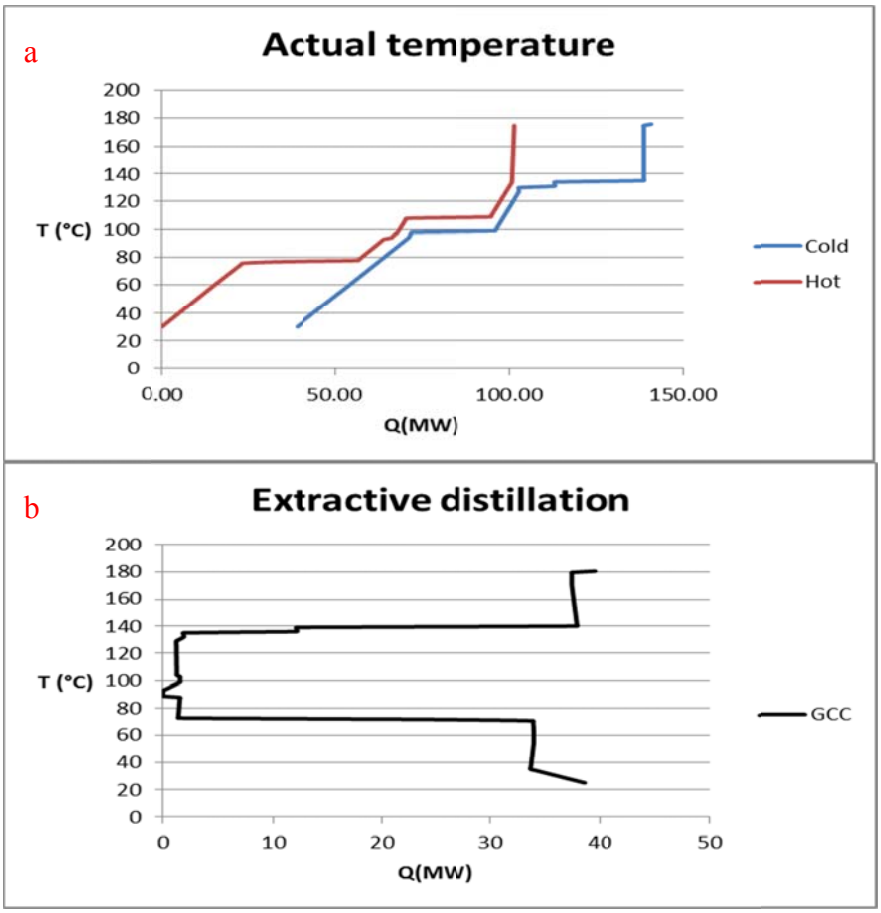

Figure 3-10 : Extractive distillation composite curves a- Actual temperature b- The grand composite curve

3.3.2.1 Energy transfer diagram of double-effect extractive distillation design

The ETD of extractive distillation flow sheets is shown in Figure 3.11.As can be observed in this figure, since there is enough temperature difference between beer column 1 and beer column 2 and enough heat for this, the rebolier of the beer column 1 can match up with the condenser of beer column 2. This figure also shows that from process point of view, the beer columns highly contribute to the energy consumption of this design and as a first-stage screening, altering the operating conditions of these columns could potentially create heat integration opportunities.

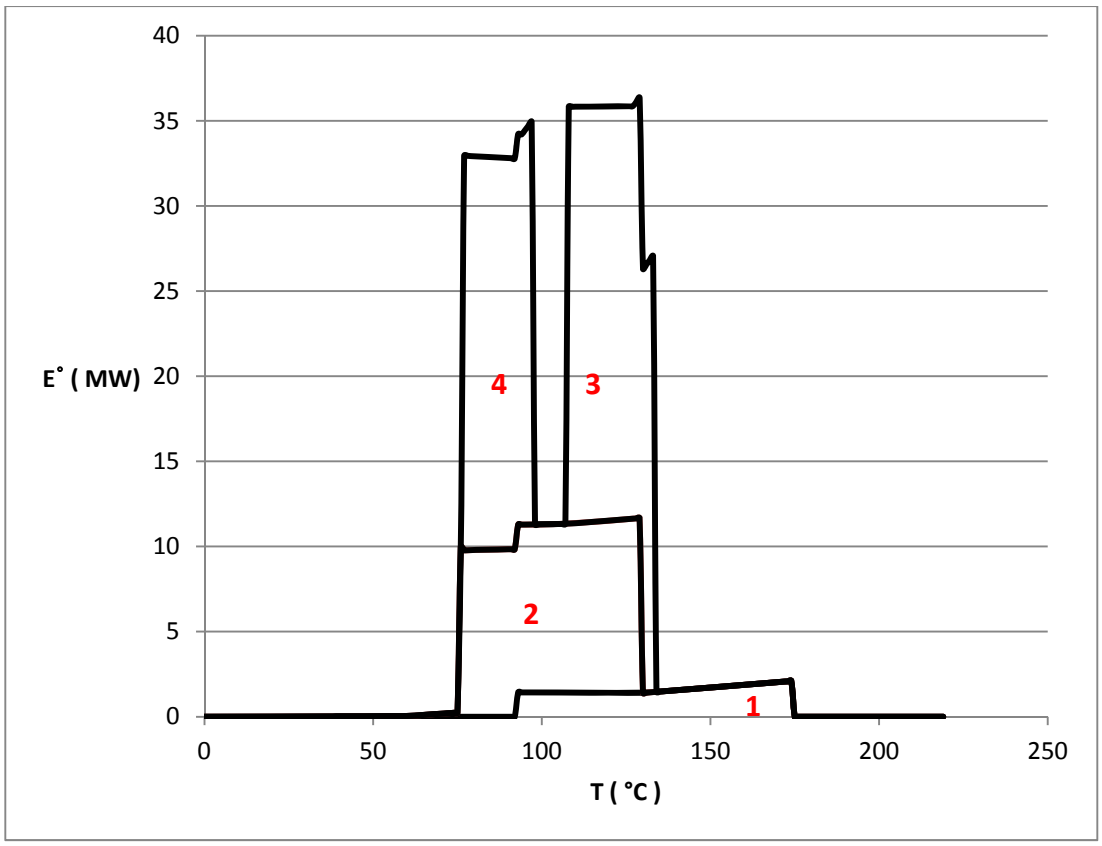

Figure 3-11 : Energy transfer diagram of the double-effect extractive distillation design, 1- Recovery column 2- Extractive column 3- Beer column2 4- Beer column 1

Figure 3.11 also shows that by reducing the operating pressure of extractive column we could potentially supply its heating demand with available heats in the beer columns. Also decreasing the pressure of the extractive column will down-translate the whole diagram and can contribute to an overall heat reduction. Since generally lower-than-ambient pressure could cause operability and controllability problems, by observing figure 3.11 it is understood that increasing the pressure of extractive column could potentially be a better option to help reduce the overall consumption. The pressure increase to the extent which relocates this column after the recovery column can potentially pave the way for integration between these two columns if minimum temperature difference is met. As mentioned before the feasibility of these process modifications should be examined in more depth in further stages.

3.3.2.2 Grid diagram of the extractive distillation design

The grid diagram of this design is shown in Figure 3.12. As this figure suggests, the exchanger $E_{2,6}$ links the condenser of beer column 2 with the reboiler of beer column 1.

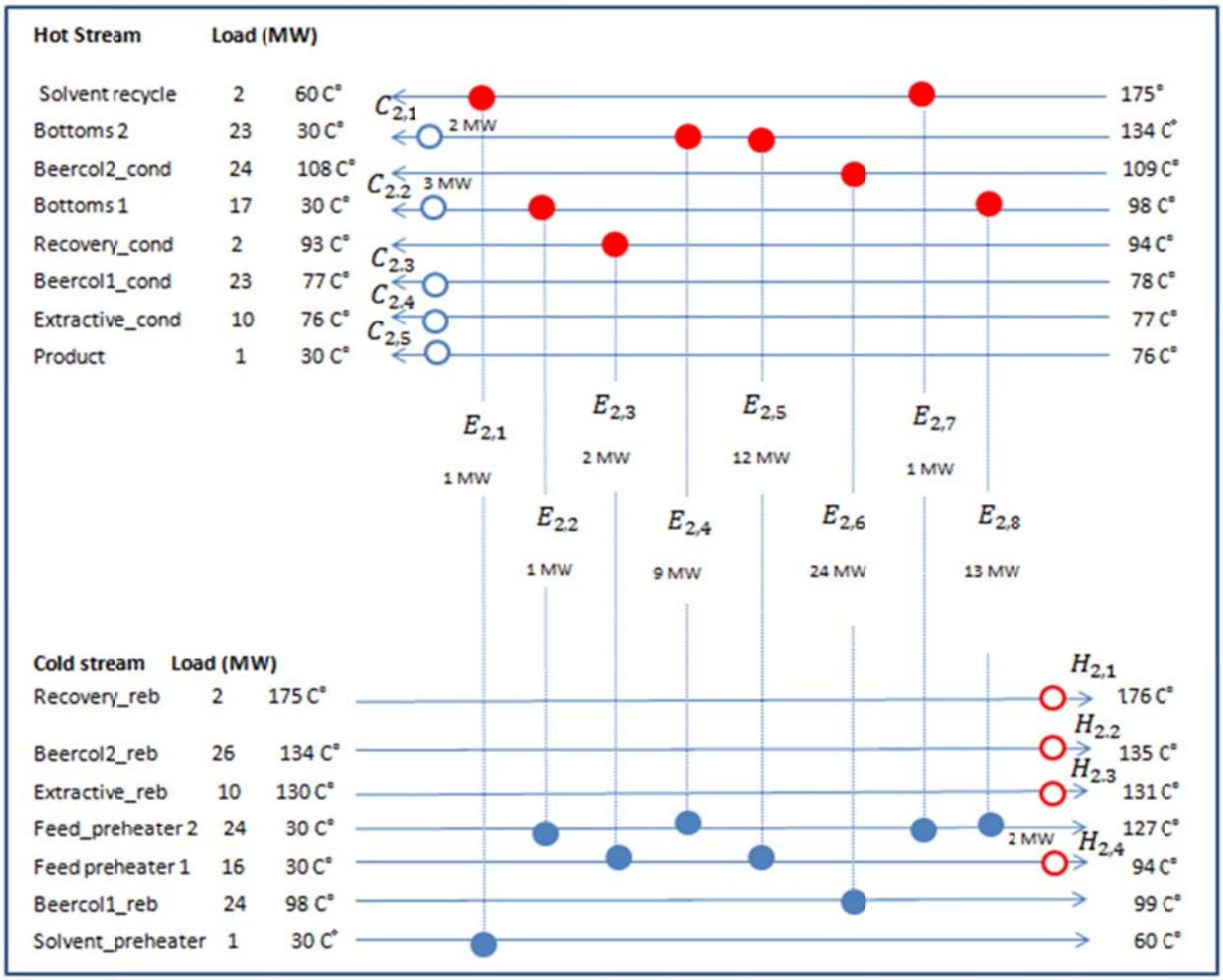

Figure 3-12 : Heat exchanger network of the double-effect extractive distillation design

3.3.3 Steam stripping

Data extractions pertaining to steam stripping design are shown in tables 3.9 and 3.10 .The composite curves shown in Figure 3.13 suggests, the pinch point happens at 39°C and the minimum heating demand for this design is about 36 MW which corresponds to almost 6 MW of internal heat recovery. This low pinch temperature that is a corollary of low operating pressure in

the design indicates that the low temperature heat demand could be supplied by low temperature utility or other sources at low temperature. The power consumption remains unchanged.

Table 3.9 : Hot streams in the Steam stripping

Stream	Cp (KJ/kg-c)	Flow rate(Kg/h)	Ts	Tt	Duty(KJ/h)	Duty(MW)
Rec_cond	1.14E+03	1.00E+05	24	23	1.14E+08	31.7
Product cooler	7.19E+00	2.16E+04	169	30	2.2E+07	6
Bottoms1	4.17E+00	4.30E+05	40	30	1.8E+07	5
Bottoms2	4.17E+00	3.00E+04	40	30	1.3E+06	0.3
Total					**1.55E+08**	**43**

Table 3.10 : Cold streams in the steam stripping

Stream	Cp (KJ/kg-c)	Flow rate(Kg/h)	Ts	Tt	Duty(KJ/h)	Duty (MW)
Stripping steam	2.72E+02	4.50E+04	30	39	1.10E+08	31
Rec_reb	2.41E+03	1.74E+04	39	40	4.2E+07	11.7
Total					**1.52E+08**	**42.2**

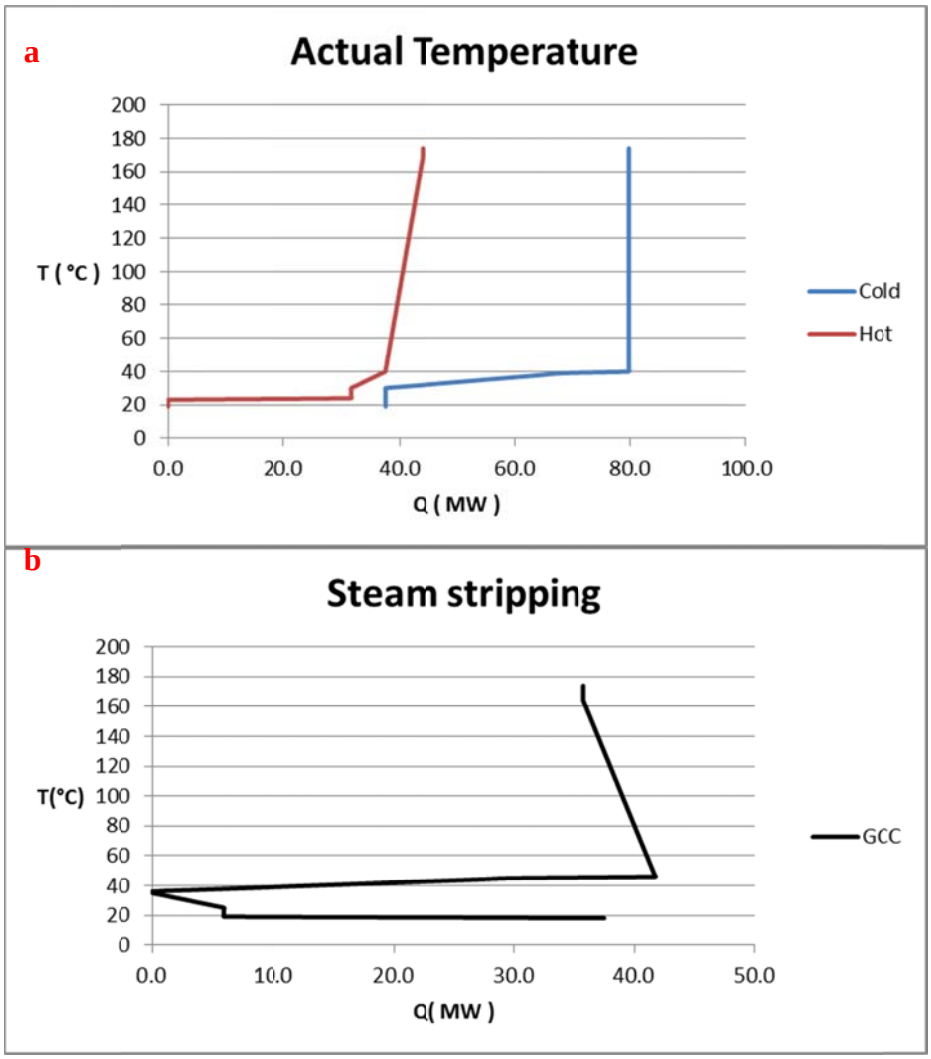

Figure 3-13 : Double-effect extractive distillation composite curves a- Actual temperature b- The grand composite curve

3.3.3.1 Energy transfer diagram of the steam stripping

The ETD of steam stripping is presented in Figure 3.14. Both the stripper and rectifier column work at low pressure and at the same range of temperature. This figure clearly suggests that altering the working pressure in either of the columns would decrease the overall heat requirement. As mentioned earlier this alteration is subject to a feasibility study and economic evaluation.

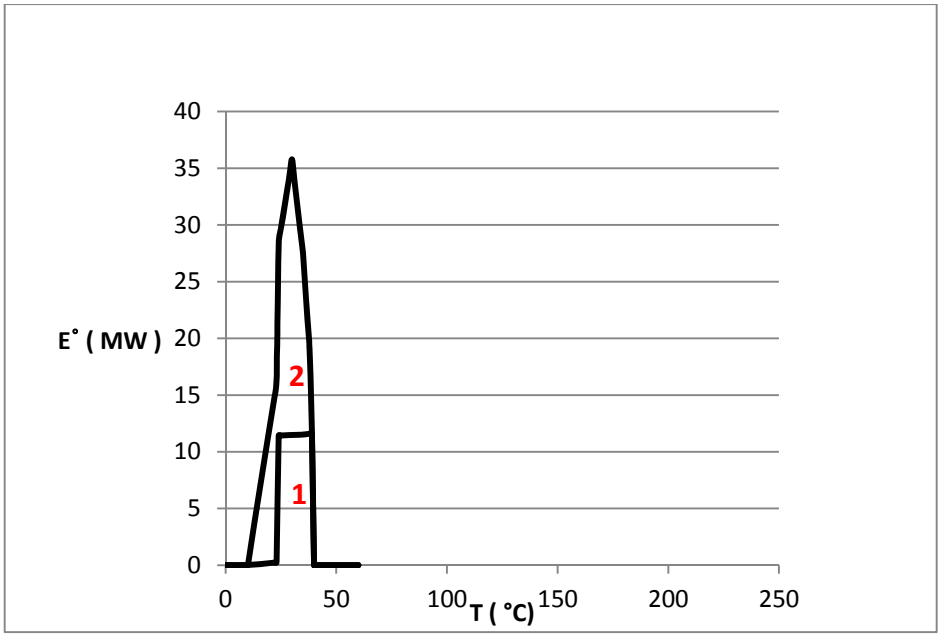

Figure 3-14 : Energy transfer diagram of steam stripping; 1- Rectifier column 2- Stripper

3.3.3.2 Grid diagram of the stripping design

The grid diagram of steam stripping is shown in Figure 3.15. Product cooler with 10 ˚C temperature difference can supply heat to the stripper for stripping agent which is steam at low temperature.

Exchanger $E_{3,1}$ as shown in this figure has a duty of 6 MW which makes this exchange happen.

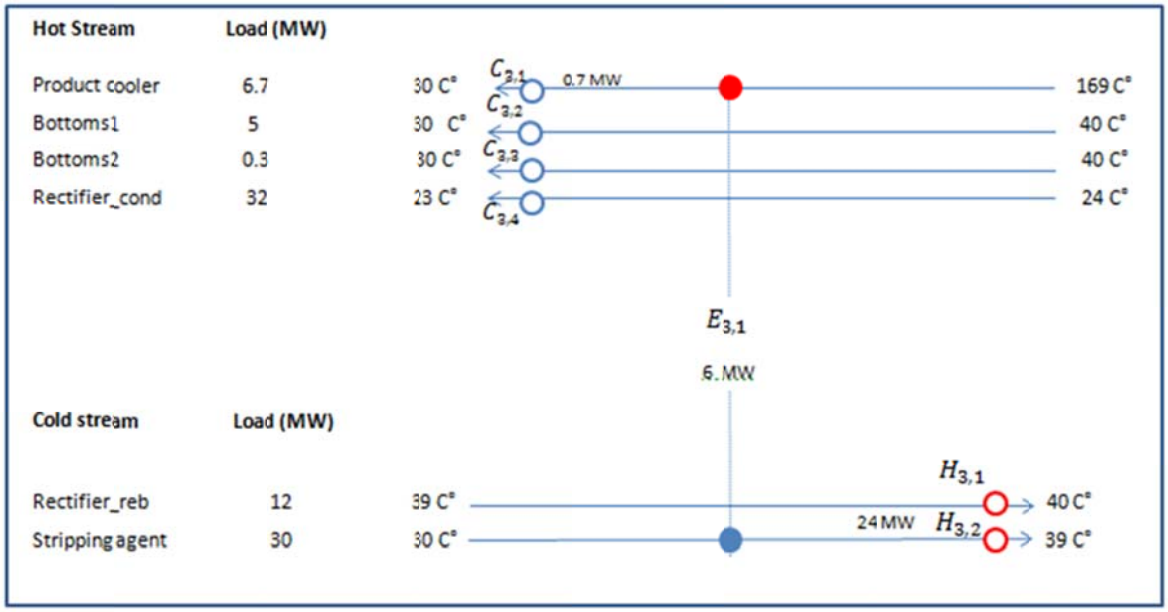

Figure 3-15 : Heat exchanger network of Steam stripping

3.3.4 Hybrid distillation-vapor permeation

The data extraction regarding hybrid distillation vapor permeation is presented in Tables 3.11 and 3.12 and the corresponding composite curves are shown in Figure 3.17. The composite curves show that after internal heat recovery the heat demand decreases to almost 49 MW which is an indication of a large recovery potential.

Table 3.11 : Hot streams in Hybrid distillation-vapor permeation

Stream	Cp (KJ/kg-c)	Flow rate(Kg/h)	Ts	Tt	Duty(KJ/h)	Duty (MW)
Beer-cond	4.13E+02	7.27E+04	113	112	3.00E+07	8
Rec-cond.	9.38E+02	9.70E+04	88	87	9.1E+07	25
Product cooler	1.34E+01	2.15E+04	105	30	2E+07	6.0
Bottoms 1	4.23E+00	3.75E+05	122	30	1.46E+08	41
Bottoms 2	4.21E+00	3.50E+04	111	30	1.19E+07	3
Total					**3.00E+08**	**83.5**

Table 3.12 : Cold streams in hybrid distillation-vapor permeation

Stream	Cp (KJ/kg-c)	Flow rate(Kg/h)	Ts	Tt	Duty(KJ/h)	Duty (MW)
Beer_reb	2.19E+03	7.59E+04	122	123	1.7E+08	46
Rec_reb	2.21E+03	5.43E+03	111	112	1.20E+07	3
Feed preheater	4.17	4.34E+05	30	100	1.27E+08	35
Total					**3.05E+08**	**84.6**

3.3.4.1 Energy transfer diagram of hybrid distillation-vapor permeation

Figure 3.16 shows the ETD of vapor permeation. The curve of membrane vapor permeation is not visible in the diagram as degradation of heat as well as heat flow is relatively small for this unit. It is understandable from the ETD that by changing the pressure of columns in order to allow for a minimum temperature difference, a heat integration opportunity is created between the beer column and the rectifier. Considering a small temperature difference between the temperature of the reboiler and the condenser in both columns, utilizing a heat pump could foster more energy saving for this system.

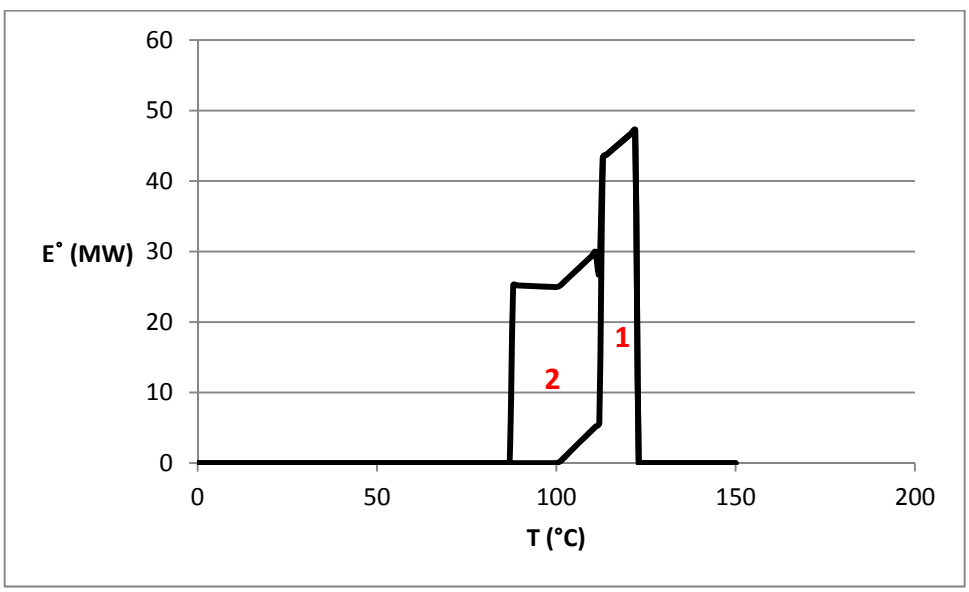

Figure 3-16 : Energy transfer diagram of the hybrid distillation-vapor permeation 1- the beer column 2- the rectifier column

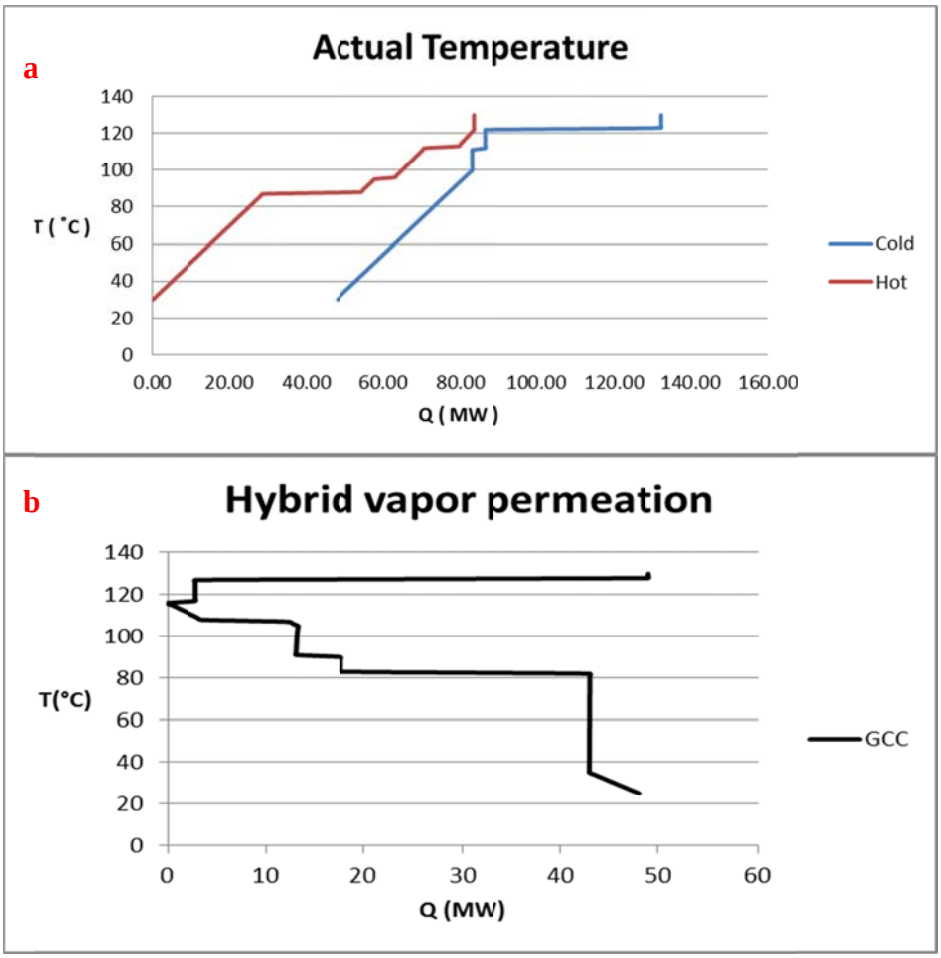

Figure 3-17 : Hybrid distillation-vapor permeation composite curves a- Actual temperature b- The grand composite curve

3.3.4.2 Grid diagram of the hybrid distillation-vapor permeation

The corresponding grid diagram pertaining to hybrid distillation-vapor permeation is depicted in Figure 3.18.

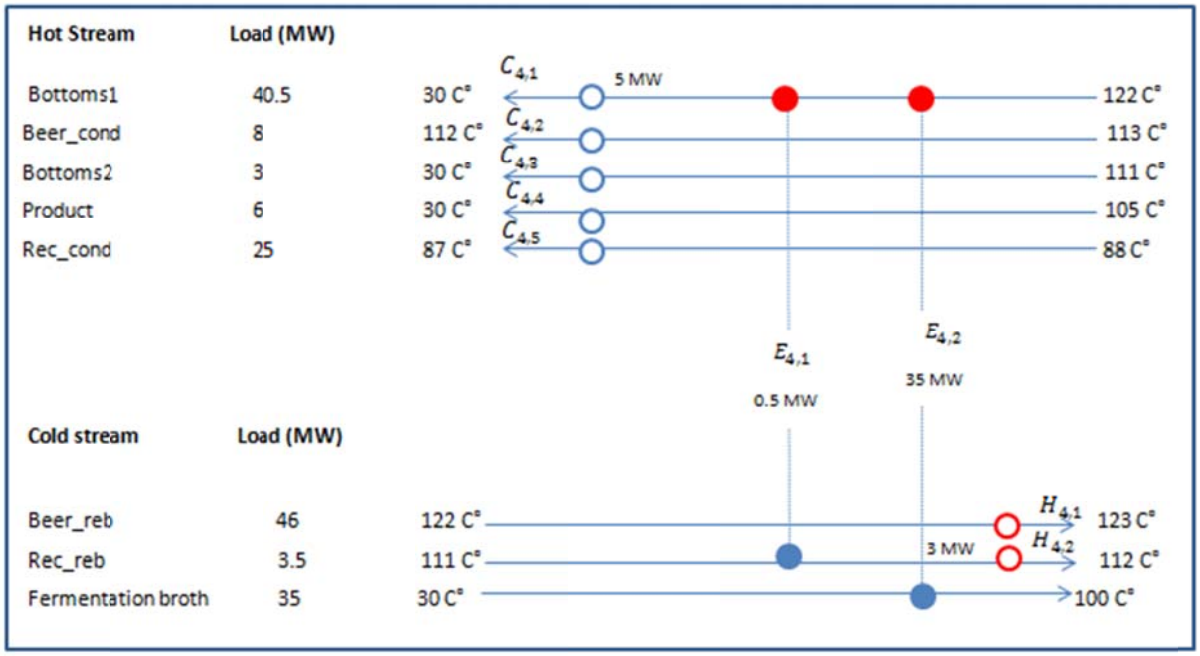

Figure 3-18 : Heat exchanger network of vapor permeation

3.3.5 Energy analysis in stand-alone with internal integration

The final results of energy consumption for all the internally-integrated design are shown in Figure 3.19. As can be seen in this figure, there is significant energy reduction in the base case, vapor permeation and extractive distillation. These designs show more than 40% reduction in energy consumption relative to their non-integrated designs. Steam stripping which inherently is an energy efficient design in terms of heat consumption has the lowest energy saving after internal integration. Electricity consumption keeps the same value for steam stripping and vapor permeation.

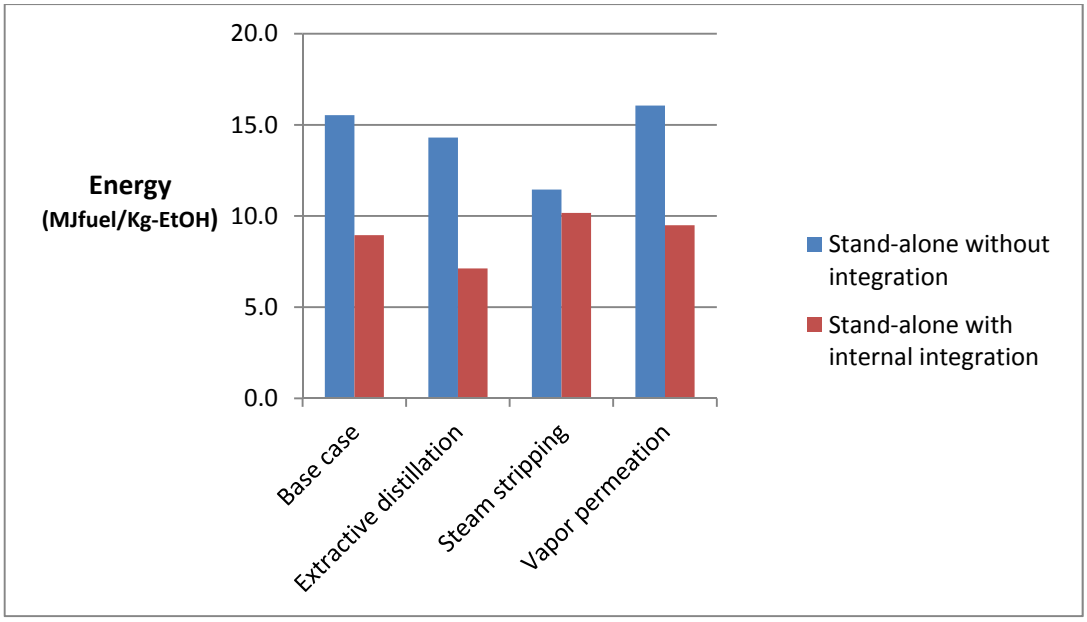

Figure 3-19 : Energy consumption in Stand-alone with internal integration

3.3.6 Economic analysis in stand-alone with internal integration

The details of economic analysis are presented in Appendix B. The cost of heat exchangers for internal heat recovery and the cost of equipment such as condensers and reboilers with new duty have been calculated and included in this analysis for each design. Energy consumption reduction as a result of internal heat recovery dramatically lowers the operating cost in internally-integrated designs. Capital costs pertaining to these designs are slightly lower than the stand-alone non-integrated cases which accentuates the fact that implementing heat integration, in these cases requires cheaper equipment and the cost associated with additional heat exchangers is justifiable considering the huge energy saving which it fosters. Base case and double-effect extractive designs exert more than 40% reduction in their operating costs relative to the stand-alone designs. The reduction in vapor permeation is slightly less than 40% and for steam stripping it's less than 10%. Similar to stand-alone non-integrated design, the total annualized cost is still in favor of double-effect extractive distillation which enjoys a relatively low capital cost.

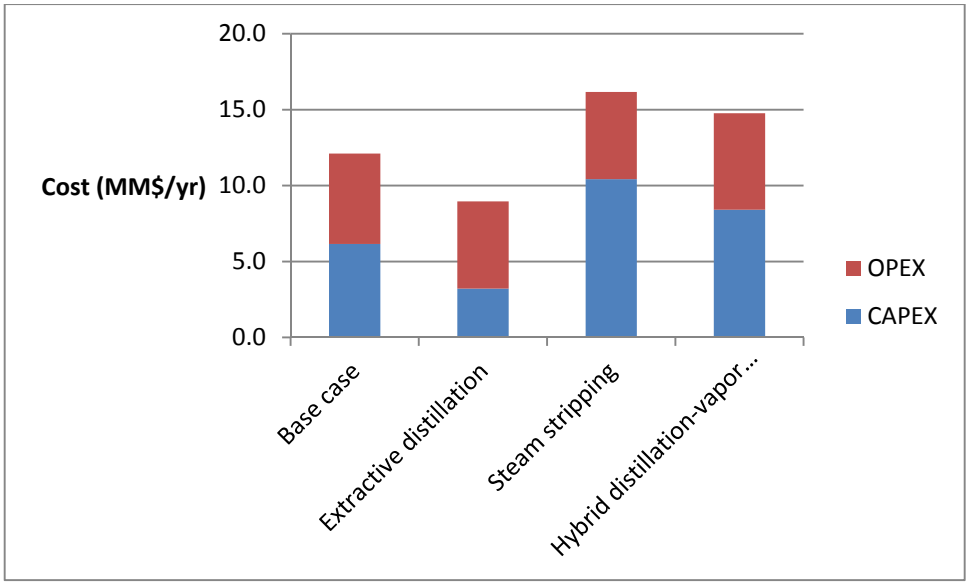

Figure 3-20 : Total annualized cost in stand-alone with internal integration

3.4 Integrated-with-Kraft designs

As stated in the methodology, in order to have grassroots designs integrated with a Kraft process, data regarding the heat exchanger network of each design in internally-integrated scenario is required to identify the possible opportunities for external heat integration with a Kraft process. The Kraft process which uses chemicals to produce pulp wood is the dominant pulping process in the pulp and paper industry with yearly production of around 130 million tons of pulp around the globe. Advantages such as high pulp strength, flexibility in processing almost all types of wood and efficient chemical recovery have made Kraft pulping a popular choice. In Kraft process chemicals such as NaOH and Na_2S are used to separate pulp from other wood constituents. Spent chemicals along with half of the wood forms a weak liquid stream called black liquor which after an evaporation stage is directed to a recovery boiler for steam and power generation as well as for recovering the used chemicals. Recovered chemicals are treated in a causticizing plant to turn into their original form (Tran and Vakkilainnen 2008). Separated pulp is sent to pulping line for being screened, bleached and finally dried to be sold as final product. Figure 3.21 schematically illustrates a simplified typical Kraft process.

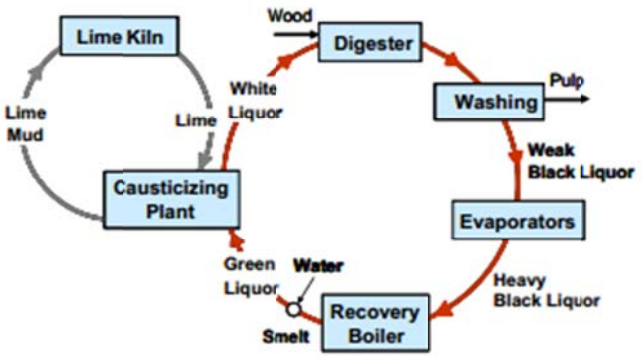

Figure 3-21 : A typical Kraft process (Tran and Vakkilainnen 2008)

3.4.1 The Kraft mill used in this study

The mill studied in this work is a model Kraft pulp typical of Scandinavian mill which has been developed and simulated in Wingems as a part of the Swedish national research program "Future Resource-Adapted Pulp Mill" (FRAM).The aim of this program is to investigate how the pulp and paper production can have less environmental impact. This model mill represents an average Scandinavian mill which produces 1,000 ADt/d of bleached market from 2,065 ADt/d of softwood. The mill representing a typical Scandinavian Kraft mill doesn't require external fuel to meet the steam demand of the process and the steam produced in the recovery boiler will suffice. The heating utility demand of this mill is 193 MW with 8 MW of LP excess steam available at the mill turbine. The heat exchanger network of this mill consists of 19 heaters, 13 coolers and 8 internal heat exchangers (Figure 3.23). In the following a brief summary of different parts of the mill is described.

- **Digester**: two-flash continuous digester which works at a temperature of 165˚C is used in this mill. The first flash unit provides steam for the chip bin and the steam from the second flash unit together with the blow-through steam from the chip bin is used for producing hot water. Medium pressure steam (MP steam) is used in the digester. Incoming white liquor is at 85˚C and is not preheated before entering the digester and pre-impregnation stage. A two-stage oxygen delignification follows the digester.

- **Bleaching**: 90% ISO brightness is achieved in the ECF (elemental chlorine-free) bleach sequence D(EOP)DD. Vacuum drum filters are used for pulp washing.

- **Pulp drying**: the pulp undergoes a screening stage before it is diluted and sent to the headbox. Before being dried in a dryer, the pulp machine which has a conventional press section gives a dryness level of 47% to the pulp. In the dryer which is of the floating web type, the outgoing air is used to preheat the incoming air which is found at 95 ˚C. After this heat exchange, low pressure steam (LP steam) is used to heat the air up to 120 ˚C.
- **Chemical recovery**: the 5.5 – effect steam recovery evaporator produces strong black liquor with 73% solid content. The stripper in the recovery steam is driven by LP steam. The stripper condenser is used to produce hot water. Hot water from the hot and water system as well as the condensate from the evaporator is used in the causticizing stage. Cold water is heated with steam in case of deficient hot water levels.
- **Steam and power**: the steam produces in the recovery boiler as mentioned before satisfies the steam demand of the whole facility, thus hog fuel is not needed and can be sold to another user. The steam turbine which generates 24.7 MW power cannot handle all the high pressure steam (HP steam); hence about 17% of this high pressure steam has to be let down to lower pressures. Almost 8 MW of LP steam is blown out to the atmosphere since there is no condensing turbine in the mill.

3.4.2 Integration through Bridge analysis

The integration of each separation design with Kraft process is done by employing Bridge method. A bridge as mentioned before is a set of modification which aims at using the heat which is expulsed to the environment to satisfy possible heat sinks in the process. This heat could be directly used to satisfy the receptor of a heater or could indirectly release the supplier of a potential heat exchanger such that this latter could provide heat to a heater. By doing so, the overall heat consumption will decrease depending on the capacity of identified bridges. As mentioned in the methodology, the data from grid diagrams of the separation techniques as well as that of the mill is used to identify the potential bridges for external heat integration. A minimum temperature difference of 10 ˚C has been considered between hot and cold streams. Table 3.13 presents the set of possible matches for heat integration with Kraft for all the separation options. The heat recovery capacity of each bridge is shown in front of each bridge. In this table the symbols $C_{n,m}$ and $H_{n,m}$ represent the coolers and heaters respectively where the

subscript “n “corresponds to the number of the design (base case =1, extractive distillation=2, steam stripping=3, hybrid vapor permeation=4) and “m “corresponds to the number of the cooler or the heater as it appears in the heat exchanger network of each separation technique. In the Kraft process, the signs C_k, H_k and E_k indicate the coolers, heaters and exchangers respectively, with the subscript K being the number of corresponding heat exchanger. The superscripts r and s defines the receptor and supplier of an exchanger respectively. For example in Table 6 the match (${C_{1,6}}^{s}{E_7}^{r}, {E_7}^{s}{E_8}^{r}, {E_8}^{s}{H_5}^{r}$) in the base case design shows that the cooler number 6 in the base case (see Figure 3.9) is coupled with the receptor of exchanger number 7 in the Kraft process(see Fig 3.22). Now that the heat demand of the receptor stream of exchanger 7 is satisfied from another source, its supplier is released and is coupled with the receptor of exchanger number 8 in the Kraft. Ultimately the released supplier of exchanger number 8 can completely satisfy the demand of the heater number 5 in the Kraft and eliminates the need for external heat utility for this stream.

Table 3.13 also shows the overall heat demand in the Kraft mill after the integration. As this table suggests, the base case and vapor permeation options have the highest heat recovery. The reason for that is the availability of heat at relatively high temperatures (> 80˚C) in these flow sheets which can completely satisfy the low-temperature demands and partially that of high-temperature in the mill. The demand in the steam stripping can be completely satisfied with the available heats in the Kraft. The low-temperature design of steam stripper as discussed before creates an opportunity to satisfy its demand via available low temperatures. In the double-effect extractive distillation, the low –temperature demands at the mill are satisfied with available heat but since this heat is not at a high temperature as the base case is, it cannot satisfy the demand of higher-temperature sinks in the Kraft.

Table 3.13 : Identified bridges and their savings for heat integration with Kraft

	Base case	Double-effect extractive distillation	Steam stripping	Hybrid vapor permeation
Bridges	${C_{1,6}}^{s}\ {H_1}^{r}$ (1.6 MW)	${C_{2,3}}^{s}{H_1}^{r}$ (1.6 MW)	${C_7}^{s}\ {H_{3,1}}^{r}$ (12.0 MW)	${C_{4,5}}^{s}{H_1}^{r}$ (1.6 MW)
	${C_{1,6}}^{s}\ {H_2}^{r}$ (1.1 MW)	${C_{2,3}}^{s}{H_2}^{r}$ (1.1 MW)	${C_7}^{s}\ {H_{3,2}}^{r}$ (7.5 MW)	${C_{4,5}}^{s}{H_2}^{r}$ (1.1 MW)
	${C_{1,6}}^{S}{H_3}^{r}$ (3.5 MW)	${C_{2,3}}^{s}{H_3}^{r}$ (2.8 MW)	${C_8}^{s}\ {H_{3,2}}^{r}$ (9.5 MW)	${C_{4,5}}^{s}{H_3}^{r}$ (3.5 MW)
	${C_{1,6}}^{S}{H_4}^{r}$ (1.0 MW)	${C_{2,4}}^{s}{E_8}^{r}, {E_8}^{s}{H_5}^{r}$ (8.0 MW)	${C_{12}}^{s}{H_{3,2}}^{r}$ (4.0 MW)	${C_{4,5}}^{s}{H_4}^{r}$ (1.0 MW)
	${C_{1,2}}^{S}{H_6}^{r}$ (1.7 MW)	${C_{2,4}}^{s}{E_8}^{r}, {E_8}^{s}{H_6}^{r}$ (1.7 MW)	${C_{13}}^{s}\ {H_{3,2}}^{r}$ (3.0 MW)	${C_{4,5}}^{s}{H_6}^{r}$ (1.7 MW)
	${C_{1,6}}^{S}{E_7}^{r}, {E_7}^{s}{E_8}^{r}, {E_8}^{s}{H_5}^{r}$ (8.0 MW)	${C_{2,4}}^{s}{E_8}^{r}, {E_8}^{s}{H_7}^{r}$ (0.3 MW)	-	${C_{4,5}}^{s}{E_7}^{r}, {E_7}^{s}{E_8}^{r}, {E_8}^{s}{H_5}^{r}$ (8 MW)
	${C_{1,6}}^{S}{E_7}^{r}, {E_7}^{s}{E_8}^{r}, {E_8}^{s}\ {H_7}^{r}$ (0.8 MW)	Available LP steam (8.0 MW)	-	${C_{4,5}}^{s}{E_7}^{r}, {E_7}^{s}{E_8}^{r}, {E_8}^{s}{H_7}^{r}$ (0.8 MW)
	${C_{1,6}}^{S}{E_7}^{r}, {E_7}^{s}{E_8}^{r}, {E_8}^{s}{H_8}^{r}$ (3.6 MW)	-	-	${C_{4,5}}^{s}{E_7}^{r}, {E_7}^{s}{E_8}^{r}, {E_8}^{s}{H_8}^{r}$ (3.6 MW)
	${C_{1,2}}^{s}\ {H_{12}}^{r}$ (6.0 MW)	-	-	${C_{4,2}}^{s}{H_{12}}^{r}$ (6.0 MW)
	Available LP steam at Kraft (8.0 MW)	-	-	Excess LP steam at Kraft (8.0 MW)
Total (MW)	**33.5**	**23.5**	**36.0**	**33.5**
Kraft (MW)	**159.5**	**169.5**	**157**	**159.5**

3.4.3 Energy analysis in integrated-with-Kraft

Figure 3.22 shows the energy consumption of each design after integration with the Kraft process. Clearly the energy consumption drops comparing to the internally-integrated scenario. This figure suggests that after integration with the Kraft process, the base case will consume less energy than the double-effect extractive distillation. This reverses the previous trend in other two scenarios. The vapor permeation acts similar to the base case except for the electricity level

which ultimately renders its overall energy consumption slightly higher than the base case. The steam stripping demand although is completely satisfied by the mill, its high power consumption contributes to a relatively high overall consumption in this design. This energy analysis result is very significant as to which technique or which method can contribute to reducing energy consumption. The result clearly shows that the base case outperforms all other techniques in integrated-with-Kraft mode while all these techniques show better energy consumption at least in terms of heat consumption in stand-alone without integration mode.

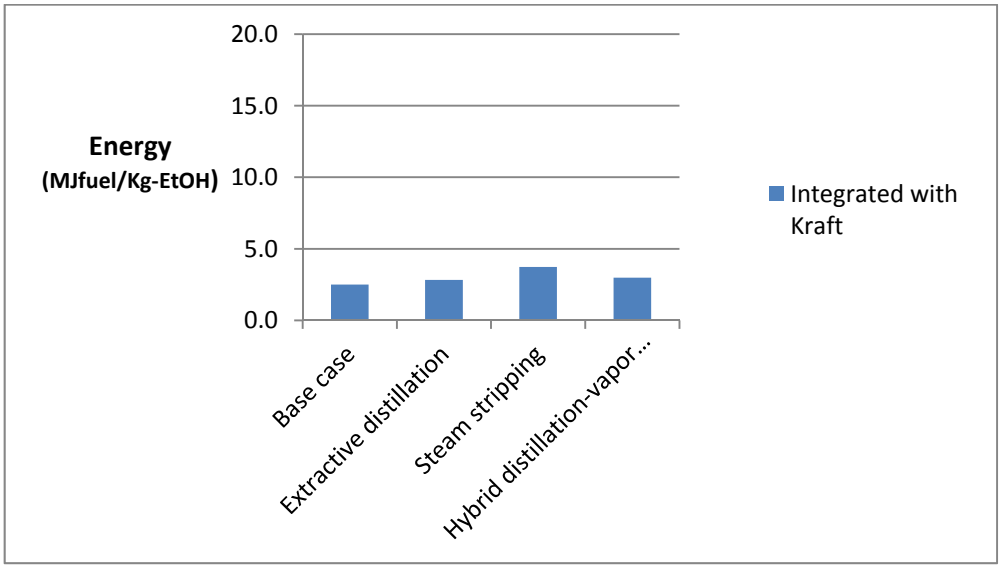

Figure 3-22 : Energy consumption in integrated-with-Kraft

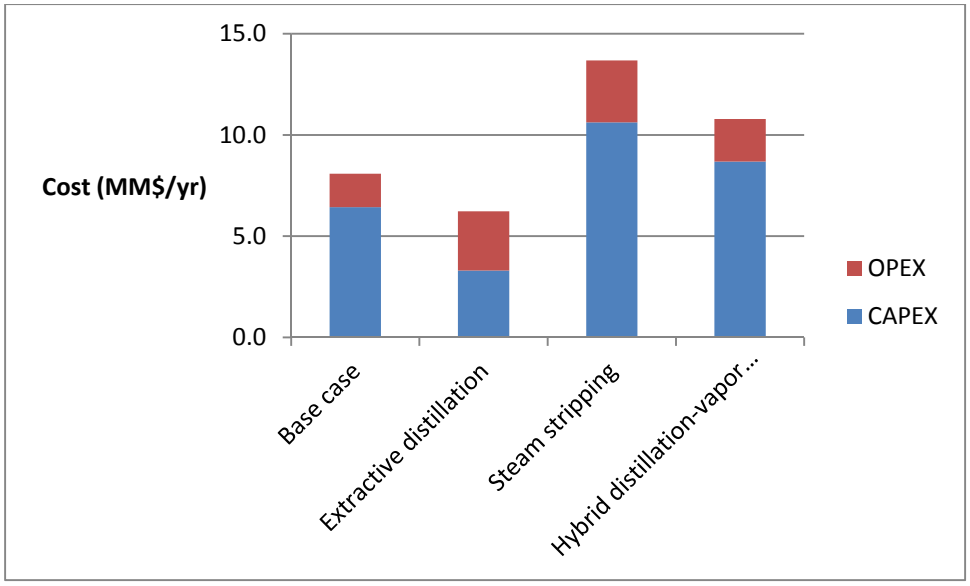

Figure 3-23 : Total annualized cost in integrated-with-Kraft

3.4.4 Economic analysis in integration with Kraft

Details of economic analysis for this scenario is found in Appendix B. in this analysis cost of additional heat exchangers pertaining to the identified bridges as well as the cost of equipment with new duties have been calculated. The CAPEX in this scenario after these considerations transpire to be slightly higher than the internally-integrated mode. As can be seen in Figure 3.23, steam stripping shows the highest capital investment cost. The lowest capital cost investment design belongs to the double-effect extractive distillation. The OPEX on the other hand is dramatically reduced in all the options after integration with Kraft. The operating costs after integration are reduced to a similar level for the base case as well as the alternatives. The total annualized cost which assembles the operating and capital cost suggests that the double-effect extractive distillation due to its low capital investment is the best option among all the other designs.

3.5 Final conclusion

Energy consumptions of all the design in three scenarios is shown in Figure 3.25. As this figure illustrates, by going towards more integrated designs we can significantly reduce the energy consumption. There are significant heat recovery opportunities for the base case, double-effect extractive and vapor permeation designs after considering Internal heat integration. There is not

much potential for steam stripping in this scenario as this design is inherently very efficient and there are not considerable energy sources available in this design for more recovery. However, steam stripping is a big consumer of electricity which adds to its overall energy consumption.

In integration with Kraft, the heat consumption is further reduced in all the designs. As can be observed in Figure 3.25, the base case has the lowest energy consumption after external integration with Kraft followed by the double-effect extractive distillation and vapor permeation with slightly higher consumption. As discussed before steam stripping although is fully satisfied in terms of heat demand but due to its relatively high power consumption remains an energy consuming option.

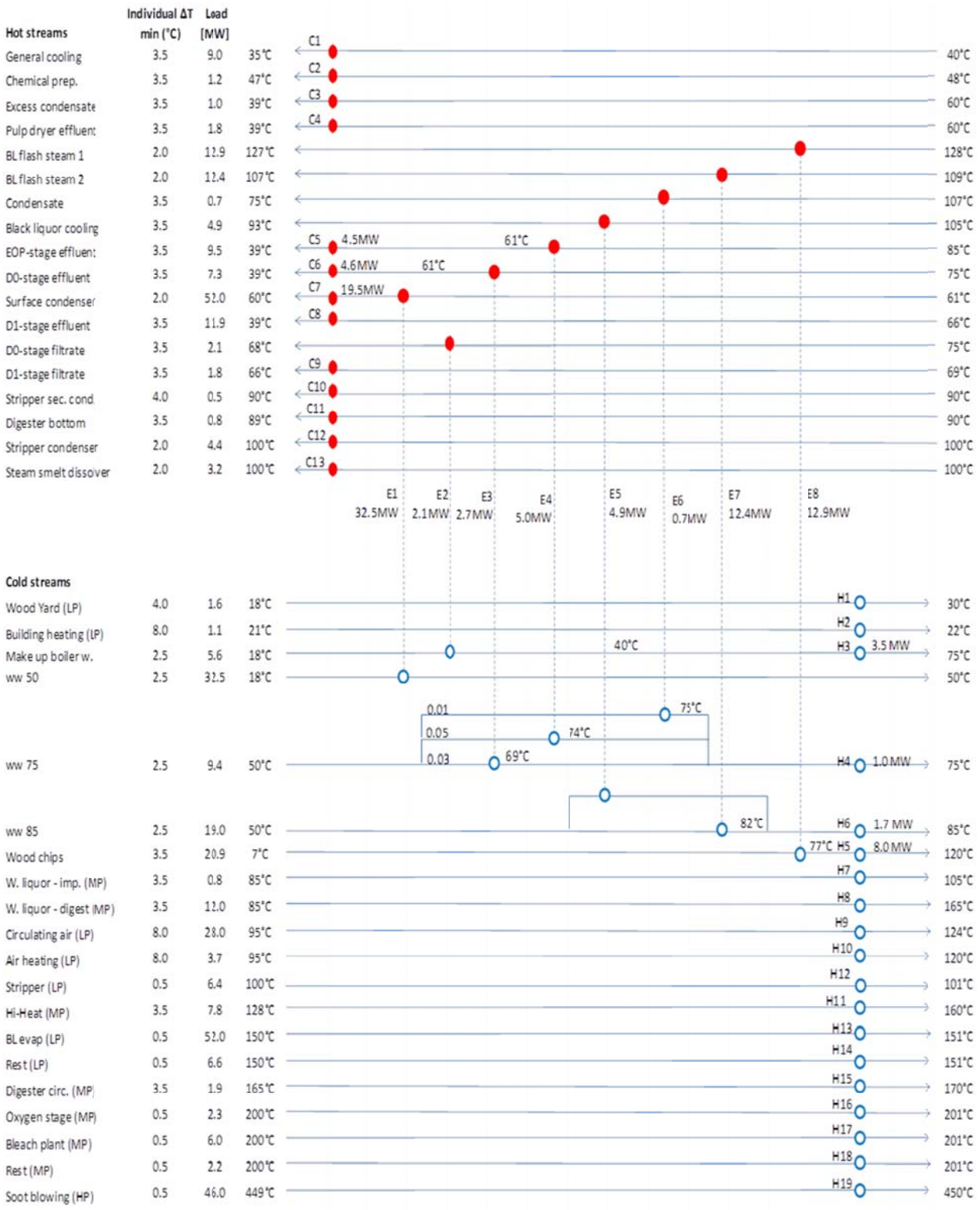

Figure 3-24 : Grid diagram of the model mill

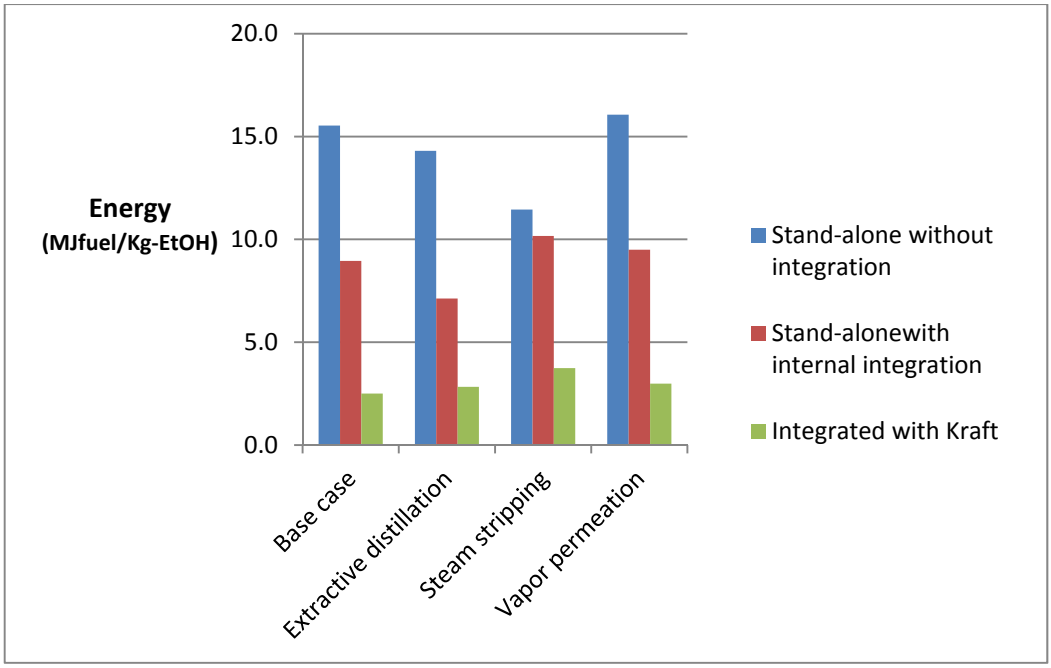

Figure 3-25 : Energy consumption in three scenarios

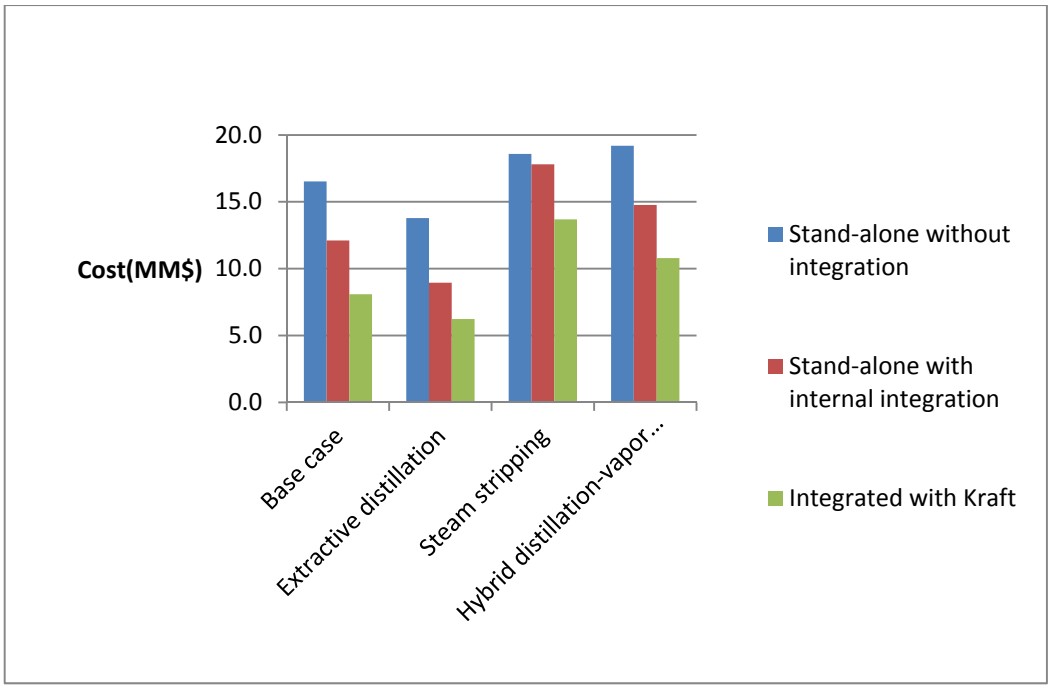

Figure 3-26 :Total annualized cost in three scenarios

As a conclusion, although alternative designs proves to be relatively more energy efficient than the base case in terms of heat demand, applying internal and external energy integration in the base case will render it the most energy efficient option. This result will be even more important if the power consumption of alternative techniques is taken into consideration. Designs such as the steam stripping and the vapor permeation consumes high amount of electricity and for instance in the case of the steam stripping, the high electricity consumption remains the main contributor to the overall energy consumption.

From economic stand point, capital investment required for a project prior to considering integration is a key factor for the success of that given project. By observing the trend of operating and capital cost diagrams presented in previous sections, it could be understood that as we go from stand-alone to more integrated designs, the operating cost significantly decreases which is the direct result of reduction in hot utility consumption. The capital cost diagram suggests that the steam stripping is the most capital intensive option followed by vapor permeation, the base case and the double-effect extractive distillation whith the lowest capital cost. Through a techno-economic analysis, Capital investment needed for each separation option and the operating cost in each of the stand-alone and integrated with Kraft are calculated and the results will determine which option is more attractive than the others. By this token and as shown in total annualized diagram in Figure 3.26, the double-effect extractive distillation will be the best option in internal and external integration scenarios.

3.6 Developed methodology

The generic methodology derived from this work is presented in Figure 3.27. This methodology could be applied to any biorefinery separation system and as discussed throughout this work is capable of identifying the integration opportunities and assessing the cost and benefits of integration and finally finding the best separation alternative in any of the stand-alone or integrated-with-Kraft modes.

According to this methodology in order to design integrated separation systems, the separation objective and desired specification must be defined in the first step. Next, separation strategies that are capable of achieving this objective should be identified and selected. As figure 3.27 shows, a mass and

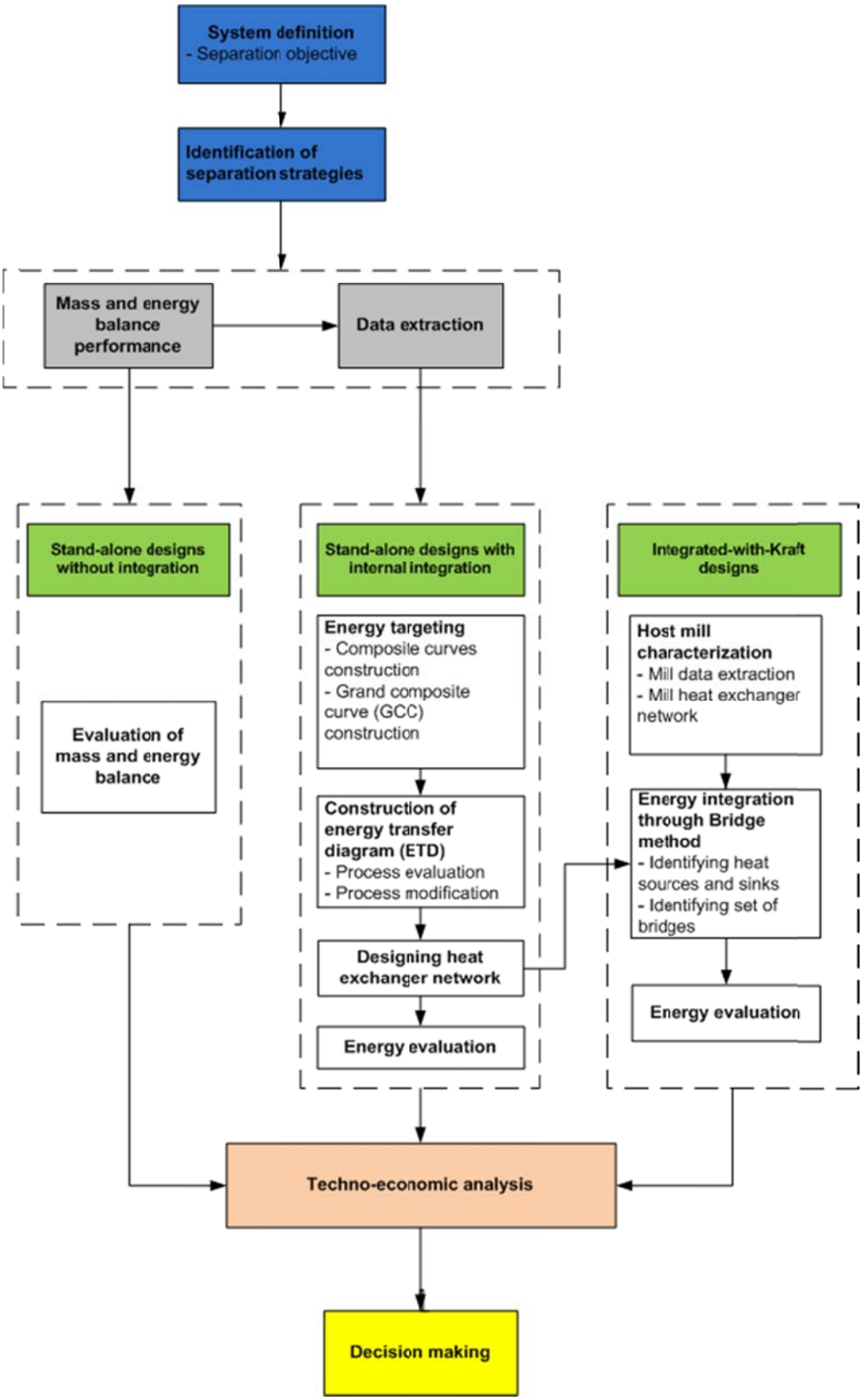

Figure 3-27 : Generic methodology

energy balance of each separation should be performed and the results which are the basics of stand-alone designs without integration will be evaluated in a techno-economic analysis.

Data regarding hot and cold streams in each separation strategy should be extracted next and these data will be subsequently used to perform an internal integration and then will be used in designing the stand-alone with internal integration flow sheets. Process modification ideas are identified in energy transfer diagram and are assessed. After internal integration and matching heat sources with heat demands in each flow sheet, the heat exchanger network corresponding to each strategy should be constructed. Ultimately results from this type of design will be evaluated in a techno-economic analysis. In order to have the designs integrated with Kraft process, data from the grass root heat exchanger network of each flow sheet will be assessed to identify the possible matches with a host Kraft mill. This will form the groundwork for the designs that will be integrated with the Kraft process. Energy consumption and cost of equipment then will be obtained and will be evaluated in a techno-economic analysis. Finally, in the end, the techno-economic evaluations which are normally manifested in the form of profitability metrics such as internal rate of return (IRR), return on investment (ROI), total annualized cost (TAC) and etc. are compared and a decision on selecting the best separation strategy will be made.

As will be discussed in the next chapter, decision making is not just done through economic metrics and other factor could significantly influence the final decision.

CHAPTER 4 GENERAL DISCUSSION AND RECOMMENDATION

4.1 General discussion

Over the past years forestry industry in North America has faced serious challenges regarding declining demand, high energy cost, aging mills and old equipment, growing competition from global producers and stricter environmental regulations. On the other hand lack of innovation and R&D development has aggravated this business and the initiatives such as mergers and downsizing have brought little comfort for this ailing sector. Hence, forestry companies have been seeking alternative business models to overcome this situation and to increase their revenue and stay competitive in the long run. While the outlook for this sector looks gloomy but advantages such as established supply chain network for securing biomass, having the required utility systems and potential available heat, have paved the way for integrating and implementing new processes along with the existing business. For the mills that are willing to enhance their economic performance forest biorefinery (FBR) could be an excellent starting point. A biorefinery which aims to produce bio-products and bio-energy could be implemented in retrofit to existing pulp and paper mill. Therefore, forestry companies by adopting a new strategic plan can produce new products and enter a new market alongside their traditional market.

On the other hand for biorefinery technology owners, in order to be profitable and successful in the short term, reducing the costs and improving the technology maturity seem to be two vital elements. Commonly, one of the important contributors to weak economics in a biorefinery is the high costs associated with downstream separation of final products. Considering the dilute nature of fermentation broth fed to the downstream separation section and the energy cost of performing such separation, biorefinery companies have tended to adopt new separation techniques to alleviate this huge operating cost. One other approach to meet this end for these companies could be a shift in the business model from stand-alone to integrated structures. Process integration both internally or externally could increase the synergies between two systems and could also decrease the operating cost. Setting up a biorefinery in proximity of a pulp and paper facility and using the available heat sources in either of these infrastructures could potentially decrease the operating and capital costs.

A systematic approach which analyzes the energy efficiency of a separation process and identifies potential opportunities for integration at the design level is necessary in order for a biorefinery to decrease its costs. Adopting new tools which aide a designer to enhance his or her understanding of the energy impact of a given design which also provides him or her with insights on process improvement is a key element in reducing the operating cost of a design. Equally important is employing an integration method which enhances the opportunities for heat recovery and at the same time limits the search space for matching sources with sinks. The Bridge method and the energy transfer diagram (ETD) tool which are used in this study meet the aforementioned objectives for energy integration and a holistic energy analysis. The goal of this work is therefore, to propose a methodology for performing a holistic energy analysis and also designing an integrated separation system for a biorefinery. The methodology also uses conventional techno-economic metrics in order to evaluate different separation techniques on a conceptual level. Three alternative separation techniques were proposed as case studies and benchmarked against a base case separation system of an ethanol biorefinery, their energy consumption as well as their potential for heat recovery in stand-alone and integrated modes were analyzed and evaluated.

4.2 Recommendations

As discussed in the conclusion of previous section, the double-effect distillation with low capital investment and low energy consumption in all three scenarios could be the option of choice for an ethanol biorefinery separation system. However there are issues which should be taken into account before adopting a new technology:

- **Processing technology risk:** Generally for companies, shifting from the common practice to a new technology involves technology risks. This risk consists of plant engineering and construction and plant operation risks. Unique risks occur during each phase which needs to be addressed carefully beforehand. Although extractive distillation is not an emerging technology and it has had a long-standing usage in the chemical industry in different applications, its implementation still requires plant engineering, plant construction, solvent storage, movement of product within the plant and etc. which all involve new risks for biorefinery management to make a decision on. To the above risks,

we should add operational risks which could have serious impacts on the operability of the system.

- **Environmental risk:** environmental regulations which have been intensified over the past years require companies to take more responsible stance on their effluents and emissions. This has obliged companies to minimize the level of chemical substances in their effluents or try to avoid using them if possible. In extractive distillation a large quantity of ethylene glycol (EG) is necessary in the extractive column to separate ethanol from the mixture. Although The US environmental protection agency has not labelled Ethylene glycol (EG) as a potential carcinogen but few cases of respiratory problems have been reported in individuals.

Considering above mentioned risks which are generally very difficult for companies to quantify and evaluate their impacts on the final economics of the project, and also the fact that integrated base case is the next best choice in terms of the total economic metric, it might be more preferable for decision makers to keep the common practice and adopt integration approach for reducing the energy consumption. It is also important to note that process integration (PI) itself requires restructuring and modifying heat exchanger network and might possibly cause some level of close interactions but if the integration is well balanced it can even enhance the controllability of the system (Kemp 2007).

4.3 Concluding words

Separation technology has seen new advancements and new technologies especially in separation of azeotropic mixtures. Membranes depending on their material type and operating parameters such as separation factor and flux have been somewhat used in the biochemical industry to overcome the vapor-liquid equilibrium constraints. As discussed earlier, eliminating the bulk of water in the studied bioethanol downstream separation is the most energy intensive separation step. Hence, in an end of pipe separation using hydrophobic membrane that allows water to pass through and retrieves the ethanol, could eliminate the need for a distillation step and will save a great amount of energy. Although hydrophobic membranes are not as advanced as the hydrophilic ones, prospective improvement in their technology will make this type of membrane a cost-effective separation approach. Another issue that should be taken into consideration is the

problem of fouling and operating life of membranes. Commonly depending on the structure and material of membranes, every 3 to 5 years they need to be replaced with a new one. Although these numbers have been increasing and technologies like ceramic membrane offers more durability, still this contributes to the total cost of the membrane system and also the downtime of the unit.

The other technique which was proposed in this work was steam stripping. This technology in slip-stream separations has attracted huge attention and a lot of academic research has been devoted to that. However, employing this technology at low pressure in end-of-pipe separations can bring about operability problems and controllability difficulties. Adding to this is the tremendous cost of generating low levels of pressure via mechanical systems which entails consumption of large amount of electricity.

From host mill stand point, it is noteworthy that energy inefficient mills generally generate more heat recovery opportunities. The mill studied in this work is a typical Scandinavian mill which is by nature very energy efficient. North American mills on the other hand are old and aging and not as much energy efficient. Therefore, energy integration becomes even more attractive in this type of mills and more energy reduction can be brought about by adopting it. Furthermore, the energy integration in mill which could make some steam available could be used to further supply the additional demand of the biorefinery or could potentially create opportunities for district heating, increasing the power production or extracting lignin that can be sold as a biofuel or used for other potential applications. These measures take even more focus because of increasing energy prices and new environmental policies. Moreover, lignin extraction can increase pulp production in a mill.

On the other hand, the overall methodology proposed in this work clearly shows that through energy integration, great energy reduction is achieved in the down-stream separation of the studied ethanol biorefinery. However, the separation strategies, designs, and specific energy results could be different in another case study. This methodology which is useful for early-stage design decision making considers the return on energy in an integrated forest biorefinery. The cost of a new boiler in integrating a biorefinery within a pulp and paper facility which is the most significant cost of the integration is shown to decrease as we go along the energy integration path in the biorefinery and with the Kraft process. This huge cost could render an integrated

biorefinery project absolutely uneconomical; therefore reducing it is a key step in the success of an integrated biorefinery.

Another important issue regarding ethanol production which should be considered is the market and regulation risk. Ethanol price is very volatile and continuous fluctuation makes it difficult for managers to have a long-term marketing plan on this product. Furthermore, government interventions to regulate this market and issues such as blend wall and RFS programs have made this market even more complex for the players to act. Therefore, shifting to another market such as that of Butanol which could be both used in fuel and chemical market seems to be a promising option for the players. Ethanol could also be catalytically converted to butanol in retrofitting the existing facility however; the technology needs improvement and more investigation.

4.4 Future work

The methodology proposed in this work can be further expanded into other parts of a biorefinery and can include pre-treatment, hydrolysis and fermentation too. Identifying the final topology of the retrofitted grid network of the Kraft process through an automated approach that identifies the possible bridges can also be pursued as future work.

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APPENDIX A ECONOMIC DATA

In this section the costs associated with each design in three different scenarios are presented. The prices have been updated using CE index. (CE index 2013= 569.5). the cost equipment have been scaled based on the six tenth equation : $\frac{Cost_2}{Cost_1} = (\frac{Capacity\ 2}{Capacty\ 1})^{Exp}$.

The exponents have been adopted from the work of Wooley et.al (1999). The price of electricity assumed to be 0.05 $/Kwh and the price of steam is 4.1 $/GJ adopted from Hydroquebec and Gas metro companies. In calculating the steam price, a natural gas boiler with efficiency of 90% was assumed for steam production. The type of heat exchangers presented in this work is shell&tube.

The base case

Stand-alone -Equipment cost)

Equipment	Base Cost($)	Year	Index at year	Sized by	Base data	New data	Exponent	Updated cost $(2013)	Sized cost($)
Beer Column	636,976	1996	382.00	Diameter(m)	3.86	3.35	0.78	949,628	850,257
Rectific. Column	525,800	1996	382.00	Flow (Kg/h)	55,300.00	58,000.00	0.78	783,882	813,578
BC Reboiller(H1,6)	158,800	1996	382.00	Duty(MW)	32.50	46.00	0.68	236,745	299,830
RC Reboiller(H2,6)	29,600	1997	387.00	Duty(MW)	4.06	3.61	0.68	43,559	40,274
BC Condenser	29,544	1996	382.00	Duty(MW)	0.92	8.30	0.68	44,045	196,642
RC Condenser	86,174	1996	382.00	Duty(MW)	20.08	23.80	0.68	128,471	144,224
Molecular Sieve	2,700,000	1998	390.00	Flow (Kg/h)	22,733.62	30,000.00	0.70	3,942,692	4,787,511
Fermentation broth preheater	58,400	1997	387.00	Area(m2)	46.00	235.54	0.68	85,940	260,927
C1,1 cooler(Botoms 1)	45,000	1997	387.00	Area(m2)	185.00	930.43	0.68	66,221	198,620
C1,3 cooler(Bottoms 2)	45,000	1997	387.00	Area(m2)	185.00	79.89	0.68	66,221	37,414
Total									**7,629,276**

Stand-alone- Operating cost)

Total steam consumption(KJ/h)	in MW	in GJ	Steam price $/Gj	Cost ($)/h	Annual cost($)
3.07E+08	85.3	3.07E+02	4.1	1,259	10,270,992

In equipment cost table, molecular sieve is a block unit which contains all the in-between coolers as well.

Base case- Internally-integrated)

Equipment	Base Cost($)	Year	Index at year	Sized by	Base data	New data	Exponent	Updated basecost ($)(2013)	Sized cost($)
Beer Column	636,976	1996	382.00	Diameter(m)	3.86	3.35	0.78	949,628	850,257
Rectific. Column	525,800	1996	382.00	Flow (Kg/h)	55,300.00	58,000.00	0.78	783,882	813,578
BC Reboiller(H 1,6)	158,800	1996	382.00	Duty(MW)	32.50	46.00	0.68	236,745	299,830
RC Reboiller(H 2,6)	29,600	1997	382.00	Duty(MW)	4.06	3.16	0.68	44,129	37,242
BC Condenser	29,544	1996	382.00	Duty(MW)	0.92	8.30	0.68	44,045	196,642
RC Condenser(C1,6)	86,174	1996	382.00	Duty(MW)	20.08	23.80	0.68	128,471	144,224
Molecular Sieve	2,700,000	1998	390.00	Flow (Kg/h)	22,733.62	30,000.00	0.70	3,942,692	4,787,511
C1,1 cooler	45,000	1997	387.00	Area(m2)	185.00	345.39	0.68	45,000	68,799
C1,3 cooler	45,000	1997	387.00	Area(m2)	185.00	79.89	0.68	66,221	37,414
Exchanger E1,1	19,040	1997	387.00	Area(m2)	84.00	36.98	0.68	28,019	16,039
Exchanger E1,2	19,040	1997	387.00	Area(m2)	84.00	1,995.76	0.68	28,019	241,554
Exchanger E1,3	19,040	1997	387.00	Area(m2)	84.00	33.12	0.68	28,019	14,879
Total									**7,507,968**

Internally integrated-operating cost)

Total steam consumption(KJ/h)	in MW	in GJ	Steam price $/Gj	Cost ($)/h	Annual cost($)
1.78E+08	49.4	1.78E+02	4.1	729	5,949,815

Integrated with the Kraft- Equipment cost)

Equipment	Base Cost($)	Year	Index at year	Sized by	Base data	New data	Exponent	Updated basecost $(2013)	Sized cost($)
Beer Column	636,976	1996	382.00	Diameter(m)	3.86	3.35	0.78	949,628	850,257
Rectific. Column	525,800	1996	382.00	Flow (Kg/h)	55,300.00	58,000.00	0.78	783,882	813,578
BC Reboiller	158,800	1996	382.00	Duty(MW)	32.50	46.00	0.68	236,745	299,830
RC Reboiller	29,600	1997	382.00	Duty(MW)	4.06	3.16	0.68	44,129	37,242
BC Condenser (C1,2)	29,544	1996	382.00	Duty(MW)	0.92	0.60	0.68	44,045	32,949
RC Condenser (C1,6)	86,174	1996	382.00	Duty(MW)	20.08	4.10	0.68	128,471	43,621
Molecular Sieve	2,700,000	1998	390.00	Flow (Kg/h)	22,733.62	30,000.00	0.70	3,942,692	4,787,511
C1,1 cooler (Bottoms 1)	45,000	1997	387.00	Area(m2)	185.00	345.39	0.68	66,221	101,244
C1,3 cooler (Bottoms 2)	45,000	1997	387.00	Area(m2)	185.00	79.89	0.68	66,221	37,414
Exchanger E1,1	19,040	1997	387.00	Area(m2)	84.00	36.98	0.68	28,019	16,039
Exchanger E1,2	19,040	1997	387.00	Area(m2)	84.00	1,995.76	0.68	28,019	241,554
Exchanger E1,3	19,040	1997	387.00	Area(m2)	84.00	33.12	0.68	28,019	14,879
Exchanger C1,6H1	19,040	1997	387.00	Area(m2)	84.00	29.70	0.68	28,019	13,817
Exchanger C1,6H2	19,040	1997	387.00	Area(m2)	84.00	19.60	0.68	28,019	10,414
Exchanger C1,6H3	19,040	1997	387.00	Area(m2)	84.00	122.66	0.68	28,019	36,246
Exchanger C1,6H4	19,040	1997	387.00	Area(m2)	84.00	51.24	0.68	28,019	20,021
Exchanger C1,2H6	19,040	1997	387.00	Area(m2)	84.00	72.69	0.68	28,019	25,395
Exchanger C1,6E7,E7E 8,E8H5	19,040	1997	387.00	Area(m2)	84.00	34.50	0.68	28,019	15,298
Exchanger C1,6E7,E7E 8,E8H5(2)	19,040	1997	387.00	Area(m2)	84.00	855.57	0.68	28,019	135,792
Exchanger C1,6E7,E7E 8,E8H7	19,040	1997	387.00	Area(m2)	84.00	46.11	0.68	28,019	18,636
Exchanger C1,6E7,E7E 8,E8H8	19,040	1997	387.00	Area(m2)	84.00	145.98	0.68	28,019	40,800
Exchanger C1,2H12	19,040	1997	387.00	Area(m2)	84.00	1,628.00	0.68	28,019	210,312
Excess LP steam Exchanger	19,040	1997	387.00	Area(m2)	84.00	155.05	0.68	28,019	42,507
Total									7,845,355

Integration with Kraft-Operating cost

Total steam consumption(KJ/h)	in MW	in GJ/h	Steam price $/Gj	Cost ($)/h	Annual cost($)
4.93E+07	13.7	4.93E+01	4.1	202	1,650,050

Double effect extractive distillation

Stand-alone-Equipment cost)

Equipment	Base Cost($)	Year	Index at year	Sized by	Basecase data	New data	Exponent	Updated base cost($)	sized cost($)
Beer Column1	636,976	1996	382.00	Diameter(m)	4.37	3.20	0.78	949,628	744,723
Beer Column 2	636,976	1996	382.00	Diameter(m)	4.37	3.35	0.78	949,628	771,814
Extrac Column	525,800	1996	382.00	Flow(Kg/h)	55,000.00	40,308.00	0.78	783,882	615,139
Recov Column	525,800	1996	382.00	Flow(Kg/h)	55,000.00	18,508.00	0.68	783,882	373,774
BC 2 Reboiler	158,800	1996	382.00	Duty(MW)	32.50	25.83	0.68	236,745	202,527
EC Reboiller	158,800	1997	387.00	Duty(MW)	32.50	10.28	0.68	233,686	106,818
RC Reboiller	29,600	1997	387.00	Duty(MW)	4.10	2.11	0.68	43,559	27,736
BC 1 Condenser	86,174	1996	382.00	Duty(MW)	20.00	22.78	0.68	128,471	140,350
EC Condenser	29,544	1996	382.00	Duty(MW)	0.92	9.72	0.68	44,045	218,879
RC Condenser	29,544	1996	382.00	Duty(MW)	0.92	1.56	0.68	44,045	62,952
Feed preheater1	58,400	1997	387.00	Area(m2)	46.00	104.52	0.68	85,940	150,170
Feed Preheater2	58,400	1997	387.00	Area(m2)	46.00	214.71	0.68	85,940	245,006
Solvent preheater	58,400	1997	387.00	Area(m2)	46.00	5.05	0.68	85,940	19,124
Feed 2 Pump	19,700	1997	387.00	Flow(Kg/h)	261,253.01	210,000.00	0.79	28,990	24,396
Recovery col.Pump	19,700	1997	387.00	Flow(Kg/h)	261,253.01	18,508.00	0.79	28,990	3,581
Bottoms1 cooler (C2,2)	45,000	1997	387.00	Area(m2)	185.00	459.11	0.68	66,221	122,864
Bottoms 2 cooler (C2,1)	45,000	1997	387.00	Area(m2)	185.00	508.54	0.68	66,221	131,710
Product cooler(C2,5)	45,000	1997	387.00	Area(m2)	185.00	70.08	0.68	66,221	34,225
Solvent recycle cooler (C2,6)	45,000	1997	387.00	Area(m2)	185.00	19.07	0.68	66,221	14,125
Solvent	29,971	2013							
Total									4,009,914

Stand-alone-Operating cost)

Total steam consumption(KJ/h)	in MW	in GJ	Steam price ($/GJ)	Cost ($)/h	Annual cost($)
2.82E+08	78.3	282	4.1	1,156	9,434,592
Ethylene glycol make-up(Kg/h)			**Price($/t)**		
72			1,800		1,057,536
Total					**10,492,128**

Internally integrated-Equipment cost)

Equipment	Original Cost($)	Year	Index at year	Sized by	Basecase data	New data	Exponent	Updated base cost	sized cost
Beer Column1	636,976	1996	382.00	Diameter(m)	4.37	3.20	0.78	949,628	744,723
Beer Column 2	636,976	1996	382.00	Diameter(m)	4.37	3.35	0.78	949,628	771,814
Extrac Column	525,800	1996	382.00	Flow(Kg/h)	55,000.00	40,308.00	0.78	783,882	615,139
Recov Column	525,800	1996	382.00	Flow(Kg/h)	55,000.00	18,508.00	0.68	783,882	373,774
BC 2 Reboiler(H2,2)	158,800	1996	382.00	Duty(MW)	32.50	25.83	0.68	236,745	202,527
EC Reboiller(H2,3)	158,800	1997	387.00	Duty(MW)	32.50	10.28	0.68	233,686	106,818
RC Reboiller(H2,1)	29,600	1997	387.00	Duty(MW)	4.10	2.11	0.68	43,559	27,736
BC 1 Condenser(C2,3)	86,174	1996	382.00	Duty(MW)	20.00	22.78	0.68	128,471	140,350
EC Condenser(C2,4)	29,544	1996	382.00	Duty(MW)	0.92	9.72	0.68	44,045	218,879
Feed preheater1(H2,4)	58,400	1997	382.00	Area(m2)	46.00	17.96	0.68	87,065	45,929
Feed 2 Pump	19,700	1997	387.00	Flow(Kg/h)	261,253.01	210,000.00	0.79	28,990	24,396
Recovery col.Pump	19,700	1997	387.00	Flow(Kg/h)	261,253.01	18,508.00	0.79	28,990	3,581
Bottoms1 cooler (C2,2)	45,000	1997	387.00	Area(m2)	185.00	200.54	0.68	66,221	69,954
Bottoms 2 cooler (C2,1)	45,000	1997	387.00	Area(m2)	185.00	148.36	0.68	66,221	56,991
Product cooler(C2,5)	45,000	1997	387.00	Area(m2)	185.00	70.08	0.68	66,221	34,225
Exchanger E2,1	19,040	1997	387.00	Area(m2)	84.00	30.98	0.68	28,019	14,219
Exchanger E2,2	19,040	1997	387.00	Area(m2)	84.00	10.15	0.68	28,019	6,659
Exchanger E2,3	19,040	1997	387.00	Area(m2)	84.00	209.94	0.68	28,019	52,235
Exchanger E2,4	19,040	1997	387.00	Area(m2)	84.00	161.26	0.68	28,019	43,658
Exchanger E2,5	19,040	1997	387.00	Area(m2)	84.00	160.33	0.68	28,019	43,487
Exchanger E2,6	19,040	1997	387.00	Area(m2)	84.00	1,302.40	0.68	28,019	180,703
Exchanger E2,7	19,040	1997	387.00	Area(m2)	84.00	38.98	0.68	28,019	16,623
Exchanger E2,8	19,040	1997	387.00	Area(m2)	84.00	716.49	0.68	28,019	120,360
Total									**3,914,782**

Internally integrated-Operating cost)

Total steam consumption(KJ/h)	**in MW**	**in GJ**	**Steam price $/Gj**	**Cost ($)/h**	**Annual cost($)**
1.40E+08	39	1.40E+02	4.1	574	4,683,840
Ethylene glycol make-up(Kg/h)			**Price($/t)**		
72			1,800		1,057,536
Total					**5,741,376**

Integration with Kraft-Equipment cost)

Equipment	Base Cost($)	Year	Index at year	Sized by	Basecase data	New data	Exponent	Updated base cost($)	sized cost($)
Beer Column1	636,976	1996	382.00	Diameter(m)	4.37	3.20	0.78	949,628	744,723
Beer Column 2	636,976	1996	382.00	Diameter(m)	4.37	3.35	0.78	949,628	771,814
Extrac Column	525,800	1996	382.00	Flow(Kg/h)	55,000.00	40,308.00	0.78	783,882	615,139
Recov Column	525,800	1996	382.00	Flow(Kg/h)	55,000.00	18,508.00	0.68	783,882	373,774
BC 2 Reboiler(H 2,2)	158,800	1996	382.00	Duty(MW)	32.50	32.50	0.68	236,745	236,745
EC Reboiller(H 2,3)	158,800	1997	387.00	Duty(MW)	32.50	10.28	0.68	233,686	106,818
RC Reboiller(H 2,1)	29,600	1997	387.00	Duty(MW)	4.10	2.11	0.68	43,559	27,736
BC 1 Condenser (C2,3)	86,174	1996	382.00	Duty(MW)	20.00	17.50	0.68	128,471	117,320
EC Condenser (C2,4)	29,544	1996	382.00	Duty(MW)	0.92	0.00	0.68	44,045	0
Feed preheater1 (H2,4)	58,400	1997	382.00	Area(m2)	46.00	17.96	0.68	87,065	45,929
Feed 2 Pump	19,700	1997	387.00	Flow(Kg/h)	261,253.01	210,000.00	0.79	28,990	24,396
Recovery col.Pump	19,700	1997	387.00	Flow(Kg/h)	261,253.01	18,508.00	0.79	28,990	3,581
Bottoms1 cooler (C2,2)	45,000	1997	387.00	Area(m2)	185.00	200.54	0.68	66,221	69,954
Bottoms 2 cooler (C2,1)	45,000	1997	387.00	Area(m2)	185.00	148.36	0.68	66,221	56,991
Product cooler(C2,5)	45,000	1997	387.00	Area(m2)	185.00	70.08	0.68	66,221	34,225
Exchanger E2,1	19,040	1997	387.00	Area(m2)	84.00	30.98	0.68	28,019	14,219
Exchanger E2,2	19,040	1997	387.00	Area(m2)	84.00	10.15	0.68	28,019	6,659
Exchanger E2,3	19,040	1997	387.00	Area(m2)	84.00	209.94	0.68	28,019	52,235
Exchanger E2,4	19,040	1997	387.00	Area(m2)	84.00	161.26	0.68	28,019	43,658
Exchanger E2,5	19,040	1997	387.00	Area(m2)	84.00	160.33	0.68	28,019	43,487
Exchanger E2,6	19,040	1997	387.00	Area(m2)	84.00	1,302.40	0.68	28,019	180,703
Exchanger E2,7	19,040	1997	387.00	Area(m2)	84.00	38.98	0.68	28,019	16,623
Exchanger E2,8	19,040	1997	387.00	Area(m2)	84.00	716.49	0.68	28,019	120,360
Exchanger C2,3H1	19,040	1997	387.00	Area(m2)	84.00	35.29	0.68	28,019	15,536
Exchanger C2,3H2	19,040	1997	387.00	Area(m2)	84.00	23.10	0.68	28,019	11,645
Exchanger C2,3H3	19,040	1997	387.00	Area(m2)	84.00	175.13	0.68	28,019	46,177
Exchanger C2,4E8, E8H6	19,040	1997	387.00	Area(m2)	84.00	872.54	0.68	28,019	137,618
Exchanger C2,4E8 , E8H5	19,040	1997	387.00	Area(m2)	84.00	189.43	0.68	28,019	48,708
Exchanger C2,4E8 ,E8H7	19,040	1997	387.00	Area(m2)	84.00	5.81	0.68	28,019	4,558
Excess LP steam Exchanger	19,040	1997	387.00	Area(m2)	84.00	255.37	0.68	28,019	59,679
TOTAL									4,031,010

Integration with Kraft-Operating cost)

Total steam consumption(KJ/h)	in MW	in GJ	Steam price $/Gj	Cost ($)/h	Annual cost($)
5.58E+07	16	5.58E+01	4.1	229	1,866,845
Ethylene glycol make-up(Kg/h)			**Price($/t)**		
72			1,800		1,057,536
Total					**2,924,381**

Steam stripping

Stand-alone – Equipment cost)

The cost of liquid ring pump and expander was obtained from equation presented in Seider et al. (2009).

Equipment	Base Cost($)	Year	Index at year	Sized by	Base data	New data	Exponent	Updated cost(2013)	Sized cost($)
Stripping column	636,976	1996	382.00	Diameter	3.86	4.60	0.78	949,628	1,088,846
Rectific. Column	636,976	1996	382.00	Diameter	3.86	5.00	0.78	949,628	1,162,016
RC Reboiller(H3,1)	158,800	1997	387.00	Duty(KJ/h)	1.17E+08	4.20E+07	0.68	233,686	116,433
RC Condenser(C3,4)	86,174	1996	382.00	Duty(KJ/h)	7.23E+07	1.14E+08	0.68	128,471	175,150
Molecular Sieve	2,700,000	1998	390.00	Flow(Kg/h)	22,733.62	27,700.00	0.70	3,942,692	4,346,238
liquid ring pump(for vacuum)	Calculation								5,372,560
Expander	Calculation								61,619
Pump 1 (bottoms1)	19,700	1997	387.00	Flow(Kg/h)	261,253.01	427,000.00	0.79	28,990	42,737
Pump 2 (bottoms2)	19,700	1997	387.00	Flow(Kg/h)	261,253.01	29,800.00	0.79	28,990	5,217
Product cooler (C3,1)	45,000	1997	387.00	Area(m2)	185.00	156.80	0.68	66,221	181,286
Cooler bottoms 1(C3,2)	45,000	1997	387.00	Area(m2)	185.00	357.55	0.68	66,221	144,210
Cooler bottoms 2(C3,3)	45,000	1997	387.00	Area(m2)	185.00	21.45	0.68	66,221	21,288
Stripping steam heater(H3,2)	58,400	1997	387.00	Area(m2)	46.00	140.40	0.68	85,940	183,540
Total									**12,717,600**

Stand-alone-Operating cost)

	in KJ/h	in MW	in GJ	price	Cost ($)/h	Annual cost($)
Total steam consumption	1.52E+08	42.2	1.52E+02	4.1($/GJ)	623	5,085,312
Electricity		7.5		0.05($/Kwh)		3,060,000
Total						**8,145,312**

Internally integrated-Equipment cost)

Equipment	Base Cost($)	Year	Index at ye	Sized by	Base data	New data	Exponent	Updated cost2013($)	Sized cost($)
Stripping column	636,976	1996	382	Diameter	3.86	4.6	0.78	949,628	1,088,846
Rectific. Column	636,976	1996	382	Diameter	3.86	5.0	0.78	949,628	1,162,016
RC Reboiller	158,800	1997	387	Duty(KJ/h)	1.17E+08	4.20E+07	0.68	233,686	116,433
RC Condenser(C3,4)	86,174	1996	382	Duty(KJ/h)	7.23E+07	1.14E+08	0.68	128,471	175,150
Molecular Sieve	2,700,000	1998	390	Flow(Kg/h)	2.27E+04	2.77E+04	0.7	3,942,692	4,497,186
liquid ring pump(for vacuum)	Calculated								5,372,560
Expander	Calculated								61,619
Pump 1 (bottoms1)	19,700	1997	387	Flow(Kg/h)	261253.01	427000.0	0.79	28,990	42,737
Pump 2 (bottoms2)	19,700	1997	387	Flow(Kg/h)	261253.01	29800.0	0.79	28,990	5,217
Product cooler (C3,1)	45,000	1997	387	Area(m2)	185	58.7	0.68	66,221	30,337
Cooler bottoms 1(C3,2)	45,000	1997	387	Area(m2)	185	357.6	0.68	66,221	103,655
Cooler bottoms 2(C3,3)	45,000	1997	387	Area(m2)	185	21.5	0.68	66,221	15,301
Exchanger E3,1	19,040	1997	387	Area(m2)	84	130.8	0.68	28,019	37,869
Stripping steam heater(H3,2)	58,400	1997	387	Area(m2)	46	113.3	0.68	85,940	158,613
Total									**12,708,927**

Internally integrated-Operating cost)

	in KJ/h	in MW	in GJ	price	Cost ($)/h	Annual cost($)
Total steam consumption	1.29E+08	36.0	1.29E+02	4.1($/GJ)	529	4,315,824
Electricity		7.50E+00		0.05($/Kwh)		3,060,000
Total						**7,375,824**

Integration with Kraft-Equipment cost)

Equipment	Base Cost($)	Year	Index at year	Sized by	Base data	New data	Exponent	Updated cost 2013($)	Sized cost($)
Stripping column	636,976	1996	382	Diameter(m)	3.86	4.6	0.78	949,628	1,088,846
Rectific. Column	636,976	1996	382	Diameter(m)	3.86	5.0	0.78	949,628	1,162,016
RC Reboiller	158,800	1997	387	Duty(KJ/h)	1.17E+08	4.20E+07	0.68	233,686	116,433
RC Condenser	86,174	1996	382	Duty(KJ/h)	7.23E+07	1.14E+08	0.68	128,471	175,150
Molecular Sieve	2,700,000	1998	390	Flow(Kg/h)	2.27E+04	2.77E+04	0.7	3,942,692	4,497,186
liquid ring pump(for vacuum)	Calculated								5,372,560
Expander	Calculated								61,619
Pump 1 (bottoms1)	19,700	1997	387	Flow(Kg/h)	2.61E+05	4.27E+05	0.79	28,990	42,737
Pump 2 (bottoms2)	19,700	1997	387	Flow(Kg/h)	2.61E+05	2.98E+04	0.79	28,990	5,217
Cooler bottoms 1	45,000	1997	387	Area(m2)	185	357.6	0.68	66,221	103,655
Cooler bottoms 2	45,000	1997	387	Area(m2)	185	21.5	0.68	66,221	15,301
Product cooler (C3,1)	45,000	1997	387	Area(m2)	185	58.7	0.68	66,221	30,337
Exchanger E3,1	19,040	1997	387	Area(m2)	84	130.8	0.68	28,019	37,869
Exchanger C7H3,2	19,040	1997	387	Area(m2)	84	163.6	0.68	28,019	44,085
Exchanger C8H3,2	19,040	1997	387	Area(m2)	84	565.4	0.68	28,019	102,463
Exchanger C12H3,2	19,040	1997	387	Area(m2)	84	33.9	0.68	28,019	15,130
Exchanger C13H3,2	19,040	1997	387	Area(m2)	84	25.5	0.68	28,019	12,442
Exchanger C7H3,1	19,040	1997	387	Area(m2)	84	317.7	0.68	28,019	69,236
Total									**12,952,282**

Integrated with Kraft-Operating cost)

	in MW	price	Annual cost($)
Electricity	7.50E+00	0.05($/Kwh)	3,060,000
Total			**3,060,000**

Hybrid distillation-vapor permeation

Stand-alone-Equipment cost)

Equipment	Base Cost($)	Year	Index at year	Sized by	Base data	New data	Exponent	Updated cost 2013($)	Sized cost($)
Beer Column	636,976	1996	382	Diameter(m)	3.86	3.35	0.78	949,628	850,257
Rectific. Column	525,800	1996	382	Flow (Kg/h)	55300	58000	0.78	783,882	813,578
BC Reboiller(H1,6)	158,800	1996	382	Duty(KJ/h)	1.17E+08	1.67E+08	0.68	236,745	301,429
RC Reboiller(H2,6)	29,600	1997	387	Duty(KJ/h)	1.46E+07	1.30E+07	0.68	43,559	40,274
BC Condenser	29,544	1996	382	Duty(KJ/h)	3.31E+06	3.03E+07	0.68	44,045	198,517
RC Condenser	86,174	1996	382	Duty(KJ/h)	7.23E+07	8.57E+07	0.68	128,471	144,224
Compressor (centrifugal)	3,415,036	1998	390	Flow (Kg/h)	3.23E+05	2.34E+04	0.34	4,986,828	2,043,043
Vapor permeation unit	From vendor	2013							5,522,600
Fermentation broth preheater	58,400	1997	387	Area(m2)	46	235.5	0.68	85,940	260,927
C4,1 cooler(Bottoms 1)	45,000	1997	387	Area(m2)	185	932.7	0.68	66,221	198,954
C4,3 cooler(Bottoms 2)	45,000	1997	387	Area(m2)	185	74.9	0.68	66,221	35,807
Total									**10,409,610**

Stand-alone-Operating cost)

	in KJ/h	in MW	in GJ	price	Cost ($)/h	Annual cost($)
Total steam consumption	3.05E+08	84.7	3.05E+02	4.1($/GJ)	1,251	10,204,080
Electricity		1,114		0.05($/Kwh)	454,512	454,512
Total						**10,658,592**

Internally integrated-Equipment cost)

Equipment	Base Cost($)	Year	Index at year	Sized by	Base data	New data	Exponent	Updated basecost 2013($)	Sized cost($)
Beer Column	636,976	1996	382	Diameter(m)	3.86	3.35	0.78	949,628	850,257
Rectific. Column	525,800	1996	382	Flow (Kg/h)	5.53E+04	5.80E+04	0.78	783,882	813,578
BC Reboiller(H4,1)	158,800	1996	382	Duty(MW)	32.5	46.4	0.68	236,745	301,429
RC Reboiller(H4,2)	29,600	1997	382	Duty(MW)	4.06E+00	3.61E+00	0.68	44,129	40,801
BC Condenser(C4,2)	29,544	1996	382	Duty(MW)	9.19E-01	8.42E+00	0.68	44,045	198,517
RC Condenser(C4,5)	86,174	1996	382	Duty(MW)	2.01E+01	2.38E+01	0.68	128,471	144,224
Compressor (centrifugal)	3,415,036	1998	390	Flow (Kg/h)	3.23E+05	2.34E+04	0.34	4,986,828	2,043,043
Vapor permeation	quote								5,522,600
C4,1 cooler(Bottoms 1)	45,000	1997	387	Area(m2)	185	345.4	0.68	66,221	101,244
C4,3 cooler(Bottoms 2)	45,000	1997	387	Area(m2)	185	74.9	0.68	66,221	35,807
Exchanger E4,1	19,040	1997	387	Area(m2)	84	7.1	0.68	28,019	5,227
Exchanger E4,2	19,040	1997	387	Area(m2)	84	1470.8	0.68	28,019	196,283
Total									**10,253,010**

Internally integrated-Operating cost)

	in KJ/h	in MW	in GJ	price	Cost ($)/h	Annual cost($)
Total steam consumption	1.76E+08	49	1.76E+02	4.1($/GJ)	723	5,901,638
Electricity		1,114		0.05($/Kwh)	454,512	454,512
Total						**6,356,150**

Integrated with Kraft-Equipment cost)

Equipment	Base Cost($)	Year	Index at year	Sized by	Base data	New data	Exponent	Updated basecost 2013($)	Sized cost($)
Beer Column	636,976	1996	382	Diameter(m)	3.86	3.35	0.78	949,628	850,257
Rectific. Column	525,800	1996	382	Flow (Kg/h)	5.53E+04	5.80E+04	0.78	783,882	813,578
BC Reboiller	158,800	1996	382	Duty(KJ/h)	1.17E+08	1.67E+08	0.68	236,745	301,429
RC Reboiller	29,600	1997	382	Duty(KJ/h)	1.46E+07	1.30E+07	0.68	44,129	40,801
BC Condenser(C1,2)	29,544	1996	382	Duty(KJ/h)	3.31E+06	8.00E+06	0.68	44,045	80,263
RC Condenser(C1,6)	86,174	1996	382	Duty(KJ/h)	7.23E+07	8.60E+06	0.68	128,471	30,212
Compressor (centrifugal)	3,415,036	1998	390	Flow (Kg/h)	3.23E+05	2.34E+04	0.34	4,986,828	2,043,043
Vapor permeation system	quote								5,522,600
C4,1 cooler	45,000	1997	387	Area(m2)	185	345.4	0.68	66,221	101,244
C4,3 cooler	45,000	1997	387	Area(m2)	185	74.9	0.68	66,221	35,807
Exchanger E4,1	19,040	1997	387	Area(m2)	84	7.1	0.68	28,019	5,227
Exchanger E4,2	19,040	1997	387	Area(m2)	84	1470.8	0.68	28,019	196,283
Exchanger C4,5H1	19,040	1997	387	Area(m2)	84	29.7	0.68	28,019	13,817
Exchanger C4,5H2	19,040	1997	387	Area(m2)	84	19.6	0.68	28,019	10,414
Exchanger C4,5H3	19,040	1997	387	Area(m2)	84	122.7	0.68	28,019	36,246
Exchanger C4,5H4	19,040	1997	387	Area(m2)	84	51.2	0.68	28,019	20,021
Exchanger C4,2H6	19,040	1997	387	Area(m2)	84	72.7	0.68	28,019	25,395
Exchanger C4,5E7, E7E8, E8H5	19,040	1997	387	Area(m2)	84	855.6	0.68	28,019	135,792
Exchanger C4,5E7, E7E8, E8H5(2	19,040	1997	387	Area(m2)	84	34.5	0.68	28,019	15,298
Exchanger C4,5E7, E7E8, E8H7	19,040	1997	387	Area(m2)	84	46.1	0.68	28,019	18,636
Exchanger C4,5E7,E7E8,E8H8	19,040	1997	387	Area(m2)	84	146.0	0.68	28,019	40,800
Exchanger C4,2E3, E3H12	19,040	1997	387	Area(m2)	84	1628.0	0.68	28,019	210,312
Excess LP steam Exchanger	19,040	1997	387	Area(m2)	84	155.0	0.68	28,019	42,507
Total									**10,589,983**

Integrated with Kraft-Operating cost)

	in KJ/h	in MW	in GJ	price	Cost ($)/h	Annual cost($)
Total steam consumption	4.93E+07	13.7	4.93E+01	4.1($/GJ)	202	1,650,050
Electricity		1,114		0.05($/Kwh)	454,512	454,512
Total						**2,104,562**

Economic evaluation

In this section the details of total capital cost which consists of direct and indirect costs are presented. The total capital cost is calculated according to the method proposed by Peters et al.(2003). According to this method a factor of 5 is used to estimate the total capital cost from the purchase cost. Direct capital cost generally includes the cost of equipment installation, piping, electrical systems, instrumentation etc. The indirect cost includes engineering and supervision, construction expenses, legal fees and etc. An additional factor of 0.34 has been considered for the cost of piping between the biorefinery and the Kraft mill in integrated with Kraft designs. The annuity factor(A) for annualizing the capital cost and calculating the total annualized cost based on a 10-year project(n) and interest rate of i=10% was calculated as 0.162.

TAC = Opex + A* total Capex , $A = \frac{i(1+i)^n}{(1+i)^n - 1}$

The result for each design is presented in following table.

Base case	CAPEX $ (purchased cost)	CAPEX $(Direct + indirect)	CAPEX($/yr) direct+indirect	OPEX ($/yr)	TAC
Stand-alone without integration	$7,629,276	$38,451,551	$6,257,813	$10,270,992	$16,528,805
Stand-alone with internal integration	$7,507,968	$37,840,160	$6,158,312	$5,949,815	$12,108,127
Integrated with Kraft	$7,845,355	$39,540,591	$6,435,049	$1,650,050	$8,085,099
Extractive distillation					
Stand-alone without integration	$4,009,914	$20,209,968	$3,289,079	$10,492,128	$13,781,207
Stand-alone with internal integration	$3,914,782	$19,730,500	$3,211,048	$5,741,376	$8,952,424
Integrated with Kraft	$4,031,010	$20,316,290	$3,306,383	$2,924,381	$6,230,763
Steam stripping					
Stand-alone without integration	$12,717,600	$64,096,703	$10,431,443	$8,145,312	$18,576,755
Stand-alone with internal integration	$12,708,927	$64,052,991	$10,424,329	$7,375,824	$17,800,153
Integrated with Kraft	$12,952,282	$65,279,502	$10,623,938	$3,060,000	$13,683,938
Hybrid membrane					
Stand-alone without integration	$10,409,610	$52,464,432	$8,538,345	$10,658,592	$19,196,937
Stand-alone with internal integration	$10,253,010	$51,675,171	$8,409,896	$6,356,150	$14,766,047
Integrated with Kraft	$10,589,983	$53,373,513	$8,686,293	$2,104,562	$10,790,855

APPENDIX B SIMULATION DETAILS

In the following, the stream data for the designs are presented. The thermodynamic model used in the simulation is NRTL.

The temperature-dependent binary parameters for ethanol, water and ethylene glycol related to NRTL model are presented in the following table (Adopted from Aspen plus V 7.2).

Component i	ETHANOL	ETHANOL	WATER
Component j	WATER	C2H6O-01	C2H6O-01
Temperature units	C	C	C
Source	APV72 VLE-IG	APV72 VLE-IG	APV72 VLE-IG
Property units:			
AIJ	-.8009000000	14.84220000	.3479000000
AJI	3.457800000	-.1115000000	-.0567000000
BIJ	246.1800000	-4664.405800	34.82340000
BJI	-586.0809000	157.5937000	-147.1373000
CIJ	.3000000000	.4700000000	.3000000000
DIJ	0.0	0.0	0.0

In designing the columns, the number of stages was estimated by Fenske shortcut method and the minimum reflux ration by Underwood equation (Luyben 2013). The values obtained were further refined and adjusted to obtain the desired specification. The feed stage locations were found empirically by observing their effects on reboiler energy consumption. In double-effect extractive distillation, the solvent-to-feed ratio was set to obtain the desired purity. The features of the base case design were adopted from Wooley et al.(1999).

Base case)

component	unit	Fermentaion brorth	Heated FB	Concentrated beer	Bottoms 1	From regeneration	Ethanol 92.5%	Bottoms 2	Superheater	Product
Total Flow	Kg/h	4.33E+05	4.33E+05	5.80E+04	3.75E+05	8.10E+03	3.00E+04	3.70E+04	3.00E+04	2.17E+04
Pressure	Kpa	101.3	101.3	188	209	150	150	185	150	140
Temperature	˚C	30	100	113	122	70	88	111	116	30
Cp	KJ/Kg-C	4.17	4.17	2.03	4.2	29.7	68.5	4.21	1.74	3.2
Vapor fraction	-	0	0	1	0	0	1	0	1	0
Ethanol	wt%	5	5	37	trace	72	92.5	trace	92.5	99.9
Ethylene glycol	wt%	0	0	0	0	0	0	0	0	0
Water	wt%	95	95	63	99.99	28	7.5	99.9	7.5	trace

Equipment	Enthalpy(KJ/h)
Feed preheater	1.27E+08
Beer_reb	1.70E+08
Beer_cond	3.00E+07
Bottoms1 cooler	1.46E+08
Rec_reb	1.30E+07
Rec_cond	8.60E+07
Bottoms2 cooler	1.26E+07
Product cooler	2.00E+07

Double-effect extractive distillation)

component	unit	Feed	13(split 1)	4(split 2)	6 (Beer1_distillate)	Bottoms 1	7 (beer2_distillate)	Bottoms 2
Total Flow	Kg/h	4.33E+05	2.23E+05	2.10E+05	1.22E+04	4.30E+07	1.17E+04	1.98E+05
Pressure	Kpa	101.3	101.3	303	101.3	124	303	331
Temperature	˚C	30	94	127	77	99	108	134
Cp	KJ/Kg-C	4.17	4.17	4.17	3.3	4.17	4.17	4.17
Vapor fraction	-	0	0	0	0	0	0	0
Ethanol	wt%	5	5	5	92	trace	92	trace
Ethylene glycol	wt%	0	0	0	0	0	0	0
Water	wt%	95	95	95	8	100	8	100

component	unit	Product	7(extrc_bottoms)	10 (recovery_distillate)	Solvent recycle	11	Make-up	13(solvent)
Total Flow	Kg/h	2.18E+04	1.85E+04	1.95E+03	1.67E+04	1.67E+04	7.20E+01	16488
Pressure	Kpa	101.3	122	101.3	110	110	101.3	101.3
Temperature	˚C	76	130	93	175	60	60	60
Cp	KJ/Kg-C	3.4	3.2	4.17	3.4	3.4	3.4	3.4
Vapor fraction	-	0	0	0	0	0	0	0
Ethanol	wt%	99.5	trace	99	trace	trace	0	0
Ethylene glycol	wt%	trace	95	trace	100	100	100	100
Water	wt%	trace	5	1	trace	trace	0	0

Equipment	Enthalpy(KJ/h)
Feed_preheater1	5.87E+07
Feed_preheater2	8.49E+07
Beercol1_cond	8.20E+07
Beercol1_reb	8.60E+07
Beercol2_cond	8.70E+07
Beercol2_reb	9.30E+07
Extrac_cond	3.50E+07
Extract_reb	3.70E+07
Recovery_con	5.60E+06
Recovery_reb	7.60E+06
Solvenr_rec cooler	6.52E+06
Make-up heater	1.20E+06

Equipment	Power(MW)
Feed_pump	0.01
Recovery_pump	8.00E-05

Steam stripping)

component	unit	Feed	Stripping agent(Water)	16(steam)	42wt% EtOH	9(out of stripper)	Bottoms 1	From regeneration	Rectfier distillate	10(out of rectifier)	Bottoms 2	8(compression)	Product
Total Flow	Kg/h	4.33E+05	4.50E+04	4.50E+04	5.10E+04	4.30E+07	4.30E+07	6.03E+03	2.77E+04	2.98E+04	2.98E+04	2.77E+04	2.17E+04
Pressure	Kpa	101.3	101.3	10	10	20	1013.3	10	10	20	101.3	101.3	101.3
Temperature	˚C	30	30	40	36	41	41	43	25	41	41	169	30
Cp	KJ/Kg-C	4.17	4.17	1.85	1.7	4.17	4.17	1.6	1.45	4.17	4.17	1.9	3.2
Vapor fraction	-	0	0	1	1	0	0	1	1	0	0	1	0
Ethanol	wt%	5	0	0	47	trace	trace	72	94	trace	trace	94	99.9
Ethylene glycol	wt%	0	0	0	0	0	0	0	0	0	0	0	0
Water	wt%	95	100	100	53	100	100	28	6	100	100	6	trace

Equipment	Enthalpy(KJ/h)
Stripper	1.10E+08
Bottoms1 cooler	1.80E+07
Rec_reb	4.20E+07
Rec_cond	1.10E+08
Bottoms2 cooler	1.30E+07
Product cooler	2.00E+07

Equipment	Power(MW)
Bottoms 1_ Pump	0.3
Bottoms 2_ pump	0.2
Liquid-ring comp.	7

Hybrid distillation-Vapor permeation)

component	unit	Fermentaion brorth	Heated FB	Concentrated beer	Bottoms 1	Ethanol 92.5%	Bottoms 2	3(compression)	Permeate	Product
Total Flow	Kg/h	4.33E+05	4.33E+05	5.80E+04	3.75E+05	2.34E+04	3.50E+04	2.34E+04	1.85E+04	2.15E+04
Pressure	Kpa	101.3	101.3	188	209	150	185	200	101.3	110
Temperature	˚C	30	100	113	122	88	111	105	30	30
Cp	KJ/Kg-C	4.17	4.17	2.03	4.2	1.66	4.21	1.71	4.17	3.2
Vapor fraction	-	0	0	1	0	1	0	1	0	0
Ethanol	wt%	5	5	37	trace	92.5	trace	92.5	5	99.9
Ethylene glycol	wt%	0	0	0	0	0	0	0	0	0
Water	wt%	95	95	63	99.99	7.5	99.9	7.5	95	trace

Equipment	Enthalpy(KJ/h)
Feed preheater	1.27E+08
Beer_reb	1.70E+08
Beer_cond	3.00E+07
Bottoms1 cooler	1.46E+08
Rec_reb	1.20E+07
Rec_cond	9.10E+07
Bottoms2 cooler	1.26E+07
Product cooler	2.00E+07

Equipment	Power(MW)
Vapor permeation	1