TECHNISCHE UNIVERSITÄT WIEN
Vienna University of Technology

Dissertation

PINCH AND EXERGY ANALYSIS OF THE

BIOETHANOL AND BIOHYDROGEN PRODUCTION PROCESSES

Ausgeführt zum Zwecke

der Erlangung des akademischen Grades

eines Doktors der technischen Wissenschaften

Unter der Leitung von

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E166 – Institut für Verfahrenstechnik,

Umwelttechnik und Technische Biowissenschaften

Eingereicht an der Technischen Universität Wien

Fakultät für Maschinenwesen und Betriebswissenschaften

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Wien, Januar 2014

ABSTRACT

The overall goal of this work was to develop methods for analyzing and evaluating the complex production concepts for biohydrogen and bioethanol production with specific regard to pinch and exergy techniques.

In order to calculate the exergy of compounds and streams of biological processes and to solve the heat exchanger network synthesis (HENS) problems for large industrial chemical plants in a systematic way, two Mathematica-based programs were developed.

For the biohydrogen production, the impact of gas-upgrading technologies, raw materials, substrate conversion in photoheterotrophic fermenter (PHF), heat integration, recirculation of effluents and residues and by-products as well as impact of glucose concentration in the thermophilic fermenter (THF) feed on the process performance were investigated from exergetic point of view.

It is shown that exergy efficiency is considerably lower for cases applying vacuum swing adsorption (VSA) compared to the process options with monoethanol amine (MEA) absorption. The process option based on feedstock thick juice has the highest exergy efficiency compared to the process option based on feedstock potato steam peelings (PSP) and wheat. Moreover, process options with 60% and 80% hydrogen yield in the PHF show that exergy efficiency is considerably decreased for the low substrate conversion in PHF.

A detailed parametric study shows that, heat integration, internal use of solid residues and increasing concentration of glucose in the THF feed as well as process improvements such as effluents recirculation reduce the irreversibilities of the process.

For the bioethanol production from lignocellulosic feedstocks, some different cases are investigated for handling stillage waste from ethanol production from exergetic point of view. The Exergy analysis shows that the exergy efficiency of bioethanol process, in which bioethanol, liquid fraction of stillage and dried solids (C5 sugars and pellets, respectively) are products, is higher than biomethane and combined heat and power (CHP) process. In

biomethane process a part of exergy is lost in the form of sludge and in CHP process the flue gas leaving system demonstrates waste exergy stream.

The pinch analysis of bioethanol production shows that a well-designed heat exchanger network increases heat integration up to 45 MW. Furthermore, the pressure and heat load modifications of distillation and evaporation units are applied to improve the heat integration and process design yielding a utility demand reduction of 15% compared to the base case.

Finally, some scenarios for a polygeneration processes for production of ethanol, electrical power, and district heat from wheat straw and wheat grain, are defined to evaluate the impact of different feed materials and process configurations with regard to exergy efficiencies.

The reference case is a wheat grain to ethanol process and yielded the highest exergy efficiency for products (ethanol and dried distillers grains (DDG)). The interim case (wheat grain and wheat straw as feedstock) was found to be more efficient producing ethanol compared to the lignocellulose case using only wheat straw to produce ethanol.

Further development and optimization of novel production concepts are possible through the methods and programs developed for exergy calculation and heat exchanger network optimization, as mentioned in the above process improvement case studies.

KURZFASSUNG

Das Ziel dieser Arbeit war es, Methoden für die Analyse und Beurteilung der komplexen Produktionskonzepte für die Biowasserstoff- und Bioethanolproduktion unter besonderer Berücksichtigung der Pinch- und Exergie-Techniken zu entwickeln.

Um die Exergie der Komponente und der Ströme von biologischen Prozessen zu berechnen und die Wärmetauschernetzwerke für industrielle Anlagen systematisch zu optimieren, wurden zwei Mathematica basierte Programme entwickelt.

Für die Biowasserstoffproduktion wurde der Einfluss von verschiedenen Parametern wie Gasreinigungstechnologien, Rohstoffen, Substratumsatz im photoheterotrophen Fermenter (PHF), Wärmeintegration, Rezirkulation von PHF-Abwässern, Nebenprodukten sowie der Einfluss der Glukose-Konzentration im thermophilen Fermenter (THF) auf die Prozessleistung exergetisch untersucht.

Es wird gezeigt, dass die Exergieeffizienz deutlich geringer ist für die Prozessvariante mit Vakuumwechseladsorption (VSA), als im Vergleich zur Prozessvariante mit Monoethanolamin (MEA) für die CO_2-Abtrennung. Die Prozessoption mit Dicksaft hat im Vergleich zu den Prozessoptionen mit Rohstoffen (dampfbehandelte Kartoffelschalen (PSP) und Weizen) die höchste Exergieeffizienz.

Außerdem zeigen die Prozessoptionen, dass je höher die Wasserstoffausbeute im PHF ist, desto höher ist die Exergieeffizienz.

Eine detaillierte Parameterstudie zeigt, dass die Wärmeintegration, interne Nutzung von festen Reststoffen, hohe Konzentration von Glukose im THF sowie die Rückführung von PHF-Abwässern, die Prozess-Irreversibilitäten reduzieren.

Für die Produktion von Bioethanol aus Lignocellulose wurden einige Fälle zur Behandlung von Schlempe aus exergetischer Sicht untersucht.

Die Exergie-Analyse zeigt, dass die Exergieeffizienz von der Bioethanolprozess (Bioethanol, Flüssigfraktion von Schlempe und getrocknete Feststoffe als Hauptprodukte) höher ist, als die Exergieeffizienz von Biogas und Kraft-Wärme-Kopplung-Prozessen (KWK).

Bei Biogas- und KWK-Prozessen geht ein Teil der Exergie in Form von Schlamm bzw. Rauchgas verloren.

Die Pinch-Analyse von der Bioethanolproduktion zeigt, dass ein gut gestaltetes Wärmetauscher-Netzwerk die Wärmeintegration bis zu 45 MW erhöht. Darüber hinaus wurden der Druck und die Wärmeleistung von Destillations- und Verdampferanlage modifiziert, um die Wärmeintegration zu verbessern.

Schließlich wurden einige Szenarien für einen Polygeneration-Prozess zur Herstellung von Ethanol, Strom und Fernwärme aus Weizenstroh und Weizenkorn definiert, um den Einfluss der verschiedenen Rohstoffe und Prozesskonfigurationen im Hinblick auf die Exergieeffizienz zu untersuchen.

Der Referenzfall ist die Bioethanolproduktion aus Weizenkorn und ergibt die höchste Exergieeffizienz für die Hauptprodukte (Ethanol und Dried Distillers Grains (DDG)).

Diese Studie zeigt, dass die Bioethanolproduktion aus Weizenkorn und Weizenstroh exergetisch effizienter ist, als die Bioethanolproduktion aus Weizenstroh alleine.

Eine Weiterentwicklung und Optimierung von neuen Produktionskonzepten ist durch die entwickelten Methoden und Programme zur Exergieberechnung und Wärmetauschernetzwerkgestaltung wie an den oben genannten Prozessverbesserungsbeispielen gezeigt werden konnte, möglich.

Für den gläubigen Menschen steht Gott am Anfang,

für den Wissenschaftler am Ende aller seiner Überlegungen.

„Max Planck"

ACKNOWLEDGEMENTS

This PhD thesis was carried out at the Institute of Chemical Engineering , Vienna University of Technology from January 2008 to January 2014 under the supervision of Prof. Dr. Anton Friedl and co-supervision of Dr. Walter Wukovits.

LIST OF PUBLICATIONS

The last part of this PhD thesis contains five journal and three peer reviewed conference papers.

Paper I: Effect of process integration on the exergy balance of a two-stage process for fermentative hydrogen production, A. Modarresi, W. Wukovits, D. Foglia and A. Friedl, Journal of Cleaner Production, 18 (2010), pp. 63-71.

Paper II: Application of exergy balances for evaluation of process configurations for biological hydrogen production, A. Modarresi, W. Wukovits and A. Friedl, Applied Thermal Engineering, 30 (2010), pp. 70-76.

Paper III: Exergy analysis of biological hydrogen production, A. Modarresi, W. Wukovits and A. Friedl, Proceedings of the 18th European Symposium on Computer Aided Process Engineering – ESCAPE 18, Lyon, France, 2008, pp. 1137-1142.

Paper IV: Evaluation of process configurations for biological hydrogen production applying mass-,energy- and exergy-balances, W. Wukovits, A. Modarresi and A. Friedl, Proceedings of the 16th European Biomass Conference & Exhibition, Valencia, Spain, 2008, pp. 2178 – 2183.

Paper V: Pinch and exergy analysis of lignocellulosic ethanol, biomethane, heat and power production from straw, A. Modarresi, P. Kravanja and A. Friedl, Applied Thermal Engineering, 43 (2012), pp. 20-28.

Paper VI: Exergy analysis of production of lignocellulosic ethanol, A. Modarresi, P. Kravanja and A. Friedl, Chemical Engineering Transactions, 25 (2011), pp. 635-640.

Paper VII: Heat integration of biochemical ethanol production from straw – A case study, P. Kravanja, A. Modarresi and A. Friedl, Applied Energy, 102 (2013), pp. 32-43.

Paper VIII: Comparison of combined ethanol and biogas polygeneration facilities using exergy analysis, P. Bösch, A. Modarresi and A. Friedl, Applied Thermal Engineering, 37 (2012), pp. 19-29.

Co-authorship statement

Paper I: Main author, responsible for exergy analysis, data evaluation and writing.

Paper II: Main author, responsible for exergy analysis, data evaluation and writing.

Paper III: Main author, responsible for exergy analysis, data evaluation and writing.

Paper IV: Co-author, responsible for exergy analysis and data evaluation.

Paper V: Main author, responsible for pinch and exergy analysis, data evaluation and writing.

Paper VI: Main author, responsible for exergy analysis, data evaluation and writing.

Paper VII: Co-author, responsible for pinch analysis and heat exchanger network synthesis.

Paper VIII: Co-author, responsible for all correspondence, literature survey and data evaluation.

Related publications not included in this PhD thesis

Mit wenig Energie mehr Wärme - Hochtemperaturwärmepumpe für den Einsatz in der Prozesstechnik (in German), S. Riepl, B. Adler, A. Friedl and A. Modarresi, Process - Chemie-Pharma-Verfahrenstechnik, 20 (2013), 3; pp. 78-79.

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Optimierung der Wärmeübertragernetzwerke an Industriestandorten (in German), A. Modarresi, A. Miltner, A. Friedl and M. Wiesinger, Chemie Technik, 40 (2011), 4, pp. 64-66.

Effect of process integration on the exergy balance of a process for biological hydrogen production, A. Modarresi, W. Wukovits and A. Friedl, Chemical Engineering Transactions, 18 (2009), pp. 391-396.

Application of mass-, energy- and exergy- balances for evaluation of process configurations for biological hydrogen production, W. Wukovits, A. Modarresi and A. Friedl, proceedings of the 18th International Congress of Chemical and Process Engineering Chisa 2008, Prague, Czech Republic, 2008, J6.3.

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I. BACKGROUND

1. BACKGROUND

1.1. INTRODUCTION

Today, the dramatic increase in world population growth rate and developing countries having not yet sufficient energy efficient technologies are two major reasons that the world fossil fuels consumption continues to rise, despite the fact that their resources are limited and non-renewable. The consequences of increasing demand for fossil fuels in the past forty years upon environment are dramatically increasing concentrations of greenhouse gases and global warming causing climate change.

World oil consumption reached a record high of 4130 million tons per year in 2012 according to BP Statistical Review of World Energy 2013 [1]. As seen in Fig. 1, the industrialized and developing countries are main consumers and since a few years the countries in the Asia-Pacific have overtaken the industrial countries (such as USA and European countries) as the world's number one users at 1389 million tons per year in 2012 representing the fastest rate of increase in oil consumption.
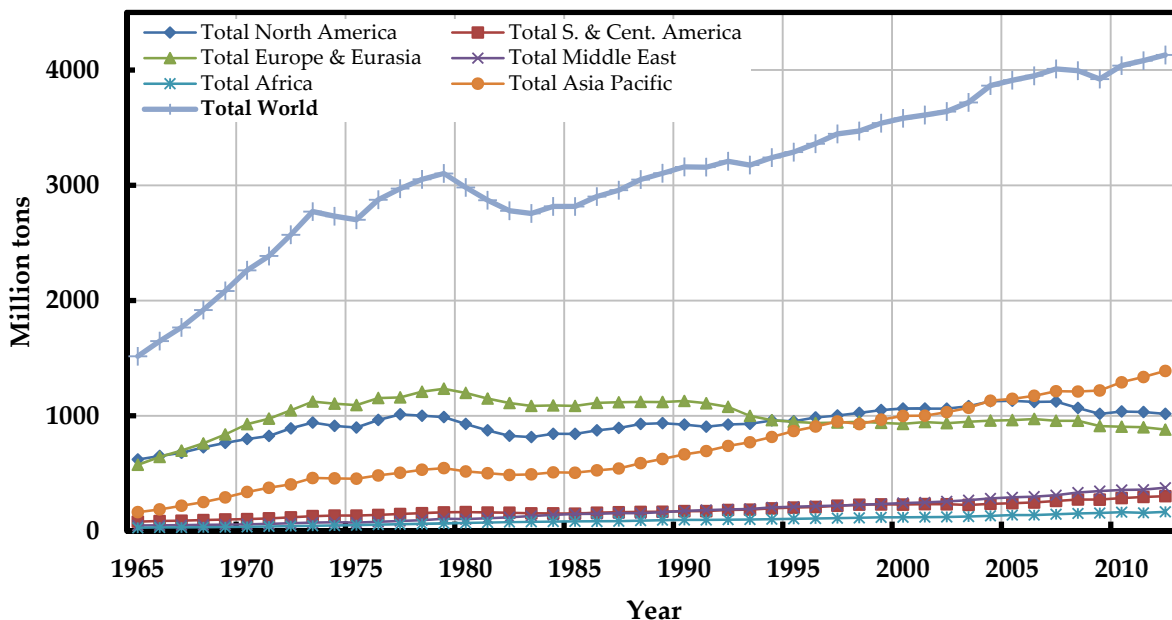
Fig. 1: World oil consumption, 1965-2012 [1]

The combustion of fossil fuels leads to releasing energy, water vapor, CO_2, pollutants such as NO_x, SO_x and particulates. The Emission of CO_2 from fossil fuels was 34.4 million tons in 2012, increasing nearly three times as in 1965. (Fig. 2)
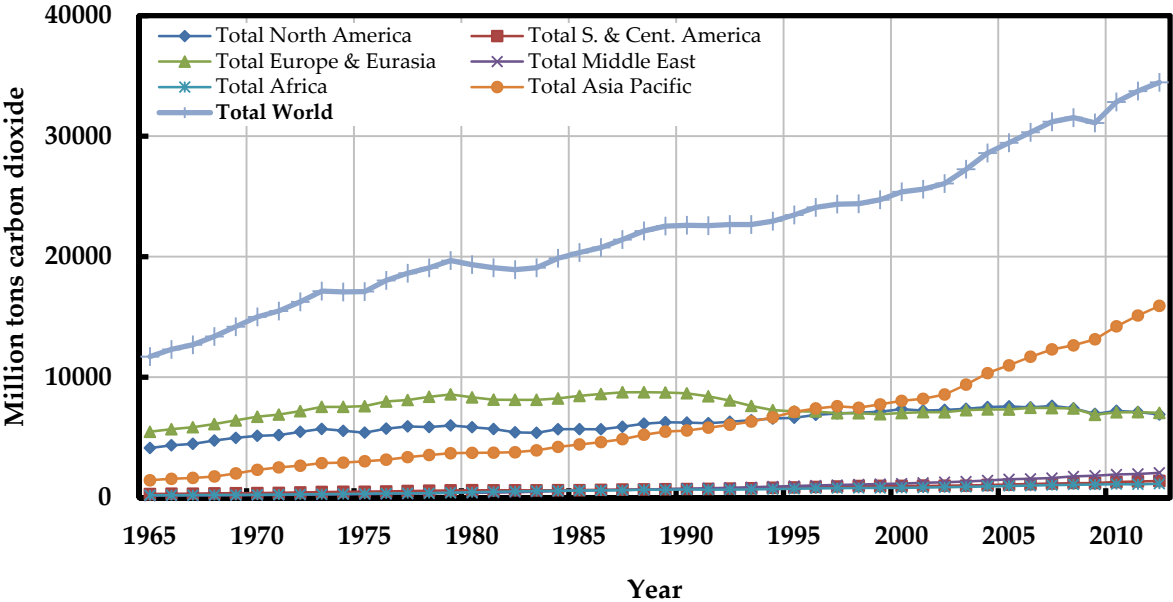
Fig. 2: World (fossil fuel) carbon dioxide emissions, 1965-2012 [1]

The global environmental problems such as diminishing oil reserves, increasing global temperature by approximately 1-3.5 °C [2] and air pollution can be reduced using alternative sources and efficient technologies such as hydrogen fuel cell. The alternative sources such as solar energy, wind power, hydroelectric energy and biomass fuel are available in large quantities, cleaner and already widely used but not nearly to their fullest potential.

The graphs in Fig. 3 show that the world biofuel production reached more than 60 million tons of oil equivalent in 2012, an increase of at least 500 percent over 2002.
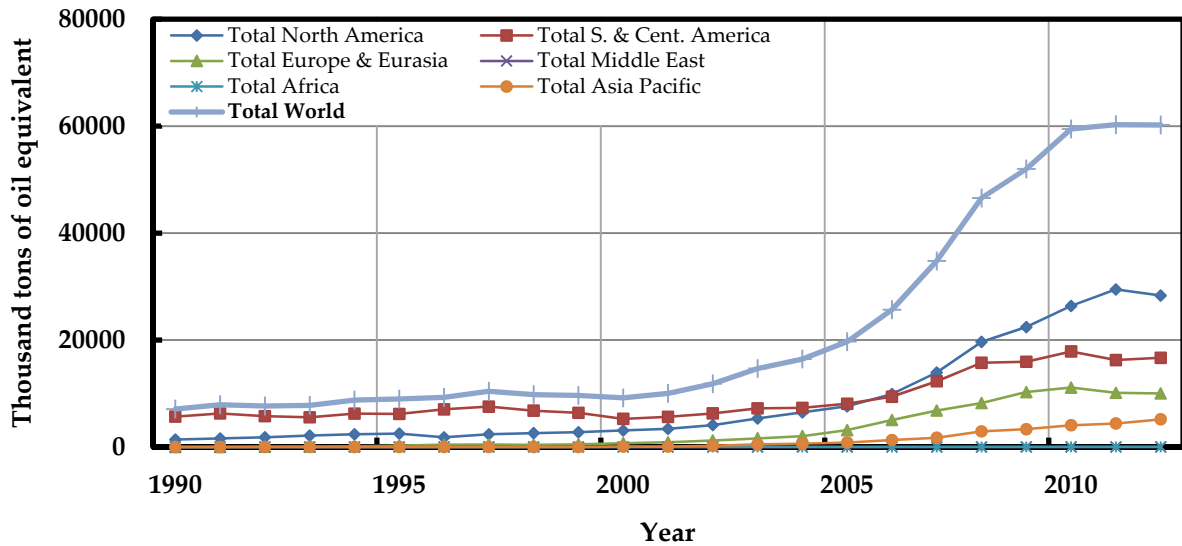
Fig. 3: World biofuel production, 1990-2012 [1]

1.2.   OBJECTIVES

In recent years, heat exchanger network optimization and exergy analysis consisting of principles from many fields of chemical engineering such as; thermodynamics, heat transfer, process simulation and modeling are two widely-used concepts and techniques of optimizing chemical engineering processes and systems.

The main objectives of this thesis are:

- To further develop a software for optimal synthesis of heat exchanger network (HEN)
- To further develop a software for exergy performance evaluation
- To analyze and improve biohydrogen and -ethanol production processes by means of above mentioned tools helping to find process irreversibility, optimum configurations and minimum external heating and cooling demand.

1.3.   APPENDED PAPERS

This work is based on 8 papers attached at the end of this thesis.

In the **first** paper, process integration options used in fermentative production of hydrogen (Hyvolution process) [4] are discussed and the energy recovery potential by

improved heat exchange between process streams was studied. In addition, exergy analysis is studied and comparisons of case studies in terms of exergy are given. Parametric studies show the influence of used feedstock, applied process parameters as well as process and heat integration measures on exergy efficiencies.

The **second** paper is a detailed study of the possibilities for process improvement and optimization into a novel process for biological production of hydrogen from biomass employing thermophilic and photo-heterotrophic bacteria (Hyvolution process) with respect to chemical exergy. It shows the strong dependence of obtained exergetic efficiency based on chemical exergy of biomass feed and produced pure hydrogen on the configuration of the overall process.

The **third** paper focuses on a powerful approach (exergy analysis) for analyzing both the quantity and the quality of energy to identify the system components with the highest thermodynamic inefficiency and the processes that cause them in Hyvolution process. The exergy content of the process streams is calculated using a MS-Excel-based tool where special attention is given to the calculation of chemical exergy of biomass- and sugar components involved in this process. Some thermodynamic efficiency measures are suggested and assessed from an exergy perspective.

In the **forth** paper process simulation was used to calculate overall mass-, energy and exergy-balances for single process steps and selected process options for the production of biohydrogen in a two stage fermentation process from feedstock wheat and corn stover (Hyvolution process) in order to improve and to obtain a competitive process for the biological production of hydrogen.

In the **fifth** paper two process analysis approaches were introduced and used to evaluate the potential for effective improvement of a complex process for production of bioethanol, biomethane, heat and power from wheat straw.

The **sixth** paper discusses an exergetic assessment of lignocellulosic ethanol production process. Parametric studies have been investigated to show the influence of the proper selection of scenarios on exergy efficiencies in more detail. A Mathematica-based program [3] has been introduced to calculate the exergy of compounds and streams by a systematic approach.

The **seventh** paper includes a base case study of ethanol production process from lignocellulosic biomass (straw) by means of pinch analysis and heat exchanger network synthesis in order to use process heat efficiently and to improve the process design.

Finally, in the **eighth** paper various polygeneration processes for production of ethanol, electrical power and district heat from wheat (grain + straw) were evaluated and analyzed from exergy point of view and compared with a standard ethanol process. Exergy analysis includes formulation of chemical and physical exergy terms, exergy losses to environment and exergy efficiencies of the processes. It was shown that the usage of valuable by-products increases the overall exergy efficiency of the process.

2. HYDROGEN PRODUCTION TECHNOLOGIES

2.1. INTRODUCTION

Hydrogen is identified as an important and promising energy carrier emitting zero environmental pollutants (water as by-product) [5], having the highest specific energy with several advantages over other energy carriers for the future. Main utilizations are in transport (as a fuel) and chemical sectors. Hydrogen can be produced using renewable and fossil sources at small and large plants involving a variety of process technologies as shown in Fig. 4. The annual consumption of hydrogen has an increase of ca. 6%. Nowadays, approximately 98% of hydrogen is produced by fossil fuel resources [6]. Hence, the hydrogen production processes must be taken into account which are most environmentally friendly and economically as well as based on alternative feedstock.

Fossil Fuels	**Water**	**Renewables**
Technology	*Technology*	*Technology*
• Steam reforming	• Electrolysis	• Gasification of biomass
• Partial oxidation	• Thermochemical	• Photofermentation
• Gasification of coal		• Dark fermentation
• Autothermal reforming		• Hybrid
• Plasma process		
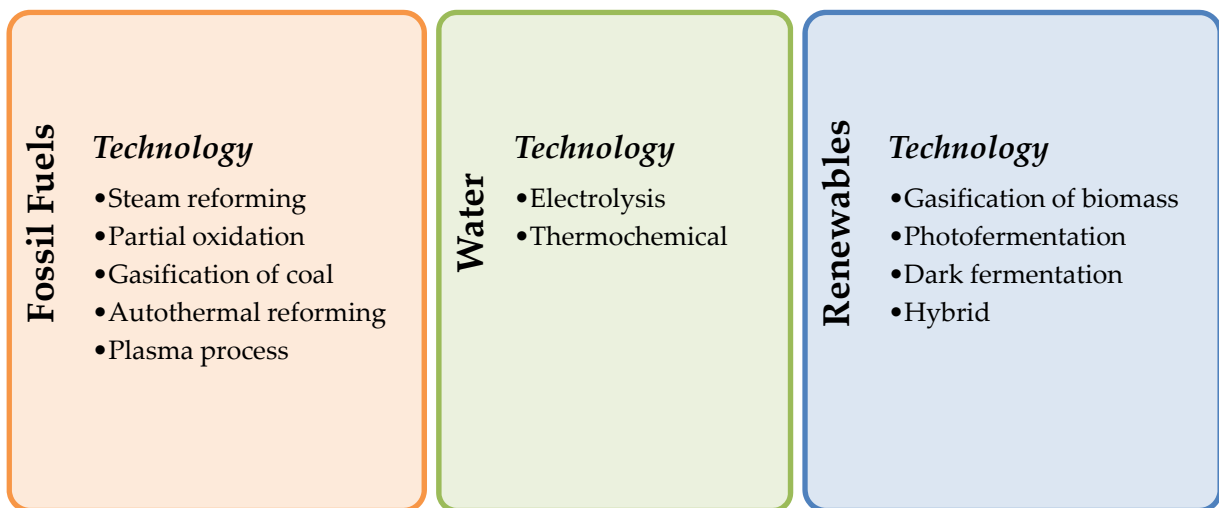
Fig. 4: Hydrogen production sources and technologies [adapted and modified from: 7]

2.2. HYDROGEN FROM FOSSIL SOURCES

Five industrial technologies producing a hydrogen rich gas from fossil fuels are as follows:

- Steam reforming (SR),
- Partial oxidation (POX),
- Coal gasification
- Auto-thermal reforming (ATR) and
- Plasma process

2.2.1. STEAM METHANE REFORMING (SMR)

Hydrogen can be mainly produced from natural gas (methane), oxygenated hydrocarbons and methanol as a raw material [8] using HP steam. This well established technology is most efficient, economical hydrogen production process and currently used to produce 48% of world hydrogen [9].

The whole process consists of three steps. In the first step, the feedstock is mixed with HP steam in the presence of Ni as catalyst [10] and hydrogen, CO and CO_2 are produced. The first step endothermic reactions for hydrocarbons are represented by Eqs. (1) and (2) [11].

$$C_mH_n + mH_2O \ (g) \rightarrow mCO + (m + 0.5 \ n) \ \mathbf{H_2} \tag{1}$$

$$C_mH_n + 2mH_2O \ (g) \longrightarrow mCO_2 + (2m + 0.5 \ n) \ \mathbf{H_2} \tag{2}$$
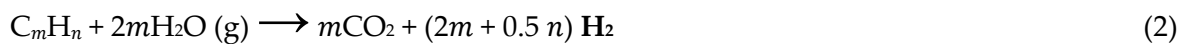
During the second step, cooled synthesis gas (CO + H_2) then reacts with additional HP steam and is converted into H_2 and CO_2. This reaction is an exothermic reaction and called "water-gas shift" as shown by Eq. (3).

$$CO + H_2O \ (g) \longleftrightarrow CO_2 + \mathbf{H_2} \tag{3}$$

The last step is a separation process using pressure swing adsorption (PSA) to remove CO, CO_2 and H_2O yielding a pure H_2 gas stream [10].

2.2.2. PARTIAL OXIDATION (POX)

This method is a non-catalytic process, in which hydrogen is produced by burning of the feedstock (natural gas (methane) or hydrocarbon) in air at high temperature because of endothermic nature of the reaction [8, 12] represented by Eq. (4).

$$C_mH_n + (0.5\ m)\ O_2 \longrightarrow m\text{CO} + (0.5\ n)\ \mathbf{H_2} \tag{4}$$

The final products of this process are carbon dioxide and hydrogen which are produced by the reaction of undesired carbon monoxide with HP steam [13] as shown in Eq. (3).

2.2.3. COAL GASIFICATION

Gasification of coal is a well established industrial process in which coal is fed into the gasifier, oxidized with oxygen or steam at high temperature and pressure because of endothermic nature of reactions and thermochemically converted into synthesis gas according to Eqs. (5) - (7).

$$C\ (s) + H_2O\ (g) \longrightarrow CO + \mathbf{H_2} \tag{5}$$

$$C\ (s) + O_2 \longrightarrow CO_2 \tag{6}$$

$$C\ (s) + CO_2 \longrightarrow 2\ CO \tag{7}$$
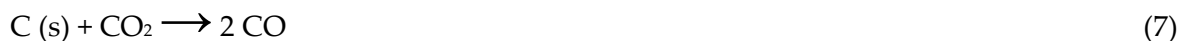
This approach is very mature and research in this area will be focused on reduction of high capital investment costs and environmental emissions as well as on improving of low energy efficiency. Basically, the coal feedstock is more available and relatively cheaper than fossil

fuel used by SMR technology. Hence coal gasification processes (e.g. fluidized bed, fixed bed or entrained flow) could be more attractive for hydrogen production than well-developed SMR approach. [14].

2.2.4. AUTOTHERMAL REFORMING (ATR)

Autothermal reforming approach is a combination of steam reforming and partial oxidation which are an endothermic (energy demanding) and an exothermic (energy releasing) process (Eqs. (1) and (4)), respectively [15]. Because of exothermic nature of the overall reaction, this process doesn't require any external heat. The produced syngas is fed into a water-gas shift reactor whereby CO is used to further produce hydrogen (Eq. (3)).

2.2.5. PLASMA REFORMING

Plasma process is considered as a high efficiency hydrogen production process in which the overall reaction is same as normal reforming reaction. This technology is expensive to be applied in the large scale, centralized hydrogen production plants.

2.3. HYDROGEN FROM WATER

2.3.1. ELECTROLYSIS

Water electrolysis process is a well-known hydrogen production process based on the separation of water molecules into hydrogen and oxygen molecule by means of electrical energy [16, 17], as represented by Eq. (8).

$$H_2O + electricity \longrightarrow 0.5\ O_2 + \mathbf{H_2} \tag{8}$$

The electrical energy can be generated by utilization of fossil fuel, industrial waste and renewable sources such as solar, wind and geothermal energy [18, 19]. Moreover, solar and nuclear energy can be utilized to supply some of the energy needs for high temperature electrolysis (HTE) using solid oxide cells [20]. A considerably reduction of needed electricity, an improvement of electrolysis reaction efficiency and use of several carbon free high temperature heat sources are some advantages of HTE.

2.3.2. THERMOCHEMICAL

The thermochemical methods are carried out using high temperature heat obtained from fossil fuels or promising energy sources such as concentrated solar energy [21, 22] to decompose water into hydrogen and oxygen [23], according to Eq. (9).

$$H_2O + heat \longrightarrow 0.5\ O_2 + \mathbf{H_2} \tag{9}$$

Alternatively, the thermal-driven chemical reactions can take place using the waste heat from nuclear plants [24, 25].

2.4. HYDROGEN FROM RENEWABLE SOURCES

2.4.1. GASIFICATION OF BIOMASS

Several biomass sources [26, 27] can be processed in the gasification process in which the feedstock is fed into a reactor (fluidized bed or fixed bed) and partially oxidized in presence of steam/oxygen and heat into a gaseous mixture consisting of CO_2, CO, CH_4, H_2,N_2 and other compounds [26]. The major biomass gasification reactions are represented by Eqs. (3), (5) - (7) and (10) – (12) [28].

$$2\ C\ (s) + O_2 \longrightarrow 2\ CO \tag{10}$$

$$C\ (s) + H_2 \longrightarrow CH_4 \tag{11}$$

$$CO + 3\ H_2 \longrightarrow CH_4 + H_2O \tag{12}$$

The moisture contained in the biomass plays a crucial role in the overall thermal process efficiency.

2.4.2. PHOTOFERMENTATION

Photosynthetic microbes (non sulphur bacteria), such as rhodobacter [29] can produce hydrogen from water and biomass in the presence of (sun) light. For instance, glucose can be converted into H_2 and CO_2 directly by means of light energy, as shown in Eq. (13).

$$C_6H_{12}O_6 + 6\ H_2O + \text{light energy} \longrightarrow 6\ CO_2 + 12\ \mathbf{H_2} \tag{13}$$
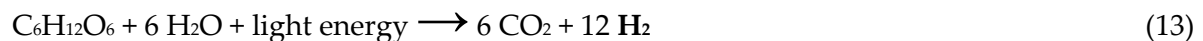
More research is required in reactor design and bacteria to produce hydrogen in large scale photo-bioreactors yielding higher efficiency and lower cost.

2.4.3. DARK FERMENTATION

Biologically, hydrogen can be produced through carbohydrate-rich substrates fermentation utilizing anaerobic bacteria and microorganisms in the dark and ambient temperature without any external energy [30, 31] or at elevated temperature up to 70 °C [4]. For example, Glucose, which is usually used as feedstock for dark fermentation, can be converted into organic acids and hydrogen according to Eqs. (14) and (15).

$$C_6H_{12}O_6 + 2\ H_2O \longrightarrow 2\ CH_3COOH + 2\ CO_2 + 4\ \mathbf{H_2} \tag{14}$$

$$C_6H_{12}O_6 + 2\ H_2O \longrightarrow CH_3CH_2CH_2COOH + 2\ CO_2 + 2\ \mathbf{H_2} \tag{15}$$
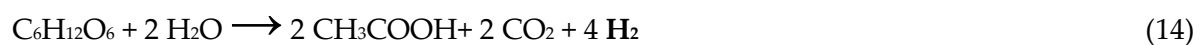
2.4.4. HYBRID

This method is a combination of dark and photo fermentation in which the organic acids produced in the first step (dark fermentation) are converted into hydrogen by sunlight and microorganisms in the second step (photo fermentation). The complete conversion of biomass into hydrogen can be achieved through this promising hydrogen production approach [4, 32 and 33], but also for this process concept further experimental research is necessary.

3. ETHANOL PRODUCTION TECHNOLOGIES

3.1. INTRODUCTION

Ethanol is widely seen as an alternative fuel used in transportation that reduces greenhouse gas emissions and global warming compared to gasoline. Ethanol is blended with gasoline for use in vehicles (**E85:** 85% ethanol, 15% gasoline and **Gasohol:** 90% gasoline, 10% ethanol) and is as an octane enhancer [34, 35]. Ethanol can be produced synthetically and biologically. The synthetic ethanol (7% world's ethanol production [36]) is made through hydration of ethylene. Bioethanol (93% world's ethanol production [36]) is produced from biomass materials through fermentation process in which lignocellulose-based biomass (low cost feedstocks), starch-based biomass (high cost feedstocks) and sugars can be fermented and converted into ethanol. The production of lignocellulosic ethanol is still under development. Ethanol production in the world grew from 49.6 billion liters in 2007 to 82.5 billion liters in 2012 as represented in the Fig. 5.
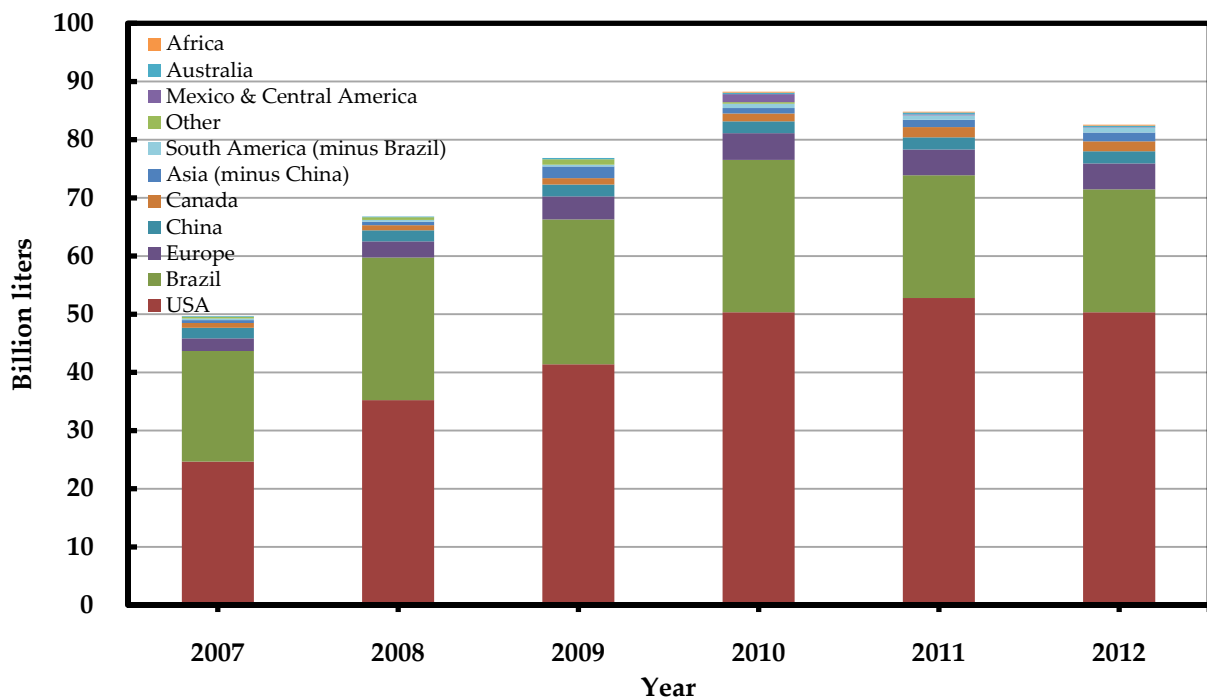
Fig. 5: World ethanol production by country/region [adapted and modified from: 37]

3.2. SYNTHETIC ETHANOL PRODUCTION

Petroleum- and coal-based ethanol (synthetic ethanol) production is a hydrolysis process (exothermic reaction) in which the steam is added to ethylene, a petroleum by-product, in presence of a catalyst as shown in Eq. (16).

$$C_2H_4 + H_2O \longrightarrow C_2H_5OH \tag{16}$$

The final product is an ethanol-water mixture that is then fed to fractional distillation step yielding a mixture of 96 wt % ethanol [38].

3.3. BIOETHANOL PRODUCTION

Bioethanol (or fermentation ethanol) can be produced from biomass feedstocks through several processes represented in Fig. 6 [39]. First, the sugar-rich and starch-based feedstocks are converted into sugar by extraction and enzymatic saccharification processes, respectively. The cellulose-based biomass need to be pre-treated using diluted acid and hydrolyzed using specialized enzymes to achieve a suitable sugar mixture for fermentation step.

After the fermentation step, bioethanol containing water should be distilled to separate the water from ethanol and achieve high concentration, purity final distillation product (up to 95 wt % ethanol). After that, bioethanol is dehydrated through molecular sieves to a concentration of at least 99.5 wt %.
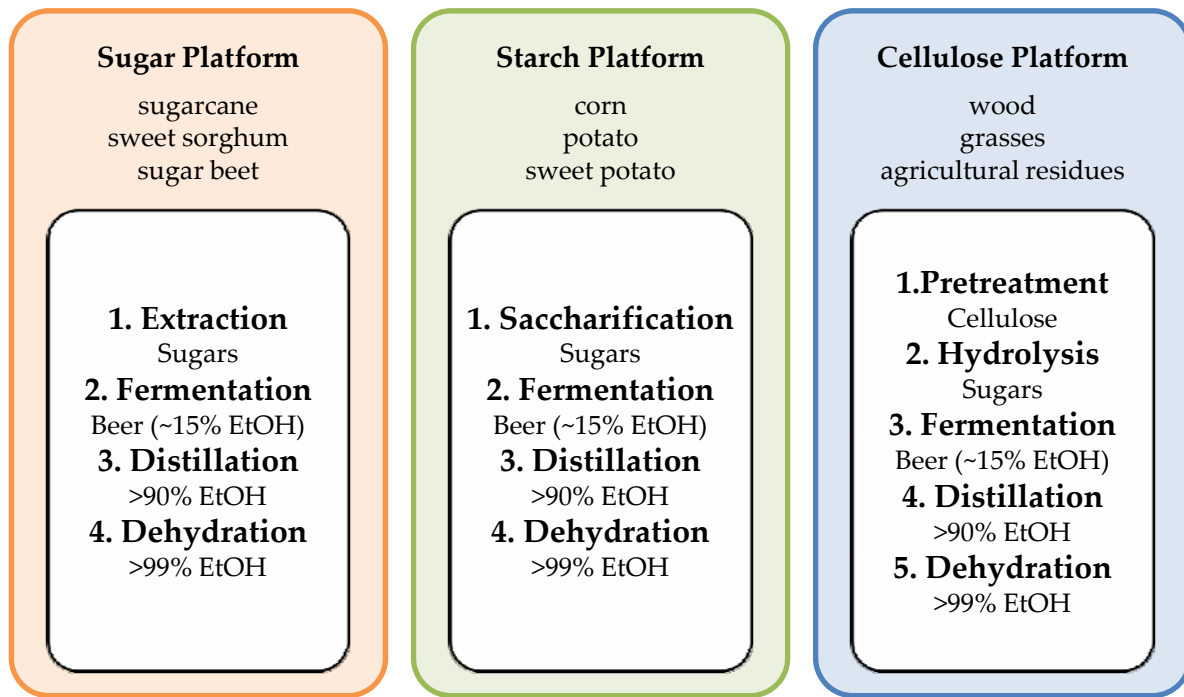
Fig. 6: Bioethanol production processes [adapted from: 39]

3.3.1. 1st GENERATION

In the first generation bioethanol production, traditional raw materials like sugarcane, potato, wheat and maize which are expensive and consumed as human food are used to produce ethanol.

The sugar-rich biomass like sugarcane can be converted to ethanol by direct fermentation of their juice made by extraction process. These processes are basically able to produce energy and power for own usage by burning the cane bagasse.

The starch-rich biomass like sorghum, rice, corn, potato and wheat, can easier produce sugars (arabinose, xylose, galactose and mostly glucose [40]) than cellulosic biomass through saccharification process which utilizes amylases as a microorganism as represented by Eq. (17) (in the case of glucose).

$$(C_6H_{10}O_5)_n + n\ H_2O \longrightarrow n\ C_6H_{12}O_6 \tag{17}$$

Ethanol and carbon dioxide are then produced through sugar fermentation according to Eq. (18) (in the case of glucose).

$$C_6H_{12}O_6 \longrightarrow 2\ C_2H_5OH + 2\ CO_2 \hspace{3cm} (18)$$

The increasing food price is affected by rising feedstock demand for first generation biofuel production [40].

3.3.2. 2nd GENERATION

Lignocellulosic material including agricultural residues such as corn stover, crop waste and wheat straw, industrial residues such as paper mill sludge and household solid waste which are cheap and contain cellulose, lignin and hemicelluloses, are used as feedstock for the second generation bioethanol production [42, 43].

3.3.2.1. BIOCHEMICAL CONVERSION

The first processing step is pretreatment of lignocellulosic materials in which complex substrates and molecules such as cellulose, hemicelluloses and lignin have to be removed using methods such as steam explosion treatment, acid-based technology, organosolv and biological pretreatment employing microorganisms [44]. Some of these pretreatment methods need to be further developed in order to be more suitable, cost effective and less energy consuming for industrial and large scale bioethanol production plants [45].

After pretreatment, a hydrolysis process is utilized [46] in which long chains of the carbohydrate polymers (cellulose and hemicellulose consisting of polymers of 6- and 5-carbon sugars respectively) are broken down using enzymes or concentrated acids in the presence of water to provide simple fermentable sugars such as glucose, xylose and arabinose. Acetic acid is produced as by-product through acid hydrolysis of hemicellulose

[47]. The main solid residue (lignin) recovered from hydrolysis of lignocellulosic materials can be utilized as a fuel or a fuel additive [48] or for power and heat providing [49].

The next process step is the mixed sugar fermentation in the presence of microorganisms according to Eqs. (18) and (19) [50].

$$3\ C_5H_{10}O_5 \longrightarrow 5\ \mathbf{C_2H_5OH} + 5\ CO_2 \tag{19}$$

A promising process is simultaneous saccharification and fermentation processes (SSF) [51] in a bioreactor in which lower amount of enzyme is required and ethanol production yield (glucose conversion to ethanol) is higher compared to the standalone fermentation step [52].

3.3.2.2. THERMOCHEMICAL CONVERSION

Bioethanol can be produced through the process based on thermochemically biomass gasification in which no bacteria and yeast are required. The raw materials containing 10-20% moisture are indirectly heated using circulation of hot olivine sand between the char combustor unit and the gasifier [53, 54] yielding a mixture of some gases according to Eq. (5). The synthesis gas produced includes some contaminants such as CO_2, H_2S and tars that should be removed [45, 50 and 54]. After gas cleanup process consisting of multiple stages, the cleaned synthesis gas (CO, H_2 and CH_4) is converted into alcohols with a conversion yield of 50% for bioethanol [45, 50], when it passes through a fixed bed reactor containing special catalysts that are designed according to desired biofuel. Produced alcohols are distilled using separation columns to obtain pure alcohols (methanol and ethanol as the main products [54]).

Generally, the unconverted synthesis gas can be combusted to provide heat and electricity for the whole site.

4. EXERGY ANALYSIS

4.1. INTRODUCTION

Conventional thermal system assessment tools are based on the first law of thermodynamics that expresses the quantity of energy entering and leaving a thermal process in which internal energy, heat, and work are conserved.

The second law of thermodynamics introduces the quality of the energy crossing a thermal process boundary.

Exergy analysis is a link between first and second law of thermodynamics (quantity and quality of energy). Because of irreversibilities within the thermal process, exergy can be destroyed (but never conserved) to generate entropy in a system in which the main part of exergy is transformed into work.

As a complement to the traditional energy analysis methods, the exergy analysis is able to identify and quantify the thermodynamic insufficiencies, irreversibilities (exergy losses) and their causes within processes and/or calculate the maximum system performance.

Hence, the combined energy and exergy analysis provides the strategies taking into account the first and second law of thermodynamics for efficient thermodynamic system improvements [55, 56].

4.2. DEFINITION

Exergy **Ex** is defined as the maximum available work obtained theoretically by bringing the open flow system **S** to equilibrium with its reference environment **E** through a reversible process [57, 58] as shown in Fig. 7.

In contrast to other thermodynamic properties, exergy is always calculated with regard to the reference state in which a temperature of 298.15 K and a pressure of 101.323 kPa are normally taken. The reference state is specified with the subscript "0".
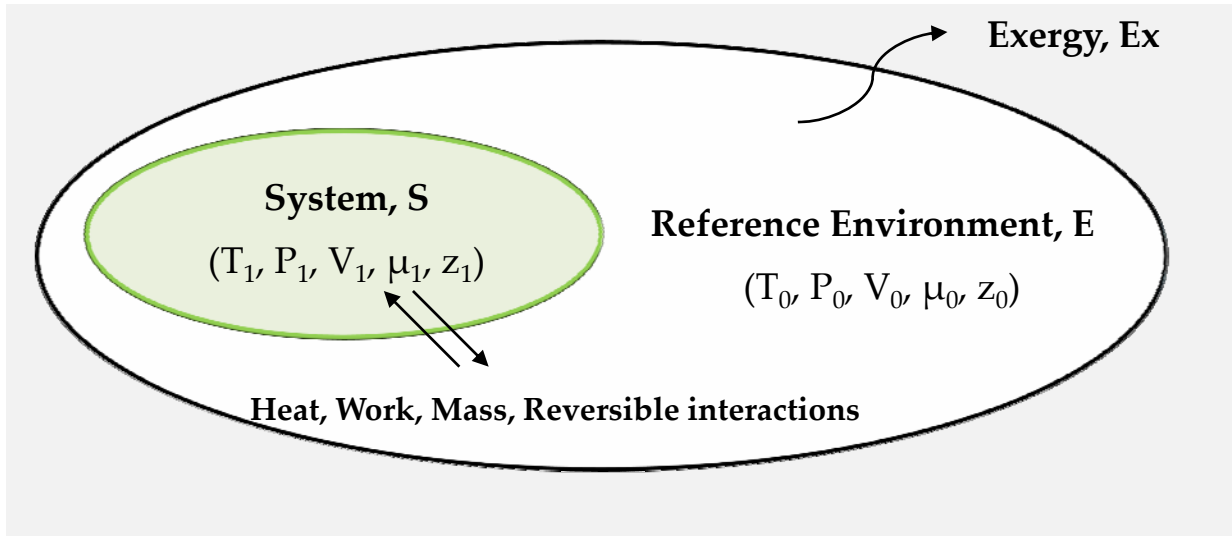
Fig. 7: Exergy definition [adapted from: 57& 58]

For an open flow steady state system, the total exergy consists of chemical, physical (consisting of thermal and mechanical exergies [59, 60]), potential and kinetic exergies [60]. The chemical exergy is associated with the difference in chemical composition of system with regard to the reference environment. The thermal and mechanical exergies depend on the temperature and pressure of the system respectively [61]. The kinetic and potential exergies are associated with the system velocity and system height assessed relative to the reference environment. These kinds of exergy are neglected in this study due to chemical nature of the studied processes.

The change in the total exergy of an open flow system can be caused through mass and energy transfer (heat interaction and work interaction) to its surroundings in which the work can be usually defined as pure exergy [62].

4.2.1. EXERGY OF HEAT FLOW

The exergy transfer associated with heat stream Q crossing the system boundaries is calculated using Eq. (20) [63].

$$Ex_Q = \left| Q \left(1 - \frac{T_0}{T} \right) \right|$$ (20)

where T_0 is the reference temperature, $\bar{T}$ is the thermodynamic equivalent temperature at which the heat transfer takes place and Q is the heat flow rate represented in Fig. 8. The opposite signs indicate that the amount of work obtained from a heat stream is always positive.
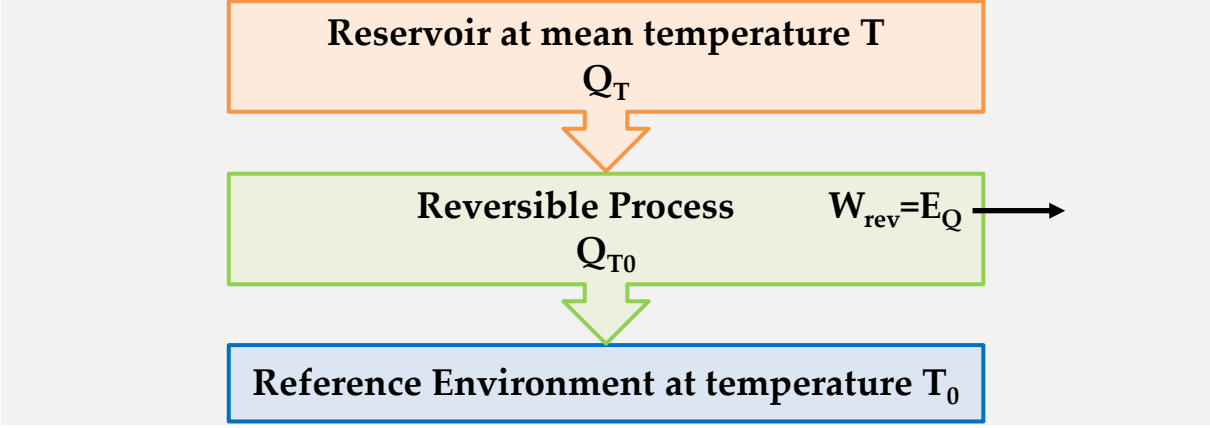
Fig. 8: Exergy of heat [adapted from: 64]

4.2.2. EXERGY OF MASS FLOW

The total amount of exergy of a mass flow is a sum of physical, chemical and mixing exergies as shown by Eq. (21) [61, 65].

$$Ex_{tot} = \dot{m}(Ex_{ph} + Ex_{ch} + \Delta_{mix}Ex) \tag{21}$$

Where $\dot{m}$ is the flow rate.

4.2.2.1. PHYSICAL EXERGY

Physical exergy is defined by Kotas [58] as follows:

"Physical exergy is equal to the maximum amount of work obtainable when the stream of substance is brought from its initial state to the environmental state defined by P_0 and T_0, by physical processes involving only thermal interaction with the environment"

In general, physical exergy can be calculated from enthalpy and entropy changes of the system by Eq. (22) [65].

$$Ex_{ph} = H - H_0 - T_0(S - S_0) \tag{22}$$

where H and S are the enthalpy and entropy of the system at the actual condition (T, P), while H_0 and S_0 are the same properties at the environmental condition (T$_0$, P$_0$).

The physical exergy of a multi-component material stream is given by Eq. (23) [65].

$$Ex_{ph} = \Delta_{actual \to 0}\left[L\left(\sum_{i=1}^{m} x_i H_i^l - T_0 \sum_{i=1}^{m} x_i S_i^l\right) + V\left(\sum_{i=1}^{m} y_i H_i^v - T_0 \sum_{i=1}^{m} y_i S_i^v\right)\right] \tag{23}$$

where x and y are the molar ratio of the i th component in the liquid (l) and vapor (v) phase, respectively. L and V are liquid and vapor fraction, respectively. Values for thermodynamic properties namely enthalpy and entropy can be obtained by means of thermochemical database such as HSC chemistry or simulation software like IPSEpro, Aspen Plus, etc. [66, 67].

4.2.2.2. CHEMICAL EXERGY

C hemical exergy can be defined as below [58]:

"Chemical exergy is equal to the maximum amount of work obtainable when the substance under consideration is brought from the environmental state to the dead state by processes involving heat transfer and exchange of substances only with the environment"

The final state of the stream when calculating chemical exergy, is dead state, which expresses that the substance is in mechanical, chemical and thermal equilibrium with the reference environment.

If the analyzed system contains substances which don't exist in the reference environment, the chemical exergy of pure substance is computed from the standard chemical exergy of reference species which are available in standard reference sources [68, 69] as shown in Eq. (24).

$$Ex_{ch,i} = \Delta G_i - \sum_j \nu_j Ex_{ch,j} \tag{24}$$

in which $Ex_{ch,i}$ denotes the standard chemical exergy of any species i, $Ex_{ch,j}$ the standard chemical exergy of the pure element j in species i, ΔG_i standard Gibbs free energy of formation of species i and ν_j denotes the stoichiometric coefficient of pure element j in species i.

The standard chemical exergy of a species i in its α phase (e.g. liquid) can be estimated from the value in its β phase (e.g. vapor) according to Eqs. (25) and (26) [65].

$$Ex_{ch,i}^{\alpha} = Ex_{ch,i}^{\beta} + \Delta_{\beta \to \alpha} G_i \tag{25}$$

$$\Delta_{\beta \to \alpha} G_i = \Delta G_i^{\alpha} - \Delta G_i^{\beta} \tag{26}$$

Finally, the chemical exergy of a multi-component material stream is given by Eq. (27) [65].

$$Ex_{ch} = L \sum_{i=1}^{m} x_i Ex_{ch,i}^{l} + V \sum_{i=1}^{m} y_i Ex_{ch,i}^{v} \tag{27}$$

Chemical exergy of complex biological substances like cellulose, etc. can be estimated from the correlations for technical fuels using the lower heating value (LHV), and mass fractions of organic material, sulphur, water and ash in the biological substances as defined by Eq. (28) [70].

$$Ex_{ch,bio} = x_{bio}(\beta . LHV) + x_S(Ex_{ch,S} - C_S) + x_{Water}Ex_{ch,Water} + x_{ash}Ex_{ch,ash} \tag{28}$$

where C_S is the calorific value of sulphur.

The factor β can be estimated from correlations developed by Szargut et al. [71] as shown in Eqs. (29) – (31).

- For solid biofuels:

$$\beta = \frac{1.044 + 0.0160\frac{H}{C} - 0.3493\frac{O}{C}\left(1 + 0.0531\frac{H}{C}\right) + 0.0493\frac{N}{C}}{1 - 0.4124\frac{O}{C}} \tag{29}$$

- For liquid vegetable oils:

$$\beta = 1.0374 + 0.0159\frac{H}{C} + 0.0567\frac{O}{C} \tag{30}$$

- For coal:

$$\beta = 1.0437 + 0.1869\frac{x_{H_2}}{x_C} + 0.0617\frac{x_{O_2}}{x_C} + 0.0428\frac{x_{N_2}}{x_C} \tag{31}$$

where H, C, O and N represent hydrogen, carbon, oxygen and nitrogen contents in the biological substance.

4.2.2.3. EXERGY OF MIXING

To determine the exergy change of mixing, we can use the concept of "property change of mixing" as discussed in general textbooks on chemical thermodynamics (e.g. Smith et al. [72]):

$$\Delta_{mix}M = M^\alpha - \sum_{i=1}^{m} x_i^\alpha M_i^\alpha \tag{32}$$

where M and M_i^α denote a thermodynamic property of a mixture and of a pure component i, respectively.

By applying above mentioned concept to the exergy as a thermodynamic property, Eq. (33) is obtained for exergy of mixing [65].

$$\Delta_{mix}Ex = \Delta_{mix}H - T_0\Delta_{mix}S \tag{33}$$

4.3. EXERGY BALANCE

The exergy balance of an open steady state system involving of multiple inlet and outlet energy and mass flows, as shown in Fig. 9, can be represented in a general form [62] in which the exergy flow leaving the system boundary is always less than the exergy flow entering the system boundary because of exergy destruction also named system irreversibility (internal exergy loss) as introduced by Eq. (34).

$$I = \sum_{IN} Ex_i + \sum_{IN} Ex_Q - \sum_{OUT} Ex_j - \sum_{OUT} Ex_Q - Ex_W \qquad (34)$$

where $\sum_{IN} Ex_i$ and $\sum_{OUT} Ex_j$ are exergy flow of all inlet and outlet material streams, respectively. $\sum_{IN} Ex_Q$ and $\sum_{OUT} Ex_Q$ are the sum of all exergy caused through heat transfer crossing the system boundary. Ex_W and I are the work and irreversibility, respectively.
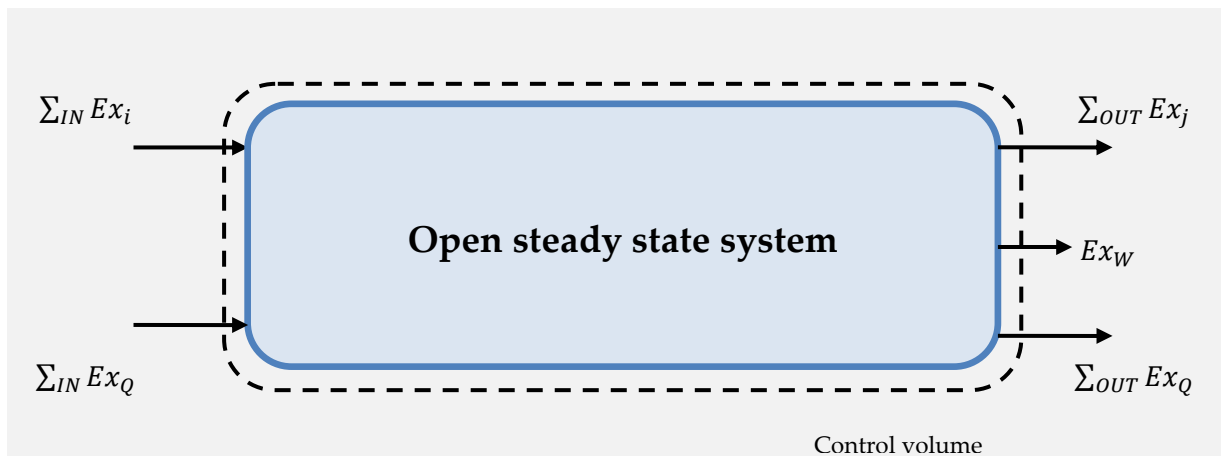
Fig. 9: Exergy balance for an open steady state system with constant volume

4.4. EXERGY EFFICIENCIES

For open steady state systems, three types of exergy efficiency definitions can be found in the literature sources [62].

- Conventional exergy efficiency

This simplest exergy efficiency is defined as the ratio of the all exergy output to the all exergy input [73]. This efficiency is used when no product can be defined.

$$\eta_{Ex,C} = \frac{\sum Ex_{OUT}}{\sum Ex_{IN}} \tag{35}$$

- Rational exergy efficiency

This exergy efficiency is defined by Kotas [58] and is given by the ratio of the desired exergy output to all exergy input.

$$\eta_{Ex,R} = \frac{\sum Ex_{Product}}{\sum Ex_{IN}} \tag{36}$$

in which $\sum Ex_{Product}$ and $\sum Ex_{IN}$ are desired exergy leaving the system and all exergy entering the system, respectively, as shown in Fig. 10. These terms can be specified for each type of system.
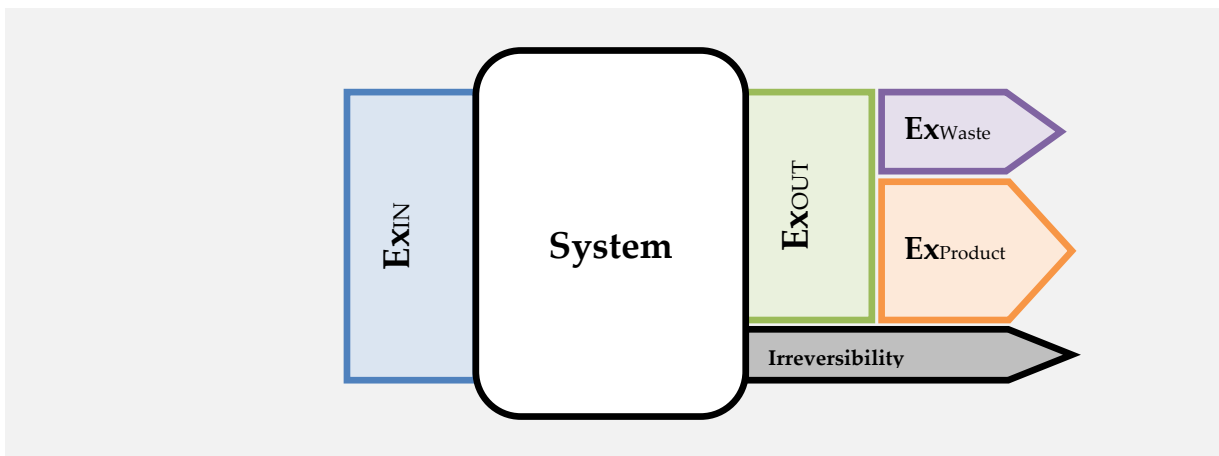
Fig. 10: The input and output of exergies for an open steady state system

- Efficiency defect

Third exergy efficiency can be defined as the ratio of irreversibilities (exergy losses) to all exergy input that is used in a system.

$$\eta_{Ex,D} = \frac{I}{\sum Ex_{IN}} \tag{37}$$

For biological processes, the overall exergy efficiency may be defined as the ratio between chemical exergy of products and biomass feeds [70].

5. PINCH ANALYSIS

5.1. INTRODUCTION

Today, heat integration and efficient energy usage (energy consumption optimization) are important concerns in many industries because of increase in fossil fuels prices, limited fossil energy resources and restrictions on carbon dioxide emissions, etc.

To integrate and reuse energy in the industrial plants, heat exchanger network (HEN) synthesis techniques are used in which pinch technology is the most widely used HEN method based on the thermodynamic principles.

The well studied HEN synthesis approaches as energy optimization system tool provide a conceptual view of energy used in thermochemical processes involving some cold process streams required to be heated up and some hot streams that need cooling energy to be cooled down as well as utilities. These approaches suggest heat recovery opportunities realized through the well-designed heat exchanger networks based on the minimum annualized cost involving equipment and external utility costs.

Several procedures and methods for HEN synthesis have been developed in the last years and briefly described by Grossmann et al. [74, 75]

5.2. METHODOLOGY

HEN synthesis techniques can be divided into two major categories: (1) sequential techniques involving HEN synthesis decomposition into sub-problems such as pinch technique based on the thermodynamic heuristic rules presented by Linnhoff et al. [76, 77] and mathematical programming such as heat load distribution (HLD) model, and (2) simultaneous techniques using a staged-superstructure based on the mixed integer nonlinear programming (MINLP) model proposed by Yee et al. [78].

HEN synthesis problems are also divided into (1) grassroot (design of the new heat exchanger network) and (2) retrofit (optimization of existing heat exchanger network). This work is focused on the pinch and simultaneous technique.

5.2.1. PINCH TECHNIQUE

Pinch technology can design heat exchanger networks for industrial processes in which after the improvement in the heat exchanged internally, the cooling and heating demands are provided by external utilities such as high pressure steam and cooling water. This appropriate approach ensures that energy saving targets are achieved by a well-designed HEN and identifies minimum energy consumption through the basic heat, material balance and graphical representation with reference to the several cold and hot process streams and utilities with given supply (T_S) and target (T_T) temperatures, heat capacity flow rate (CP = mass flow rate x specific heat capacity) and other specifications in the total site.

The heat capacity of process streams is assumed to be constant for simplicity of the procedure. Therefore, stream energy content can be calculated from the enthalpy change of a stream between its inlet and outlet temperatures according to Eq. (38) [79].

$$Q = \int_{T_S}^{T_T} CP\, dT = CP(T_T - T_S) = \Delta H \qquad (38)$$

The cold and hot process streams can be plotted on the enthalpy change-temperature diagram in which the hot and cold composite curves are shown by the red and blue lines, respectively as represented in Fig. 11.

The line slope of hot and cold composite curves is calculated according to the heat availability and demand in each temperature interval of the process. The composite curves meet each other at the pinch point. The system can be divided into two separate sub-systems, namely, above and below the pinch point. To achieve maximum heat exchanged internally, HEN structure and design must be based on the usage of external cooling and heating utilities only below and above the pinch, respectively as well as on the no heat transfer through the pinch.

A minimum temperature difference (ΔT_{min}) is specified for the whole system as minimum force of heat exchange with regards to the total annual cost that can be estimated from external cooling and heating energy, and heat exchangers costs [80].

The above mentioned composite curves show that heat can be internally exchanged between process streams, where both curves overlap. Furthermore, composite curves provide information about minimum cooling and heating demand as well as the maximum heat integration for the total site. This energy saving technique was described in some detail by Smith et al. [80].
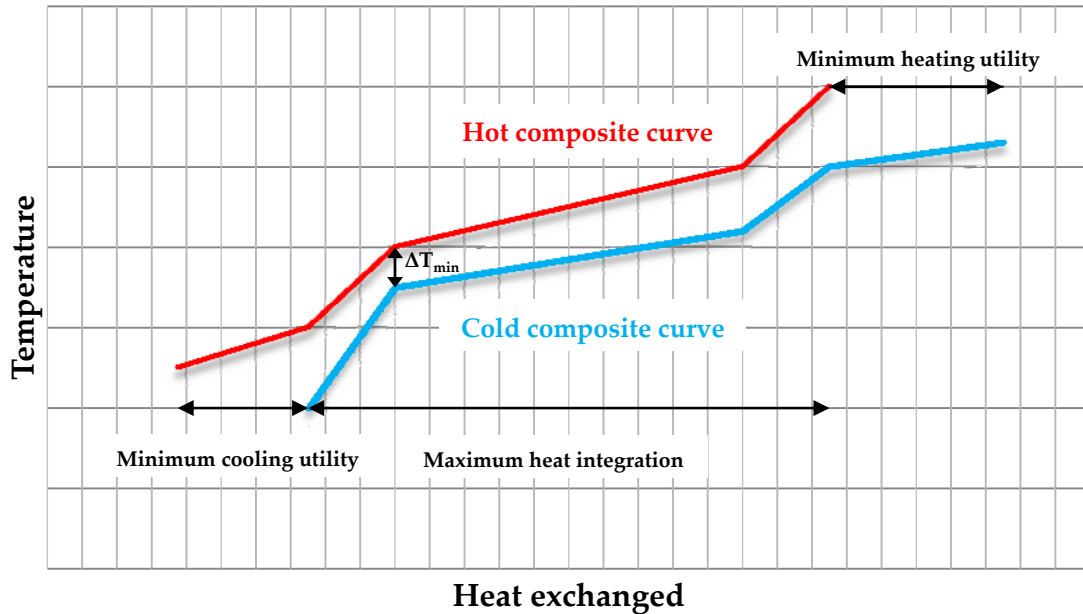
Fig. 11: Composite curves [adapted from: 80]

5.2.2. SIMULTANEOUS TECHNIQUE

This HEN synthesis approach is based on the simultaneous optimization of utilities and equipment costs. Some assumptions such as isothermal stream mixing and no phase change can be usually used to construct an optimal-designed heat exchanger network.

This model provides a Mixed Integer Nonlinear Programming (MINLP) objective function and some constraints that can be solved through the advanced mathematical optimization techniques described by Grossmann et al. and Belotti et al. [74, 81 and 82] with regards to the problem size.

Fig. 12 illustrates a two stage superstructure for four process streams given in the HEN synthesis problem. The hot process streams (HPS) and cold process streams (CPS) can be split at each stage. It's assumed that split streams are mixed isothermally to reduce the

complexity of the MINLP model. The external coolers and heaters are placed at the end of the hot and cold process streams, respectively.
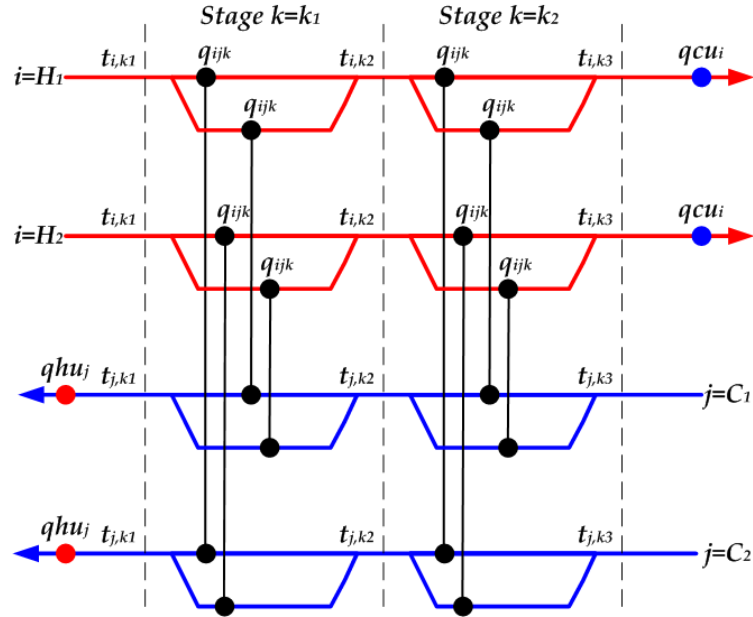
Fig. 12: Staged-superstructure [adapted from: 78]

The MINLP model can be formulated as follows [83-85]:

- Total heat balance for each process stream

$$(Tin_i - Tout_i)CP_i = \sum_k \sum_j q_{ijk} + qcu_i \tag{39}$$

$$(Tout_j - Tin_j)CP_j = \sum_k \sum_i q_{ijk} + qhu_j \tag{40}$$

where variables q_{ijk}, qcu_i and qhu_j are heat exchanged between hot stream i and cold stream j in stage k, heat exchanged between hot stream i and cold utility, and heat exchanged between cold stream j and hot utility, respectively. Tin_i, $Tout_i$ and CP_i are inlet temperature, outlet temperature and heat capacity flow rate of stream i, respectively.

- Total heat balance for each stage

$$(t_{i,k} - t_{i,k+1})CP_i = \sum_j q_{ijk} \tag{41}$$

$$(t_{j,k} - t_{j,k+1})CP_j = \sum_i q_{ijk} \tag{42}$$

where variables $t_{i,k}$ and $t_{j,k}$ are temperature of hot stream i and cold stream j at the hot end of stage k, respectively.

- Inlet temperatures

$$Tin_i = t_{i,1} \tag{43}$$
$$Tin_j = t_{j,NOK+1} \tag{44}$$

where NOK the total number of stages.

- Decrease in the temperatures

$$t_{i,k} \geq t_{i,k+1} \tag{45}$$
$$t_{i,NOK+1} \geq Tout_i \tag{46}$$
$$t_{j,k} \geq t_{j,k+1} \tag{47}$$
$$Tout_j \geq t_{j,1} \tag{48}$$

- Load of the heating and cooling utilities

$$(t_{i,NOK+1} - Tout_i)CP_i = qcu_i \tag{49}$$
$$(Tout_j - t_{j,1})CP_j = qhu_j \tag{50}$$

- Logical constraints for streams and utilities

$$q_{ijk} - Q_{i,j}^{max} z_{ijk} \leq 0 \tag{51}$$
$$qcu_i - Q_i^{max} zcu_i \leq 0 \tag{52}$$
$$qhu_j - Q_j^{max} zhu_j \leq 0 \tag{53}$$

where binary variables z_{ijk}, zcu_i and zhu_j are existence of heat exchanger unit between hot stream i and cold stream j, hot stream i and cold utility, and cold stream j and hot utility, respectively.

$$z_{ijk}, zcu_i, zhu_j = 0, 1 \qquad (54)$$

Q^{max} is an upper limit for heat exchange in which $Q_{i,j}^{max}$ is equal to the minimum heat content of the two process streams.

$$dt_{ijk} \leq t_{i,k} - t_{j,k} + \Delta T^{max}(1 - z_{ijk}) \qquad (55)$$

$$dt_{ij,k+1} \leq t_{i,k+1} - t_{j,k+1} + \Delta T_{i,j}^{max}(1 - z_{ijk}) \qquad (56)$$

$$dtcu_i \leq t_{i,NOK+1} - Tout_{cu} + \Delta T_{i,cu}^{max}(1 - zcu_i) \qquad (57)$$

$$dthu_j \leq Tout_{hu} - t_{j,1} + \Delta T_{j,hu}^{max}(1 - zhu_j) \qquad (58)$$

where dt_{ijk}, $dtcu_i$, and $dthu_j$ are temperature approaches for heat exchanger unit between hot stream i and cold stream j at temperature location k, hot stream i and cold utility, and cold stream j and hot utility, respectively.

$\Delta T_{i,j}^{max}$ is an upper bound for the temperature difference that can be estimated by Eq. (59).

$$\boldsymbol{if} \ Tin_i - Tin_j < \Delta T_{min} \ \rightarrow \ \Delta T_{i,j}^{max} = abs[Tin_i - Tin_j] + \Delta T_{min}$$
$$\boldsymbol{else} \ \Delta T_{i,j}^{max} = \max\{0, Tin_i - Tin_j, Tout_j - Tout_i\} \qquad (59)$$

▪ Additional limits (lower and upper bounds)

$$Tout_i \leq t_{i,k} \leq Tin_i \qquad (60)$$

$$Tin_j \leq t_{j,k} \leq Tout_j \qquad (61)$$

$$0 \leq q_{ijk} \leq \min\{(Tin_i - Tout_i)CP_i, (Tout_j - Tin_j)CP_j\} \qquad (62)$$

$$0 \leq qcu_i \leq (Tin_i - Tout_i)CP_i \qquad (63)$$

$$0 \leq qhu_j \leq (Tout_j - Tin_j)CP_j \qquad (64)$$

$$dt_{ijk} \geq \Delta T_{min} \qquad (65)$$

$$dtcu_i \geq \Delta T_{min} \qquad (66)$$

$$dthu_j \geq \Delta T_{min} \tag{67}$$

$$LMTD_{ijk} \geq \Delta T_{min} \tag{68}$$

$$LMTD_{i,cu} \geq \Delta T_{min} \tag{69}$$

$$LMTD_{j,hu} \geq \Delta T_{min} \tag{70}$$

where $LMTD_{ijk}$, $LMTD_{i,cu}$ and $LMTD_{j,hu}$ are logarithmic mean temperature difference between hot stream i and cold stream j, hot stream i and cold utility and cold stream j and hot utility. The Chen's approximation [86] is used to approximate the logarithmic mean temperature difference (LMTD) as shown in Eqs. (71) – (73).

$$LMTD_{ijk} = \left[dt_{ijk} dt_{ij,k+1} \left(\frac{dt_{ijk} + dt_{ij,k+1}}{2} \right) \right]^{1/3} \tag{71}$$

$$LMTD_{i,cu} = \left[dtcu_i (Tout_i - Tin_{cu}) \left(\frac{dtcu_i + (Tout_i - Tin_{cu})}{2} \right) \right]^{1/3} \tag{72}$$

$$LMTD_{j,hu} = \left[dthu_j (Tin_{hu} - Tout_j) \left(\frac{dthu_j + (Tin_{hu} - Tout_j)}{2} \right) \right]^{1/3} \tag{73}$$

Finally, the objective function can be defined as the minimization of the total annual costs (TAC) including operation and investment costs as shown by Eq. (74).

$$\text{minimize } \{ \sum_i \sum_j \sum_k CF_{ij} z_{ijk} + \sum_i CF_{icu} zcu_i + \sum_j CF_{jhu} zhu_j + \sum_i CCU qcu_i + \sum_j CHU qhu_j +$$

$$\sum_i \sum_j \sum_k C_{ij} \frac{q_{ijk}}{(U_{ij} LMTD_{ijk})} + \sum_i C_{icu} \frac{qcu_i}{(U_{i,cu} LMTD_{i,cu})} + \sum_j C_{jhu} \frac{qhu_j}{(U_{j,hu} LMTD_{j,hu})} \} \tag{74}$$

where, CCU and CHU are unit cost of cooling and heating utility, respectively, and C_{ij}, C_{icu} and C_{jhu} represent the area cost coefficients, and CF_{ij}, CF_{icu} and CF_{jhu} are fixed charges for heat exchangers. U_{ij}, $U_{i,cu}$ and $U_{j,hu}$ are overall heat transfer coefficients and represented by Eqs. (75) – (77).

$$U_{ij} = \left[\frac{1}{h_i} + \frac{1}{h_j} \right]^{-1} \tag{75}$$

$$U_{i,cu} = \left[\frac{1}{h_i} + \frac{1}{h_{cu}} \right]^{-1} \tag{76}$$

$$U_{j,hu} = \left[\frac{1}{h_{hu}} + \frac{1}{h_j} \right]^{-1} \tag{77}$$

where h_i, h_j, h_{cu} and h_{hu} are film heat transfer coefficients.

Some literature on the HEN synthesis based on simultaneous methods considered pure and multi-component phase changes that are common in the industrial chemical plants, such as in the evaporators and condensers.

Ponce-Ortega et al. [83] proposed a new MINLP model based on the work of Yee et al. [78] to deal with isothermal phase changes for pure component streams.

The temperature-enthalpy relations are nonlinear for multi-component phase change and assumption of isothermal phase change for mixture streams leads to inaccurate and unacceptable heat exchanger networks. Therefore, Hasan et al. [87, 88] presented a MINLP formulation dealing with mixtures and non-isothermal phase changes in HENS problems.

5.2.2.1. UTILITY OPTIMIZATION

Most of the current non-graphic approaches for HEN synthesis allow only one type of heating and cooling utility with reference to their final temperatures such as staged-superstructure [78].
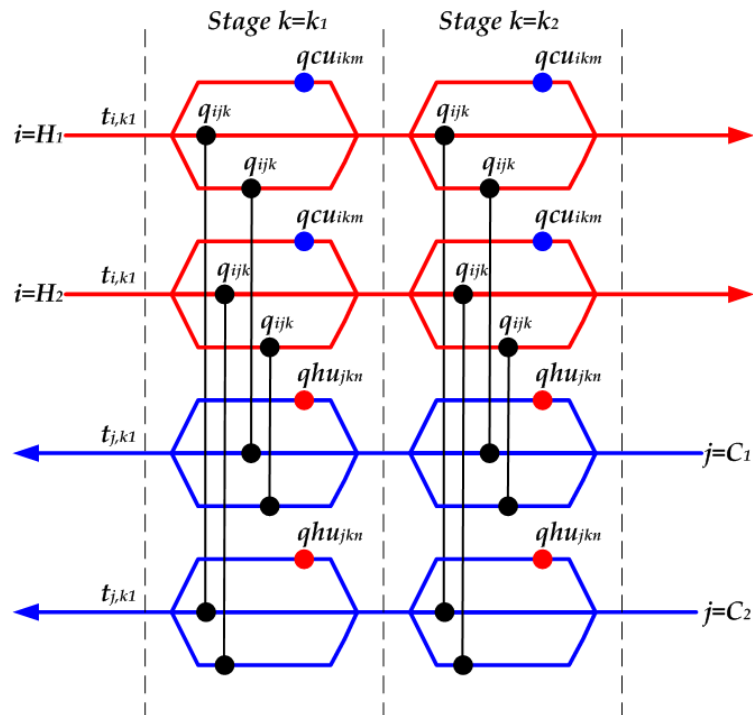
Fig. 13: Staged-superstructure for HENS including multiple utilities [adapted from: 88]

However, the different types of utilities such as steam and cooling water at different levels are commonly used in the chemical industries and processes.

Ponce-Ortega et al. [89] developed a new MINLP model based on the staged-superstructure for HEN synthesis involving multiple utilities in which the intermediate location of multiple utilities is allowed and optimal placement of them is addressed within each stage of superstructure unlike the original MINLP model as shown in Fig. 13.

II. RESULTS

6. PAPERS

Papers are sorted by topic, author and year of publication.

6.1. PAPER I

Effect of process integration on the exergy balance of a two-stage process for fermentative hydrogen production

A. Modarresi, W. Wukovits, D. Foglia and A. Friedl
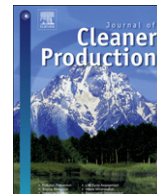
Effect of process integration on the exergy balance of a two-stage process for fermentative hydrogen production

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ABSTRACT

In this paper, a process for the fermentative production of hydrogen is analysed with respect to its exergy efficiency. Parametric studies show the influence of used feedstock, applied process parameters as well as process and heat integration measures on exergy efficiency. It is shown that heat integration and recirculation of fermentor effluents reduce process irreversibilites and the amount of exergy leaving the process in waste streams. Nevertheless, depending on the used feedstock, a large amount of exergy leaves the process via by-products. Internal use of by-products and waste materials for providing process heat could increase chemical exergy efficiency up to 74%.

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1. Introduction

Hydrogen is considered being one of the most important carbon free energy carriers of the future. At the moment most of used hydrogen is produced from fossil fuels via steam reforming. To be able to establish a sustainable hydrogen economy, hydrogen has to be produced from renewable resources. During the last years, besides biomass gasification, extensive research in the field of fermentative production of hydrogen by applying bacteria was carried out. However, the experience shows that single stage processes are not efficient from the point of view of hydrogen yield, since only part of feedstock is converted to hydrogen. A promising way is a 2-stage process consisting of a thermophilic fermentation step followed by a photoheterotrophic fermentation step (Bartacek et al., 2007; Das et al., 2008; Redwood et al., 2009; Claassen et al., 2006). New research in this area is mainly focused on the selection of feedstock, optimization of yield and the rate of hydrogen production. Only little emphasis is put yet into optimization of the overall process based on process and heat integration. Additionally to mass and energy balances, exergy analysis is a powerful technique for determining and improving the efficiency of processes. In this paper, exergy analysis is performed on a novel process for the fermentative production of hydrogen, combining a thermophilic fermentation with a consecutive photoheterotrophic fermentation step.

2. Process description and process model

The novel process for the fermentative production of hydrogen investigated in the FP6 project HYVOLUTION consists of pre-treatment (PTR), thermophilic fermentation (THF), photo(hetero-trophic) fermentation (PHF) as well as gas-upgrading (Gas-Upg) as illustrated in Fig. 1. The process usually starts with an appropriate pre-treatment of biomass to provide a suitable feedstock for thermophilic fermentation. In HYVOLUTION process, starch and sugar based as well as lignocellulosic residues from agriculture and food processing are used as feedstocks for fermentative hydrogen production. In this paper we focus on starch and sugar based feedstocks represented by potato steam peels (PSP) and thick juice respectively. Whereas processing of thick juice does not need any pre-treatment, the pre-treatment procedure of PSP consists of a liquefaction and saccharification step. During pre-treatment starch is converted into fermentable glucose. The sugar-containing substrate − glucose in case of feedstock PSP and sucrose in case of thick juice − is diluted and then heated up to 70 °C before it is fed into the thermophilic fermentor (THF). In this first fermentation step, thermophilic bacteria growing at 70 °C produce hydrogen gas and organic acids as the main by-products following Eq. (1) or (2).

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 4H_2 + 2CO_2 \qquad (1)$$

$$C_{12}H_{22}O_{11} + 5H_2O \rightarrow 4CH_3COOH + 8H_2 + 4CO_2 \qquad (2)$$

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Nomenclature

Eff	exergy efficiency, %
PSP	potato steam peels
PTR	pre-treatment
THF	thermophilic fermentor/fermentation
PHF	photo(heterotrophic) fermentor/fermentation
HAc	acetic acid
Gas-Upg	gas-upgrading
C	calorific value, kJ/kg
Ex	molar exergy, kJ/mol
EX	exergy flow rate, kJ/s
I	irreversibility, kJ/s
HHV	higher heating value of biomass, kJ/kg
LHV	lower heating value of biomass, kJ/kg
VSA	vacuum swing adsorption
x	mole fraction in liquid phase, mol/mol
y	mole fraction in vapour phase, mol/mol
β	ratio of the chemical exergy to LHV, -
η	efficiency, %
V	vapour fraction, −
L	liquid fraction, −
H	molar enthalpy, kJ/mol

Rel. irr.	relative irreversibility, %
S	molar entropy, kJ/(mol K)

Superscripts

l	in liquid phase
v	in vapour phase
m	number of components

Subscripts

ash	ash
bio	biomass
chem	chemical
in	input
Liquid	liquid biomass
out	output
phys	physical
prod	product
Q	heat
S	sulphur
Solid	solid biomass
W	work
0	reference state

The liquid effluent from THF is again diluted and finally fed into the photo fermentor (PHF). In this second fermentation step operated at 30 °C photoheterotrophic bacteria convert acetic acid (HAc) existing in the effluent of the thermophilic fermentor to further hydrogen and carbon dioxide following Eq. (3):

$$CH_3COOH + 2H_2O \rightarrow Light + 4H_2 + 2CO_2 \qquad (3)$$
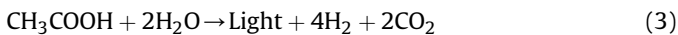
To obtain pure hydrogen (97 vol%), finally carbon dioxide has to be separated from produced gas. In the present study vapour swing adsorption is assumed to be used for gas-upgrading resulting in the loss of 10% of produced hydrogen. After gas-upgrading carbon dioxide can be collected to be used:

- For carbonation of soft drinks
- To improve plant growth in greenhouses
- For refrigerating and cooling systems
- As a raw material for chemical synthesis.

Investigation and optimization of the different process steps within HYVOLUTION project is mainly based on experimental work. Process simulation is used in order to combine and integrate the single process steps and to optimize the overall process,. The commercial software package Aspen Plus® (V7.1, Aspen Technology, Inc., Burlington, USA, 2008) was selected to predict the behaviour of HYVOLUTION process using basic mass and energy balances, phase and chemical equilibrium as well as reaction kinetics. A scheme of overall HYVOLUTION process depicting considered process and heat integration options is shown in Fig. 1. The simulation model as well as mass and heat balances for different process options are taken from Foglia et al. (2010).
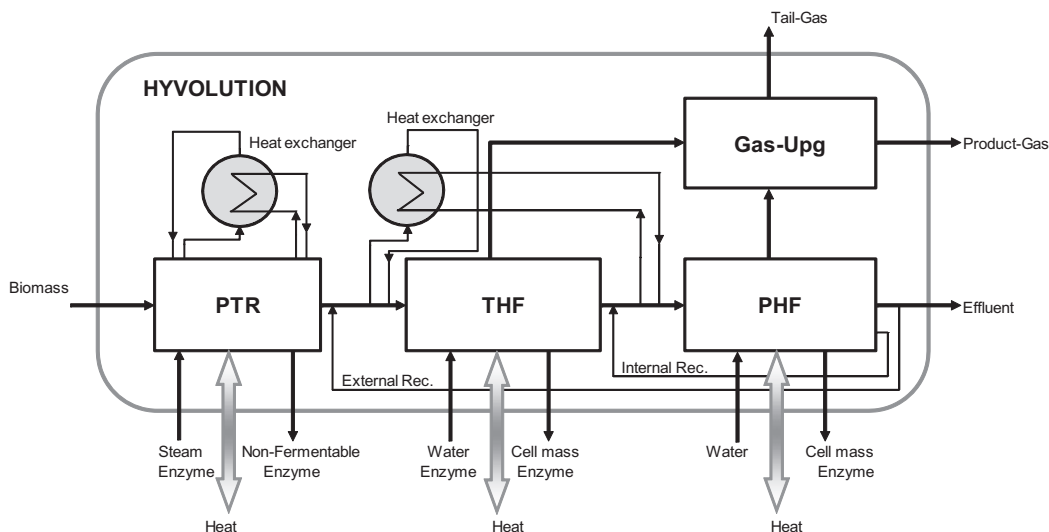

Fig. 1. HYVOLUTION process illustrating heat integration and effluent recirculation streams.

3. Exergy analysis and exergy efficiencies

Exergy is defined as the maximum obtainable work while a system contacts with its environment reversibly. Exergy analysis is a useful approach to identify the kind, location and quantity of thermal and material losses in chemical and thermal processes (Szargut and Styrylska, 1964). Exergy analysis identifies the system components with the highest thermodynamic inefficiency and the processes that cause them. This technique is widely used during the analysis and improvement of the efficiency of processes. For a given chemical or thermal process exergy is the portion of the total energy of the system that is available for conversion to useful work. In contrast to energy, exergy can be lost. Exergy losses are caused by internal irreversibilities of processes. Therefore, during the optimization of a process irreversibilities should be minimized. The concept of exergy change, transfer and destruction can be used to develop an exergy balance similar to energy. However, the concept of exergy analysis only considers a thermodynamic point of view and should be seen as an additional option for optimization. It is often considered as confusing and gives no information on the economic feasibility of a process.

3.1. Calculation of exergy

The exergy content of a stream in a chemical process is calculated as the sum of three components: chemical exergy, physical exergy and the exergy change of mixing. The latter could be neglected for most practical processes. The total exergy flow rate of a material stream at actual conditions therefore can be obtained from Eq. (4):

$$EX = EX_{Chem} + EX_{Phys} \tag{4}$$

where EX_{Chem} and EX_{Phys} are chemical and physical exergy, respectively. The chemical exergy of a multi-component material stream is given by (Hinderink, 1996):

$$EX_{Chem} = L \sum_{i=1}^{m} x_i Ex_{Chem,i}^l + V \sum_{i=1}^{m} y_i Ex_{Chem,i}^v \tag{5}$$

In which $Ex_{Chem,i}^l$ and $Ex_{Chem,i}^v$ denote the standard chemical exergy of a species i in liquid and vapour phase, respectively. The physical exergy is obtained from enthalpy and entropy differences between actual and reference state ($T_0 = 298.15$ K, $p = 1$ bar) following Eq. (6):

$$Ex_{Phys} = H - H_0 - T_0(S - S_0) \tag{6}$$

The physical exergy of a multi-component material stream can be written as (Hinderink, 1996):

$$Ex_{Phys} = \left[L\left(\sum_{i=1}^{m} x_i H_i^l - T_0 \sum_{i=1}^{m} x_i S_i^l\right) + V\left(\sum_{i=1}^{m} y_i H_i^v - T_0 \sum_{i=1}^{m} y_i S_i^v\right) \right]_{reference}^{actual} \tag{7}$$

Standard chemical exergy is tabulated for many species. Otherwise, for defined species it can be calculated from the Gibb's free energy of formation. Chemical exergy of biomass can be accurately predicted using statistical correlations based on data from elemental analysis and the lower heating value (Ptasinski et al., 2006):

$$Ex_{Chem,bio} = x_{bio}(\beta \times LHV_{bio}) + x_S(Ex_{Chem,S} - C_S) + x_{water}Ex_{Chem,water+} + x_{ash}Ex_{Chem,ash} \tag{8}$$

The factor β is the ratio of the chemical exergy to the lower heating value (LHV) of the organic fraction of biomass, C_S is the calorific value of sulphur and x_{bio} is the mass fraction of biomass.

Eqs. (9a) and (9b) are used to calculate the factor β of solid and liquid biomass, respectively (Szargut and Styrylska, 1964):

$$\beta_{Solid} = \frac{1.044 + 0.016\frac{H}{C} - 0.3493\frac{O}{C}\left(1 + 0.0531\frac{H}{C}\right) + 0.0493\frac{N}{C}}{1 - 0.4124\frac{O}{C}} \tag{9a}$$

$$\beta_{Liquid} = 1.0374 + 0.0159\frac{H}{C} + 0.0567\frac{O}{C} \tag{9b}$$

H/C, O/C and N/C denote for the atomic ratios in the biomass formula. Higher heating values (HHV) of biomass can be accurately calculated by the following correlation (Channiwala and Parikh, 2002):

$$HHV_{Fuel} = 0.3491x_C + 1.1783x_H - 0.1034x_O - 0.0151x_N + 0.1005x_S - 0.0211x_{ash} \tag{10}$$

where x_C, x_O, x_H, x_N, x_S and x_{ash} are the mass and the ash fractions in wt% of dry material and HHV the heating value in MJ/kg. The correlation is developed for a wide range of fuels, covering the whole range from coal to biomass. HHV is converted to LHV via the enthalpy of evaporation for water formed during combustion.

Other thermodynamics properties of biomass, which are not exactly known due to the not well-defined structure of biomass, are obtained from correlations such as modified Kopp's rule for the calculation of heat capacities (Hurst and Harrison, 1992).

3.2. Exergy efficiencies

For real processes the exergy input always exceeds the exergy output due to irreversibilities mentioned above. The exergy balance of a process is represented by Eq. (11):

$$I = \sum_{in} EX_j - \sum_{out} EX_k + \sum_{in}(EX_Q + EX_W) - \sum_{out} EX_Q \tag{11}$$

Eq. (11) considers the exergy of all input and output material streams, the sum of all thermal exergy and work (EX_Q, EX_W) involved in a process as well as the irreversibility I of the process. The output exergy usually consists of the exergy of product and waste streams leaving the process.

Besides the relative irreversibility — the ratio of irreversibility to total exergy input to the system, Eq. (13) — three different definitions of exergy efficiency are introduced by Cornelissen (1997). Simple exergy efficiency, Eq. (12), expresses the ratio of total exergy output and total exergy input of a process. Rational exergy efficiency, Eq. (14), presents the ratio of exergy of the product to the total exergy input. Another option is to use the chemical exergy efficiency, defined as the ratio between chemical exergy of the product and the chemical exergy of input, expressed in Eq. (15).

$$\eta_{ex,1} = \frac{EX_{out}}{EX_{in}} \tag{12}$$

$$rel.\ Irr. = \frac{I}{EX_{in}} \tag{13}$$

$$\eta_{ex,3} = \frac{EX_{prod}}{EX_{in}} \tag{14}$$

$$\eta_{ex,4} = \frac{EX_{Chem,prod}}{EX_{Chem,bio}} \tag{15}$$

3.3. Mathematica-based exergy calculator package

A tool based on Mathematica (V6.0.3.0, Wolfram Research, Inc., Champaign, USA, 2008) has been developed to calculate the exergy of compounds and streams of HYVOLUTION process in a systematic way. The structure of the model for exergy calculation is shown in Fig. 2. The exergy of the system is calculated according to the following steps:

1. Identify the material streams and composition.
2. Read the thermodynamic properties and chemical exergy databank.
3. Calculate the chemical exergy for each material stream according to its composition.
4. Calculate the physical exergy for each material stream according to the temperature and pressure of the stream.
5. Calculate the total exergy for the material stream.
6. Calculate the different types of exergy efficiency.

The chemical exergy of components is taken from a databank. Used values were compiled from literature or calculated from the correlations given above. The calculation of thermodynamic properties is based on polynomial functions to obtain temperature dependent values of specific heat, entropy and enthalpy.

Mass and energy balances for the investigated process options are provided with the process simulation tool Aspen Plus® and are based on the process model and process parameters described above. For detailed process parameters as well as mass and energy balances (see Foglia et al., 2010). Data necessary for the calculation of exergy of process streams are read automatically from the results of the process simulation tool by a routine based on Mathematica Scripting Language. The heating and cooling demand of the process are modelled as material streams (e.g. steam, cooling water) in the exergy package.

4. Results

Exergy analysis of fermentative hydrogen production has been performed for two raw materials, potato steam peelings (PSP), a starch containing residue from food processing, and thick juice, a sucrose based feedstock available as intermediate of sugar beet processing. Balances are scaled to the production of 60 kg/h of pure hydrogen (97 vol%) considering 10% hydrogen losses in the gas-upgrading unit.

All considered cases are based on a substrate concentration of 10 g/L sugar and 40 mM of acetic acid at the inlet of thermophilic fermentor and photo fermentor, respectively. In the Base Case 80% of substrate (sucrose/glucose) is converted into hydrogen in THF and 80% of acetic acid into hydrogen in PHF. It is assumed, that in both fermentors 15% of substrate is used to produce cell mass and 5% of feedstock are not converted in the fermentors. For the conversion of sugar to hydrogen an overall yield of 70% of the theoretical maximum will be obtained.

While experimental investigation in THF showed that a conversion of substrate to hydrogen of about 80% (wt) is possible, actual results suggests the reduction of substrate conversion to hydrogen in PHF to 60% resulting in a higher feedstock, water and heat demand necessary to produce 60 kg/h of hydrogen compared to the Base Case (Foglia et al., 2010). The effect of reduced substrate conversion on the exergy efficiency of the process is represented by the Engineering Case. Both cases – Base Case and Engineering Case – include neither internal and external recirculation nor any heat recovery step depicted in Fig. 1.

In order to reduce the heat and water demand in the process, the recirculation of fermentor effluents has been introduced into the process (Fig. 1). Results in process simulation showed that only a combination of recirculation of photo fermentor effluent to the inlet of photo fermentor and the inlet of thermophilic fermentor – referred to internal and external recirculation, respectively is feasible in the process (Foglia et al., 2009). Replacing dilution water in the
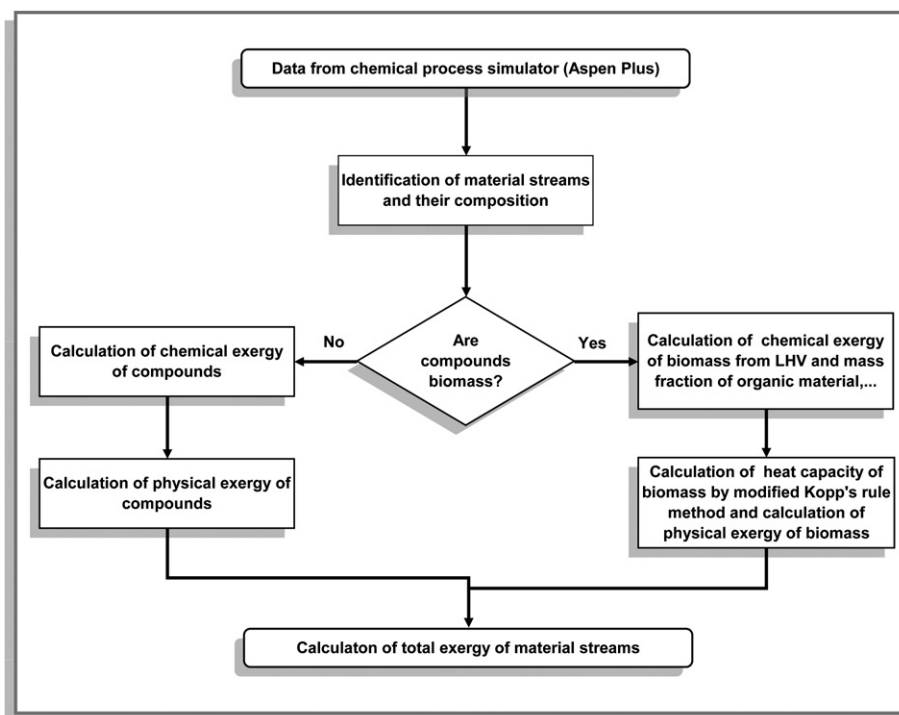

Fig. 2. Structure of algorithm used for calculation of exergy of process streams.

thermophilic fermentation step by recirculation of thermophilic reactor effluent is not possible due to an increase of osmotic pressure in the system. Effluent recirculation is defined as percentage of replacement of dilution water in the process/process step.

While recirculation of effluents reduces the water demand of the process up to 90%, applicable recirculation options only slightly reduce the heat demand of the process. A reduction of heat demand finally was obtained by the introduction of two heat exchangers. One heat exchanger is used in the pre-treatment step, the other heat exchanger is placed at the inlet of the THF to preheat the reactor inlet with the outlet stream of the fermentor. For both heat exchangers a minimum temperature approach of 5 °C is defined. Simulation results show a reduction of 30% and 85% of the heat demand in pre-treatment and THF, respectively (Foglia et al., 2010).

As seen in earlier work (Wukovits et al., 2008; Modarresi et al., 2010) obtained exergy efficiency strongly depends on the definition of products. Besides the calculation of exergy efficiency of the different process options, parameter studies investigating the influence of definition of products on rational exergy efficiency ($\eta_{ex,3}$) and chemical exergy efficiency ($\eta_{ex,4}$) were performed. These studies represent the use of different by-products besides the main product hydrogen, giving a surplus of information to be used to find options for process improvement (Modarresi et al., 2010).

4.1. Impact of raw materials

Fig. 3 compares the exergy efficiencies of HYVOLUTION process based on feedstock PSP and thick juice. Feedstock characteristics, process parameters as well as mass and energy balances are taken form (Foglia et al., 2010). Additionally, Fig. 3 shows the exergy efficiency of feedstock wheat. These results are taken from a previous study assuming a dry matter content of 90% as well as a starch content of 70% based on dry matter for the feedstock (Modarresi et al., 2010).

According to Fig. 3 the process option based on wheat has the highest value of efficiency 1 followed by PSP. Reason for this ranking is the content of water as well as the fraction of fermentable components (starch/sugar). Wheat contains the lowest mass fraction of water (about 10%) compared to PSP and thick juice. Furthermore, the ratio of fermentable components to non-fermentable fraction in this feedstock is high. Therefore the ratio of waste to product for wheat is less than for PSP.

Efficiency 1 for the process option based on thick juice is surprisingly lower than the efficiency of a process operated with PSP, although the sucrose content of thick juice is almost double of the starch content of PSP and comparable to the starch content of wheat. The irreversibilites of thick juice and PSP based processes are quiet

comparable with 8332 MJ/kg and 8185 MJ/kg. However, total exergy input (thick juice: 468,445 MJ/kg; PSP: 71,803 MJ/kg) and output (thick juice: 38,613 MJ/kg; PSP: 63,617 MJ/kg) for both process options differ considerably, explaining the unexpected large differences for values of efficiency 1 and relative irreversibility.

Efficiency 3A, representing the ratio of exergy of the product stream to the total exergy input to the process, shows a completely different behaviour for considered feedstock options than observed for efficiency 1. The process option based on feedstock thick juice shows the highest rational exergy efficiency followed within narrow margins by feedstock wheat. Efficiency 3A of the process option based on feedstock PSP is considerably lower. Thick juice consists almost of sugar and water, with only few other components hardly leading to material losses in form of non-fermentables. Therefore, the use of sugar thick juice produces less waste than the use of starchy materials PSP and wheat needing pre-treatment and showing a lower ratio of fermentables to non-fermentables. Especially feedstock PSP shows a low content of fermentables (starch) resulting in the lowest rational exergy efficiency of feedstock options under consideration.

The same trend can be observed for efficiency 4A which describes the ratio of chemical exergy of hydrogen to the chemical exergy of used biomass. As observed for feedstock thick juice efficiency 3A and efficiency 4A are almost double compared to feedstock PSP.

4.2. Impact of substrate conversion in PHF

Comparing Base Case and Engineering Case, thus process options with 80% and 60% hydrogen yield in PHF, respectively, show almost no differences in efficiency 1 (Fig. 4), although the Engineering Case needs larger amounts of feedstock, water and heat input. Constant efficiency 1 is explained by the fact that the overall process changes only slightly and the definition of efficiency 1. Since all input and output streams are considered for the calculation of exergy efficiency, a larger amount of feedstock and utility demand does not show up in the results, since excess water and not consumed feedstock are released from the process, but exergy of these components is not lost.

In contrast, efficiencies 3A and 4A clearly reflect the larger amount of feedstock and utility demand of the process due to lower hydrogen yield in the Engineering Case. For both feedstock options, efficiency 3A and 4A are considerably decreased for the Engineering Case.

4.3. Impact of heat integration

Optimization of the process from the point of view of heat demand by introduction of heat integration is an important step
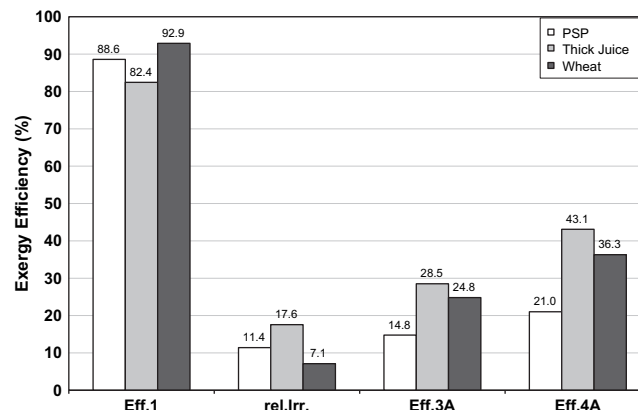
Fig. 3. Comparison of different raw materials for Base Case.
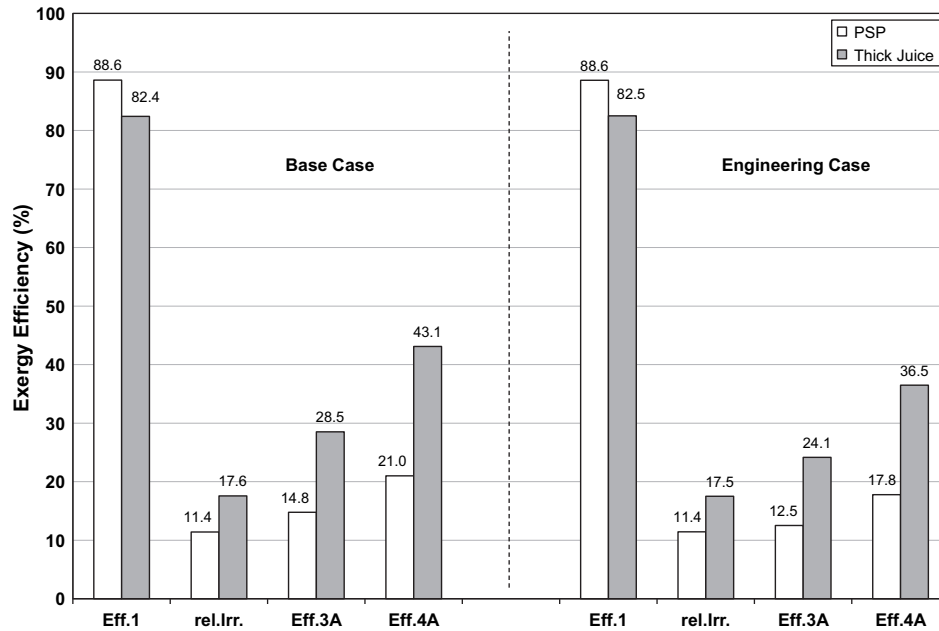
Fig. 4. Effect of substrate conversion in PHF on exergy efficiencies.

towards an economic process. However exergy analysis shows that the influence of heat integration on exergy efficiency is low for the considered process as illustrated in Fig. 5. In fermentative hydrogen production the process is carried out at a temperature between 30 °C and 70 °C. Only during pre-treatment of feedstock slightly higher temperature is needed. Due to the low temperature level lost exergy is negligible and heat integration does not influence on exergy balance and exergy efficiencies as it does in the energy balance.

As seen in Fig. 5, efficiency 1 is increased for PSP for the heat integrated case, while for the process option based on thick juice, efficiency 1 is decreasing. This could be explained by the fact that with introduction of heat integration, on the one hand the energy demand of the process decreases on the other hand additional exergy losses are introduced by the heat integration circuits in both

heat exchangers. Furthermore, besides the reduction of heat input the temperature level of the involved heat exchanging streams has an important impact on the exergy efficiency. Lower temperature levels due to heat integration of THF contribute to the decrease of efficiency 1 for the integrated process option of feedstock thick juice. Per definition efficiency 4 is not changing, since it only describes the ratio of chemical exergies.

4.4. Impact of internal and external recirculation of effluents

From a process integration point of view, recirculation of effluent of PHF to both fermentors considerably reduces the water demand of the process. As seen in the Fig. 6 by applying internal and external recirculation, also the exergy efficiencies are
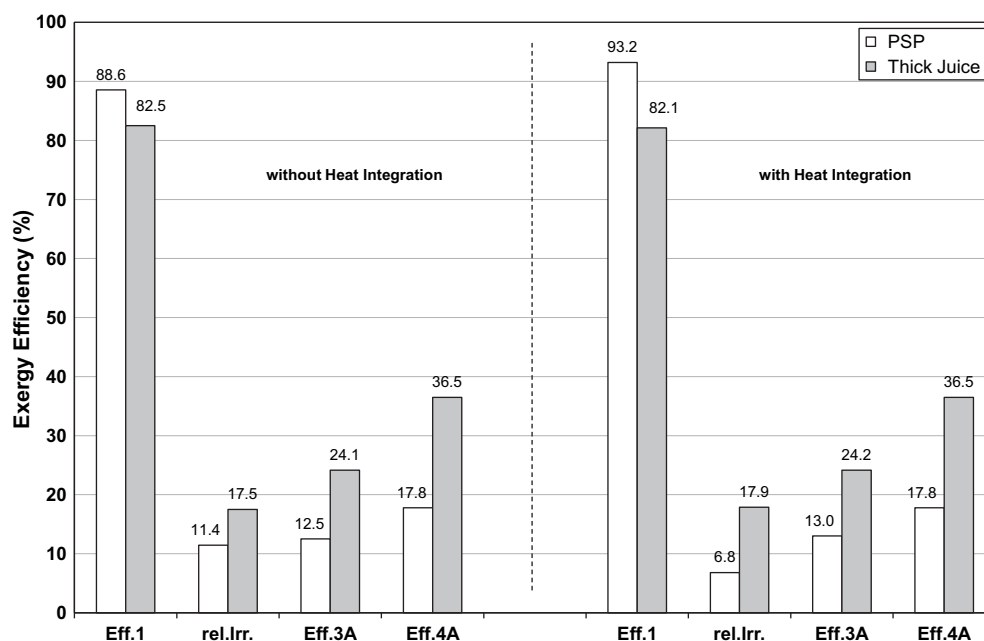
Fig. 5. Influence of heat integration on exergy efficiencies for Engineering Case.
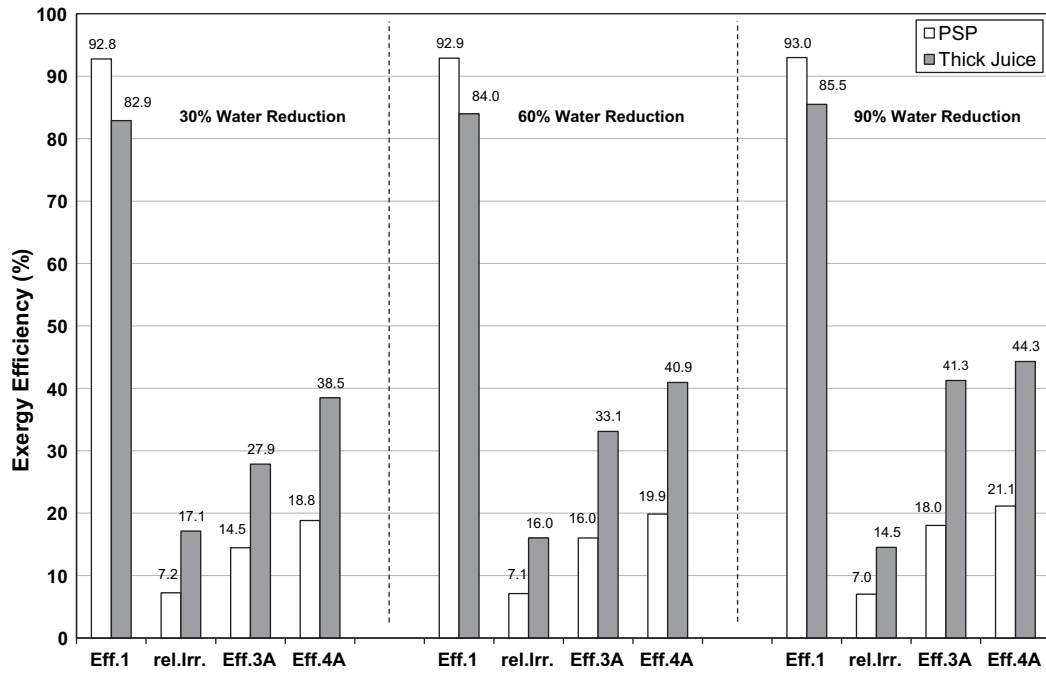
Fig. 6. Effect of internal and external recirculation of effluents on exergy efficiencies.

improved, especially for the process operated with feedstock thick juice. The level of increasing efficiency depends on the amount of recirculated effluent. The larger the amount of recirculated effluent, and thus the reduction of the demand of fresh water, the higher is the value of exergy efficiency. The reason is that reuse of the effluent exiting from PHF provides the possibility to consume

further materials which would leave the process unused without effluent recirculation.

Fig. 7 shows that heat integration and effluent recirculation have a visible effect on the distribution of the total exergy entering the process to the total exergy of product, by-product and waste streams. Heat and process integration reduce considerably the
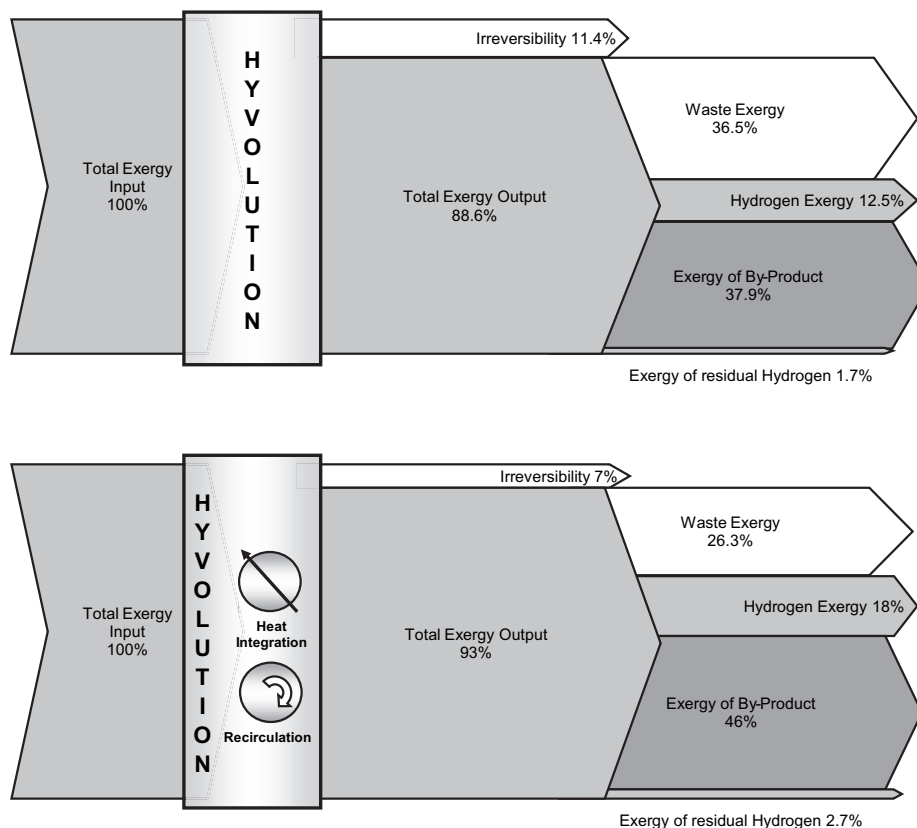
Fig. 7. Grassmann's diagram for feedstock PSP with and without heat integration and effluent recirculation (90% reduction of dilution water) for Engineering Case.
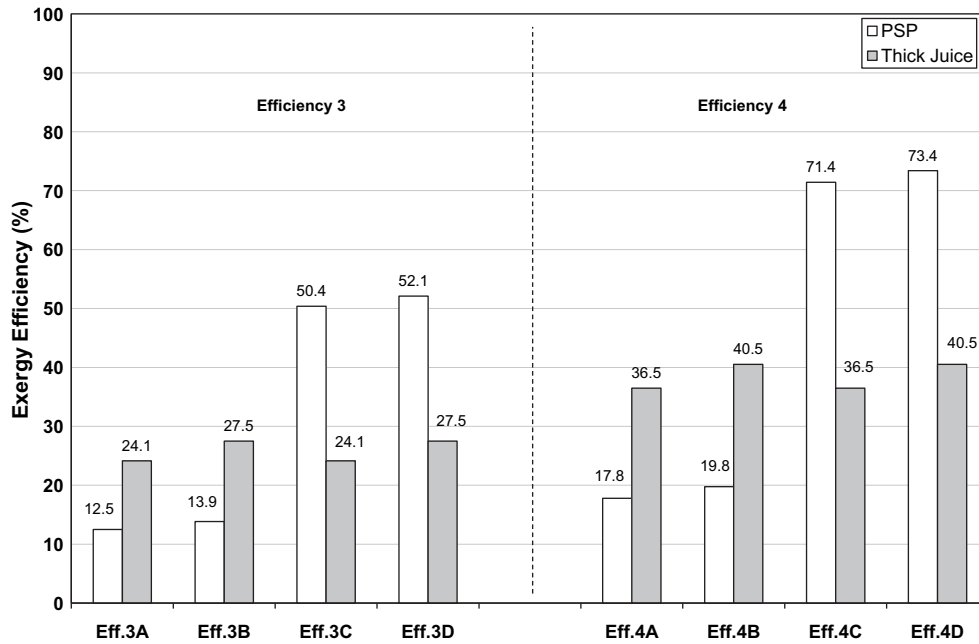
Fig. 8. Effect of residues and by-products on exergy efficiencies for Engineering Case (without heat integration).

relative irreversibilities in the process for PSP. Furthermore less exergy is lost as waste stream.

4.5. Impact of residues and by-products

Although introduction of heat integration and effluent recirculation reduces exergy losses in the process, a considerable part of the exergy of process input is found in by-products and not in the produced hydrogen.

Fig. 8 shows the results of a parametric study on product definition, representing the maximum possible improvement of exergy efficiency using off-streams and by-products in the process internally.

Efficiencies 3A ($\eta_{ex,3}$) and 4A ($\eta_{ex,4}$) refer to the product-gas (hydrogen, 97 vol%) as sole product of the process. Additionally to the product-gas, lost hydrogen in the tail-gas of adsorbers for gas-upgrading could be considered as a product by using the exergy content of hydrogen to provide process heat (efficiencies 3B and 4B). In the same way solid residues form pre-treatment of PSP could be used by combustion or via fermentation of biogas, represented by efficiencies 3C and 4C. Efficiencies 3D and 4D finally refer to the use of both, tail-gas as well as non-fermentables. Investigated options are summarized in Table 1.

Following the definition of efficiencies 3 and 4 – see Eqs. (14) and (15) - it has to be underlined that in the case of rational exergy efficiency (efficiency 3) the term product comprises the exergy of the whole product stream. For the product stream in HYVOLUTION process this includes chemical exergy of hydrogen as well as remaining traces of impurities (carbon dioxide and water vapour) and physical exergy according to the temperature and pressure of the stream. In the case of chemical exergy efficiency,

only chemical exergy of hydrogen in the product stream is used to calculate the efficiency by relating it to the chemical exergy of the feedstock put into the system.

While the use of hydrogen in tail-gas only gives a modest improvement of efficiencies (Fig. 8, Eff. 3B and Eff. 4B) for both feedstock options, the internal use of solid residues exiting from pre-treatment in case of feedstock PSP increases rational and chemical exergy efficiency of the process by more than double (Fig. 8, Eff. 3C and Eff. 4C), as a result of the low ratio of fermentable starch to non-fermentables in this feedstock option. Considering the low content of non-fermentables and the missing pre-treatment step for thick juice an improvement of exergy efficiency is not observed here. Nevertheless, for both feedstock options also the cell mass produced in both fermentors could be used to further increase the rational and chemical efficiency of the process. This option was not taken into consideration yet in the presented balances.

It has to be underlined that in all cases the presented values refer to the maximum obtainable exergy, not considering additional process steps necessary to access this exergy content as well as exergy losses probably caused by these additionally necessary process steps, which might influence efficiencies 3 and 4, but also efficiencies 1 and relative irreversibility.

Due to these selected constrains, efficiency 1 and relative irreversibility remain unchanged during the parametric study presented here.

5. Conclusions

Exergy analysis is not only applicable to high temperature processes, but also gives useful insights to fermentation processes, pointing out options for process improvement and optimization of feedstock use. However, presented data clearly show, that obtained results need a careful interpretation in view of different possible definitions of exergy efficiency. Whereas the recirculation of PHF effluent to the reactor inlets of both – PHF and THF – increases all considered exergy efficiencies, the reduction of acetic acid to hydrogen conversion in PHF – increasing feedstock and water demand – is only reflected by an increase of rational and chemical

Table 1
Investigated options of product definition representing the use of by-products.

Exergy efficiencies	Product(s)
Eff3A, Eff4A	Product-gas
Eff3B, Eff4B	Product-gas, tail-gas
Eff3C, Eff4C	Product-gas, non-fermentables
Eff3D, Eff4D	Product-gas, tail-gas, non-fermentables

exergy efficiency. Recirculation of effluents improves the rational exergy efficiency of the process based on feedstock thick juice from 24.2% to 41.3% and the chemical exergy efficiency from 36.5% to 44.3%.

Heat integration only slightly contributes to an improvement of exergy efficiency of the process. Depending on the reduction of the heat demand and the temperature level in the process, heat integration measures could even decrease exergy efficiency due to additional exergy losses caused by the introduced heat exchanger cycles. Nevertheless, process and heat integration reduce the relative irreversibilities of the HYVOLUTION process operated with PSP from 11.4% to 7.0%. Exergy leaving the process via waste streams decreases from 36.5% to 26.3% of total exergy input whereas after the introduction of the described integration options 18% of total exergy input to the process leaves the process in the form of produced hydrogen compared to 12.5% in the non-integrated case.

The study clearly shows, that depending on the feedstock, rational and chemical exergy efficiency could be considerably improved through the internal use of by-products for instance to provide process heat. In the case of PSP the use of solid residues from feedstock pre-treatment could raise rational and chemical exergy efficiency up to 54.1% and 73.4%, respectively.

However, exergy analysis only illuminates the thermodynamic efficiency of a process. Hence it has to be seen as an additional source of information besides mass and energy balances to evaluate and improve the process.

Acknowledgments

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6.2. PAPER II

Application of exergy balances for evaluation of process configurations for biological hydrogen production

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Application of exergy balances for evaluation of process configurations for biological hydrogen production

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ARTICLE INFO

ABSTRACT

Exergy analysis was applied to a novel process for biological production of hydrogen from biomass employing thermophilic and photo-heterotrophic bacteria. The exergy content of the process streams is calculated using a MS-Excel spreadsheet.

The scrutinized process incurs an exergy loss of 7–9% of the total exergy input. The efficiency based on chemical exergy of biomass feed and produced pure hydrogen refers to 36–45% depending on the configuration of the overall process. The results presented in the paper underline the strong dependence of obtained exergetic efficiency from definition of products and shows options for process improvement and optimization.

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1. Introduction

Hydrogen will be an important energy carrier in the future. Presently hydrogen is almost completely produced from fossil fuels or by electrolysis of water. To make the future hydrogen economy fully sustainable, renewable resources instead of fossil fuels have to be employed for hydrogen production. Besides biomass gasification, hydrogen from biomass can also be produced in a non-thermal way using bacteria.

During the last years, different anaerobic and photo-heterophic fermentation processes were investigated to produce biohydrogen. However, single stage processes currently do not work economically. A promising way for the production of hydrogen from biomass in a non-thermal way is a 2-stage bioprocess consisting of a thermophilic fermentation step followed by a photo-heterotrophic fermentation [1–4].

Most research currently is performed concerning the selection of microorganisms, optimization of yield and rate of hydrogen production as well as reactor design. Only a few studies are aiming at the design of the whole production process including feedstock pre-treatment and gas-upgrading as well as additional process steps to successfully combine both fermentation processes and remove hydrogen from the fermentation broth.

To obtain an economic and competitive overall process for the biological production of hydrogen from biomass, careful selection of upstream and downstream processes as well as optimal integration of all steps in terms of minimizing residual streams and heat demand is crucial. Besides mass and energy balance, exergy analysis will be applied to the novel process for non-thermal production of hydrogen from biomass as a selection criterion for the most efficient hydrogen production route.

2. Hyvolution process

The novel approach for the non-thermal hydrogen production from biomass in Hyvolution is based on a combined bioprocess employing thermophilic and photo-heterotrophic bacteria, to provide a high hydrogen production efficiency (see Fig. 1) [5].

The process starts with the necessary pre-treatment of biomass to provide a suitable feedstock for thermophilic fermentation (THF). Starch and sugar containing as well as lignocellulosic biomass will be considered as feedstock. The ultimate objective finally is the use of residues from agriculture and food processing (molasses, potato steam peelings, wheat bran, straw) for the production of biohydrogen. For a first evaluation of the overall process, a starch-based feedstock was selected, represented by wheat, due to the known pre-treatment procedure. For feedstock wheat, a dry matter content of 90% as well as a starch content of 70% based on dry matter was assumed. The pre-treatment of wheat is a conventional and proven liquefaction and saccharification process. The milled feedstock is first mixed with water to 35 wt.% solid mixture. α-amylase

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Nomenclature

|			
C	calorific value, kJ/kg	*Subscripts*	
Ex	molar exergy, kJ/mol	ash	ash
EX	exergy flow rate, kJ/s	bio	biomass
F	molar flow rate, mol/s	chem	chemical
I	irreversibility	ex	exergetic
HAc	acetic acid	feed	feedstock
HHV	higher heating value of biomass, kJ/kg	in	input
LHV	lower heating value of biomass, kJ/kg	mix	mixing
MEA	MEA (Mono-Ethanol-Amine)-absorption/desorption	out	output
PHF	photo-heterotrophic fermentation	phys	physical
PRE	pre-treatment	prod	product
THF	thermophilic fermentation	Q	heat
VSA	vacuum swing adsorption	S	sulphur
x	mole fraction	water	water
β	ratio of the chemical exergy to LHV	W	work
η	efficiency, loss		

is added and the mixture is heated to 105 °C with direct steam and kept at 95 °C for 2 h. Finally, the liquefied feedstock is fed to the saccharification reactor and mixed with gluco-amylase. A residence time of 72 h at 60 °C gives an overall conversion of starch in the pre-treatment of about 97%.

In the first fermentation step, thermophilic bacteria growing at temperatures of at least 70 °C produce hydrogen gas and organic acids as the main by-products. Depending on the fermentation pathway of the bacteria and built by-products, different amounts of hydrogen per mole of sugar are yielded. Assuming that glucose is the substrate and acetic acid is the main by-product, the thermophilic fermentation can be represented by the following reaction:

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 4H_2 + 2CO_2 \tag{1}$$
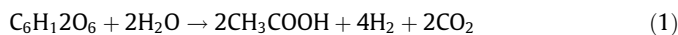
Experimental results in the thermophilic fermentation step requested a decrease of hydrogen partial pressure in the fermenter due to inhibitory effects. In case of glucose-based feedstock, a maximum hydrogen partial pressure of 20 kPa was identified giving optimum productivities and yields under the applied conditions [3,6]. To lower the hydrogen partial pressure in the thermophilic fermenter, it was suggested to apply gas-stripping. Since used thermophilic bacteria are very sensitive to oxygen, an inert gas has to be used. Nitrogen is not applicable since it can be hardly separated from hydrogen during gas-upgrading. Finally stripping with CO_2 was identified as a feasible option, since it is produced in the process and available after gas-upgrading. Produced acetic acid (HAc) can be used as substrate for hydrogen production in a consecutive photo-heterotrophic fermentation step (PHF). Based on acetic acid as substrate the reaction can be written as:

$$CH_3COOH + 2H_2O + light \rightarrow 4H_2 + 2CO_2 \tag{2}$$
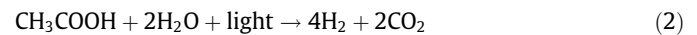
Through the combination of thermophilic fermentation with photo-heterotrophic fermentation, almost complete conversion of the substrate to hydrogen and carbon dioxide can be obtained, resulting in up to 75% conversion efficiency or 9 moles of hydrogen per mole of glucose [5,7]. Basic process data for the thermophilic and photo-heterotrophic fermentation step used for calculation of mass and heat balances are summarized in Table 1.

To provide pure hydrogen, finally carbon dioxide has to be separated from produced gas. Due to fluctuations in quantity and quality of the raw gas produced in the bioreactors, a specific gas treatment is required. In this paper, the industrial state-of-the-art systems adsorption (VSA, vacuum swing adsorption) and amine absorption/desorption (MEA) were chosen for gas-upgrading since they are well-documented processes with well-known performance. Finally, a novel membrane contactor will be evaluated and integrated in Hyvolution process. In lab scale experiments, this system demonstrated highly efficient carbon dioxide separation from gas mixtures of biological origin [8].

Investigation and optimization of the different process steps within the Hyvolution project is mainly based on experimental work. Focus is given to the selection of microorganisms and the optimization of process parameters of the different process steps to increase hydrogen yield and productivity as well as to decrease by-product formation. However, optimization of single steps might not give a satisfactory overall process. Therefore, process simulation is used to combine and integrate the single process steps
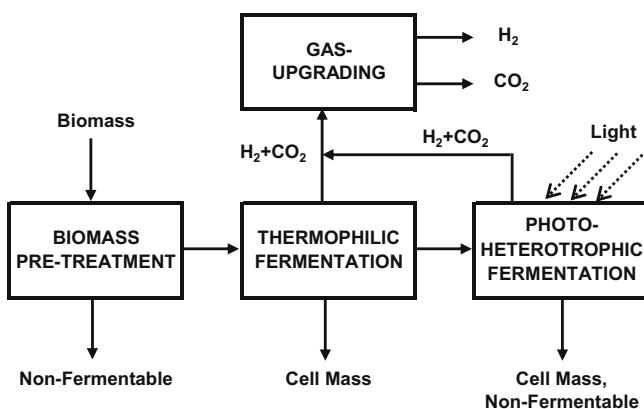
Fig. 1. Scheme of Hyvolution-process.

Table 1
Basic settings for pre-treatment, thermophilic fermentation (THF) and photo-heterotrophic fermentation (PHF) for feedstock wheat.

Plant capacity	60 kg/h Hydrogen
Feedstock	Wheat
Conversion starch	97% (wt)
Conversion substrate to hydrogen	80% (wt) per fermentation step
Conversion substrate to cell mass	15% (wt) per fermentation step
Substrate losses	5% (wt) per fermentation step
Temperature THF	70 °C
pH THF	6.5
Substrate concentration THF	50 g/l Glucose
Temperature PHF	30 °C
pH PHF	7.3
Substrate concentration PHF	100 mM Acetic acid

and finally select process routes by comparing the performance of different unit operations and design options. The commercial software package ASPENplus® was selected to predict the behaviour of Hyvolution process using basic mass balances, energy balances, phase and chemical equilibrium as well as reaction kinetics. Software package and simulation models, which are based on experimental data, are described in [9,10]. Mass and energy balances based on different substrate concentration in thermophilic and photo-heterotrophic fermenter are presented in [11] for starch based as well as lignocellulosic feedstock.

3. Exergy analysis

In general, exergy analysis is applied to identify the type, location and magnitude of thermal losses [12]. Exergy is calculated as the sum of three components – chemical exergy, physical exergy and the exergy change of mixing. The total exergy flow rate of a material stream at actual conditions can be obtained from

$$EX = F \cdot (Ex_{chem} + Ex_{phys} + \Delta Ex_{mix}). \tag{3}$$

Chemical exergy, physical exergy as well as exergy change of mixing are calculated following the procedure described in [13].

Chemical exergy of biomass (see Eq. (4)) can be estimated using lower heating values and data from elemental analysis [14,15]:

$$Ex_{chem,bio} = x_{bio} \cdot (\beta \cdot LHV_{bio}) + x_S \cdot (Ex_{chem,S} - C_S) + x_{water}$$
$$\cdot Ex_{chem,water} + x_{ash} \cdot Ex_{chem,ash}. \tag{4}$$

The factor β is the ratio of the chemical exergy to the lower heating value (LHV) of the organic fraction of biomass and C_S is the calorific value of sulphur. Higher heating values (HHV) of biomass can be accurately calculated by the correlation developed by Channiwala and Parikh [16]. For further details on calculation of chemical exergy of biomass see [13,17].

For real processes, the exergy input always exceeds the exergy output. This unbalance is caused by exergy losses due to irreversibilities:

$$\sum_{in} Ex_j + \sum_{in} (Ex_Q + Ex_W) = \sum_{out} Ex_k + \sum_{out} Ex_Q + I \tag{5}$$

Eq. (5) considers the exergy of all entering and leaving material streams, the sum of all thermal exergy and work interactions (Ex_Q and Ex_W) involved in a process as well as the irreversibility I of the system [18]. The exergy output usually consists of the exergy of product and waste streams leaving the system. Cornelissen [19] discusses three types of exergetic efficiency given in Eqs. (6a)–(6c). Simple exergetic efficiency expresses the ratio of exergy output (exergy of output streams) and exergy input (exergy of input streams). Eq. (6b) represents the exergy losses of the process. Rational exergetic efficiency (see Eq. (6c)) is initially defined by Kotas [20]. This efficiency is given by the ratio of exergy of product streams to the exergy input. Another possibility is to use the chemical exergetic efficiency, defined as the ratio between chemical exergy of product and chemical exergy of feedstock, presented in Eq. (6d).

$$\eta_{ex,1} = \frac{Ex_{out}}{Ex_{in}} \tag{6a}$$

$$\eta_{ex,2} = \frac{I}{Ex_{in}} \tag{6b}$$

$$\eta_{ex,3} = \frac{Ex_{prod}}{Ex_{in}} \tag{6c}$$

$$\eta_{ex,4} = \frac{Ex_{chem,prod}}{Ex_{chem,feed}} \tag{6d}$$

4. Mass and energy balances

Presented overall process balances are calculated for the production of 60 kg/h of pure hydrogen (99.7 vol.%) corresponding to approximately 2 MW of thermal power (based on lower heating value) without considering heat integration and recirculation of effluents within the process. The overall balances include the increased feedstock demand when applying VSA for gas upgrading due to hydrogen losses in the VSA-unit (25%). The following process options are investigated:

- Feedstock wheat, no stripping, MEA
- Feedstock wheat, CO_2-stripping, MEA
- Feedstock wheat, no stripping, VSA

Key data concerning overall mass and energy balances for selected process options are summarized in Table 2.

Besides biomass feed and water demand, cumulative heat demand and minimum heat demand as well as estimates for the demand of electric power are given. Minimum heat demand follows from the construction of hot and cold composite curve (Q-T-graph). "cell mass" and "non-fermentable" refers to biomass produced in the process in form of cell mass and remaining non-fermentable solids from feedstock, respectively. Production of heat and energy from residues, by-products as well hydrogen losses are not considered yet.

For further details on heat and mass balances see [11,21].

5. Exergy balances and exergetic efficiency

A MS-Excel spreadsheet has been developed to calculate in a fast and systematic way the exergy of compounds and streams of Hyvolution process. The calculation of necessary thermodynamic properties are based on integrated polynomial functions for the values of specific heat, entropy and enthalpy, using the same correlations as in the used process simulation tool, to ensure full compatibility with the solutions for mass and energy balance. For more details on exergy calculation see [13,17].

Fig. 2 shows the exergy balance of the process option without stripping and gas-upgrading by VSA obtained from the developed MS-Excel spreadsheet. It is important to consider the magnitude of exergy of the material streams involved in the process compared to the exergy of incoming and outgoing heat and work streams, resulting from the dominance of chemical exergy in the process.

5.1. Exergy of overall process

Fig. 3 shows the exergetic efficiency of the different process steps in terms of simple exergetic efficiency ($\eta_{ex,1}$), exergy losses also referred as irreversibilities ($\eta_{ex,2}$), rational exergetic efficiency ($\eta_{ex,3}$) and chemical exergetic efficiency ($\eta_{ex,4}$) according to Eqs. (6a)-(6d). Products in the calculation of rational exergetic efficiency as well as chemical exergetic efficiency include the purified hydrogen stream and pure hydrogen, respectively. In case of rational exergetic efficiency the term product comprises the exergy of the whole product stream (stream "hydrogen", see Fig. 2). This includes chemical exergy of hydrogen as well as remaining traces of impurities (CO_2 and water vapour), physical exergy and exergy change of mixing. In case of chemical exergetic efficiency, only chemical exergy of pure hydrogen is considered as usable product. A hydrogen content of 99.7 vol.% is assumed in the product stream.

The results show that the highest efficiency is achieved for the process option without stripping and applying gas-upgrading by MEA-absorption. Largest exergy losses occur in the process option applying CO_2-stripping, but are comparable to the option without

Table 2
Key data concerning overall mass- and energy-balances for selected process options.

	No stripping, VSA	No stripping, MEA	CO$_2$-stripping, MEA
Flow rate feedstock (kg/h)	1212	970	970
Flow rate water (kg/h)	70,000	56,000	56,000
Flow rate strip-gas (CO$_2$) (kg/h)	0	0	1710
Flow rate cell mass (kg/h)	103	82.5	82.5
Flow rate non-ferment (kg/h)	295	236	236
Concentration H$_2$ raw gas (mol/mol)	64.0	64.0	34.0
Electric power (kW)	210	70	120
Heat flow (kJ/s)	1430	1650	2570
Min. heat flow (kJ/s)	1230	1100	2200
H$_2$ losses (%)	25	0	0

stripping and gas-upgrading by VSA. Since exergy losses for the option with CO$_2$-stripping are higher compared to cases without stripping, alternative measures for the reduction of hydrogen par-

tial pressure in the thermophilic fermentation step are recommended from the exergetic point of view.

Compared to the process options with MEA-absorption, rational and chemical exergetic efficiency are considerably lower for cases applying VSA. Main reasons are the high hydrogen losses during regeneration of VSA and the connected higher feedstock demand to obtain 60 kg/h pure hydrogen. Results indicate that this process step needs improvement. Losses might be reduced by re-designing the process step and using inert gas instead of purified hydrogen for flushing during the regeneration of the adsorber. This will reduce, but not completely avoid hydrogen losses in this process step.

Exergy losses obtained for the investigated process options are between 7% and 9%. The efficiency based on chemical exergy of biomass feed (wheat) and produced pure hydrogen refers to 36–45% depending on the configuration of the overall process. The obtained results correspond with data [18] for anaerobic digestion of biomass to H$_2$ as well as to biogas production with 36% and 46%, respectively.

Exergetic efficiencies of further process options as well as of the different involved process steps are available from [17,21].
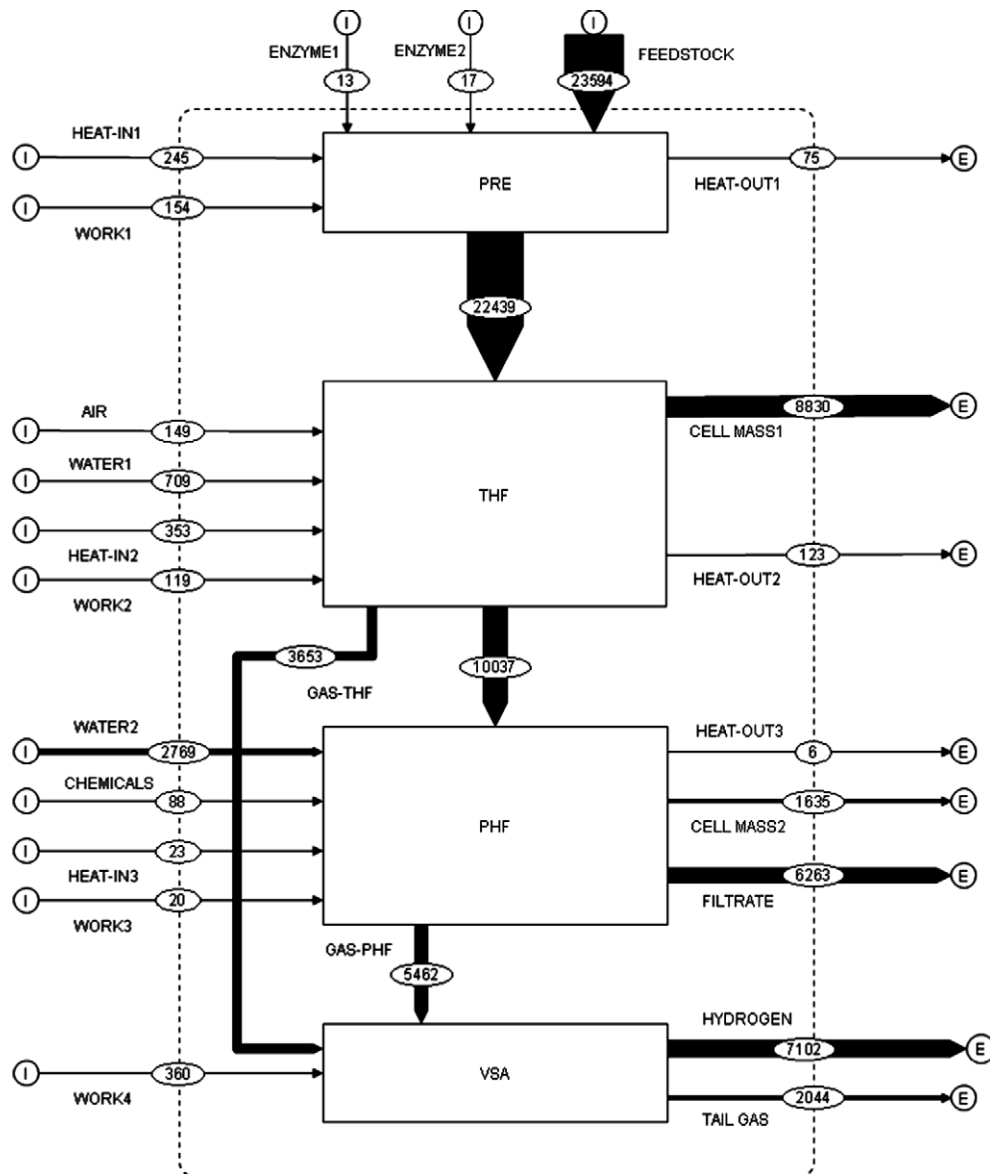
Fig. 2. Exergy balance of process option without stripping; gas-upgrading by VSA [MJ/h].
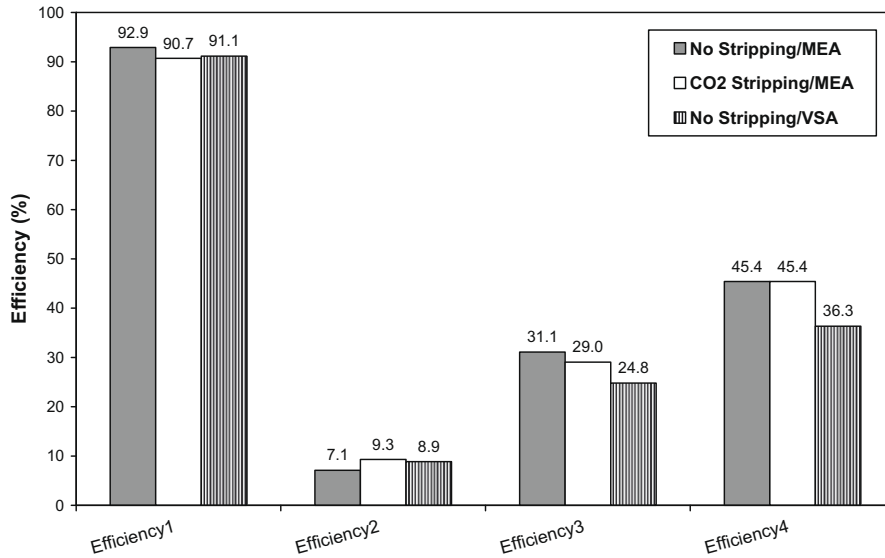
Fig. 3. Overall exergetic efficiency of investigated process options.

Differences in results compared to the actual paper are due to different definition of especially rational exergetic efficiency as well as the fact of slightly changed stream composition for the removal of cell mass from the process streams.

5.2. Parameter study on product definition

As seen in earlier work [11], obtained exergetic efficiency strongly depends on the definition of products. Figs. 4 and 5 present the results of a parameter study investigating the influence of definition of products on rational exergetic efficiency ($\eta_{ex,3}$) and chemical exergetic efficiency ($\eta_{ex,4}$), respectively. Results are used to find options for process improvement.

Case "H_2" describes the base case considering only pure hydrogen stream or pure hydrogen as product of the process as described above. Case "$H_2 + H_2(tail)$" describes an option where hydrogen in the tail gas of VSA step is used for example to produce heat and power by combustion. This case is only considered for chemical

exergetic efficiency ($\eta_{ex,4}$), since rational exergetic efficiency always considers the whole stream, including also the content of CO_2 (Case "$H_2 + H_2(tail) + CO_2$"). Considering the tail gas as a product increases rational exergetic efficiency of the process option applying VSA from 25% to 32% due to the high hydrogen content of the tail gas, while the slightly increase of efficiency of the process options with MEA-absorption is caused only by CO_2. Attention has to be given to the interpretation of the high chemical exergetic efficiency ($\eta_{ex,4}$) of the process options applying CO_2-stripping in Fig. 4. The high efficiency for cases considering CO_2 as a usable product only results from definition of $\eta_{ex,4}$, where all CO_2 leaving the process is considered as a product, but entering stripping gas is not included in the input term. As defined above (see Eq. (6d)), only chemical exergy of used feedstock is considered in the input term for calculation of this efficiency.

A significant increase of exergetic efficiency of the overall process can be achieved, when defining remaining biomass as usable product of the process. Exergetic efficiencies almost double as
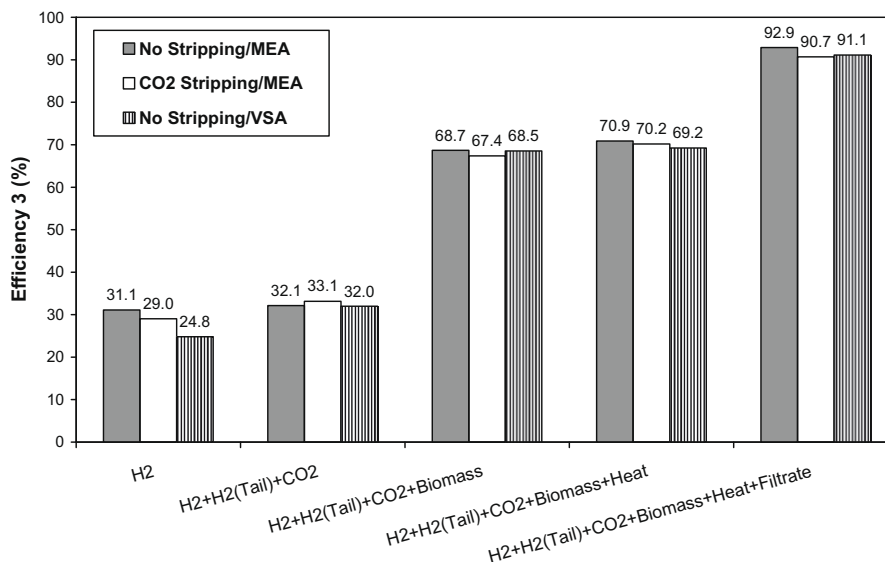
Fig. 4. Parameter study on product definition – rational exergetic efficiency (efficiency 3).
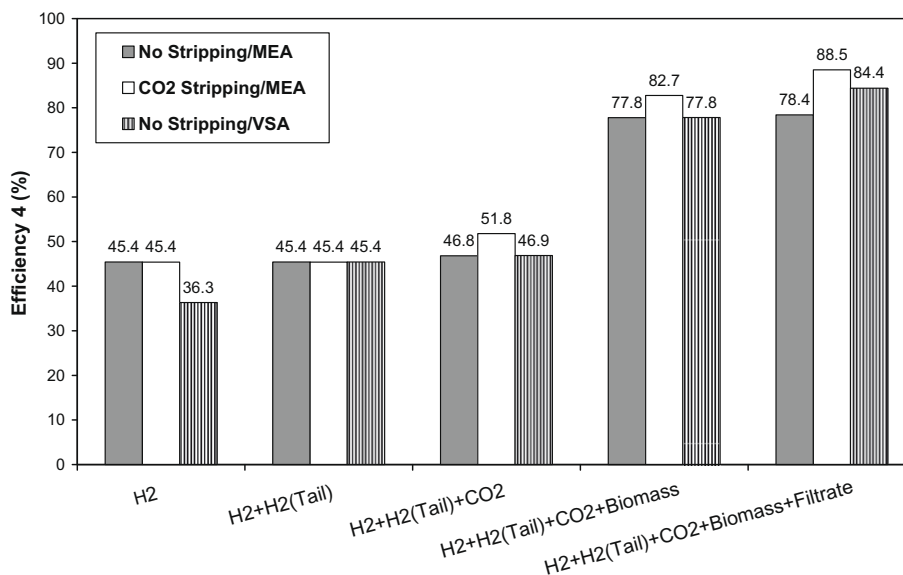
Fig. 5. Parameter study on product definition – chemical exergetic efficiency (efficiency 4).

follows from Figs. 4 and 5 Remaining biomass refers to biomass produced in the process in form of cell mass and non-fermentable solids from feedstock, respectively. Cell mass produced during fermentation might be re-introduced to the process as feedstock or source of nutrients or might be used to produce heat and power together with the non-fermentable fraction. A separate investigation was not possible, since so far a separation of non-fermentables after pre-treatment step is not foreseen in the process. Non-fermentables are removed after thermophilic fermentation together with the cell mass produced in this process step.

Introducing released heat to the portfolio of usable products shows that from the exergetic point of view the contribution of heat integration to the increase of exergetic efficiency of the process is negligible due to the strong impact of chemical exergy compared to physical exergy. Nevertheless, heat integration plays an important role from the point of view of energy demand and economic evaluation (see Table 2 as well as [11]).

A further increase of exergetic efficiency will result from the (re-) use of process effluents to replace tap water or the application of effluents as a liquid fertilizer in agriculture.

6. Conclusions

Exergy analysis was applied to a novel process for biological production of hydrogen. The exergy content of the process streams was calculated using a MS-Excel spreadsheet showing good agreement with literature.

The process scrutinized by the Hyvolution project incurs an exergy loss of 7–9% in reference to the total exergy input. A chemical exergetic efficiency of 36–45% was obtained without considering any heat and process integration.

A parameter study underlines the strong dependence of obtained exergetic efficiency from definition of obtained products and shows options for process improvement and optimization. Following the results, it is recommended to avoid hydrogen losses or to use the chemical exergy of hydrogen in the tail gas to produce heat and power for the process. Most important contribution to an increase of exergetic efficiency comes from (re-) use of produced cell mass and non-fermentables as well as effluent from process as feedstock or nutrient, for heat and power generation or fertilizer, respectively. From the exergetic point of view, the contri-

bution of heat integration to the increase of exergetic efficiency is negligible for the investigated low temperature process.

The calculated improvement of exergetic efficiencies only represents a theoretical maximum. Impact on exergy balance and exergetic efficiency has to be investigated in more detail considering also additional process steps necessary to implement the suggested process improvements.

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6.3.   PAPER III

Exergy analysis of biological hydrogen production

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Exergy analysis of biological hydrogen production

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Abstract

Exergy is defined as the maximum work obtainable while the system contacts with environment reversibly. Exergy analysis is a powerful approach for analysing both the quantity and the quality of energy. This concept identifies the system components with the highest thermodynamic inefficiency and the processes that cause them.

Exergy analysis was applied to a novel process for biological production of hydrogen from biomass in a combined bioprocess employing thermophilic and phototrophic bacteria. The exergy content of the process streams is calculated using MS-Excel program. Calculation of exergy incorporates chemical exergy, physical exergy and exergy of mixing. Special attention is given to the calculation of chemical exergy of biomass- and sugar components involved in the process.

Keywords: Exergy analysis; Biomass; Biological hydrogen production

1. Introduction

Since fossil fuels are estimated to last for only a few more decades at the current rate of consumption, a search for other sources of energy has become unavoidable. Hydrogen will be an important energy carrier in the future. At the moment hydrogen is almost completely produced from fossil fuels or from electrolysis of water. To make the future hydrogen economy fully sustainable, renewable resources have to be employed for hydrogen production. Besides biomass gasification, hydrogen from biomass can also be produced in a non-thermal way using bacteria. A promising way for the production of hydrogen from biomass in a non-thermal way seems to be a 2-stage bioprocess consisting of a thermophilic fermentation step to produce hydrogen, CO_2 and intermediates followed by a photo-heterotrophic fermentation, in which all intermediates will be converted to further hydrogen and CO_2.

Exergy analysis identifies the type, location and magnitude of thermal losses. Identification and quantification of these losses allows evaluation as well as improvement and optimisation of the hydrogen production process from the energetically point of view.

2. "Hyvolution"-process

The main aim of the Integrated Project "Hyvolution" is the development of a two-stage fermentation process for the economical production of hydrogen from biomass raw materials (Fig. 1). The process starts with the necessary pre-treatment of biomass to provide a suitable feedstock for thermophilic fermentation. In the first fermentation step thermophilic bacteria growing at temperatures of at least 70ºC produce hydrogen gas and organic acids as the main by-products. Depending on the fermentation pathway of the bacteria and built by-products different amounts of hydrogen per mole of sugar are yielded. Assuming that glucose is the substrate and acetic acid is the main by-product, the thermophilic fermentation can be represented by the following reaction:

$$C_6H_{12}O_6 + 2H_2O \rightarrow 4H_2 + 2CO_2 + 2C_2H_4O_2$$
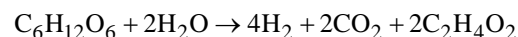
Produced acetic acid can be used as substrate for hydrogen production in a consecutive photo-fermentation step. Based on acetic acid as substrate the reaction can be written as:
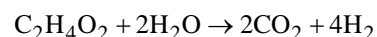
$$C_2H_4O_2 + 2H_2O \rightarrow 2CO_2 + 4H_2$$

Through the combination of thermophilic fermentation with photo-fermentation, complete conversion of the substrate to hydrogen and carbon dioxide can be obtained, resulting in 75% conversion efficiency or 9 moles of hydrogen per mole of glucose [1-4]. To provide pure hydrogen, carbon dioxide has to be separated from produced gas.
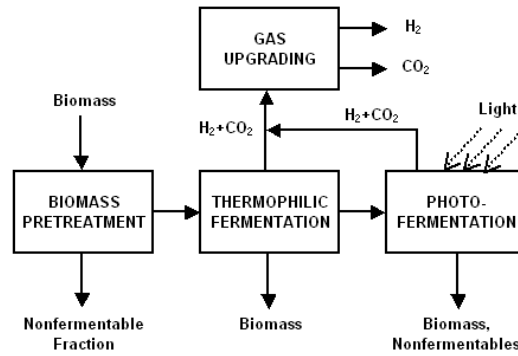
Figure 1: Scheme of "Hyvolution"-process

3. Calculation of exergy

The concept of exergy change, transfer and destruction can be used to develop an exergy balance similar to energy.

3.1. Exergy of conventional components

Exergy will be calculated as the sum of three components; chemical and physical exergy and the exergy change of mixing. The total exergy flow rate of a material stream at actual conditions can be obtained from Eq. (1):

$$EX = F(Ex_{chem} + Ex_{phys} + \Delta_{mix} Ex) \tag{1}$$

For real processes the exergy input always exceeds the exergy output. This unbalance is due to irreversibilities, also named exergy destruction and is represented by Eq. (2):

$$\sum_{IN} Ex_j + \sum_{IN} Ex_Q - Ex_W = \sum_{OUT} Ex_k + \sum_{OUT} Ex_Q + I \tag{2}$$

Eq. (2) considers the exergy flow of all entering and leaving material streams, the sum of all thermal exergy and work interactions (Ex_Q and Ex_W) involved in a process and the irreversibility I of the system [5]. The exergy output usually consists of the exergy of product and waste streams leaving the system. Exergy of waste streams represents exergy losses. Cornelissen [6] discusses three types of exergetic efficiency given in Eq. (3a-c). Simple exergetic efficiency expresses all exergy input as used exergy, and all exergy output as utilised exergy (Eq. (3a)). Rational efficiency, see Eq. (3b), is initially defined by Kotas [7]. This efficiency is given by the ratio of the desired exergy output to the exergy used. Other possibilities to represent the exergetic efficiency of a process are percent of exergy losses or the chemical exergetic efficiency, defined as the ratio between chemical exergy of product gas and biomass feed, presented in Eq. (3c) and Eq. (3d), respectively.

$$\eta_{ex,1} = \frac{Ex_{out}}{Ex_{in}}, \ \eta_{ex,2} = \frac{Ex_{pr}}{Ex_{in}}, \ \eta_{ex,3} = \frac{I}{Ex_{in}}, \ \eta_{ex,4} = \frac{Ex_{Chem,Gases}}{Ex_{Chem,Biomasses}} \tag{3a-d}$$

$Ex_{Chem,Gases}$ is the exergy of gases produced and $Ex_{Chem,Biomass}$ represents the exergy of biomass feeds consumed.

3.2. Exergy of biomass components

Chemical exergy of biomass can be estimated using lower heating values and data from elemental analysis [8, 9]:

$$Ex_{chem,bio} = x_{bio}(\beta.LHV_{Org}) + x_S(Ex_{chem,S} - C_S) + x_{water}Ex_{chem,water} + x_{ash}Ex_{chem,ash} \tag{4}$$

The factor β is the ratio of the chemical exergy to the lower heating value (LHV) of the organic fraction of biomass and C_S is the calorific value of sulphur. Higher heating values (HHV) of biomass can be accurately calculated by the correlation developed by Channiwala and Parikh [10]:

$$HHV_{Fuel} = 0.3491x_C + 1.1783x_H - 0.1034x_O - 0.0151x_N + 0.1005x_S - 0.0211x_{ash} \tag{5}$$

Where X_C, X_H, X_O, X_N, X_S and X_{ash} are the mass fractions of elements and ash (all in wt%) of dry material following from elemental analysis and HHV the heating value in MJ/kg. LHV is obtained from HHV considering enthalpy of evaporation of water formed during combustion.

Table 1 shows data from elemental analysis [11], LHV, the ratio β between the chemical exergy and LHV, and chemical exergy for selected biomasses, where Caldi and Rhodobacter (Rhodo-B) are bacteria used in the process.

Table 1: Chemical exergies and heating values of different type of biomass

Biomass	Beta	N	C	H	O	LHV (MJ/kg	HHV (MJ/kg)	Ex_{chem} (kJ/kg biomass)
Starch	1.15	0	6	10	5	17.52	17.68	20122
Glucose	1.17	0	6	12	6	14.23	16.30	16707
Enzyme	1.12	0.2	1	1.8	0.5	24.97	24.98	28046
Caldi	1.12	0.17	1	1.76	0.53	24.07	24.07	27049
Rhodo-B	1.11	0.14	1	1.76	0.38	28.26	28.26	31299

4. Results of exergy analysis and discussion

An Excel program has been developed to calculate in a fast and systematic way the exergy of compounds and streams of "Hyvolution"-process. Exergy analysis of biological hydrogen production has been performed for starch based feedstock at two different concentration of glucose (10g/l and 50g/l) for a plant size of 50 kg/hr produced hydrogen. Gas-upgrading unit was not included to the analysis. Furthermore no recycle streams as well as measures towards heat-integration are considered yet. Stream data are provided using process simulation [12]. The calculation of necessary thermodynamic properties are based on integrated polynomial functions for the values of specific heat, entropy and enthalpy, using the same correlations like in the simulation tool, to be fully compatible with the calculation of mass- and energy-balance. Table 2 summarises flow rate, temperature, pressure, and exergy flow rate, calculated for the process flow-sheet given in Fig. 2.
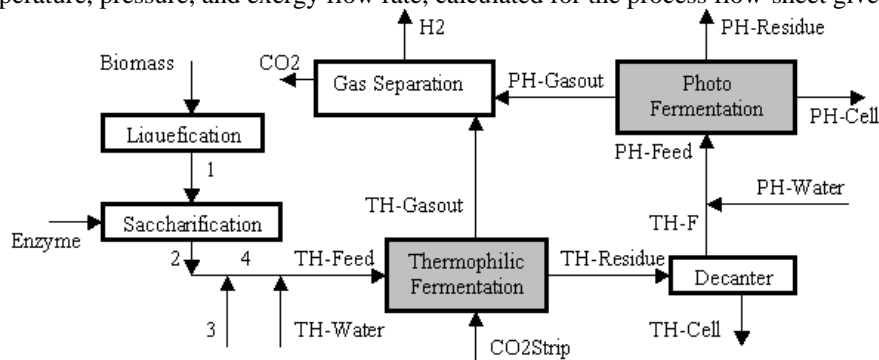
Figure 2: Flow-sheet of "Hyvolution" -process

Table 2: Flow rate, temperature and exergy flow rate of the main process streams (P = 1 bar)

Process stream	10g/l Glucose			50g/l Glucose		
	Flow rate (kg/hr)	T (°C)	Total exergy flow rate (MW)	Flow rate (kg/hr)	T (°C)	Total exergy flow rate (MW)
Biomass	1562	105.0	4.240	1562	105.0	4.240
PRE-ENZ2	3.9E-01	20	0.003	3.9E-01	20	0.003
TH-Water	9061	20	0.260	51668	20	1.488
TH-Feed	10841	25.2	4.146	53448	21.0	4.747
CO2Strip	1579	39.6	0.195	2318	39.6	0.286
TH-Gasout	1662	15	0.829	1657	15	0.827
TH-Residue	10793	70	3.287	54145	70	4.134
TH-Cell	577	64.6	0.371	2708	66.5	0.408
PH-Gasout	150	15	0.952	393	15	0.988
PH-Cell	388	30	1.034	388	30	1.034
PH-Residue	74334	30	1.953	74107	30	2.000
PH-Water	64656	20	0.912	23451	20	0.331
PH-Feed	74872	26.1	3.848	74888	52.4	4.033
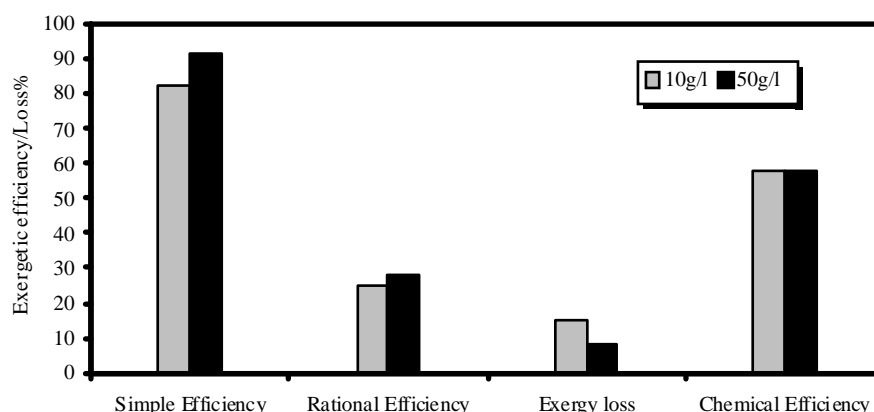
Figure 3: Exergy efficiencies of "Hyvolution"-process (without gas separation units)

Fig. 3 compares the different exergy efficiencies (see also Eq. (3a-d)) for processes using glucose concentrations of 10 g/l and 50 g/l in the feed of the thermophilic fermenter. Simple exergetic efficiency and rational efficiency increase with increasing concentration of glucose, while the total exergy losses (internal and external) decrease. During the process, the exergy contained in the biomass is converted into chemical and physical exergy of the product gas. Part of the exergy of biomass is lost due to process irreversibilities. The resulting exergetic efficiency based on chemical exergy at standard conditions is 57.6%. Calculation is based on a chemical exergy of the biomass feed and final gas products of 2.74 MW and 1.58 MW respectively. The rational exergetic efficiency at standard conditions is 28% and 25% (without recycle streams and heat-integration) for 50g/l glucose and 10g/l glucose respectively, what is calculated as the ratio between the exergy of useful process output and the exergy of the process input including biomass and utilities (process-steam, etc.).

In order to optimise "Hyvolution"-process from the exergetic point of view and to reduce the waste exergy occurring in the process, produced biomass (bacteria) should be considered as useful product and recycled back into process. Furthermore emphasis should be given to use a high glucose concentration in the feed.

5. Summary and Outlook

Exergy analysis was applied to a novel process for biological production of hydrogen. The exergy content of the process streams was calculated using MS-Excel program, incorporating chemical exergy, physical exergy and exergy of mixing with special attention to the calculation of chemical exergy of biomass- and sugar-components involved in the process.

For "Hyvolution"-process an exergy loss of 8-15% of the total exergy input depending on the process parameters was found. The efficiency based on chemical exergy refers to 57%, while for overall exergetic efficiency at standard conditions is 28% and 25% calculated for 50g/l glucose and 10g/l glucose respectively. The exergetic efficiencies of "Hyvolution"-process (without recycle streams and heat integration) are comparable to the anaerobic digestion of biomass to H_2 and biomass to biogas with 36% and 46% respectively [5].

The results of exergy analysis will be used to improve and optimise hydrogen production from the energetically point of view throughout the development of the process. To improve the accessibility of the exergy of the process streams, it is planned to implement the calculation of exergy in the used process simulation tool to provide the stream data. The calculation algorithm will also consider chemical exergy.

6. Acknowledgement

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Nomenclature

C_S	Calorific value of sulphur, kJ/kg
Ex	Molar exergy, kJ/mol
EX	Exergy flow rate, kW
F	Molar flow rate, mol/s
HHV	Higher heating values of biomass, kJ/kg
I	Irreversibility
LHV	Lower heating values of biomass, kJ/kg
P	Pressure, kPa
Q	Molar heat, kJ/mol
T	Temperature, °C
x	Mole fraction
X	Mass fraction
β	Ratio of the chemical exergy to the LHV of the organic fraction of biomass
η_{ex}	Exergy efficiency, exergy loss

Subscripts

chem	Chemical part
mix	Mixing part
phys	Physical part
Q	Heat part
W	Work part
ex	Exergy
in	Input
out	Output
pr	Product
waste	Waste

6.4. PAPER IV

Evaluation of process configurations for biological hydrogen production applying mass-, energy- and exergy-balances
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Proceedings of the 16th European Biomass Conference & Exhibition, Valencia, Spain,

2008, pp. 2178 – 2183

EVALUATION OF PROCESS CONFIGURATIONS FOR BIOLOGICAL HYDROGEN PRODUCTION APPLYING MASS-, ENERGY- AND EXERGY-BALANCES

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ABSTRACT: Process simulation was used to calculate overall mass- and energy-balances for single process steps and selected process options for the production of biohydrogen in a two stage fermentation process from feedstock wheat. Options with and without CO_2-stripping has been investigated applying different gas-upgrading processes. Besides mass- and energy-balance also the exergetic efficiencies of process steps as well as overall process options have been provided. Results show that it is strongly recommended to avoid applying CO_2-stripping for the reduction of hydrogen partial pressure in the thermophilic fermentation step, since even minimum heat demand of this process option exceeds the 2 MW of thermal power obtainable from the produced 60 kg/h of H_2. Obtained mass-, energy- and exergy balances will be used to further improve and optimize HYVOLUTION-process to finally obtain an economic and competitive overall process for the biological production of hydrogen from biomass.
Keywords: biological hydrogen production, biomass conversion, hydrogen

1 INTRODUCTION

Hydrogen will be an important energy carrier in the future. At the moment hydrogen is almost completely produced from fossil fuels or by electrolysis of water. To make the future hydrogen economy fully sustainable, renewable resources instead of fossil fuels have to be employed for hydrogen production. Besides biomass gasification, hydrogen from biomass can also be produced in a non-thermal way using bacteria.

During the last years different anaerobic and photo-fermentation processes were investigated to produce biohydrogen. But single stage processes at the moment do not work economically. A promising way for the production of hydrogen from biomass in a non-thermal way seems to be a 2-stage bioprocess consisting of a thermophilic fermentation step followed by a photo-heterotrophic fermentation.

Most research at the moment is performed concerning selection of micro-organisms, optimization of yield and rate of hydrogen production as well as reactor design.

Only a few studies are aiming at the design of the whole production process including feedstock pretreatment and gas upgrading as well as additional process steps to successfully combine both fermentation processes and remove hydrogen from the fermentation broth.

To obtain an economic and competitive overall process for the biological production of hydrogen from biomass, careful selection of upstream and downstream processes as well as optimal integration of all processes in terms of minimizing residual streams and heat demand is crucial. Besides mass- and energy-balance, exergy analysis will be applied to the novel process for the non-thermal production of hydrogen from biomass to provide the most efficient hydrogen production route.

In this paper, the application of mass-, energy- and exergy balances to improve and optimize the hydrogen production process will be shown.

2 HYVOLUTION PROCESS

The novel approach in HYVOLUTION for the non-thermal hydrogen production from biomass is based on a combined bioprocess employing thermophilic and phototrophic bacteria, to provide high hydrogen production efficiency (see Fig. 1).

The process starts with the necessary pretreatment of biomass to provide a suitable feedstock for thermophilic fermentation (THF). Starch and sugar containing as well as lignocellulosic biomass will be considered with a special focus on residues from food processing. In the first fermentation step thermophilic bacteria growing at temperatures of at least 70ºC produce hydrogen gas and organic acids as the main by-products.

Figure 1: Scheme of "Hyvolution"-process

Depending on the fermentation pathway of the bacteria and built by-products different amounts of hydrogen per mole of sugar are yielded. Assuming that glucose is the substrate and acetic acid is the main by-product, the thermophilic fermentation can be represented by the following reaction:

$$C_6H_{12}O_6 + 2H_2O \rightarrow 4H_2 + 2CO_2 + 2C_2H_4O_2$$

Produced acetic acid (HAc) can be used as substrate for hydrogen production in a consecutive photo-fermentation step (PHF). Based on acetic acid as substrate the reaction can be written as:

$$C_2H_4O_2 + 2H_2O \rightarrow 2CO_2 + 4H_2$$

Through the combination of thermophilic

fermentation with photo-fermentation, complete conversion of the substrate to hydrogen and carbon dioxide can be obtained, resulting in 75% conversion efficiency or 9 moles of hydrogen per mole of glucose [1-4].

To provide pure hydrogen, finally carbon dioxide has to be separated from produced gas. Due to fluctuations in quantity and quality of the raw gas produced in the bioreactors, a specific gas treatment is required. In this paper, the industrial state-of-the-art gas-upgrading systems gas adsorption (VSA, vacuum swing adsorption) and amine absorption/desorption (MEA) are considered. A novel membrane contactor will be evaluated and integrated in the HYVOLUTION process. In lab scale experiments this system demonstrated highly efficient carbon dioxide separation from gas mixtures of biological origin [5].

3 MASS- AND ENERGY-BALANCES

Investigation and optimization of the different process steps within HYVOLUTION project is mainly based on experimental work. Focus is given to the selection of micro-organisms and the optimization of process parameters of the different process steps to increase hydrogen yield and decrease by-product formation. But optimization of single steps might not give a satisfactory overall process. Therefore process simulation is used to combine and integrate the single process steps and finally select process routes by comparing the performance of different unit operations and design options. The commercial software package ASPENplus® was selected to predict the behavior of Hyvolution-process using basic mass balance, energy balance, phase and chemical equilibrium as well as reaction kinetics. Software package and simulation models, which are based on experimental data, are described in [6].

Table I: Basic settings for pretreatment, thermophilic fermentation (THF) and photo-fermentation (PHF)

Plant capacity [*]	60 kg/h Hydrogen
Feedstock	Wheat
Conversion starch	97 % (wt)
Conversion substrate to hydrogen	80 % (wt)
Conversion substrate to cell mass	15 % (wt)
Substrate losses	5 % (wt)
Temperature THF	70 °C
pH THF	6.5
Substrate concentration THF	50 g/l Glucose
Temperature PHF	30 °C
pH PHF	7.3
Substrate concentration PHF	100 mM Acetic Acid

[*] see also text

For a first evaluation of the overall process starch-based feedstock was selected, represented by wheat. The pretreatment of wheat is a conventional and proven liquefaction and saccharification process. The milled feedstock is first mixed with water to 35 wt% solid mixture. Alfa-amylase is added and the mixture is heated to 105°C with direct steam and kept at 95°C for 2 hours. Finally the liquefied feedstock is fed to the saccharification reactor and mixed with gluco-amylase. A residence time of 72 hours at 60°C gives an overall conversion of starch in the pretreatment of about 97%. Basic process data for thermophilic- and photo-fermentation step are summarized in Table I.

Substrate concentration of 50 g/l glucose and 100 mM acetic acid (HAc) at thermophilic- and photo-fermenter inlet, respectively, represent a feasible outlook based on latest project results.

Experimental results in the thermophilic fermentation step requested a decrease of hydrogen partial pressure in the fermenter due to inhibitory effects. In case of glucose based feedstock a maximum hydrogen partial pressure of 20 kPa was identified. To lower the hydrogen partial pressure in the thermophilic fermenter, it was suggested to apply gas-stripping. Since used thermophilic bacteria are very sensitive to oxygen, some inert gas has to be used. Nitrogen is not applicable since it can be hardly separated from hydrogen during gas-upgrading. Finally stripping with CO_2 was identified as a feasible option, since it is produced in the process and available after gas-upgrading.

For the first simulation of HYVOLUTION process vacuum swing adsorption (VSA) and MEA-absorption/desorption (MEA) were chosen for gas-upgrading since they are well documented processes with well known performance.

Presented overall process balances are calculated for the production of 60 kg/h of pure hydrogen (99,7 vol%) corresponding to approx. 2 MW of thermal power (based on lower heating value) considering hydrogen losses depending on used gas-upgrading method. When investigating feedstock pretreatment and fermentation steps, calculations assume the production of 60 kg/h of hydrogen in the raw product gas not considering possible losses during gas-upgrading for easier comparison. All results are based on calculations without heat integration and recirculation of effluents within the process.

Besides cumulative heat- and cooling- demand (summation of heat input/output of the different units) expressed as heat flow, also the minimum heating and cooling demand following from the construction of hot and cold composite curve (Q-T-graph) is presented. Minimum heating and cooling demand gives the best case concerning heat integration. It has to be considered that calculated minimum heat demand represents a theoretical value not including engineering as well economic considerations! A minimum temperature difference of 10°C is assumed for these data. Results for the following process options will be presented based on feedstock wheat:

- Pretreatment, THF (without stripping), PHF, VSA
- Pretreatment, THF (without stripping), PHF, MEA
- Pretreatment, THF (with CO_2-stripping), PHF, MEA

4 EXERGY-BALANCE/EXERGETIC EFFICIENY

Mass- and energy-balances are complemented by the exergetic efficiencies of the overall process as well as the different process steps. The exergy-balance of the process and the involved process steps is calculated using MS-Excel program. Special attention was given to the proper calculation of chemical exergy of biomass- and

sugar components involved in the process.

Exergy analysis identifies the type, location and magnitude of thermal losses. Identification and quantification of these losses allows evaluation as well as improvement and optimization of the hydrogen production process from the energetically point of view. Exergy is calculated as the sum of three components; chemical and physical exergy and the exergy change of mixing.

The total exergy flow rate of a material stream at actual conditions can be obtained from Eq. 1:

$$EX = F\left(Ex_{chem} + Ex_{phys} + \Delta_{mix}Ex\right) \qquad \text{(Eq. 1)}$$

Chemical exergy of biomass (Eq. 2) can be estimated using lower heating values and data from elemental analysis [7, 8]:

$$Ex_{chem,bio} = x_{bio}\left(\beta \cdot LHV_{bio}\right) + x_S\left(Ex_{chem,S} - C_S\right) + $$
$$+ x_{water}Ex_{chem,water} + x_{ash}Ex_{chem,ash} \qquad \text{(Eq. 2)}$$

The factor β is the ratio of the chemical exergy to the lower heating value (LHV) of the organic fraction of biomass and C_S is the calorific value of sulphur.
For real processes the exergy input always exceeds the exergy output. This unbalance is due to irreversibilities, also named exergy destruction and is represented by Eq. 3:

$$\sum_{in} Ex_j + \sum_{in} Ex_Q + Ex_W = \sum_{out} Ex_k + \sum_{out} Ex_Q + I \qquad \text{(Eq. 3)}$$

Eq. 3 considers the exergy of all entering and leaving material streams, the sum of all thermal exergy and work interactions (Ex_Q and Ex_W) involved in a process as well as the irreversibility I of the system [9]. The exergy output usually consists of the exergy of product and waste streams leaving the system. Cornelissen [10] discusses three types of exergetic efficiency given in Eq. 4a-c. Simple exergetic efficiency expresses the ration of exergy output (exergy of output streams) and exergy input (exergy of input streams). Eq. 4b represents the exergetic losses of the process. Rational efficiency (Eq. 4c) is initially defined by Kotas [11]. This efficiency is given by the ratio of exergy of product streams to the exergy input. Another possibility is to use the chemical exergetic efficiency, defined as the ratio between chemical exergy of product and chemical exergy of feedstock, presented in Eq. 4d.

$$\eta_{ex,1} = \frac{Ex_{out}}{Ex_{in}} \qquad \text{(Eq. 4a)}$$

$$\eta_{ex,2} = \frac{I}{Ex_{in}} \qquad \text{(Eq. 4b)}$$

$$\eta_{ex,3} = \frac{Ex_{prod}}{Ex_{in}} \qquad \text{(Eq. 4c)}$$

$$\eta_{ex,4} = \frac{Ex_{chem,prod}}{Ex_{chem,feed}} \qquad \text{(Eq. 4d)}$$

The calculation of necessary thermodynamic properties are based on integrated polynomial functions for the values of specific heat, entropy and enthalpy, using the same correlations like in the used process simulation tool, to be fully compatible with the calculation of mass- and energy-balance. For more details on exergy calculation see [12].

5   RESULTS

A total of 970 kg/h of wheat containing 610 kg/h starch has to be provided to obtain 60 kg/h of hydrogen in the raw product gas (without considering losses in gas-upgrading). Calculated cumulative heat flow for pretreatment equals 219 kJ/s. Pretreatment of wheat provides quite high sugar concentration (0.29 kg/kg) in the product stream of hydrolysis.

Figure 2 and 3 represent details to mass and energy balance for thermophilic fermentation (THF) and photo-fermentation (PHF) scaled to obtain 60 kg/h hydrogen in the raw gas after fermentation. Results are generated for feedstock wheat without CO_2-stripping to reduce hydrogen partial pressure in THF and without integration of both process steps in terms of energetic coupling or recirculation of effluents.
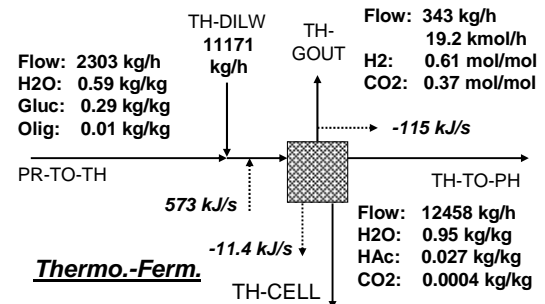
Figure 2: Simplified mass and energy balance for thermophilic fermenter (THF; wheat, 60 kg/h hydrogen in raw gas, 50 g/l glucose,100 mM HAc, without stripping)
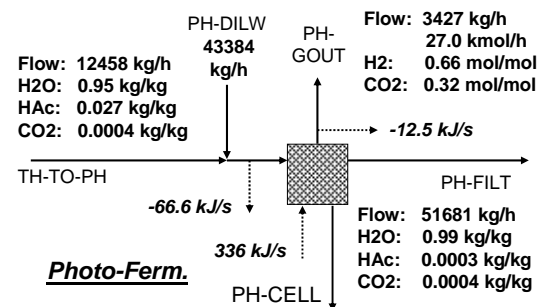
Figure 3: Simplified mass and energy balance for photo-fermenter (PHF; wheat, 60 kg/h hydrogen in raw gas, 50 g/l glucose, 100 mM HAc, without stripping)

Mass balances show a high water demand (54555 kg/h) for the fermentation steps since especially for PHF substrate concentration in the feed stream has to be very low following from experimental results. After the pretreatment step the substrate stream to the thermophilic fermenter (THF) has to be diluted from approx. 300 g/l to

50 g/l of sugars. Another dilution step is necessary for the substrate stream entering the photo-fermenter (PHF). Besides high reactor volumes this dilution strongly influences the energy balance of the system, resulting in a heat flow of 573 kJ/s for adjusting the fermentation temperature of 70°C in the THF.

Figure 4 shows the results of sensitivity studies concerning the effect of substrate concentration and preheating of process water for diluting THF-feed on process performance. Glucose concentration was varied from 10-200 g/l. Substrate concentration to PHF was kept constant at 100 mM HAc. From Figure 4 follows, that heat flow for preheating THF-feed can be decreased below 25 kJ/s. But it becomes also clear that without measures towards increase of HAc-concentration in PHF-feed total heat flow to operate fermentation steps will lie at approx. 500 kJ/s (without heat integration). On the other hand Figure 4 shows that the use of preheated (e.g. introduction of heat integration) dilution water contributes to the decrease of necessary heat flow for temperature adjustment of THF-feed. Instead of preheating dilution water, effluent from the PHF could be used for dilution purpose in the THF-step. Recirculation of reactor effluents and reusing effluent from PHF for substrate dilution in THF also reduces demand of fresh water. Nevertheless a challenge remains the reduction of fresh water demand in PHF.

When comparing mass balances of THF and PHF for cases with and without CO_2-stripping, differences are negligible except gas flow rate and product gas composition coming from THF, which changes due to the introduction of a strip-gas stream of approx. 1700 kg/h (39 kmol/h) CO_2 (see also Table II). Necessary heat flow for THF increases significantly from -11.4 kJ/s to +208/kJ/s for keeping temperature constant due to evaporation of water. At the same time recovered heat flow in the condenser after THF increases due to the higher product gas flow.

Figure 4: Results of sensitivity study on the influence of substrate concentration on necessary heat flow to adjust temperature in fermentation steps
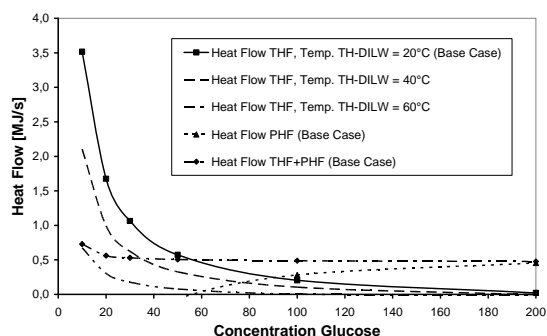
Table II: Composition and flow rate of raw product gas from thermophilic fermenter (THF) and photo-fermenter (PHF)

		Flow rate [kmol/h]	H_2-content [mol/mol]
No stripping	THF	19.2	0.62
	PHF	27.0	0.66
	THF+PHF	46.2	0.64
CO_2-stripping	THF	58.8	0.20
	PHF	27.1	0.66
	THF+PHF	85.9	0.34

Introduction of a CO_2-strip-gas-stream increases the raw gas flow rate to the gas-upgrading unit to approx. the double. Furthermore hydrogen concentration in the raw gas is lowered from approx. 64 vol% to approx. 34 vol% leading to conditions where VSA (vacuum swing adsorption) can not be employed any more. Additionally, fluctuations in gas flow rate, but mainly in gas-composition, over the day/night cycle complicate selecting and properly sizing/rating of the gas-upgrading equipment.
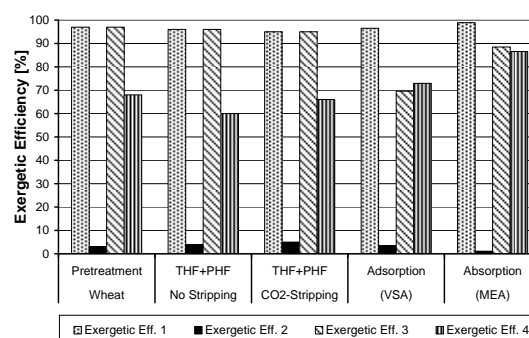
Figure 5: Exergetic efficiency of process steps

Fig. 5 shows the exergetic efficiency of the different process steps in terms of simple exergetic efficiency ($\eta_{ex,1}$), exergetic losses ($\eta_{ex,2}$), rational exergetic efficiency ($\eta_{ex,3}$) and chemical exergetic efficiency ($\eta_{ex,4}$). Products in the calculation of rational exergetic efficiency include product gas, substrates going to a downstream step, produced cell mass as well as non-fermentables. The term product comprises the whole product stream. Following this definition product gas of fermentation steps include both, produced hydrogen and carbon dioxide. This product definition is also the reason for the higher chemical exergetic efficiency for the combination of fermentation steps applying CO_2-stripping compared to the option without stripping. Important to consider is the high exergetic efficiency of MEA-absorption/desorption compared to VSA.

Table III: Key data concerning overall mass- and energy-balances for selected process options (Feedstock wheat, 50 g/l sugar in THF, 100 mM HAc in PHF)

		No-strip. VSA	No-strip. MEA	CO_2-strip. MEA
Feedstock	[kg/h]	1212	970	970
Water	[kg/h]	70000	56000	56000
Strip-gas (CO_2)	[kg/h]	0	0	1710
H_2 in raw gas	[mol/mol]	64.0	64.0	34.0
Heat flow	[kJ/s]	1430	1650	2570
Min. heat flow	[kJ/s]	1230	1100	2200
Electric power	[kW]	210	70	120
Cell mass	[kg/h]	103	82.5	82.5
Non-fermentable	[kg/h]	295	236	236
H_2 losses	[%]	25	0	0

Key data concerning mass- and energy-balance of the

investigated overall process routes are summarized in Table III. Results are based on the production of 60 kg/h of pure hydrogen without heat integration and recirculation of effluents within the process. The overall balances consider the increased feedstock demand when applying VSA for gas upgrading due to hydrogen losses in the VSA-unit (25%). Besides biomass feed and water demand, cumulative heat demand and minimum heat demand as well as estimates for the demand of electric power are given. "Cell Mass" and "Non-Fermentable" refers to biomass produced in the process in form of cell mass and non-fermentable solids from feedstock, respectively. Production of heat and energy from residues, by-products as well hydrogen losses are not considered yet!

Somewhat surprising is the fact that when looking at the minimum heat flow rate for the process option without CO_2-stripping. The option with MEA-absorption/desorption gives a lower value compared to the option applying VSA. In contrast to the data for the cumulative heat flow rate where it is the other way round. Different reasons can be identified to explain these finding. First of all for the VSA-option 25% more feedstock has to be used due to hydrogen losses during gas-upgrading, resulting in a higher heat flow. A decrease of hydrogen losses in VSA from 25% to 10% will change situation. Second reason are better (theoretical) options for heat integration when applying MEA-absorption/desorption. A detailed investigation from the engineering point of view is necessary to clarify whether all integration options included in the calculation of minimum heat flow are feasible.

From Table 3 it can further seen that for the option with CO_2-stripping even the minimum heat flow rate exceeds the approx. 2 MW thermal power being produced from the obtained 60 kg/h of pure hydrogen. Fig. 6 summarizes the exergetic efficiencies for the investigated process options.
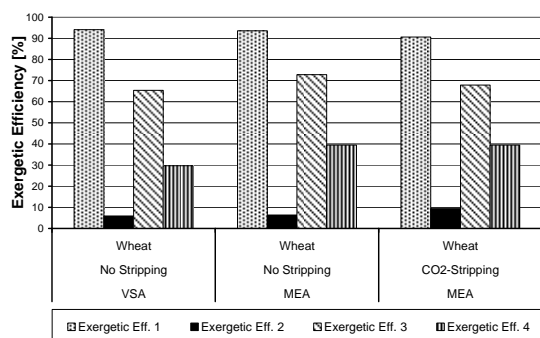
Figure 6: Overall exergetic efficiency of investigated process options

Simple exergetic efficiency and exergy losses of the process option without gas stripping are comparable. But rational as well as chemical exergetic efficiencies are higher applying MEA-absorption/desorption due to the high hydrogen losses during gas-upgrading using VSA. To produce the same amount of pure hydrogen more feedstock has to be used. While simple exergetic efficiency for process options with CO_2-stripping is the lowest, rational and chemical exergetic efficiency are higher than for case without stripping and using VSA for gas-upgrading.

Exergy losses of process options lie between 6 % and 9.5 % and include the low temperature of heat of the process steps. The efficiency based on chemical exergy of biomass feed (wheat) and produced pure hydrogen refers to 30-45% depending on the configuration of the overall process. The obtained results correspond with data [9] for anaerobic digestion of biomass to H2 as well as to biogas production with 36 % and 46%, respectively.

6 SUMMARY AND OUTLOOK

The paper summarizes simulation results of single process steps and selected process routes for the production of biohydrogen in a two stage fermentation process from feedstock wheat. Options with and without CO_2-stripping has been calculated applying different gas-upgrading processes. Besides mass- and energy-balance also the exergetic efficiency of process steps as well as overall process options have been provided. From the presented result follows that further investigation and improvement of the process is necessary to finally obtain an efficient overall process.

It is strongly recommended to avoid CO_2-stripping for reduction of hydrogen partial pressure in the thermophilic fermentation, since it decreases process performance.

Results of exergy analysis reflect the results of mass- and energy-balances, but also contribute with new insight. During interpretation the results of the exergetic analysis it has to be taken care to carefully consider the definition of used exergetic efficiencies. Furthermore it has to be clear, that for the investigated low temperature process chemical exergy exceeds the contribution of physical exergy to the overall exergy of the process streams by far.

During further simulation of the process measures towards process and heat integration will be considered. The first step comprises the recirculation/reuse of effluent streams of the different process steps to reduce water and heat demand. Attention has to be given to the concentration of fermentation products which build-up and might cause inhibitory effects. Additionally also formation and build-up of by-products will be considered. In a second step heat integration will be applied to the improved process.

7 ACKNOWLEDGEMENT

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9   NOMENCLATURE AND ABBREVIATIONS

C	Calorific value, kJ/kg
Ex	Molar exergy, kJ/mol
EX	Exergy flow rate, kJ/s
F	Molar flow rate, mol/s
I	Irreversibility
LHV	Lower heating values of biomass, kJ/kg
x	Mole fraction
β	Ratio of the chemical exergy to LHV
η	efficiency, loss

Subscripts

ash	Ash
bio	Biomass
$chem$	Chemical
ex	Exergetic
in	Input
mix	Mixing
out	Output
$phys$	Physical
$prod$	Product
Q	Heat
S	Sulphur
W	Work

Abbreviations

HAc	Acetic acid
MEA	MEA (Mono-Ethanol-Amine)-absorption/desorption
PHF	Photo-fermentation
THF	Thermophilic fermentation
VSA	Vacuum swing adsorption

6.5. PAPER V

Pinch and exergy analysis of lignocellulosic ethanol, biomethane, heat and power production from straw

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Pinch and exergy analysis of lignocellulosic ethanol, biomethane, heat and power production from straw

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ABSTRACT

In this work a complex process for production of bioethanol, biomethane, heat and power from the wheat straw is introduced and analyzed with regard to pinch and exergy analysis. The pinch analysis is focused on the bioethanol production where a well-designed heat exchanger network increases heat integration up to 45 MW. To obtain optimal total site external hot and cold utilities demands at different temperature levels as well as maximum power generated by steam turbine, an integrated steam cycle composite curve has been added to the grand composite curve of the "background process". The exergy analysis takes into account three production sections separately and exergy efficiencies are calculated to find the quantity of irreversibilities the bioethanol processes. The results from exergy analysis show that the bioethanol process has the highest exergy efficiency because of usage of stillage for other processes in which a considerable part of exergy entering is converted into irreversibility because of heat losses and non reacting unknown material produced as material losses.

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1. Introduction

In the past few years, the use of biomass for biofuel production is increased because of increasing energy demand and avoiding the global warming and greenhouse gas emissions (GHG) caused by fossil fuel consumption [1]. Bioethanol as the major biofuel used in transportation and as a clean and sustainable resource compared to the fossil fuels, is produced by simultaneous enzymatic saccharification and fermentation (SSF) process where fermentable sugars extracted from different feedstock are enzymatically saccharified, fermented and converted to ethanol. Some studies have shown that greenhouse gas emissions released through bioethanol production from starchy crops are high compared to production from lignocellulosic materials such as straw [2]. In this study, a complex process producing bioethanol, biomethane as well as combined heat and power (CHP) from straw is analyzed from energy and exergy point of view. Main by-products generated during the bioethanol process are fed into other sub-processes as feedstock. Pfeffer et al. [19] performed an energy analysis of a polygeneration process in which bioethanol, biogas, heat (steam) and power are produced from wheat and residues of bioethanol production process to decrease external energy demand. Macedo

et al. [3] studied that during bioethanol production from sugarcane, need of fossil fuel consumed to supply required process energy is much lower compared to corn as feedstock. One of the challenges during bioethanol processing is the reduction of utility demands by means of process heat integration [4]. Morandin et al. [21] suggested some heat integration improvements to a combined sugar and biofuel production process coupled with a CHP system fueled with bagasse as well as multi effect evaporation unit by means of integrated composite curve of steam cycle in which different CHP system configurations are investigated. Besides mass and energy balance exergy analysis can be applied to identify, exergy dissipations (irreversibilities) from exergy saving point of view. A few investigations on bioethanol production process combined with CHP system have previously been published from energy and exergy point of view. Most of the recent studies have been focused on the pinch or exergy analysis and have not considered the both of them. Ojeda et al. [5] have applied energy and exergy analysis with heat integration approach which suggest some process improvements resulting in minimization of residual waste streams and a new heat exchanger network. Tovazhnyansky et al. [26] applied pinch technique to conserve energy in the sodium hypophosphite production plant and investigated influence of energy and equipment (heat exchanger) cost on minimum temperature difference to obtain well-designed cost-effective heat exchanger network according to the optimum minimum temperature difference.

2. Process description

In Fig. 1 the combined production of ethanol, biomethane, heat and power from straw is schematically illustrated. A more detailed description can be found in Lassmann et al. [6]. According to the main products, the total process can be divided in three sections as following:

2.1. Bioethanol production process

Before the steam explosion unit, straw with 90% dry matter (DM) content is reduced in size, moistened to reach 35% DM content and then preheated. Steam explosion takes place at 190 °C after addition of 1% (wt/wt) SO_2 based on DM. Secondary steam recovered at two pressures levels can be used to heat other parts of
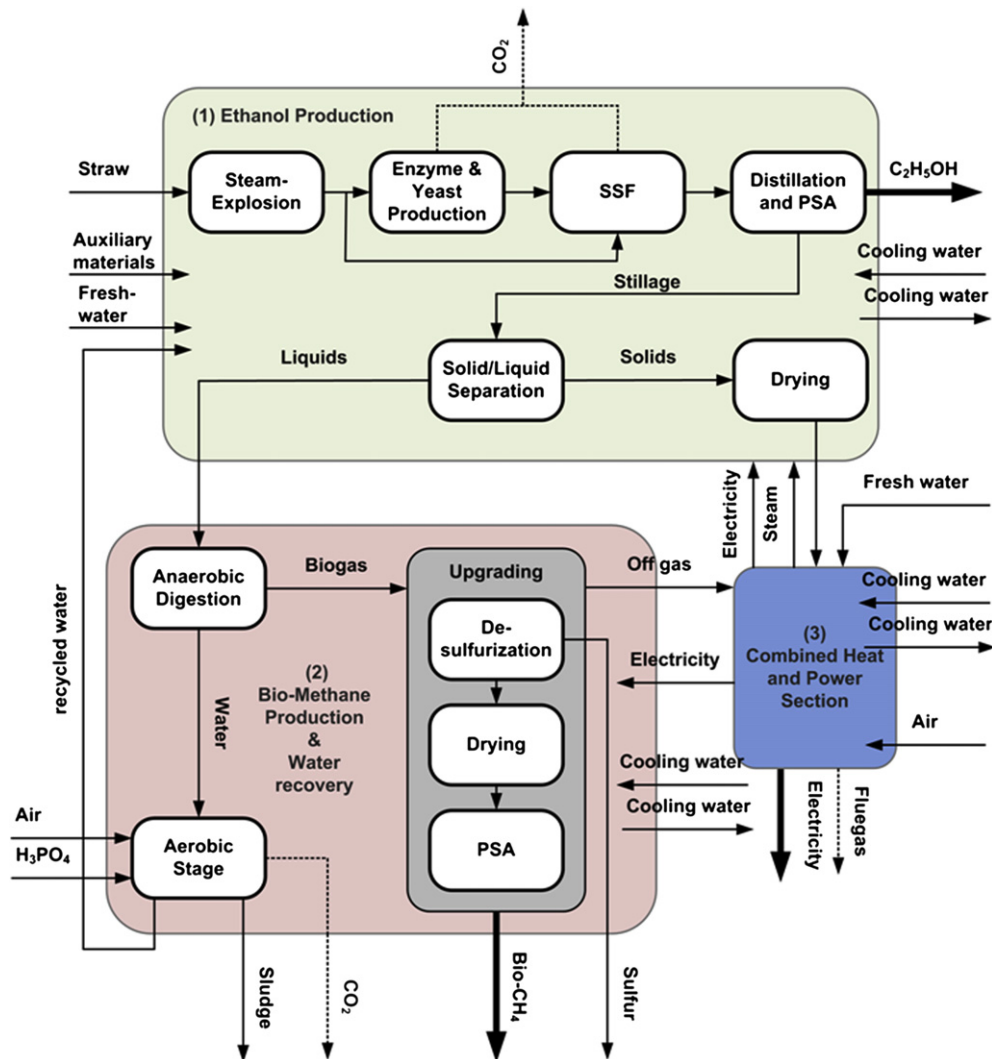

Fig. 1. Combined production of ethanol, biomethane, heat and power from straw.

the process [7]. Thereafter it is sent to the biomethane section. In steam explosion, 80% of hemicelluloses sugars are released as monomers, 15% are degraded. For cellulose 10% of sugars are released as monomers and 2% degraded. Heat losses are assumed to be 10% of total heat transferred.

The slurry leaving steam pretreatment is neutralized using aqueous NH_3, cooled and split into three streams. Minor parts are used to produce enzymes and yeast, whereas the major fraction is directly sent to simultaneous saccharification and fermentation (SSF). For yeast propagation, the low C_6 sugar content of pretreated straw should be increased. Hence beet molasses are added to reach approximately equal amounts of C_6 sugars from straw and molasses. 60% of C_6 sugars fed into yeast propagation are converted to yeast and 35% are converted to CO_2 and H_2O, corresponding to a biomass/sugar yield of approximately 0.5 kg/kg. In contrast to yeast, enzyme producing microorganism "*Trichoderma reesei*" can also utilize C_5 sugars, hemicelluloses and cellulose. We assumed that 50% of carbohydrates are converted to CO_2 and H_2O, 35% are converted to enzyme and 10% are converted to biomass, corresponding to an enzyme/sugar yield of 0.28 kg/kg. SSF is performed for 72 h at 37 °C and 12% (wt/wt) water insoluble solids (WIS). Cellulose to C_6 conversion and C_6 to ethanol conversion are both set with 92%, yielding a final ethanol concentration of approximately 4% (wt/wt). In this context it must be noted, that all CO_2 released from the bioreactors originates from straw and is thus climate neutral. The beer from SSF is sent to distillation for recovery of ethanol. As suggested by Sassner [7], distillation is performed in two parallel stripper columns and one rectifier column. For heat integration purposes, the columns are operated at different pressures. Mass flows and reflux ratios are chosen in a way, which guarantees optimal heat recovery. Hence, heat only has to be supplied at the reboiler of the high pressure stripper column and removed at the condenser of the vacuum rectifier column. The head product from the rectifier is compressed, superheated and sent to pressure swing adsorption (PSA), where a 99.5% (wt/wt) ethanol product is obtained. 25% of that product are used for regeneration of the loaded bed and thereafter returned to the rectifier. The remaining product is condensed and cooled and ready for use as a fuel. Ethanol containing vapors from SSF and ethanol condensation are sent to the scrubbing system. In accordance with emission standards for volatile organic carbon final ethanol concentration in the vapors leaving the scrubber are set to reach 100 mg C/N m³. The stillage leaving distillation contains mainly water but also large amounts of insoluble and soluble solids. In order to be economically viable and ecologically friendly, by-products and process heat should be obtained from the stillage. Therefore insoluble solids are separated from soluble solids and water. For the solid fraction a DM content of 50% and a recovery of 99% for insoluble solids are assumed. Drying of the solids to 90% DM can be performed using a superheated steam dryer operating at 4 bar Sassner [7]. The dried solids containing mainly lignin are incinerated in the CHP section. Secondary steam obtained in the dryer is used for process heating purposes and thereafter sent to the biomethane section, as well as the liquid fraction obtained in the solid–liquid separation step.

2.2. Biomethane production and recovery of process water

The liquid fraction of the stillage as well as condensed vapors from steam explosion and drying are cooled and thereafter sent to an anaerobic digestor (AD). Here organic substances are converted to biogas containing mainly CH_4 and CO_2 but also H_2S. Moreover anaerobic sludge is formed. We assumed that 75% and 15% of the chemical oxygen demand (COD) are converted to biogas and sludge, respectively. The remaining 10% leaves AD together with the waste water. For modeling biogas production we applied a modified version of the Buswell equation [8], which takes formation of H_2S into account.

In order to obtain biomethane the raw biogas is desulfurized, dried and upgraded using PSA. Due to the very low H_2S concentrations allowed in the PSA more than 99% of H_2S have to be removed in the desulfurization step. Sulfur removal is performed using a biological system, in which absorption of H_2S in water and biological oxidation to sulfur occur spatially separated [9]. Thus, no oxygen is added to the desulfurized biogas. For removal of water and other condensable compounds, the biogas is compressed and cooled. Thereafter CO_2 is separated from CH_4 using PSA. It is assumed, that 3% of CH_4 are lost in the off gas, which is combusted together with insoluble solids in the CHP section. The product gas contains 98% (vol/vol) of methane and can be injected to the natural gas grid or used to supply a filling station for natural gas vehicles.

The waste water from AD is sent to an aerobic water treatment (AWT) stage, where the remaining 10% of COD fed into AD are converted to CO_2, water and aerobic sludge. Addition of H_3PO_4 is necessary to meet the phosphorus demand of the aerobic microorganisms. Water leaving the AWT can be recycled to the process unrestrictedly. Sludge produced in AD and AWT is concentrated mechanically (thickened) and can be recycled to farming land to replace mineral fertilizer or incinerated.

In this work, climate relevant emissions during biogas production and upgrading are not considered.

2.3. Combined heat and power (CHP) section

The dried solids and off gas from biogas upgrading are combusted at 820 °C. CO_2 emissions formed during combustion can be considered climate neutral, since they originate from biomass. In this study complete conversion to CO_2, H_2O and N_2 is assumed. However, in a complete LCA study based on simulations from this work [23], typical CH_4 and N_2O emissions of biomass combustion systems are considered. The hot flue gases are used to generate primary steam at 650 °C and 65 bar. Part of the flue gas leaving the boiler is recycled to combustion to keep the temperature low. The excess amount leaves the system at 120 °C. Steam generated in the boiler drives a condensing turbine with 2 extraction ports. Electricity is produced and steam required for the process is extracted at 20 and 4 bar. Steam, which is not extracted for process needs, is condensed at 50 °C using cooling water. Isentropic and mechanical efficiency of the turbine are set to 87 and 97%. Electrical and mechanical efficiency of the generator are both set to 97%. The electricity generated in the CHP section is used to power other sections of the process. Excess electricity leaves the system as a product and can be sold to the grid. Residual ash from the CHP section can be returned to farming land to replace mineral fertilizer.

3. Process simulation

Flowsheet simulations were carried out using the steady state simulation software IPSEpro. A library containing the necessary unit operations and capable of handling the complex materials was constructed by Schausberger et al. [10] and is improved and augmented continuously.

Operating time was set at 8000 h/y for ethanol plant capacity of 100,000 t/y. Annual amounts of biomethane and electricity produced were evaluated from mass balances and modeling assumptions.

4. Exergy analysis and exergy efficiencies

Exergy analysis is able as an appropriate thermodynamic technique based on the second law to identify the location, quality and

quantity of thermal and material losses in chemical and thermal processes as shown by Szargut et al. [11] and as recently discussed in more detail for different chemical process concepts by Asprion [25]. The exergy of a material streams, heat flow and work flow can be calculated according to the procedure introduced by Hinderink et al. [12]. Chemical exergy of fuels can be calculated by means of Szargut's correlation [11]. In almost the same manner chemical exergy of biomass is calculated using lower heating value (LHV) and mass fraction of substances in the biomass presented by Ptasinski et al. [13]. Modarresi et al. [14,18] applied exergy analysis to the novel process for the fermentative production of hydrogen (Hyvolution) consisting of a photo fermentor followed by a thermophilic fermentor operated at 70 °C. The result pointed out that some process improvements can be achieved by recirculation of fermentor effluents and internal use of by-products to provide process heat. Moreover, exergy efficiency was increased through the use of solid residues from pretreatment of potato steam peels feedstock. To calculate the chemical exergy of streams of the "Hyvolution" process, a chemical exergy database for biomass components was developed. In this study, because of different material streams and types of feedstock compared to the hyvolution process, specific chemical exergy of the new biomass components has been evaluated. In contrast to "Hyvolution" process, some units of the bioethanol plant are operated at high temperature which affects physical exergy of material streams.

4.1. Mathematica-based exergy calculator

A program based on Mathematica (V7.01.0) has been developed to calculate the exergy of compounds and material streams of the process in an automatic way. First, the required data for analysis is extracted from software simulator IPSEpro and is entered into exergy tool in which a large chemical exergy databank prepared as Excel file is used to calculate the chemical exergy of streams whereas thermal properties correlations for calculation of physical exergy can be easily collected from simulator databank. The procedure is able to calculate the different exergy efficiencies with regard to production processes. The algorithm approach for exergy calculation is shown in Fig. 2.

4.2. Exergy efficiencies

Two definitions of exergy efficiency introduced by Cornelissen [15] were calculated. Simple exergy efficiency, Eq. (1), expresses the ratio of total exergy leaving the system and total exergy entering the system boundaries. Rational exergy efficiency, Eq. (2), presents the ratio of exergy content of useful products to the total exergy input. In this work, exergy efficiencies were used to show impact of by-products and irreversibilities, Eq. (3), on the process improvement.

$$\eta_1 = \text{Ex}_{\text{Out}}/\text{Ex}_{\text{In}} \tag{1}$$

$$\eta_2 = \text{Ex}_{\text{Product(s)}}/\text{Ex}_{\text{In}} \tag{2}$$

$$\eta_3 = 1 - \eta_1 \tag{3}$$

5. Pinch analysis

Pinch analysis introduced originally by Linnhoff et al. [17] is a thermodynamic technique based on the so-called grand composite curve (GCC) and composite curves (CC) to determine the minimum hot and cold utilities demand when maximum heat integration is reached. The major objective of pinch analysis is the identification of utility and heat exchanger network capital cost targets. Hence heat exchanger network satisfying these targets is synthesized and then optimized to achieve minimum total annual cost.

The data of thermal process streams which don't have changes in composition and should be heated up (cold streams) or cooled down (hot streams), can be extracted and tabulated as a set of streams with their supply and target temperatures as well as their heat contents obtained from mass flows and specific enthalpy data according to the guideline presented by Kemp [20]. As a brief explanation of pinch analysis technique, each thermal process stream is plotted by a line on the temperature−heat content diagram in which slope of the line is equal to the heat content
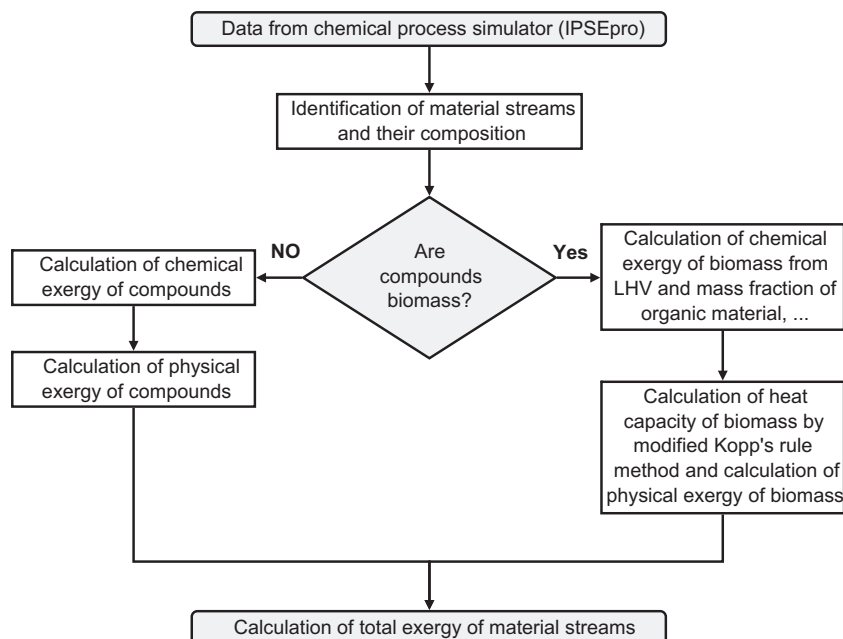
Fig. 2. Structure of algorithm approach used for calculation of exergy of process streams [14,18].
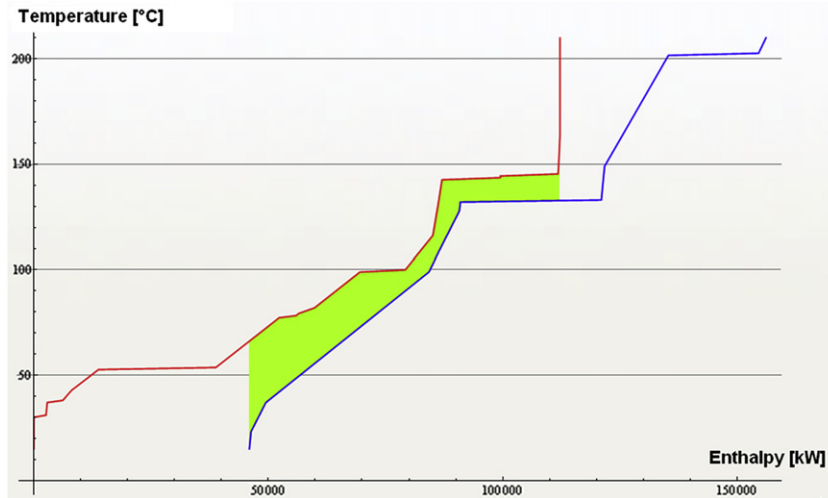
Fig. 3. Composite curves for combined bioethanol and biomethane production process (minimum temperature approach of 10 °C).

divided by temperature difference. The hot composite curve (shown as the red line in Fig. 3) is constructed by adding enthalpy changes of hot process streams according to temperature intervals. The cold composite curve involving cold process streams (shown as the blue line in Fig. 3) is similarly constructed. After CC construction, hot composite curve is shifted to the right until where minimum temperature difference between hot and cold composite

curve is reached. This point of shortest distance between two curves is known as "pinch point". For more details about construction of composite curves and grand composite curve as well as HEN synthesis see [22]. Furthermore, maximum heat integration, minimum hot and cold utility demand can be read off from CCs. After these steps, a heat exchanger network based on the results from pinch analysis has to be designed to increase process

Table 1
Process streams of bioethanol, biomethane process and CHP system.

Cold streams	Stream part	T_{in} [°C]	T_{out} [°C]	Heat [kW]
Bioethanol production				
Preheat straw for SE	Preheat straw for SE	23.15	99.00	14,088
Generate Steam for SE	Heat water for SE	15.00	201.70	8489
	Evaporate water for SE	201.70	202.70	19,023
Preheat mash for distillation	Heat mash for distillation to 99 °C	37.00	99.00	20,624
Preheat mash for distillation stripper 3 bar	Heat mash for distillation to130 °C	99.00	127.80	5064
Heat distillation stripper 3 bar	Heat bottom stripper 3 bar	132.00	133.00	30,022
Superheat steam to PSA	Superheat steam to PSA	108.00	130.00	192
Superheat drying steam	Superheat drying steam	149.00	210.00	13,100

Hot streams	Stream part	T_{in} [°C]	T_{out} [°C]	Heat [kW]
Bioethanol production				
Condense and cool steam from SE 4 bar	Condense SE 4 bar steam	143.60	142.60	12,350
	Cool SE 4 bar steam	143.60	37.00	2601
Condense and cool steam from SE 1 bar	Condense SE 1 Bar steam	99.96	98.96	9301
	Cool SE 1 bar steam	98.96	37.00	1083
Cool pretreated biomass	Cool pretreated biomass	99.00	42.80	10,704
Cool reactor yeast production	Cool reactor yeast production	31.00	30.00	1598
Cool reactor enzyme production	Cool reactor enzyme production	31.00	30.00	957
Cool reactor SSF	Cool reactor SSF	38.00	37.00	2913
Condense head product rectification	Condense head rectifier	53.65	52.65	24,476
Condense and cool ethanol product	Cool EtOH product	130.00	78.30	303
	Condense EtOH product	78.30	77.30	3027
	Cool EtOH product	78.30	30.00	460
Cool and condense regenerate from PSA	Cool regenerate from PSA	137.30	82.00	146
	Condense regenerate from PSA	82.00	79.34	1831
Condense and cool secondary steam from dryer	Cool secondary steam dryer	149.00	145.37	45
	Condense secondary steam	145.37	144.37	12,253
	Cool secondary steam condensate	145.37	37.00	2628
Biomethane production				
Cool feed to AD	Cool feed to AD	116.2	37	22,635
Cool compressed biogas	Cool compressed biogas	163.40	50.00	2287
Condense water biogas upgrading	Condense water biogas upgrading	50.00	30.00	649
CHP				
Cool flue gas combustion	Cool flue gas combustion	820	120	117,531
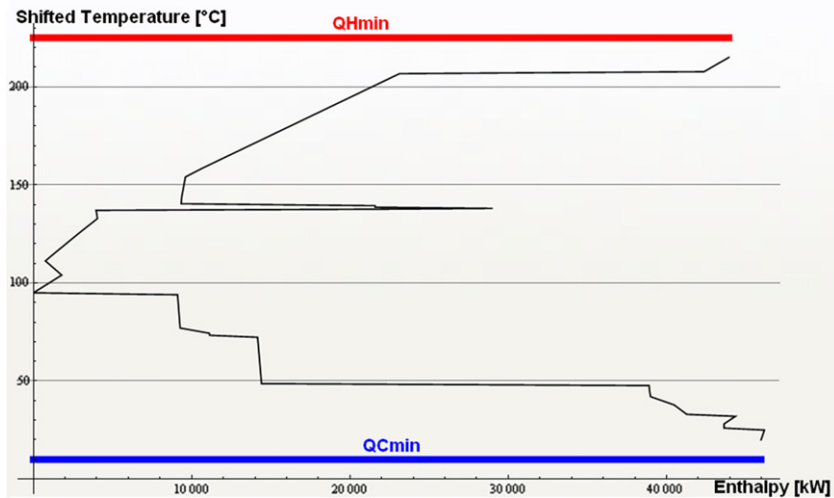
Fig. 4. Grand composite curve for combined bioethanol and biomethane production process (minimum temperature approach of 10 °C).

heat integration and to reduce the utilities demands. However, finding a cost-effective network which results in the optimal energy recovery can be done with a heat exchanger network software based on the mathematical programming. To optimize steam network in CHP plant, in which electricity, primary and secondary steam are generated, integrated grand composite curves have to be constructed for steam cycle and the background process including flue gas stream [24] (For interpretation of the references to color in this paragraph, the reader is referred to the web version of this article.).

5.1. Mathematica-based HEN synthesis and pinch analyzer

In order to solve the heat exchanger network synthesis problems which are large scale for industrial plants in the systematic way, a mathematica-based program involving three sub-programs is developed. The first section deals with the pinch technology in which CCs and GCC can be drawn and total annual cost of heat

exchanger network synthesized is minimized. The second sub-program introduces the methodology for synthesis of heat exchanger networks consisting isothermal process streams based on the super structure procedure presented by Ponce-Ortega et al. [16]. The last part of program presents the retrofitting of existing networks. The software is called "TVTHENS". The software Mathematica is chosen as a programming language because it is able to solve the large industrial problems with lower computing time compared to another MINLP solver. The core of the program is the minimization of capital and energy cost of the whole heat exchanger network simultaneously.

6. Results and discussion

6.1. Pinch analysis results

The above-mentioned approach was applied to the combined bioethanol and biomethane production process. Table 1 presents
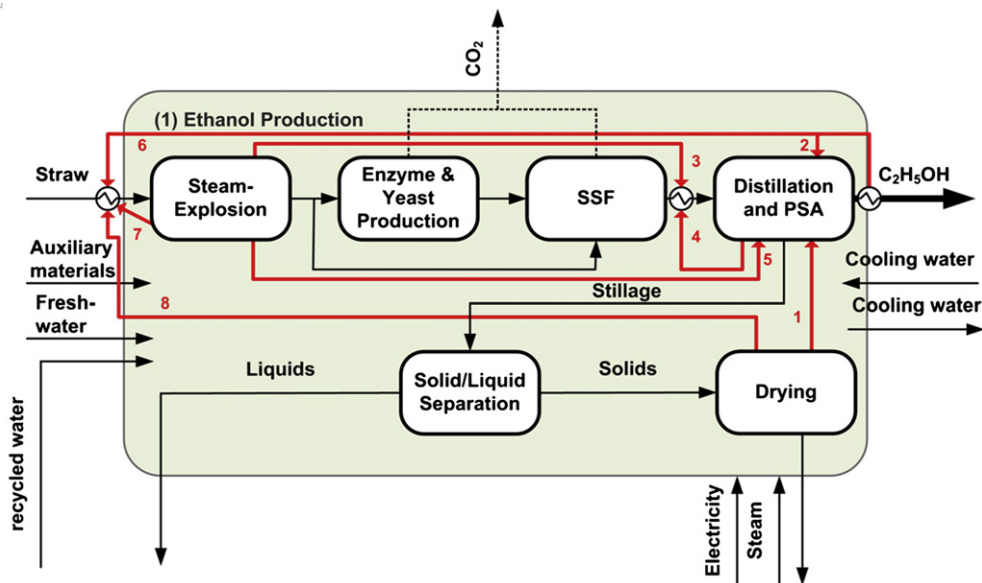
Fig. 5. The most important internal heat exchanging in the bioethanol production process proposed by "TVTHENS".
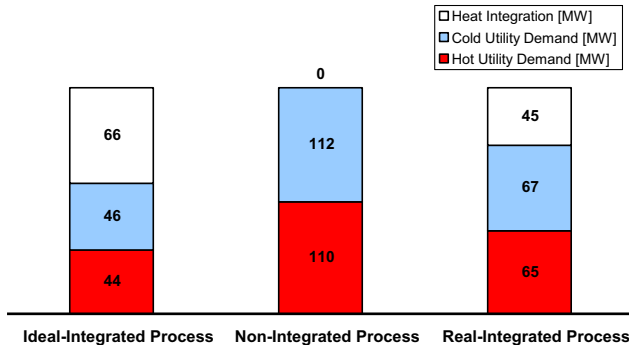
Fig. 6. Comparison between non-integrated and integrated combined bioethanol and biomethane production process.

the thermal process streams investigated for pinch analysis in which flue gas leaving the boiler is excluded because it's used to generate primary steam. To take phase change into account during the pinch analysis, some process streams were divided into stream parts. The pinch analysis of bioethanol and biomethane production process based on the composite curves shows that around 66 MW of heat could be integrated between hot and cold process streams if the process is optimal integrated. The minimum cold utility demand (46 MW) and minimum hot utility demand (44 MW) can be interpreted from Fig. 3 or Fig. 4. In comparison with the utilities demand of the non-integrated bioethanol (112 MW) and bio-methane production process (110 MW), heat integration potential is noticeable. To reach the maximum heat integration between hot and cold process streams, a well-designed heat exchanger network has to be structured. Thermal integration considering some forbidden matches between streams because of technical/safety reasons determined by "TVTHENS" shows that around 45 MW would be saved by utilization of heat released during the steam explosion treatment (Q3,Q5,Q7), drying (Q1,Q8) and bioethanol cooling (Q2,Q6) for mash preheating before introducing it into the distillation columns, feed and stripper heating as shown in Fig. 5. It's to be noted that high pressure steam used in the steam explosion and drying unit, cooling water used in the SSF, yeast and enzyme production reactor as well as cooling water for biogas
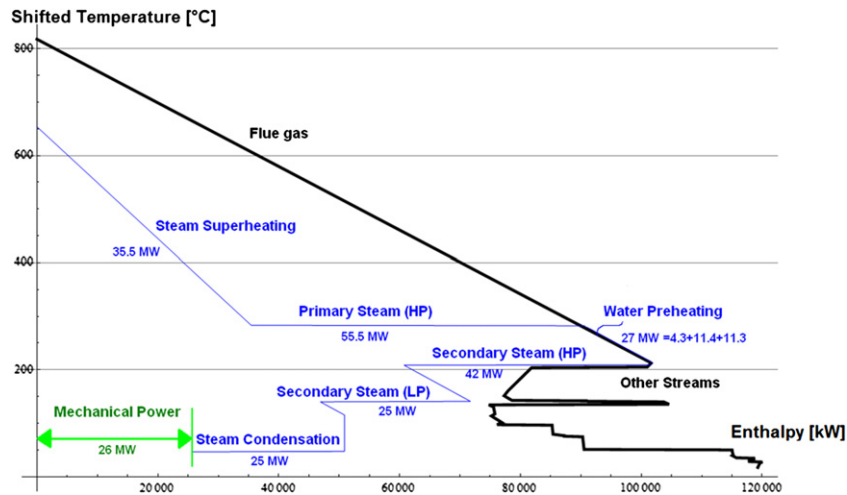
Fig. 7. Integrated composite curve: steam network.

	Total process	Ethanol process Product=ethanol	Ethanol process Product=ethanol By-product=liquid fraction of stillage	Ethanol process Product=ethanol By-product=dried solids	Ethanol process Product=ethanol By-product=liquid fraction of stillage+dried solids	Biomethane process Product=bioCH4	CHP process Products=steam+ electricity
Exergy Efficiency 1 (%)	66.6	87.8	87.8	87.8	87.8	84.0	58.2

Fig. 8. Simple exergy efficiency of the total process and sub-processes.

Fig. 9. Rational exergy efficiency of the total process and sub-processes.

cooling can not be replaced with other process streams due to technical restrictions. The total amount of energy required for heating and cooling of the above mentioned units are about 40 and 8.4 MW, respectively. Additionally, some process streams such as slurry and liquids fed to AD consist of the large amounts of insoluble and soluble solids which limit heat recovery of these process streams by commonly used heat exchangers (22.6 MW). Hence, after implementation of heat transfer limitation between process streams thermal integrated process needs around 65 MW hot utility and 67 MW cold utility. That means thermal integration between process streams reduces steam and cooling water consumption up to 40% which leads to the significant utilities cost reduction as seen in Fig. 6. Hot and cold composite curves are demonstrated in Fig. 3. Grand composite curve which allows to choice cheaper utility levels in the existing plant in which process streams are normally heated or cooled using several utility levels, is constructed from composite curves and is shown in Fig. 4. As seen, available waste heat at 90 °C (around 9 MW) can be used as a heat source for the heat pumps (hot water generation) and absorption chillers (chilled water generation). The pinch point found for combined bioethanol and biomethane production process lies at 95 °C considering the minimum temperature difference of 10 °C.

Total site heat integration can be demonstrated through the integrated grand composite curves introduced by Maréchal et al. [24]. As seen in Fig. 7, steam network integrated composite curve (blue curve) and other process streams (black curve) including flue gas show that secondary steam generated at two pressures levels by steam turbine can provide sufficient heat for bioethanol production process in which it's impossible to meet the maximum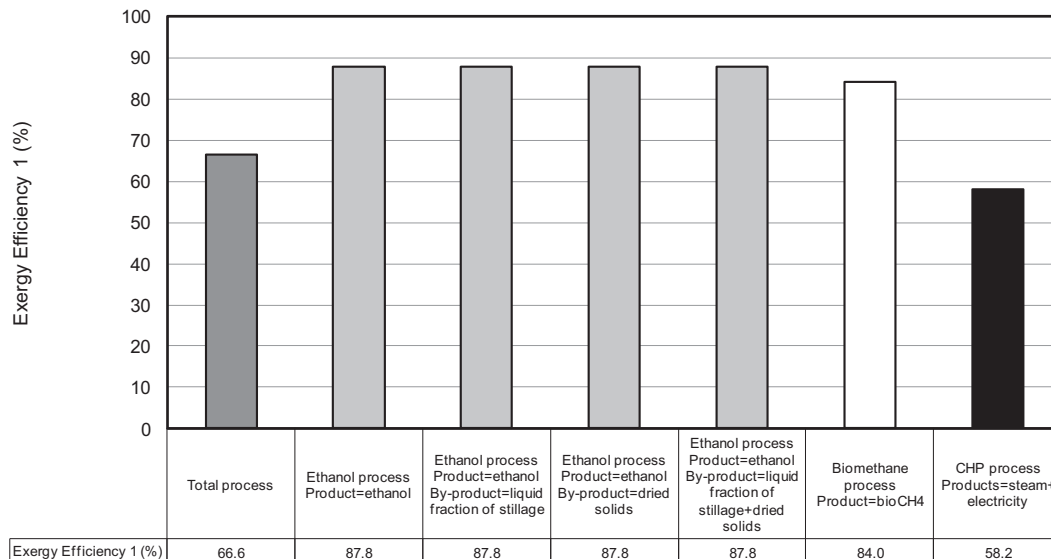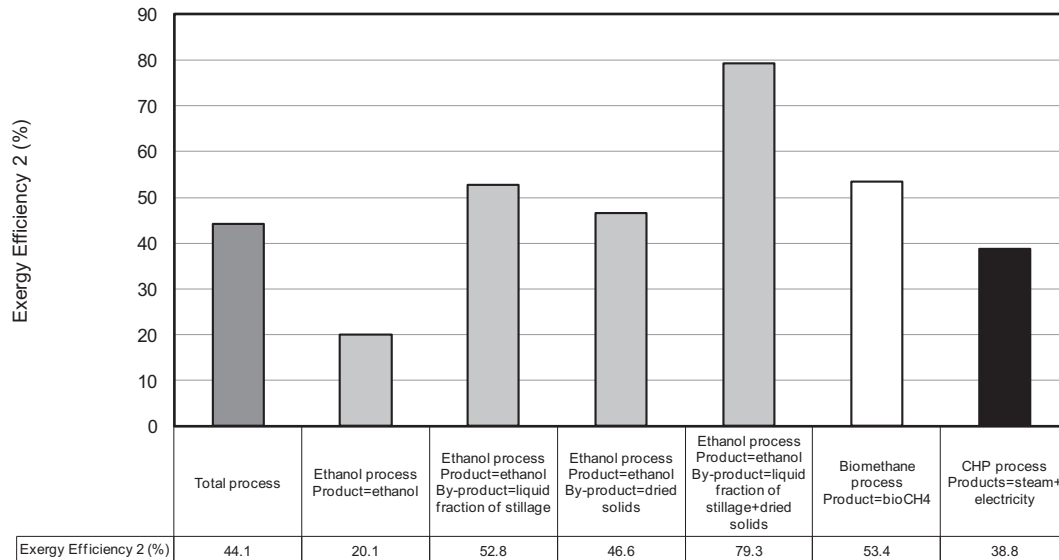 heat integration because of some restrictions mentioned in this work. It's to be noted that HP secondary steam used in the steam explosion is directly injected and mixed with the material stream and going out from the steam cycle boundary. After generating necessary steam for the bioethanol production process, additionally around 26 MW mechanical power are co-generated in the CHP system, which results in a net electricity production of 25 MW.

6.2. Exergy analysis results

After applying pinch analysis, exergy analysis has been evaluated. Because of reduction of external utilities requirements

without any changes in the amount of feedstock and products, exergy efficiency of total process was increased compared to the non thermal integrated bioethanol process. For exergy analysis, total process is broken down into three production sections to analyze each one separately and independently from other ones. Additionally exergy analysis was applied to total process to establish the impact of each section on the other section and on the total process. The simple exergy efficiency of bioethanol (with regard to different by-products), biomethane and CHP process and total process is shown in Fig. 8. In bioethanol production, the major exergy input is biomass entering steam explosion, and the major exergy outputs are bioethanol, liquid fraction from stillage as feed for biomethane production and dried solids combusted in CHP process. In biomethane process, the main exergy input is the liquid fraction and the main exergy streams leaving process are biomethane and sludge. The generated steam and electricity and flue gas indicate the leading exergy output streams and dried solids are the main exergy input during CHP process. As seen in Fig. 8 irreversibilities of bioethanol, biomethane and CHP process are about 12%, 16% and 42% of input exergy attributed to heat losses and non reacting unknown materials.

Waste fraction has been reduced by providing liquid fraction and dried solids. Thus the rational exergy efficiency of bioethanol process is higher than two other processes. In biomethane process a part of exergy is lost in the form of sludge and in CHP flue gas
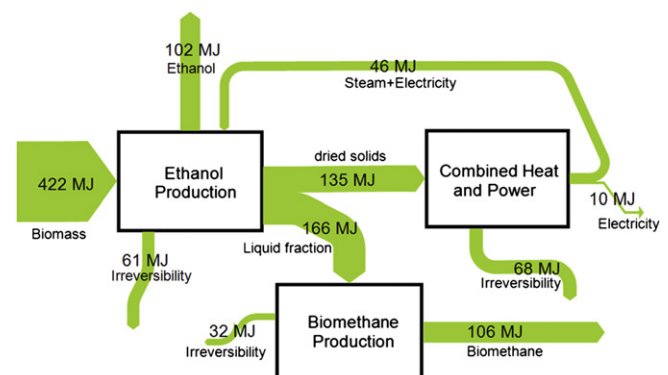

Fig. 10. Exergy flow diagram of the lignocellulosic ethanol production.

leaving system demonstrates waste exergy stream as shown in Fig. 9. Exergy efficiency of biomethane process can be increased if sludge-derived fertilizer is produced or sludge is incinerated.

7. Conclusions

In this paper, bioethanol, biomethane as well as combined heat and power process were analyzed from exergetic and thermodynamic point of view. Pinch analysis was evaluated to determine the minimum utilities demand. The required process streams data was extracted from software IPSEpro. The synthesis heat exchanger network showed that heat released in the steam explosion, dryer and product cooling can be used to preheat the feed and mash stream. As result, hot and cold utility demand can be reduced by 40%. Integrated grand composite curves showed that maximum 26 MW mechanical power can be generated by steam turbine in CHP plant in which 70 MW secondary steam at two pressure levels are co-generated to cover bioethanol production process heat demands.

Additionally exergy analysis was performed to calculate system irreversibilities and to identify material and heat losses as waste stream. The results show that the bioethanol production process has the highest exergy efficiency because of usage of stillage for other processes where it can be converted to biomethane in an anaerobic digestor and combusted in a boiler generating steam which drives a turbine to generate electricity used as energy resources in bioethanol process. Exergy flow diagram (Sankey diagram) is demonstrated in Fig. 10. As shown a considerable part of exergy entering biomethane and CHP process is converted into irreversibility because of heat losses and non reacting unknown material produced in these compared to bioethanol production process.

In the next study, "column pinch analysis" will be performed to optimize and modify operation of the stand-alone distillation columns from energy point of view. To investigate it, the condenser (hot process stream) and reboiler streams (cold process stream) should be taken out. After the distillation column data extraction, it will be demonstrated as a box on the grand composite curve of the rest of the process which is called as the "background process". If the distillation column lies across the pinch, it's recommended to change its operating temperature and pressure to fit the column above or below the pinch point which allows additional opportunities to reduce external hot and cold utilities demands [20]. Research outlook will be providing more results about HENs by means of program "TVTHENS".

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6.6. PAPER VI

Exergy analysis of production of lignocellulosic ethanol

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Exergy Analysis of the Production of lignocellulosic Ethanol

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Exergy analysis is applied to a process for production of bio-ethanol from lignocellulosic. A tool based on Mathematica has been developed to calculate the exergy of compounds and streams of lignocellulosic ethanol production process. The whole process was simulated using the suitable chemical process simulation software (IPSEpro). Some different scenarios are analyzed for handling stillage waste from ethanol production. Parametric studies show the influence of the proper selection of scenario on exergy efficiency. It is shown that process integration reduces process irreversibilites. Internal use of waste streams for providing process heat and electricity as well as generation of some useful by-products such as animal feed and pellets using additional steps could increase exergy efficiency.

1. Introduction

Today production of bio-ethanol from lignocellulosic materials is a suitable chemical process according to some reasons. First, the greenhouse gas mitigation potential compared to both, fossil fuels and bio-ethanol from starchy crops is high (Eisentraut, 2010) and second usage of additional acreage can be avoided if residual materials from food production or forest industry are employed.

In this work we investigate the production of ethanol from straw from an exergetic point of view. Several production scenarios for a process based on steam pretreatment with acid impregnation and enzymatic hydrolysis are compared using the steady state process simulation software IPSEpro. Besides mass and energy balance, exergy analysis is applied to the bio-ethanol production of from lignocellulosic. To obtain an economic and competitive overall process, careful selection of upstream and downstream processes as well as optimal integration of all steps in terms of minimizing residual streams and heat demand is crucial.

Please cite this article as: Modarresi A., Kravanja P. and Friedl A., 2011, Exergy analysis of the production of lignocellulosic ethanol, Chemical Engineering Transactions, 25, 635-640

DOI: 10.3303/CET1125106

2. Process Description

Figure 1 summarizes the scenarios considered in this work. As can be seen, the scenarios are identical as far as the upstream process, ethanol recovery and stillage separation is concerned.
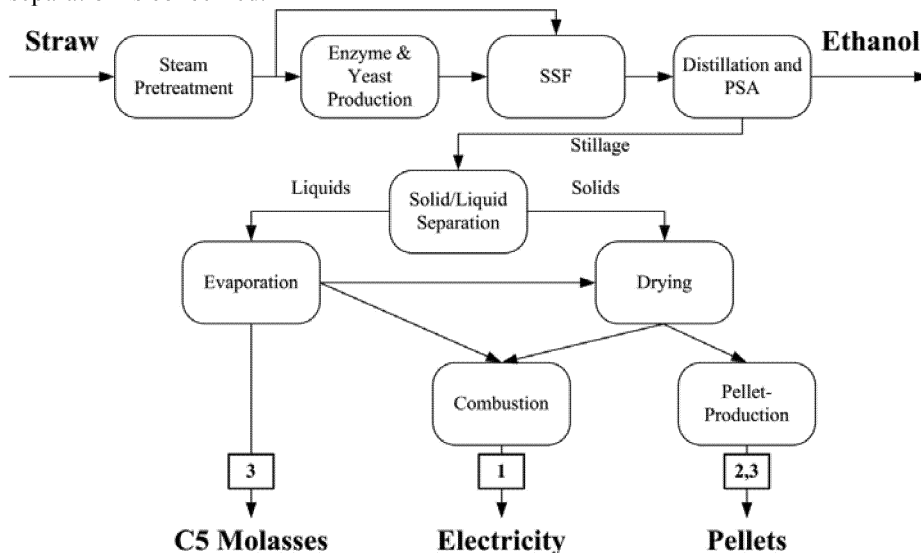
Figure 1: Schematic summary of process scenarios for the production of ethanol from straw.

For all the scenarios process steam is generated by burning part of the stillage reducing the processes' demand for fossil energy largely. In scenarios 2 and 3 electricity is bought from the grid whereas in scenario 1, electricity is produced on-site. For scenarios 2 and 3 the byproducts pellets (Scenario 2 and 3) and C5-molasses (Scenario 3) are produced. Ethanol production capacity is 100,000 t/y.

2.1 Upstream process, ethanol recovery and purification
The upstream process consists of the process steps steam pretreatment, enzyme production, yeast propagation and simultaneous saccharification and fermentation (SSF). For ethanol recovery a heat integrated distillation system is used. Ethanol purification is realized using pressure swing adsorption.

2.2 Stillage utilization
The stillage from distillation is sent to a filter press, separating liquids and soluble solids from insoluble solids. The liquid fraction containing most of the soluble solids is concentrated in a 5 effect evaporation train working. Insoluble Solids are dried to 90% drymatter in a superheated steam dryer. Now several ways to utilize the residual streams exist, as indicated by the numbers 1 through 3 in Figure 1.

2.2.1. Combined Heat and Power
In scenario 1 the dried insoluble solids as well as the concentrated soluble are burnt in the boiler. Steam is produced and expanded in a turbine to produce electricity for the process. Excess electricity can be sold to the grid. Process steam is extracted at the two pressure levels required.

2.2.2. Pellets
In scenario 2 process electricity is supplied from the grid. The dried insoluble solids are pelletized and can be sold as solid fuel. Concentrated soluble solids (65%drymatter) burnt to provide process heat. Since the energy content of the concentrated soluble solids is more than sufficient to meet the processes heat demand, excess solubles are dried and pelletized together with the insoluble solids.

2.2.3. C5-Molasses
In scenario 3 process electricity is supplied from the grid. The dried solids are used as fuel for the boiler, whereas the concentrated solubles (C5 sugars and other soluble components) can be sold as a product. Since the energy content of the dried solids exceeds the processes heat demand, a small amount of excess solids are pelletized and sold.

3. Exergy Analysis and Exergy Efficiencies

Exergy analysis is a useful approach to identify the kind, location and quantity of thermal and material losses in chemical and thermal processes (Szargut and Styrylska, 1964).

3.1 Exergy efficiencies
Two different definitions of exergy efficiency are introduced by (Cornelissen, 1997). Simple efficiency, Eq. (1), expresses the ratio of total exergy output and total exergy input of a process. Rational efficiency, Eq. (2), presents the ratio of exergy of the product to the total exergy input. Another option is to use the chemical efficiency, defined as the ratio between chemical exergy of the product and the chemical exergy of input, expressed in Eq. (3).

$$\eta_1 = \frac{Ex_{Out}}{Ex_{In}} \tag{1}$$

$$\eta_3 = \frac{Ex_{Product(s)}}{Ex_{In}} \tag{2}$$

$$\eta_4 = \frac{Ex_{Chem,Product(s)}}{Ex_{Chem,biomass}} \tag{3}$$

3.2 Mathematica-based exergy calculator
A tool based on Mathematica (V7.01.0) has been developed to calculate the exergy of compounds and streams of bio-ethanol production process in a systematic way (Hinderink et al., 1996). The structure of the model for exergy calculation is shown in Figure 2.
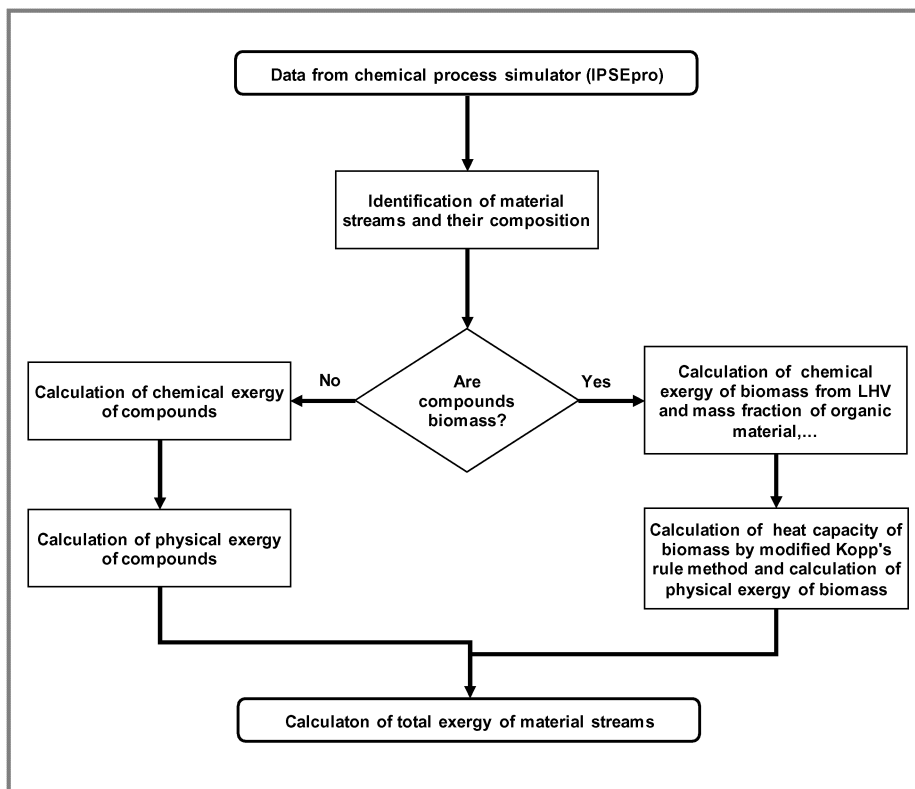
Figure 2: Structure of algorithm used for calculation of exergy of process streams (Modarresi et al., 2010).

4. Results

Although introduction of combustion step for producing process electricity reduces exergy losses in the process, a considerable part of the exergy of process input is found in by-products such as C5 sugars as well as pellets and not in the produced bio-ethanol. It should be noticed that C5-Molasses would be feedstock for other chemical processes. Investigated scenarios are summarized in Table 1.

Table 1: Investigated options of product definition representing the use of by-products.

Exergy Efficiencies	Scenario	Product(s)
Eff_3A, Eff4A	1	Ethanol
Eff_3D, Eff4D	1	Ethanol, electricity
Eff_3A, Eff4A	2	Ethanol
Eff_3D, Eff4D	2	Ethanol, Pellets
Eff_3A, Eff4A	3	Ethanol
Eff_3D, Eff4D	3	Ethanol, C5-Molasses, Pellets

Efficiencies 3A and 4A refer to the produced bio-ethanol as sole product of the process. Additionally to the bio-ethanol, other residuals could be considered as by-products to provide process heat and electricity (efficiencies 3D and 4D)

4.1 Exergy efficiency of overall process

Figure 3 shows the exergetic efficiency of the different cases in terms of simple exergetic efficiency 1, rational exergetic efficiency 3 and chemical exergetic efficiency 4 according to Eq. (1-3). Introducing drying and evaporation steps, the exergetic efficiencies 1, 3 and 4 are increased. The amount of increase of (η,3) and (η,4) corresponds with the amount of usable by-products following from mass- and energy-balance. Highest increase in efficiency 3 occurs when considering residual biomass from the process as valuable product (pellets and C5-Molasses). Due to the strong impact of chemical exergy compared to physical exergy in the investigated low temperature process there is a small difference between efficiency 3D and 4D. As can be seen, total exergy efficiency ranges from 44.5% for scenario 1 to 69.7% for scenario 2.

4.2 Parameter study on product definition

As seen Figure 3 presents the results of a parameter study investigating the influence of definition of products on rational exergetic efficiency (η,3) and chemical exergetic efficiency (η,4).

Figure 3: Exergetic efficiency of the different cases in terms of simple, rational and chemical exergetic efficiency

A significant increase of exergetic efficiency of the overall process can be achieved, when defining remaining biomass as usable product of the process or when producing electricity internally.

5. Conclusions

Exergy analysis was applied to a process for biological production of ethanol. A promising chemical exergetic efficiency of 24.2 % was obtained without considering any by-products. A parameter study underlines the strong dependency of obtained exergetic efficiency on the obtained products and shows options for process improvement and optimization. Following the results, it is recommended to produce electricity (pure exergy) by combustion of residuals to use the chemical exergy of solids. Most important contribution to an increase of exergetic efficiency comes from (re-) use of C5 sugars and pellets for heat and power generation or for sale. The calculated improvement of exergetic efficiencies only represents a theoretical maximum. Impact on exergy balance and exergetic efficiency has to be investigated in more detail considering also additional process steps necessary to implement the suggested process improvements.

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6.7.   PAPER VII

Heat integration of biochemical ethanol production from straw – A case study

P. Kravanja, A. Modarresi and A. Friedl
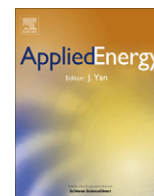
Heat integration of biochemical ethanol production from straw – A case study

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HIGHLIGHTS

▶ We perform heat integration of ethanol production from straw.
▶ In pinch analysis distillation and evaporation design are examined in detail.
▶ Via pinch analysis the design is improved and the utility targets reduced by 15%.
▶ For the improved design an efficient heat exchanger network was obtained.
▶ For this network 50% of residual materials suffice to provide process heat.

ABSTRACT

Ethanol produced from lignocellulosic biomass is a desired, renewable fuel that can help to reduce our dependence on oil. In order to achieve the commercial deployment of this fuel good economic and environmental performance are mandatory. Both these targets are tackled by the efficient use of process heat. This work deals with the heat integration of the biochemical production of ethanol from straw. Process simulation and pinch analysis are applied to investigate a base case design of the production process. The energy intensive unit operations distillation and evaporation are in the focus of this pinch analysis. Pressure and heat load modifications of these sections are applied to improve the process design. For this improved process design a heat exchanger network is synthesized. Energy stream and pinch analysis revealed that process residues easily suffice to provide the investigated process with heat. The design modifications of the distillation and evaporation sections lead to increased heat integration. Consequently, a 15% reduction of the utility targets compared to the base case is obtained in the improved design. The heat exchanger network for the improved design is simple, yet the increase in utility consumption compared to the utility targets is quite modest. As a result, in the network only 51% of waste biomass suffice to provide the process with heat. The exceeding biomass can be used for the recovery of energy or material by-products, which highlights the need for efficient polygeneration concepts.

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1. Introduction

It is widely accepted that bioethanol from lignocellulosic feedstock should play an important role in the energy system of the future. This consensus, based on several appealing features of the fuel and the technology, is expressed in policies in both, the EU and the US [1–3]. Bioethanol is a renewable fuel that reduces our dependence on oil, has very good combustion properties and can be applied to the existing car fleet when blended at low concentrations [4]. The greenhouse gas mitigation potential of lignocellulosic ethanol is high compared to both, fossil fuels and bioethanol from starchy crops [5,6]. Ultimately, the food vs. fuel debate can be avoided, when lignocellulosic waste materials are used for the production of bioethanol.

At present, the technology is limited to the demonstration scale. For commercial production lignocellulosic ethanol has to be economically feasible and environmentally friendly. A common strategy to achieve this goal is to provide process heat by burning the lignin-rich process residues and thereby avoid the use of external, fossil fuels [7–10]. Another way to reach this goal is to increase the process efficiency by means of process integration. For this task, pinch technology can be employed in different ways.

A first strategy is to use pinch technology to improve the core process design. Using this approach, Fujimoto et al. [11] found that a heat pump can significantly improve the process efficiency of a lignocellulosic ethanol production process based on concentrated acid hydrolysis. Another strategy to increase process efficiency by means of pinch technology is to optimize the CHP or polygeneration system associated with utility allocation. Zhang et al. [12] used this approach to investigate different polygeneration options for a lignocellulosic ethanol process employing two-stage dilute acid

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hydrolysis and significantly improved process efficiency. Ultimately, Morandin et al. [13] combined the two strategies and used pinch analysis for parameter optimization of the core process as well as for validation of different CHP systems. For a process producing ethanol and sugar from sugarcane parameter optimization resulted in a heat demand reduction of one third. In addition, the net power output of the associated CHP system was maximized.

1.1. Aim and scope of the paper

In this work we aim to thermally integrate the biochemical production process of ethanol from straw using pinch analysis and heat exchanger network synthesis. The process under consideration is made up of the unit operations steam pretreatment, on-site enzyme and yeast production and simultaneous saccharification and co-fermentation (SSCF) of C5 and C6 sugars to convert straw to ethanol. The ethanol product is recovered and purified by means of distillation and pressure swing adsorption. The stillage from distillation is treated using solid–liquid separation, multi-stage evaporation and superheated steam drying of solid residues.

We start our work with a base case flowsheet model of the process and aim to (i) find options to improve this base case design and (ii) create a fully integrated flowhsheet model of the improved process design. Thereto we apply pinch analysis and heat exchanger network synthesis. As a result of this procedure, a heat exchanger network and the utility requirement of the fully integrated production process are obtained. The mass balances for the process can be closed and general conclusions about the technology can be drawn. Future work will be dedicated to further process analysis (e.g. exergy analysis, economic evaluation or life cycle analysis).

2. Methodology

The methodology followed in this work is schematized in Fig. 1. First, a flowsheet model of the base case design for the production process is developed. From this flowsheet model, data is extracted for pinch analysis. The pinch analysis focuses on the energy intensive downstream unit operations distillation and evaporation. Following a well-established procedure [14], these unit operations are analyzed separately from the background process. The findings from this pinch analysis allow us to derive modifications of the process design. These modifications concern the above mentioned unit operations distillation and evaporation and include a change of (i) the number of stages in these unit operations, (ii) the temperature

level of the stages and (iii) the heat load of the stages. These design modifications aim at increased heat integration and are implemented to create a flowsheet model of the thus obtained improved process design. Again, data extraction and pinch analysis are performed for the improved design in order to assess the proposed design modifications. Thereto the utility targets of the base case design and the improved design are compared. To complete this heat integration study, a heat exchanger network is developed for the improved process design.

2.1. Flowsheet simulations

Steady state flowsheet simulations are performed using the equation oriented software "IPSEpro". The software was developed for simulation of power plants [15]. Hence, detailed property data and unit operations are available for power plant computations only. For simulation of the process considered in this work a suitable model library was developed [16]. Due to "IPSEpro's" equation oriented solving approach input and output information can be exchanged arbitrarily and complex flowsheets including recycle streams converge quickly. For heat integration, thermal process data obtained from simulations with IPSEpro is extracted, exported to Microsoft Excel and from there imported to the pinch analysis and heat exchanger network software described in Sections 2.2 and 2.3.

2.2. Pinch analysis

Pinch analysis is a powerful methodology to determine options for process heat recovery. In this work it is carried out using the pinch analysis module of the software "TVTHENS". "TVTHENS" was developed at the Vienna University of Technology using the computational software program "Mathematica". After data extraction (see Section 3.1) and energy stream investigation according to [14,17], thermal data of the cold streams needing heating and hot streams needing cooling are entered into "TVTHENS" via Microsoft Excel. Based on these data and a specified minimum temperature difference ΔT_{min} of 10 °C that is applied in pinch analysis throughout this work, composite curves and grand composite curves representing the minimum heating and cooling demands are constructed by a graphical approach introduced by Salama [18]. For streams without phase change constant heat capacities are assumed. To deal with isothermal streams involved in the process, it is assumed that these streams have 1 °C temperature difference during phase
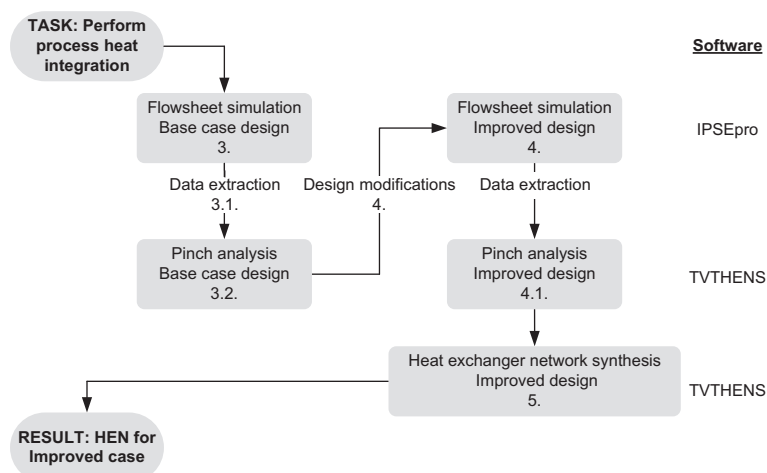
Fig. 1. Methodological workflow and simulation tools used. The numbers indicate the respective sections of the text. HEN: Heat exchanger network. Numerals stand for the respective sections of the text.
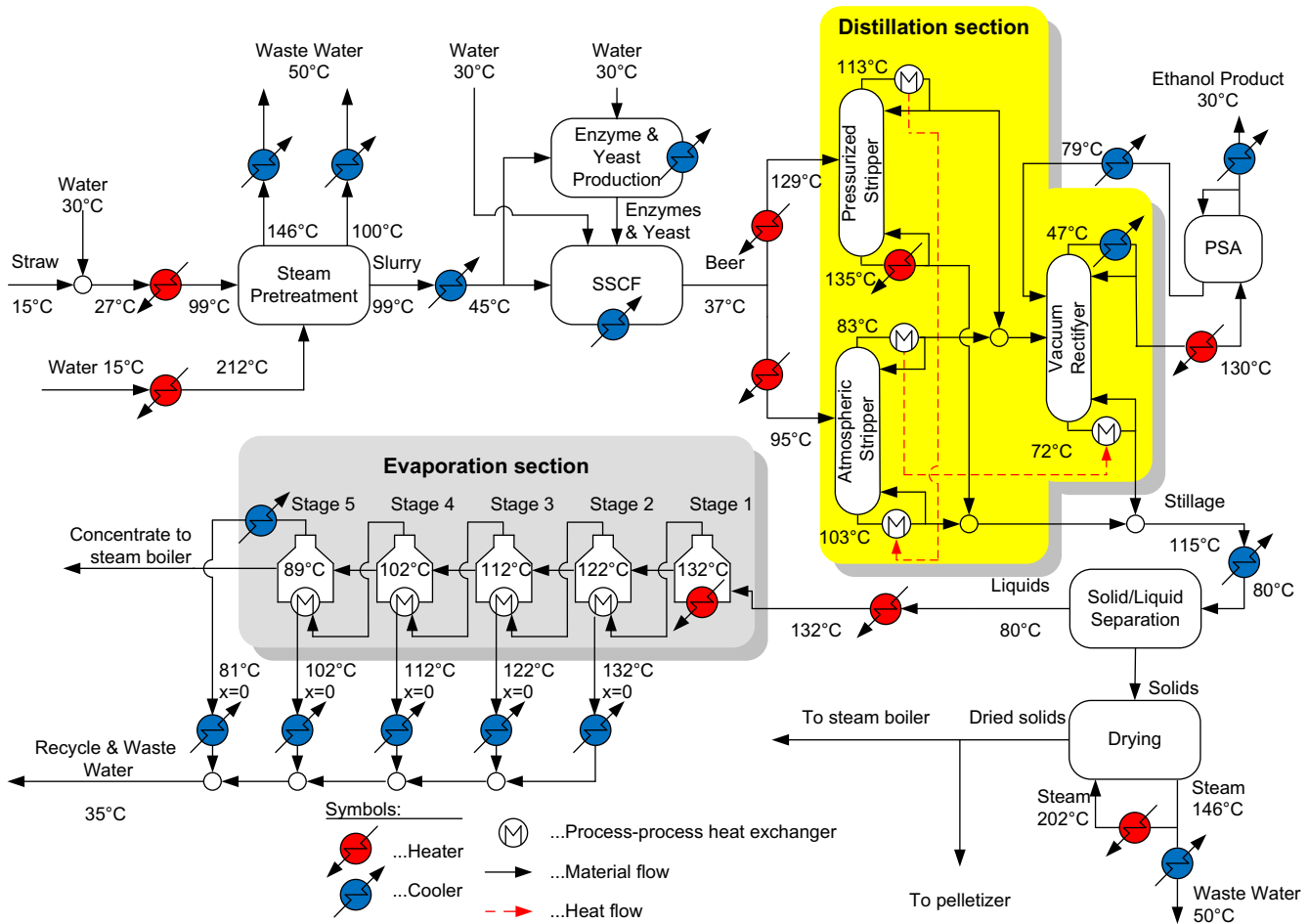
Fig. 2. Scheme of the base case design including stand-alone optimized distillation and evaporation section. SSCF: simultaneous saccharification and co-fermentation. PSA: pressure swing adsorption. For simplicity reasons yeast and enzyme production are unified in one block.

change. Fore more details about the pinch analysis principles applied see [14,17].

2.3. Heat exchanger network synthesis

Heat exchanger network synthesis was performed with the respective program module of "TVTHENS". The program module for heat exchanger network design considers process streams that undergo both sensible and latent heat changes (e.g. streams in the multi stage evaporation) and utilizes an extended mixed integer linear programming (MILP) model proposed by Ponce-Ortega [19]. This model is based on the superstructure formulated by Yee and Grossmann [20] in which the total annual cost including utility and heat exchanger costs is minimized. The "Mathematica" optimization package makes it possible to reduce computational time for industrial scale problems. The network synthesis was performed with for a ΔT_{min} of 10 °C. In order to keep the network simple, stream splitting was excluded in the network synthesis.

3. Base case design

Fig. 2 shows the base case design of the process. This design builds on the work at Lund University, Sweden [9,21,22] and employs efficiently integrated stand-alone solutions for the thermal separation units distillation and evaporation. The mass and energy balances are calculated for an ethanol production capacity of 100,000 t/y and operating time of 8000 h/y.

Shredded straw (90 dry matter, DM) is wetted to reach a moisture content of 65% and preheated close to the boiling temperature of water. The moistened and preheated straw is impregnated with SO_2 and steam pretreated at 190 °C. Heat losses are assumed to amount to 10% of total heat transferred. As suggested by Wingren [23], the flashing after steam pretreatment is performed in two steps, first at medium pressure (MP) at approx. 4.3 bar and then at atmospheric pressure (AP). Flashing yields saturated secondary steam at the respective levels. After condensation and cooling to 50 °C the condensates from steam pretreatment have to be disposed of.

The hot slurry after steam pretreatment is neutralized using $NH_4(OH)$, cooled to 45 °C and split into three streams. The major part of the slurry is directly fed to SSCF where both, C6 and C5 sugars are fermented to ethanol. Minor parts of the slurry are used for enzyme production (EP) and yeast propagation (YP). The mass flows of the streams to EP and YP are a result of the conversions in the bio-reactors on the one hand and enzyme and yeast requirements in SSCF on the other hand. SSCF is performed at 37 °C, whereas yeast propagation and enzyme production are performed at 30 °C. The slurry however, is only cooled to 45 °C, since dilution with colder water is necessary to decrease the solid content and the concentration of inhibitors formed in the pretreatment. Moreover, the bioreactors require cooling to remove heat released from the respective reactions.

After conversion of sugars to ethanol in SSCF the beer stream contains approx. 6 w/w% ethanol. This stream is split into two streams, preheated and fed to the thermally integrated three

column distillation section. As suggested by Wingren, this section consists two parallel stripper columns, one operated at elevated pressure and one under atmospheric conditions, and a vacuum rectifier column [21]. The pressurized stripper requires heat at MP level. Condenser heat from the pressurized stripper is used to heat the atmospheric stripper whose condenser heat in turn is used to heat the vacuum rectifier. The split ratio of the feed stream and the distillation operating conditions are chosen in a way, that no external heat is necessary to heat atmospheric stripper or the rectifier. To compensate for heat losses in the columns, the reboiler heat duties are approx. 5% lower than the condenser heat duties by which they are supplied. To enable heat exchange between hot and cold streams a ΔT of 10 °C is assumed. Condensation heat at the head of the rectifier has to be removed at 47 °C. The 92 w/w% ethanol head product is compressed, superheated to 130 °C and sent to a pressure swing adsorption (PSA) unit. In PSA ethanol is purified to 99.5 w/w%. 25% of the purified ethanol is used to purge the loaded bed. The regenerate obtained from purging is condensed and returned to the rectifier. Purified ethanol is condensed and cooled to 30 °C.

The stillage stream from distillation contains all the solids, water and by-products of prior conversion steps. This stream is cooled to 80 °C and sent to a filter press where liquids and soluble solids are separated from insoluble solids. A dry matter content of 45% of the solid fraction and 99% recovery of insoluble solids are assumed. The liquid fraction containing most of the soluble solids is preheated for evaporation and concentrated to 65% DM in a 5 stage co-current evaporation train. The feed stage is operated at a pressure requiring MP steam, whereas the last stage is operated at 0.5 bar. In each stage heat losses are assumed to amount to 10%. Operating pressures in the stages 1–5 are set to 2.9, 2.1, 1.5, 1 and 0.5 bar resulting in 10 °C ΔT between the stages (see Fig. 2). Complete condensation ($x = 0$) is assumed, when the vapors from stages 1–4 are used for heat exchange with subsequent stages. The boiling point elevation was considered using an empiric expression [24]. The condensed vapors from the first four stages are cooled to 35 °C. Vapor from the last stage is condensed and cooled to 35 °C. A part of the condensate can be recycled to the process [24], the rest is disposed of. The concentrate from evaporation is sent to the steam boiler.

For drying of insoluble solids a superheated steam dryer working at MP level can be employed [21]. During the drying the water content is reduced to 10%. The steam serving as drying medium is produced from water evaporated from the solids. In a closed loop the steam is superheated indirectly [25]. In addition excess MP steam that can be used elsewhere in the process is produced. After condensation and cooling to 50 °C this stream has to be disposed of. Again, heat losses are assumed to amount to 10%. As indicated in Fig. 2, hot utilities are provided by feeding parts of the dried solids together with the concentrate from evaporation to a steam boiler. Excess solids can be pelletized and sold.

A flowsheet model of this process design was developed in "IPSEpro". The overall process ethanol yield is 70.4%, based on C6 and C5 sugars available in the raw material. 446,000 t of straw (252 MW) are thus required annually to produce 100,000 t of ethanol (93 MW). Moreover, some 150,000 t of dried solids (84 MW) and 112,000 t of evaporation concentrate (56 MW) are obtained. The corresponding energy flows in parentheses are based on the lower heating value (LHV). The lower heating values for biomass streams were calculated using the PLS model of Friedl et al. [26].

3.1. Data extraction for pinch analysis

All hot and cold process streams extracted from a flowsheet model of the base case design are listed in Table 1. To cover the entire process utility demand the cooling of bio-reactors operated in

batch-mode is also included. To check and improve their design the energy intensive distillation and evaporation sections are singled out from the background process [14]. As described in Section 3 and shown in Fig. 2, the thermal separation units distillation and evaporation are designed in a way that external heat is only required at the first stage operated at the highest pressure and external cooling is only required at the last operated at the lowest pressure. Consequently, for the base case all other hot or cold streams of the distillation and evaporation sections are either not listed in Table 1 (condenser of the press. stripper, vapors evap. stage 1 and 2, heat evap. stages 2, 3 and 5) or the respective data is not included (n.i.) in Table 1. As indicated in Fig. 2, heating the feed to distillation and evaporation as well as cooling of the stillage and condensed vapors are covered in the background process [14]. Hot utility generation in the steam boiler is not included. However, steam for pretreatment is included, because this stream is a reactant in the pretreatment step and not a true utility [17].

By summing up all the heat loads of all cold and hot streams, the maximum hot and cold utility requirement $Q_{HU,max}$ and $Q_{CU,max}$ of the base case are obtained. They amount to 113.3 and 100.2 MW, whereof 71.1 and 71.0 MW are required for heating and cooling of the background process. The remaining 42.3 and 29.2 MW are needed to heat and cool the distillation and evaporation sections. Almost 40% of hot utility are thus required to heat these energy intensive unit operations even though energy efficient multi-stage solutions have been implemented. This finding clearly illustrates why these sections should be in the focus of the following pinch analysis.

3.2. Pinch analysis of the base case

To perform pinch analysis of the base case design, the extracted data was entered to "TVTHENS" (see Section 2.2). The resulting grand composite curves (GCCs) are shown in Fig. 3.

Fig. 3a shows the GCC of the background process separated from the distillation and evaporation sections. These sections are represented as boxes [14]. The hot and cold utility targets $Q_{HU,min}$ and $Q_{CU,min}$ of the background process both account for approx. 30 MW. Hence, 41 MW of heat can potentially be recovered in the background process. The pinch point of the background process is located at a shifted temperature T^* of 141 °C, the condensation temperature of MP steam obtained from steam pretreatment and drying. This location of the pinch point indicates that the background process cannot fully absorb the heat from steam pretreatment and drying. As shown in Fig. 3a, some 11 MW of excess heat are obtained in that way.

The distillation and evaporation sections are well placed below the pinch of the background process [15]. However, the 11 MW of excess heat at MP level do not suffice to provide heat for both thermal separation units. Hence, integrating the distillation and evaporation sections could potentially lead to further energy savings.

Fig. 3b shows the overall grand composite curve, representing the entire base case process including distillation and evaporation. The overall process utility targets $Q_{HU,min}$ and $Q_{CU,min}$ thus obtained amount to 61 MW and 48 MW. By subtracting the targets from the 113 MW and 100 MW representing the maximum hot and cold utility requirement $Q_{HU,max}$ and $Q_{CU,max}$ of the base case one finds a heat recovery of 52 MW corresponding to a 46% and 52% reduction of hot and cold utility consumption. Comparing the 52 MW to the 41 MW of heat recovery in the background process reveals that the integration of the distillation and evaporation sections with the background process leads to an increase in heat integration by 11 MW. This integration is due to utilization of excess MP steam from the background process, which can be used to heat the distillation or evaporation. This option for heat recovery is reflected in the very sharp pocket at a T^* of 141 °C. It is important to note that

Table 1
Hot and cold streams in the background process, distillation section and evaporation section. Streams differing in the base case and improved case are shown in bold characters. For these streams data for the base case are indicated before the backslash whereas data for the improved case are indicated after the backslash.

Stream description	Alias	T_{in} (°C)	T_{out} (°C)	$T_{Phasechange}$ (°C)	$Q_{Phasechange}$ (MW)	Q_{total} (MW)
Background process cold streams						
Straw to SP	C01	27	99			9.2
Steam for SP	C02	15	212	211	13.8	20.0
Beer to atm. stripper	**C03**	**37**	**95**			**6.4/13.6**
Beet to press. stripper	**C03a**	**37/–**	**129/–**			**11.5/–**
Vapors to PSA	C04	105	130			0.2
Feed to evap. section	C05	80	133			10.3
Superheat drying steam	C06	150	202			13.5
Background process hot streams						
MP steam from SP + dryer	H01	146	50	146	19.2	23.0
AP steam from SP	H02	100	50	100	6.9	7.6
Slurry from SP	H03	99	45			7.2
Yeast production	H04	30	29			1.2
Enzyme production	H05	30	29			0.7
SSCF	H06	37	36			3.4
Ethanol product	H07	130	30	79	3.0	3.8
Regenerate from PSA	H08	137	78	79	1.8	2.0
Stillage	**H09**	**116/101**	**80**			**8.0/4.6**
Condensate evap. stage 1	**H10**	**132/134**	**35**			**4.0/5.5**
Condensate evap. stage 2	**H11**	**122/124**	**35**			**3.4/4.6**
Condensate evap. stage 3	**H12**	**112/113**	**35**			**2.9/3.7**
Condensate evap. stage 4	**H13**	**102/66**	**35**			**2.3/0.9**
Condensate evap. stage 5	**H14**	**81/–**	**35/–**			**1.5/–**
Distillation section cold streams						
Reboiler press. stripper	**CD0**	**134/–**	**135/–**	**134/–**	**18.7/–**	**18.7/–**
Reboiler atm. stripper	**CD1**	**n.i./103**	**n.i./104**	**n.i./103**	**n.i./28.6**	**n.i./28.6**
Reboiler vac. rectifyer	**CD2**	**n.i./72**	**n.i./73**	**n.i./72**	**n.i./28.6**	**n.i./17.3**
Distillation section hot streams						
Condenser press. stripper	**HD0**	**n.i./ –**	**n.i./ –**	**n.i./ –**	**n.i./ –**	**n.i./ –**
Condenser atm. stripper	**HD1**	**n.i./84**	**n.i./83**	**n.i./84**	**n.i./26.8**	**n.i./26.8**
Condenser vac. rectifyer	**HD2**	**48**	**47**	**48**	**11.6/12.1**	**11.6/12.1**
Evaporation section cold streams						
Heat evap. stage 1	**CE1**	**132/134**	**133/135**	**132/134**	**23.6/32.1**	**23.6/32.1**
Heat evap. stage 4	**CE4**	**n.i./73**	**n.i./74**	**n.i./73**	**n.i./16.6**	**n.i./16.6**
Evaporation section hot streams						
Vapors evap. stage 3	**HE3**	**n.i./114**	**n.i./113**	**n.i./114**	**n.i./25.3**	**n.i./25.3**
Vapors evap. stage 4	**HE4**	**n.i./73**	**n.i./66**	**n.i./73**	**n.i./16.8**	**n.i./16.8**
Vapors evap. stage 5	**HE5**	**89/–**	**81/–**	**89/–**	**17.6/–**	**17.6/–**

n.i.: stream not included because it is fully integrated; –: stream does not exist in the improved design, SP: steam pretreatment; pres.: pressurized; atm.: atmospheric; vac.: vacuum; PSA: pressure swing adsorption; MP: medium pressure; AP: atmospheric pressure; SSCF: simultaneous saccharification and co-fermentation; evap.: Evaporation.

the pinch point of overall process has shifted to 95 °C, the condensation temperature of AP steam. This is because in the overall process MP steam is entirely consumed. However, in Fig. 3b, it can be seen that now AP steam obtained from steam pretreatment does not contribute to the heat integration. In an improved process design, this heat should be utilized.

To determine major options for heat recovery in the background process one should keep in mind, that the region above the overall pinch (95 °C) is a heat sink and the region below the overall pinch is a heat source [14]. Hot streams above the overall pinch and cold streams below the overall pinch can thus be fully integrated (see Table 1). The most prominent cold streams below the pinch are (i) the straw before pretreatment (C01), (ii) the water for steam pretreatment (C02), (iii) the beer before distillation (C03 and C03a) and (iv) the feed to evaporation (C05). On the other hand, the most important hot streams above the pinch are (i) the stillage (H09) and (ii) the condensates from evaporation (H10–H13). These hot and cold streams thus provide the greatest potential for heat recovery in the background process.

To sum up, the base case design has significant potential for heat integration and utility reduction. This potential originates from (i) the background process as such and (ii) the excess MP steam from pretreatment and drying that can be used to integrate the distillation and evaporation with the background process.

However, the heat integration could be further improved e.g. by integrating the distillation and evaporation sections and shifting some of the heat demand from the MP to the AP level.

4. Improved process design

In principle, there are several strategies available to reduce the utility consumption in the prevailing heat recovery problem. Due to the capital-energy trade-off decreasing ΔT_{min} or increasing the number of stages in the distillation or evaporation sections are not considered acceptable options. Certainly, the strategy followed in this work relies on pinch based process modifications resulting in an increased integration of the thermal separation units. Thereto pressure modifications that result in temperature shifts of the heat loads are applied. Admittedly, in this context some limitations must be considered.

In the base case design both, distillation and evaporation are placed below the pinch. In principle, energy savings could be obtained by increasing the operating pressure and thereby shifting one of the sections or parts thereof above the pinch. For the evaporation stages and the stripper columns, this is not feasible due to the degradation and fouling of sugars and other organic compounds above 140 °C. Since no easily degradable compounds enter
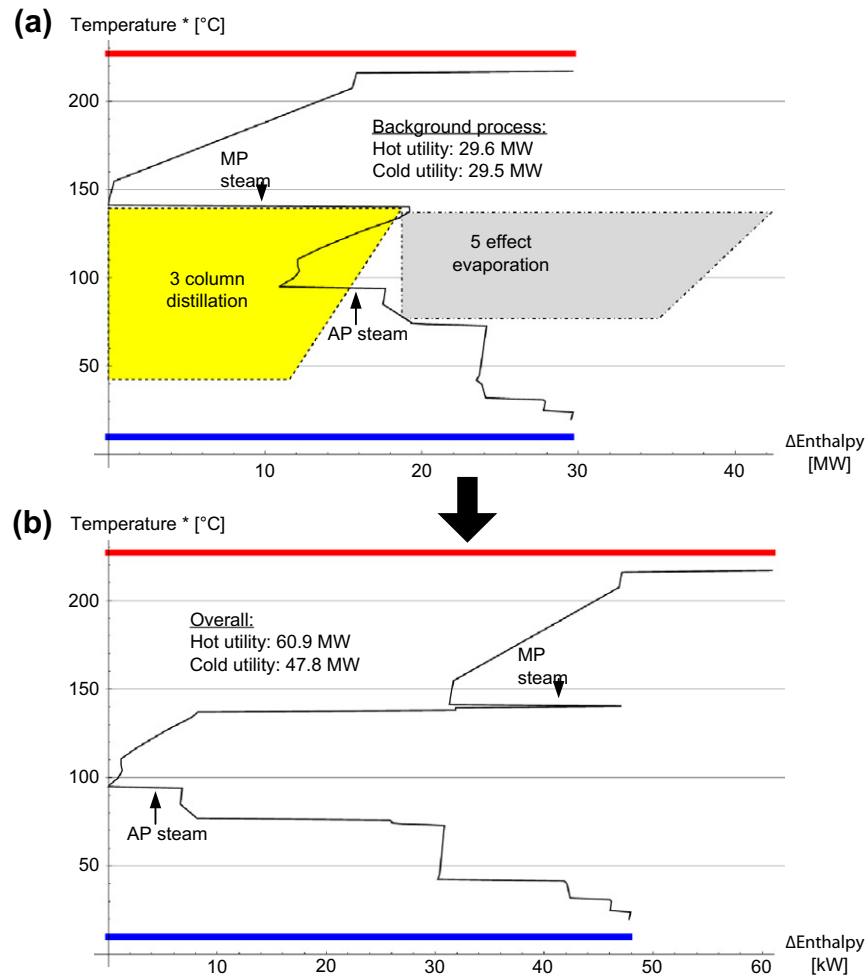
Fig. 3. Grand composite curves (GCCs) of base case. (a) GCC of background process. Distillation and evaporation are represented separately as boxes. (b) Overall GCC including the thermal separation units.

the rectification, it could potentially be shifted above the pinch. However, as can be seen in Fig. 3a, the background process could absorb the heat released at the condenser of the distillation only at temperatures above 200 °C. The associated increase of material cost and the requirement for an additional hot utility level makes this option unattractive.

On the other hand, process modifications resulting in very low temperatures and pressures should also be avoided, since vacuum generation is capital intensive and requires a lot of electricity. When very low pressures are applied, a potential heat load reduction thus corresponds to an undesired increase in electricity consumption.

Summing up, the following restrictions were applied in altering the design of the distillation and evaporation sections:

- No increase of stages in evaporation or distillation compared to the base case.
- No reduction of ΔT_{min}.
- No decrease of condensation temperatures/pressures compared to the base case.
- No heating above 135 °C.

Applying these restrictions, design modifications of the thermal separation sections were performed. Following the graphical approach described by Smith [14], heat loads and temperature levels were modified to increase the heat integration. The resulting improved design with integrated distillation and evaporation sections is shown in Fig. 4. Compared to the base case design the pressurized

stripper column and one evaporation stage are removed from the design. This reduction of stages is necessary to enable the integration of the distillation and evaporation section under the conditions listed above.

The first stage of the co-current evaporation train still requires MP steam. The heat released by condensation of the vapors from the third evaporation stage is used to supply the reboiler of the atmospheric stripper column, whose condenser duty in turn is used to heat the rectification column and the fourth stage of evaporation, both operated under vacuum.

The improved design was implemented in "IPSEpro". The stream data extracted from a converged flowsheet simulation of the improved case are in shown in Table 1. Streams differing from the base case are shown in bold characters. Altered data are indicated after the backslashes. As can be seen in Table 1, the modifications of the distillation and evaporation sections also affect the background process. The removal of the pressurized stripper results in reduced heat and cooling duties for preheating the beer and cooling the stillage, whereas the modification of the evaporation section only results in changed cooling requirements of the condensate streams.

4.1. Pinch analysis of the improved design

As for the base case, pinch analyses with a ΔT_{min} of 10 °C were carried out using the stream data from Table 1. The resulting grand composite curves (GCCs) are shown in Fig. 5.
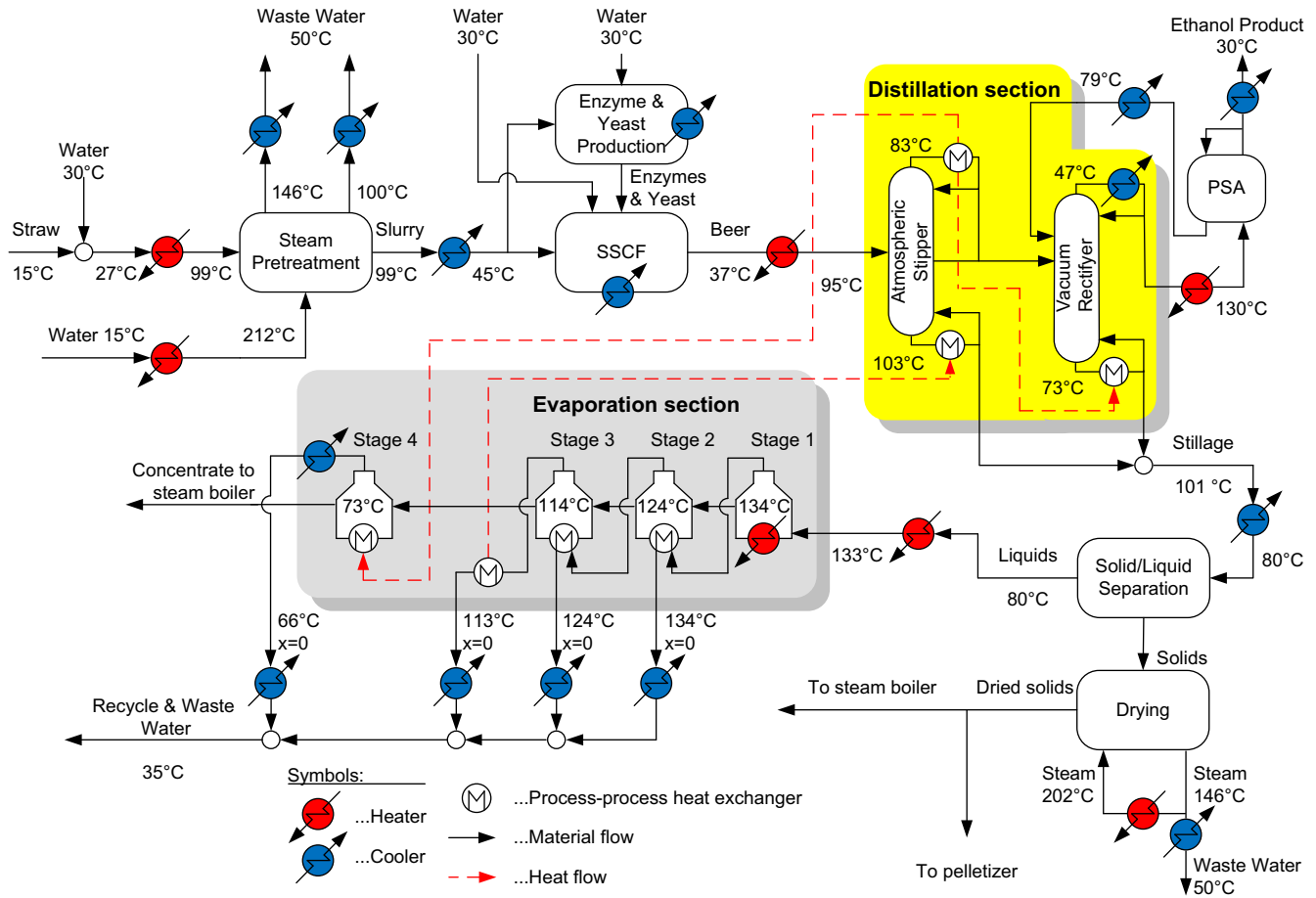
Fig. 4. Scheme of the improved design including integrated distillation and evaporation sections. SSCF: simultaneous saccharification and co-fermentation. PSA: pressure swing adsorption.

Corresponding to Fig. 3a, in Fig. 5a the grand composite curve of the background process is shown separately from the distillation and evaporation boxes. In the improved design the hot and cold utility targets $Q_{HU,min}$ and $Q_{CU,min}$ of the background process amount to approx. 30 MW and 31 MW. The slightly higher cold utility target for the background process compared to the base case is due to a lower heat demand below the pinch which results in decreased heat integration.

The integration of the distillation and evaporation is clearly visible. Since the distillation was shifted below the first three stages of evaporation, in the improved design MP steam is only required to heat the first evaporation stage and consequently the requirement at MP level is reduced compared to the base case. As can be seen, the heat duty of the evaporation is shifted towards the stages 1–3 whereas the last stage is designed with a smaller heat duty. This shifting of heat loads is beneficial for another reason also: The higher solids loading in the last stage result in a lower heat transfer. Even though the heat duty of the atmospheric stripper column has significantly increased compared to the base case, it can almost entirely be covered by the condensation of vapors from the third evaporation stage. In turn, the rectifier column and the 4th evaporation stage can, to a large extent, be supplied by the condensation heat released at the head of the stripper column.

The increased heat integration is also reflected in Fig. 5b, which shows the overall grand composite curve for the improved design. As a result of the increased integration, the overall hot and cold utility targets $Q_{HU,min}$ and $Q_{CU,min}$ for the improved design are lowered to 52 MW and 40 MW compared to 61 MW and 48 MW for the base case. This is a reduction by 14% and 16% which is attained

in spite of the reduction of stages in both distillation and evaporation.

For heat integration between distillation and evaporation a ΔT only slightly above ΔT_{min} was adopted and consequently only rudiments of pockets indicate the respective heat recovery at T^* of 110 and 80 °C. One should bear in mind, that pockets of heat recovery are only displayed when ΔT_{min} is exceeded. The increased integration between the background process and the thermal separation units is clearly visible by the pocket that is formed between 95 and 80 °C. Here AP steam from steam pretreatment can be used to cover that portion of the heat requirement of the vacuum rectifier and the last evaporation stage that cannot be provided by the condenser of the stripper column.

5. Heat exchanger network synthesis

For the improved design described in Section 4, a heat exchanger network shall be developed. To that end the methodology described in Section 2.3 is applied. The network determines the actual utility consumption and thereby allows closing the mass and energy balances of the straw to ethanol process.

When designing the heat exchanger network, some process characteristics have to be considered. The heat exchangers realizing the integration between distillation and evaporation as described in Section 4.1 are prescribed. Due to batch operation the bioreactors (HO4–H06) cannot be integrated with other process streams. However, to facilitate a direct comparison of the network with the energy targets developed in Section 3.2, H04–H06 are
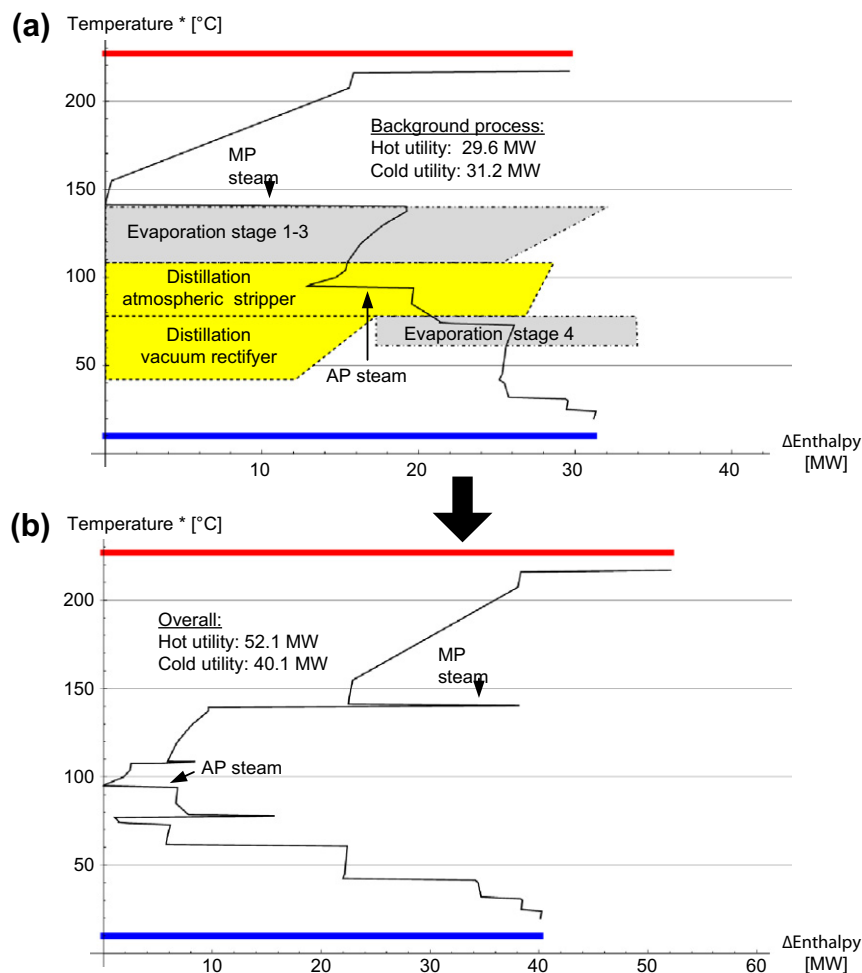
Fig. 5. Grand composite curves (GCCs) of the improved case. (a) GCC of background process. Distillation and evaporation are represented separately as boxes. (b) Overall GCC including distillation and evaporation.

included in the problem but excluded from heat exchange with other streams. There are several streams containing water insoluble solids (C01, C03, H03, H09), which can cause difficulties in heat exchangers. Certainly, heat exchange between two streams containing water insoluble solids makes things worse and is consequently forbidden. For similar reasons streams containing insoluble solids are also excluded from heat exchange with the distillation and evaporation sections. The moistened straw entering steam pretreatment (C01) is very high in insoluble solids and consequently poses a particular problem to heat transfer equipment. It is desirable to heat this stream without any further moistening i.e. steam injection. There is equipment available that can fulfill this task [27], however the heat transfer will be lower than in other heat exchangers. Consequently, for this stream the ΔT_{min} was set to 25 °C. The stream data of the improved case, as listed in Table 1, was used as input for the heat exchanger network synthesis.

5.1. Network for the improved design

The grid diagram of the network resulting from calculations with "TVTHENS" is shown in Fig. 6. With only 14 process–process heat exchangers (HX) a heat recovery of 100 MW is attained. In addition 8 hot utility (HU) and 14 cold utility (CU) heat exchangers with a heat and cooling duty of 61.4 and 49.3 MW have to be implemented. Compared to the targets (see Section 4.1), these val-

ues correspond to a very modest increase of only 18% of hot and 23% of cold utility consumption. All process–process and utility heat exchangers are listed in Table 2.

As can be calculated from data in Table 2, the integration of the distillation and evaporation sections with the background process via utilization of MP and AP steam (HX2 and HX3) amounts to 26.4 MW. Adding this value to the 52.2 MW of prescribed integration between the parts of distillation and evaporation (HX12, HX13 and HX14) results in a total heat recovery of 78.5 MW in the distillation and evaporation section. Comparing this value to 61.4 MW of hot utility consumption for the entire network underlines the significance of well-designed solutions for the distillation and evaporation in the process under investigation.

But also the background process' potential for heat recovery (see Section 3.2) is exploited in the network. Here, a major contribution to heat recovery is achieved through preheating the beer to distillation (C03) using the condensation of the vaporous ethanol product (HX5), condensates from evaporation (HX10 and HX11) and condensed MP steam from pretreatment and drying (HX1). In this way 11 MW of heat can be recovered and hot utility consumption for preheating the beer is reduced by 86%. Thus, only nine heat process–process exchangers are responsible for 90% of heat recovery. Minor contributions to the overall heat recovery are attained through (i) preheating the straw for steam pretreatment (C01) using regenerate from PSA (HX6) and evaporation condensate (HX8), (ii) heating the feed to evaporation (C05) using

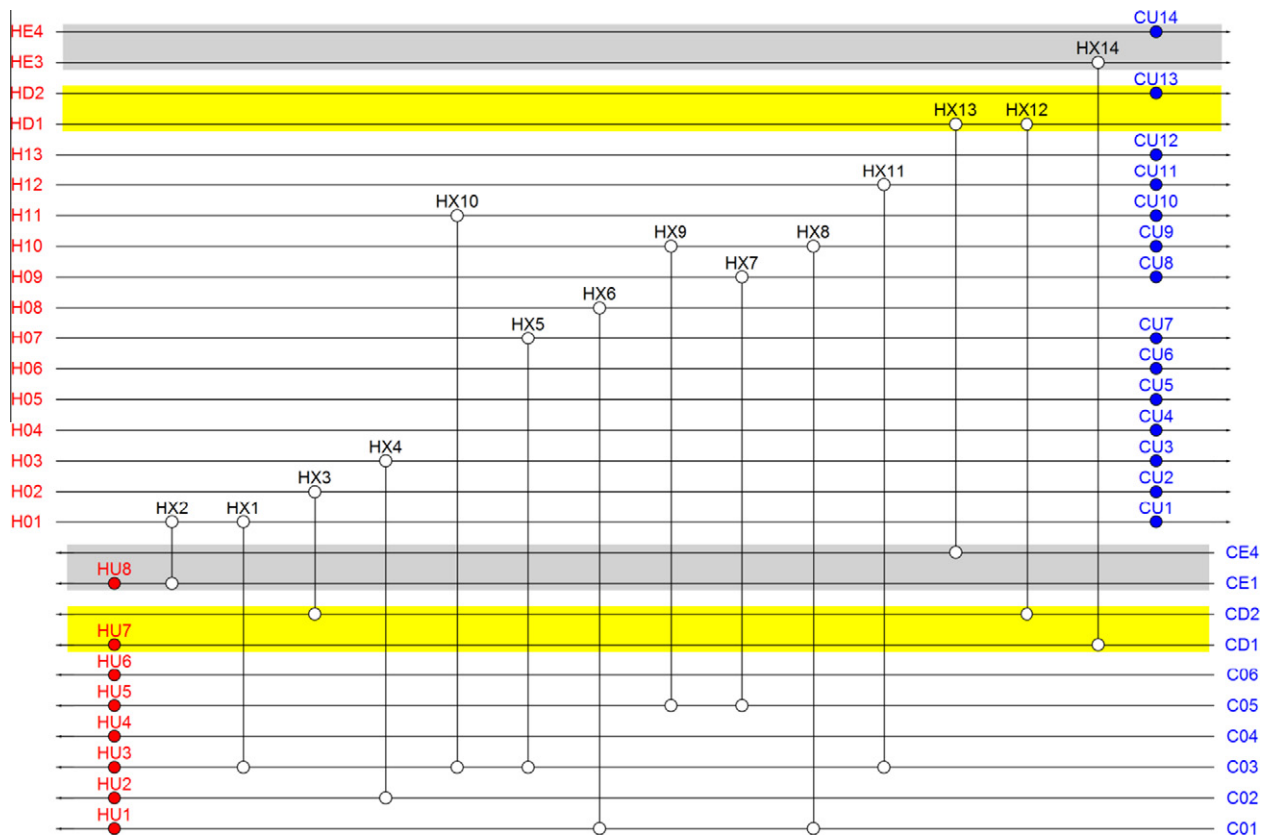**Fig. 6.** Grid diagram of the network. HX: process–process heat exchanger. HU: hot utility heat exchanger. CU: cold utility heat exchanger. Streams of distillation and evaporation are shown with a shaded background.

the hot stillage (HX7) and evaporation condensate (HX9) and (iii) preheating water, that is used to generate steam for the pretreatment (C02) via the hot slurry obtained from pretreatment (HX4).

Due to unsuitable temperature or technical restrictions some streams cannot be integrated at all and must entirely be covered by utilities. To be specific, these are the cold streams C06 (superheat drying steam) and C04 (vapors to PSA) which both must be superheated well above the pinch and the hot streams H04, H05 and H06 (cooling of bioreactors) that cannot be integrated due to batch operation (see Section 5).

6. Discussion

In Fig. 7 the utility consumption of the scenarios is summarized. The base case design of the process was derived from literature and employs efficiently integrated stand-alone solutions for the thermal separation units distillation and evaporation. Via pinch analysis it was found that the base case has a potential for 52 MW or 50% of heat recovery (see also Base case maximum vs. Base case target in Fig. 7). To a large extent this high potential can be attributed to the provision of secondary MP steam by the pretreatment and drying unit operations. The pinch analysis also revealed that AP steam from the pretreatment is not used efficiently in the base case and that a utilization of this heat source could further increase the heat recovery.

Consequently, design modifications of the distillation and evaporation sections were implemented to create an improved design of the process. To be specific, the two sections were integrated by reducing the number of stages and shifting the heat loads to different temperature levels. As a result, the utility targets were reduced by another 9 MW (or ca. 15% of the base case utility targets, see also Fig. 7). It is important to note that the increased heat integration causing this further reduction is twofold: First, between the distillation and evaporation section and second, between the background process and the thermal separation sections. To be specific, AP that could not be utilized in the base case design can be efficiently used to heat the vacuum rectifier or the 4th stage of the evaporation section. It is worth noting that this further utility reduction was achieved even though the process was simplified, namely the number of stages in both the distillation and the evaporation section were reduced. This clearly demonstrates the suitability of the technique applied and the necessity to optimally integrate the thermal separation units with the background process.

For the improved design of the process, a heat exchanger network was developed by simultaneous minimization of utility and heat exchanger cost. With only 14 process–process heat exchanger the obtained network is relatively simple but at the same time guarantees a high heat recovery. The increase of hot and cold utility consumption compared to the improved design targets amount to only 9 MW (or ca. 20% of the improved design utility target, see also Fig. 7). Almost no increase in utility consumption is observed when the base case targets are used as a reference. However, in this context it must be noted that increased heat integration between different sections of the process comes at a price, since it limits process flexibility and operability, especially during startup and maintenance. Ultimately, the question whether the proposed design and network could be implemented in a real facility remains to be answered by more detailed engineering.

The utility requirement of the obtained network allows closing the mass and energy balances of the process. In Table 3 the most prominent mass and energy flows of the process are listed. Comparing the hot utility requirement to the material related energy

Table 2
List of heat exchangers in the network. Heat exchanger of the distillation and evaporation sections are shown in bold characters.

HX Name	Heat (MW)	Hot process streams				Cold process streams			
		Stream description	Alias	T_{in} (°C)	T_{out} (°C)	Stream description	Alias	T_{in} (°C)	T_{out} (°C)
Process-process heat exchangers									
HX1	2.3	MP steam from SP and dryer	H01	145	86	Beer to distillation section	C03	76	86
HX2	**19.3**	**MP steam from SP + dryer**	**H01**	**146**	**145**	**Heat evap. stage 1**	**CE1**	**134**	**135**
HX3	**7.1**	**AP steam from SP**	**H02**	**100**	**89**	**Reboiler vac. rectifyer**	**CD2**	**72**	**73**
HX4	2.3	Slurry from SP	H03	99	83	Generate steam for SP	C02	15	89
HX5	3.3	Ethanol product	H07	130	78	Beer to distillation section	C03	51	65
HX6	2.0	Regenerate from PSA	H08	137	78	Straw to SP	C01	42	57
HX7	2.0	Stillage	H09	101	91	Feed to evap. section	C05	80	91
HX8	1.9	Condensate evap. stage 1	H10	101	67	Straw to SP	C01	27	42
HX9	1.9	Condensate evap. stage 1	H10	134	101	Feed to evap. section	C05	91	100
HX10	2.6	Condensate evap. stage 2	H11	124	75	Beer to distillation section	C03	65	76
HX11	3.2	Condensate evap. stage 3	H12	113	47	Beer to distillation section	C03	37	51
HX12	**10.2**	**Condenser atm. stripper**	**HD1**	**84**	**83**	**Reboiler vac. rectifyer**	**CD2**	**72**	**73**
HX13	**16.6**	**Condenser atm. stripper**	**HD1**	**84**	**83**	**Heat evap. stage 4**	**CE4**	**73**	**74**
HX14	**25.3**	**Vapors evap. stage 3**	**HE3**	**114**	**113**	**Reboiler atm. stripper**	**CD1**	**103**	**104**
Hot utility heat exchangers									
HU1	5.4					Straw to SP	C01	57	99
HU2	17.7					Generate steam for SP	C02	89	212
HU3	2.2					Beer to distillation section	C03	86	95
HU4	0.2					Vapors to PSA	C04	105	130
HU5	6.3					Feed to evap. section	C05	100	133
HU6	13.5					Superheat drying steam	C06	150	202
HU7	**3.3**					**Reboiler atm. stripper**	**CD1**	**103**	**104**
HU8	**12.8**					**Heat evap. stage 1**	**CE1**	**134**	**135**
Cold utility heat exchangers									
CU1	1.4	MP steam from SP and dryer	H01	86	50				
CU2	0.5	AP steam from SP	H02	89	50				
CU3	4.9	Slurry from SP	H03	83	45				
CU4	1.2	Yeast production	H04	30	29				
CU5	0.7	Enzyme production	H05	30	29				
CU6	3.4	SSCF	H06	37	36				
CU7	0.5	Ethanol product	H07	78	30				
CU8	2.6	Stillage	H09	91	80				
CU9	1.8	Condensate evap. stage 1	H10	67	35				
CU10	2.1	Condensate evap. stage 2	H11	75	35				
CU11	0.5	Condensate evap. stage 3	H12	47	35				
CU12	0.9	Condensate evap. stage 4	H13	66	35				
CU13	**12.1**	**Condenser vac. rectifyer**	**HD2**	**48**	**47**				
CU14	**16.8**	**Vapors evap. stage 4**	**HE4**	**73**	**66**				

MP: medium pressure; SP: steam pretreatment; AP: atmospheric pressure; PSA: pressure swing adsorption; evap.: evaporation; atm.: atmospheric; SSCF: simultaneous sacchrification and co-fermentation; vac.: vacuum.
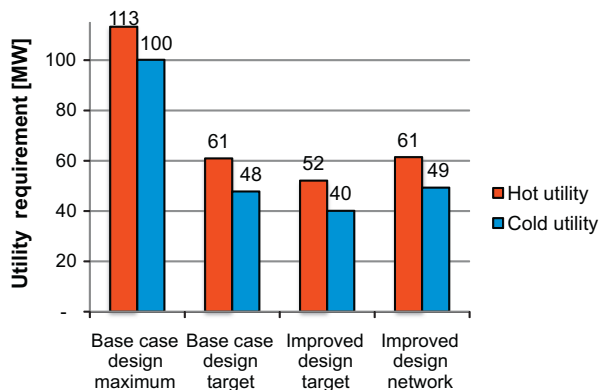
Fig. 7. Utility consumption for the different cases.

Table 3
Most important mass and energy flows for the process including the hot utility consumption for the non-integrated base case and the network. Material related energy flows are based on the lower heating value (LHV).

	Mass flow (t/y)	Energy flow (MW)
Straw (10% DM)	446,455	252
Concentrate (65% DM)	112,401	56
Dried solids (90% DM)	149,933	84
Ethanol	100,000	93
Hot utility base case max.	n.a.	113
Hot utility network	n.a.	61

flows of the process highlights the significance of heat integration for the prevailing process. The energy contained in residual materials (concentrate and dried solids) sums up to 140 MW, while the maximum hot utility consumption of the base case amounts to 113 MW. Hence, assuming a total efficiency of 85% for steam

generation and distribution, the energy contained in the residual materials barely matches the hot utility requirement of the process. On the other hand, for the network developed in this work only 51% of the residual materials suffice to supply the process with heat. The remaining 49% (or 68 MW) can be used for recovery of energy or material by-products. Relating this energy available for by-product recovery to the 93 MW of energy flow of ethanol, the actual product, illustrates the importance of efficient polygeneration concepts. These concepts are necessary to increase the overall efficiency and profitability for ethanol production from straw. In this context, it must be mentioned that within this work we assumed a high conversion of sugars during ethanol

fermentation (SSCF); for a lower conversion of sugars efficient polygeneration concepts become even more important.

Some options for polygeneration have been discussed previously [6]. Generally speaking, when assessing different polygeneration concepts, it must be considered that some of these concepts can be designed to perfectly fit to the current process design (e.g. production of electricity or electricity and district heat in a Rankine cycle [6]), whereas other concepts may require a modification of the current process design and integration. The latter is the case for polygeneration concepts that (i) provide heat in excess to the process requirement or at different temperature levels, or for concepts that (ii) do not require some of the process units in the current design (e.g. drying or evaporation). Coproduction of biogas via anaerobic digestion and biogas upgrading to biomethane [6] shall be mentioned as one example for a polygeneration concept that would require a modification of the current design.

7. Conclusion

Process simulation and pinch analysis were used to analyze and improve the design of biochemical ethanol production from straw. The analysis was started with a base case design, which was derived from the literature and included multi stage stand-alone solutions for the energy intensive thermal separation units distillation and evaporation. The following can be concluded:

- Energy self sufficient production of ethanol from straw can be realized by utilizing process residues to provide heat.
- Pinch analysis showed that due to highly integrated stand alone solutions for distillation and evaporation on the one hand, and secondary MP steam provided from pretreatment and drying on the other hand, the base case design has a high potential for heat recovery.
- The pinch analysis also revealed that the process design can be improved by adapting the design of the thermal separation units, namely the number of stages, the temperature levels and the heat loads.
- In the improved design thus obtained, further heat recovery and a reduction of the utility requirement were achieved, even though the number of stages in both distillation and evaporation were reduced which demonstrates the suitability of the method applied.
- Optimized stand-alone solutions for the energy intensive multi-stage unit operations are a good starting point in the design procedure; however, for optimal use of process heat, these units must be adapted to the background process.

For the improved design a heat exchanger network was synthesized. Thereto utility and heat exchanger cost were minimized simultaneously. With the network thus obtained, it is possible to determine the actual utility requirement in a possible production facility. Regarding the heat exchanger network the following can be concluded:

- The increase compared of utility requirement compared to the targets is modest, even though a rather simple network was designed.
- This demonstrates the suitability of the approach applied for heat exchanger network synthesis, namely simultaneous minimization of utility and heat exchanger costs.
- For the process under investigation, some 50% of process residues suffice to provide process heat.
- This underlines the importance of efficient polygeneration concepts for ethanol produced from straw.

8. Future work

Based on the results of this work, a complete flowsheet model that includes the utility system can be generated. Thereafter further process and energy system analysis such as energy or exergy analysis, techno-economic analysis or life cycle analysis can take place. Based on our findings, we believe that further research shall be dedicated to development of efficient polygeneration concepts, which will lead to higher energy efficiency as well as better economic and environmental performance. When these goals are attained, the production of ethanol from lignocellulosic biomass certainly soon will become a commercial reality.

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6.8. PAPER VIII

Comparison of combined ethanol and biogas polygeneration facilities using exergy analysis

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Comparison of combined ethanol and biogas polygeneration facilities using exergy analysis

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ARTICLE INFO

ABSTRACT

Polygeneration processes for production of ethanol (2500 t/y, anhydrous), electrical power, and district heat from wheat (grain + straw) were evaluated via exergy analysis and compared with a standard ethanol process that yields DDG as a supplementary product. A tool was developed to account for exergy in processes utilizing biological matter based on major classes of biomolecules (carbohydrates, lignin, lipids and protein) and ash. This allows for an estimation of the exergy of complex streams that occur throughout the conversion process. Standard ethanol production from wheat grain yielded an exergy efficiency of 37.9% for ethanol and 60.9% for products (ethanol and DDG). The interim case (wheat grain + straw) was found to be more efficient producing ethanol (47.4%), since the stillage was used to supply utilities. Wheat straw only facilities have limited ethanol efficiency since only part of the raw material was converted into ethanol. As was shown with the lignocelluloses only scenario using the stillage to produce valuable products can raise the overall performance of the process potentially to 68.7%.

1. Introduction

The industry can rely on a proven and robust process using starch-rich source materials that can be stored and processed conveniently to produce ethanol. Or, industry can advance beyond these First Generation processes. Lignocellulosic materials are the essence of Second Generation biofuels. Some of these source materials (e.g. straw from grain production and corn stover) are agricultural residues, others such as hardwoods, softwoods and grasses are grown dedicated for use in energy production.

These Second Generation biofuels have (in general) a lower hexose content than for example maize or wheat grain. However, in addition to hexoses these raw materials contain significant amounts of pentose-sugars and lignin.

The heterogeneous structure of lignocellulose requires additional process steps to realize the full potential. A polygeneration process that yields fuel, heat, and electricity can be more effective in minimizing wasted heat and unwanted by-products. This polygeneration process productively uses what would otherwise be underutilized side streams as a fuel, to increase the total energy output of the process and increase exergy efficiencies. This can be exergy in a chemical form (ethanol and methane) or a physical form (electricity,

steam and hot water). In recent times, several scenarios have been proposed to more fully utilize lignocellulosic source material for the production of ethanol [1,2]. They have in common that the production facility is optimized for ethanol production in conjunction with the maximum utilization of the side streams that occur during the processing. Side streams may include: low temperature heat, organic matter or carbon dioxide formed during fermentation [3]. Recently Bösch et al. [4] studied dual temperature single-step dilute acid hydrolysis method compared with two-step single-temperature dilute acid hydrolysis of biomass for ethanol production.

The agricultural residue of feedstock growth is often used to provide the utility steam of the process via incineration as with bagasse. A good example of this process is ethanol production from sugar cane. By combusting the residue in its native form a considerable amount of exergy is irrecoverably lost that could be saved if processed differently.

Another drawback of incineration alone is that elements such as nitrogen or phosphor in a bioavailable form are lost for later recirculation to the soil and therefore have to be substituted by mineral fertilizers that have a negative impact on the life cycle analysis [5].

The main goal of these facilities is the conversion of low-value source materials to high value energy forms.

It is in the nature of polygeneration concepts to yield a broad spectrum of products. To have a common ground for the comparison

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Notation

AD	Anaerobic digestion
BC	Beer column
c	Concentration [%w/w]
CD	Cellulose digestion
Cp	Specific heat [kJ/kgK]
CS	CO_2 scrubber
DDG	Dried distillers grains
DM	Dry material [kg/kg]
EF	Ethanol fermentation
EtOH	Ethanol [−]
Ex	Specific exergy [kJ/kg]
EX	Exergy [kJ]
GB	Gas boiler
GE	Gas engine
GS	Gas scrubber
LHV	Lower heating value [kJ]
MT	Mashing tub
p	Pressure [bar]
PV	Pervaporation unit
RC	Rectification column

SG	Steam generator
SP	Steam pretreatment
T	Temperature [°C]
VP	Vacuum pump
W	Mass fraction [kg/kg]
w	Weight
YP	Yeast propagation
β	Ratio of the chemical exergy to the LHV of the organic fraction of biomass [−]
η	Efficiency [−]
λ	Percentage excess air

Subscripts

chem	chemical
H, O, C, N	hydrogen, oxygen, carbon, nitrogen
i	class of biomass (carbohydrates, lignin, proteins, lipids, ash, water)
mix	Mixing
mono	monomeric
phys	physical
poly	polymeric

of these products, exergy analysis is applied [6]. It provides a reasonable foundation for the comparison of a wide variety of process streams that occur throughout the conversion process. Furthermore exergy analysis is a tool to identify the energy and exergy losses within the system which decrease the system performance [17] and to determine the most efficient process to convert biological matter to energy carrier as demonstrated by Modarresi et al. for a hydrogen generation process [7,8]. Past exergy studies by Gassner et al. [19] demonstrated that the application of a polygeneration process can have a significant impact on the process performance. With proper heat integration-polygeneration can totally recover the exergy potential of a process formulated as an optimization problem. Zhang et al. [18] also offered evidence that by applying the results of exergy analysis to a novel hybrid polygeneration system, there was an improvement in the system performance. Pfeffer et al. [20] applied an energy integration technique to improve the efficiency of a bio-ethanol production process in which heat and power are both generated from residues of the process. This study showed that rectification and distillation plants can be heat-integrated which significantly reduce external energy demand.

This paper focuses on the comparison by simulation of different processes where polygeneration could be applied. The reference case is a conventional wheat corn to ethanol process. The study is limited to an analysis of the processes themselves. Feedstock production, fertilizer use, and transport (among many other factors) are not accounted for in our calculations.

This work highlights the constraints and effects when moving on from First to Second Generation ethanol production processes (including an interim stage) in conjunction with polygeneration. As a foundation for the comparisons between these examples of applying polygeneration, exergy analysis was chosen in order to compare a large domain of parameters than has been common in the past.

2. Material and methods

2.1. Process description

Five scenarios are defined to evaluate the impact of different feed materials and process configurations; a reference case

represented by a state of the art facility based on wheat grain, two interim processes that utilize both wheat grain and straw and two straw only facilities. The production target was chosen appropriate for a process supplied from regional production (uptime 320 d/y, output 2500 t/y anhydrous ethanol (0.3%w/w H_2O, EN15376 [9])). Cases that yield electric energy are specified to generate 1400 kW with a part thereof diverted to power the facilities. The remainder is assumed to be available the public power grid. For the analysis the unit operations were summarized in four distinct processes:

- Ethanol production:
  ○ starch-based: milling, mashing, liquefaction, saccharification, yeast propagation, ethanol fermentation, distillation and dehydration
  ○ lignocellulose-based: cellulose digestion, yeast propagation, fermentation, distillation and dehydration
- Utilities: biogas production, combustion of biogas or methane in combustion chamber or engine, steam generation for steam utilities (district heat)
- DDG: separation and drying of stillage to DDG
- Steam pretreatment: decomposition of wheat straw for ethanol/biogas fermentation

2.1.1. Process 0 (P0): reference case

In this conventional process, starch-rich raw material (e.g. wheat grain), is milled, enzymatically hydrolyzed and fermented to obtain an ethanol-rich mash. This mash is further distilled and dehydrated by a membrane process to yield anhydrous ethanol. The stillage is then separated and dried to become dried distillers grains (DDG) used as a livestock fodder rich on proteins.

The combustion of natural gas supplies the energy to power process utilities. The utility steam ($p = 5$ bar) drives the distillation columns of the ethanol process and liquefaction as well as the dryer of the DDG process. The solubles from the stillage are not further utilized in this scenario, as shown in Fig. 1.

2.1.2. Process 1: interim case
2.1.2.1. Scenario 1a (P1a): without power generation. The ethanol process is equivalent to the reference scenario. The stillage from

ethanol separation and additional pretreated wheat straw are fed to the anaerobic digestion unit. The biogas is fed into a combustion chamber where it is utilized to supply for all the steam utilities ($p = 12.6$ bar). The increase of pressure over the reference scenario is necessary due to the use of steam pretreatment used in all cases but Process 0, as represented in Fig. 2.

2.1.2.2. Scenario 1b (P1b): with power generation. Anaerobic digestion of stillage and pretreated wheat supplies biogas to a combustion engine that generates electricity. Since the off heat of the engine is not sufficient to supply for all steam utilities additional biogas is required to feed the combustion chamber (see Fig. 2).

2.1.3. Process 2: lignocellulose case
2.1.3.1. Scenario 2a (P2a): without power generation. The lignocellulose scenario uses wheat straw to produce ethanol. With the ethanol fermentation process only hexose sugars are fermented. The remaining pentoses are metabolized in the anaerobic digestion step. The straw is steam pretreated, enzymatically hydrolyzed, fermented and dewatered. The stillage is further processed as in Process 1 by the addition of steam pretreated wheat straw, anaerobic digestion, combustion in a combustion chamber and steam generation, as seen in Fig. 3.

2.1.3.2. Scenario 2b (P2b): with power generation. Anaerobic digestion of stillage and pretreated wheat straw supplies biogas to a combustion engine that generates electricity. Since the flue gas of the engine is not sufficient to supply the whole process with steam a combustion chamber as well fed with biogas provides the remainder (see Fig. 3).

2.2. Process simulation

The ethanol production facilities in combination with (or without) steam pretreatment, biogas production and combustion creates a network of high complexity. To approach this problem, the authors facilitated an existing model library for ethanol production based on the simulation tool IPSEpro, an equation oriented industrial simulation package [10]. The simulation software is used to compute the energy, exergy and mass balances of the different process scenarios (see Fig. 4). According to work done earlier [11] the heat exchanger network of the process and the downstream of the ethanol production were optimized to reduce the specific energy uptake. Table 1 reports the parameters with the highest significance for the analysis. The steam consumption of the steam pretreatment process is estimated by a model that accounts for the heat up of the feed material and the headspace in the reactor (unpublished).
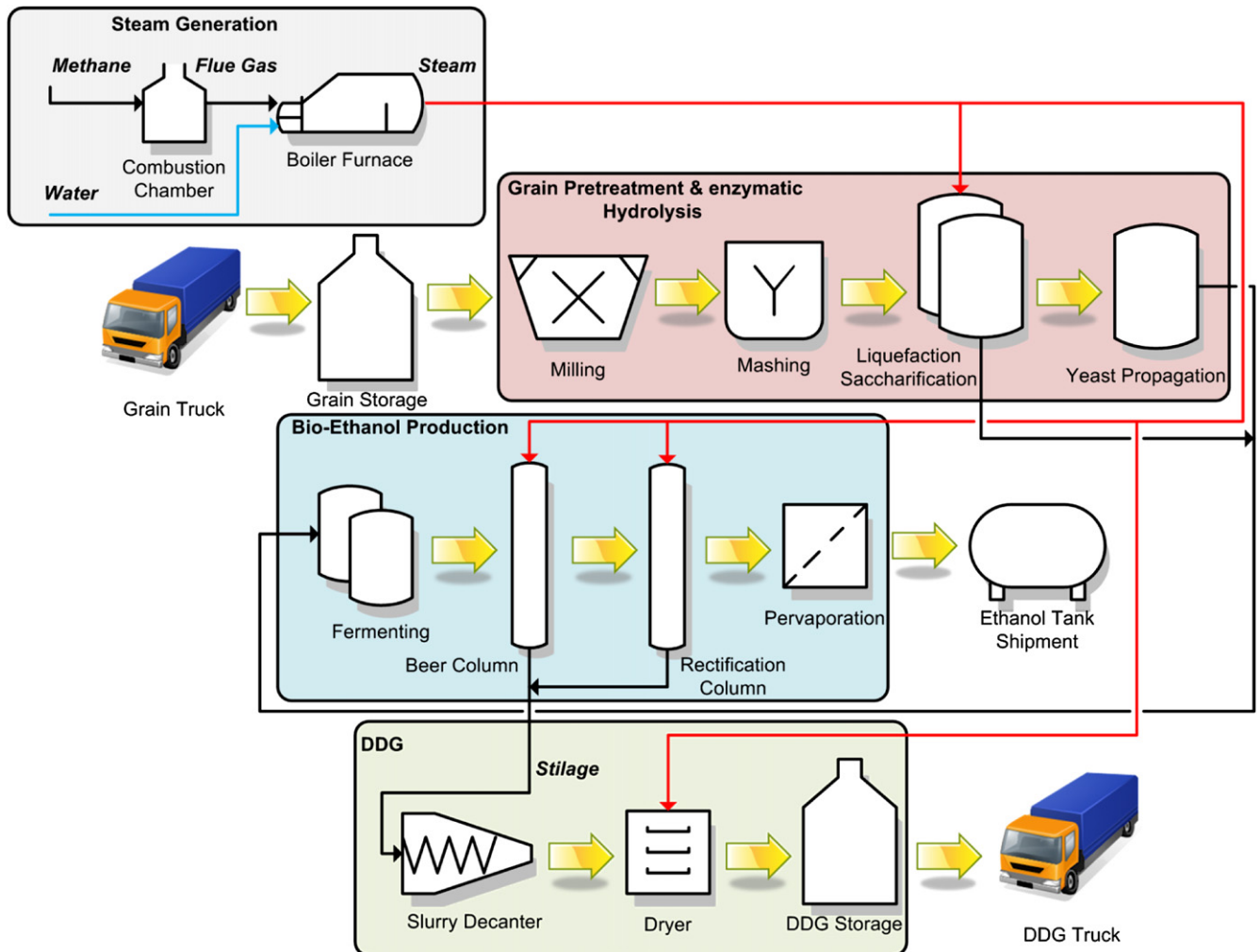

Fig. 1. Process 0 (P0), reference case, ethanol from grain, DDG from stillage, methane supplies utilities, no power generated.

Fig. 2. Process 1 (P1a, P1b), interim case, ethanol from grain, utilities from stillage and straw via anaerobic fermentation, electricity and district heat not generated in P1a.

2.3. Exergy

Exergy analysis is an appropriate technique to identify the irreversibilities in chemical processes which is recently discussed in some details by Asprion [21].

The total exergy of a multicomponent material stream is given by

$$EX = EX_{Chem} + EX_{Phys} + EX_{mix} \qquad (1)$$

where EX is the total exergy of the stream, EX_{Chem} the chemical exergy of the substances, EX_{Phys} the physical exergy and EX_{mix} the exergy of mixing. The last parameter is negligible for this application due to its minimal magnitude.

The system boundaries for the calculation are borders of the facility. EX_{Input} is defined as the sum of all input streams

$$EX_{Input} = EX_{Grain} + EX_{Straw} + EX_{Methane} + EX_{Power} \qquad (2)$$

EX_{Output} is defined as the sum of all streams leaving the system boundaries

$$EX_{Output} = EX_{Ethanol} + EX_{Biogas} + EX_{DDG} + EX_{Power}$$
$$+ EX_{DistrictHeat} + EX_{Anaer.Dig.Res.} + EX_{Effluents} \qquad (3)$$

The term Exergy of Effluents (CO_2, low temperature water, solubles from stillage, engine off heat) summarizes all low exergy streams that leave the process without yielding a product to close the exergy balance of the system. The loss of exergy (Irreversibility) by the process is defined as

$$Irreversibility = EX_{Input} - EX_{Output} \qquad (4)$$

2.3.1. Chemical exergy

Chemical exergy analysis is performed according to the method proposed by Szargut et al. [12]. Chemical exergy of starch-based and lignocellulosic biomass is calculated from the correlations for technical fuels using the LHV as followed:

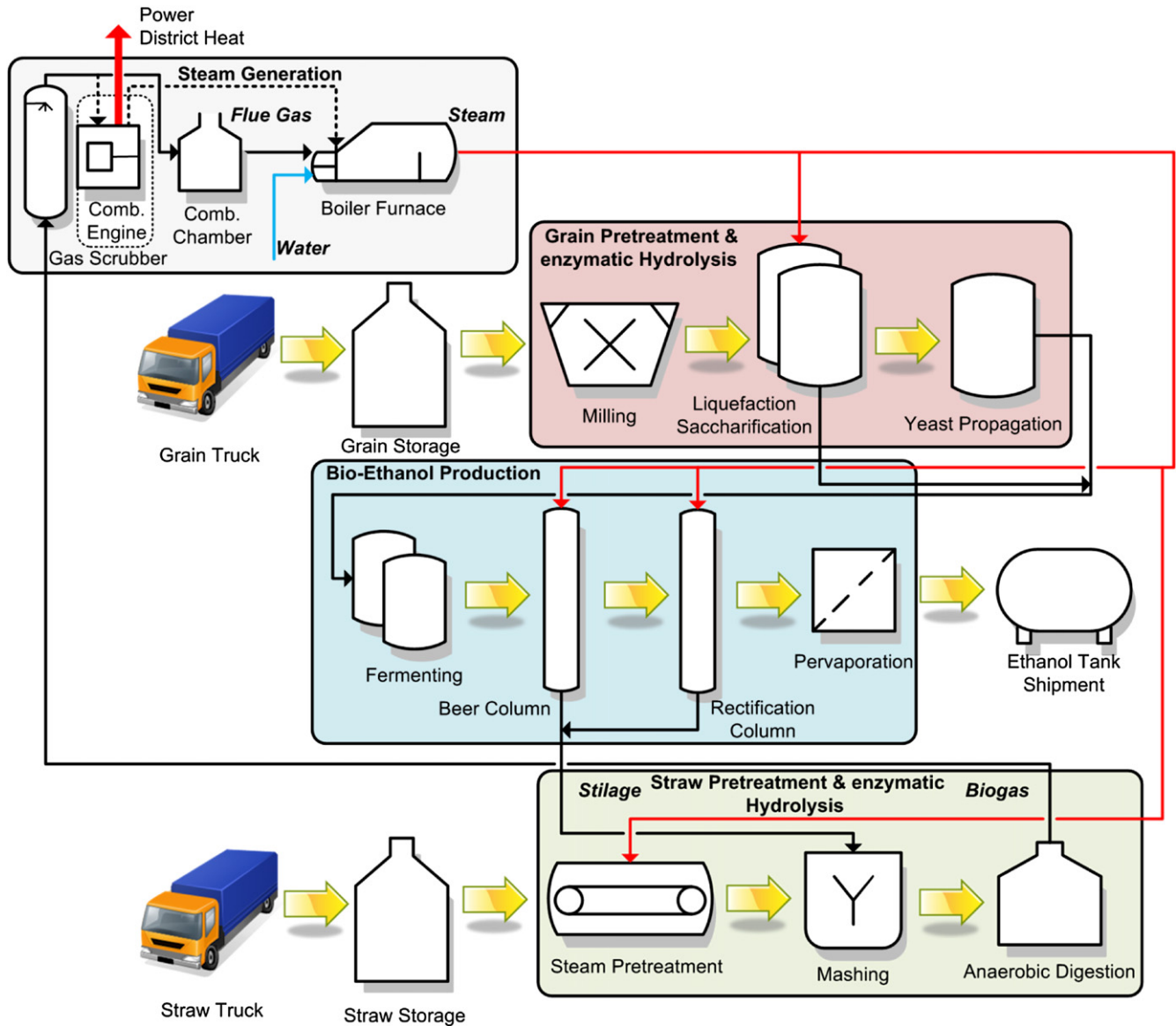$$Ex_{Chem,i} = \beta_i LHV_i \qquad (5)$$
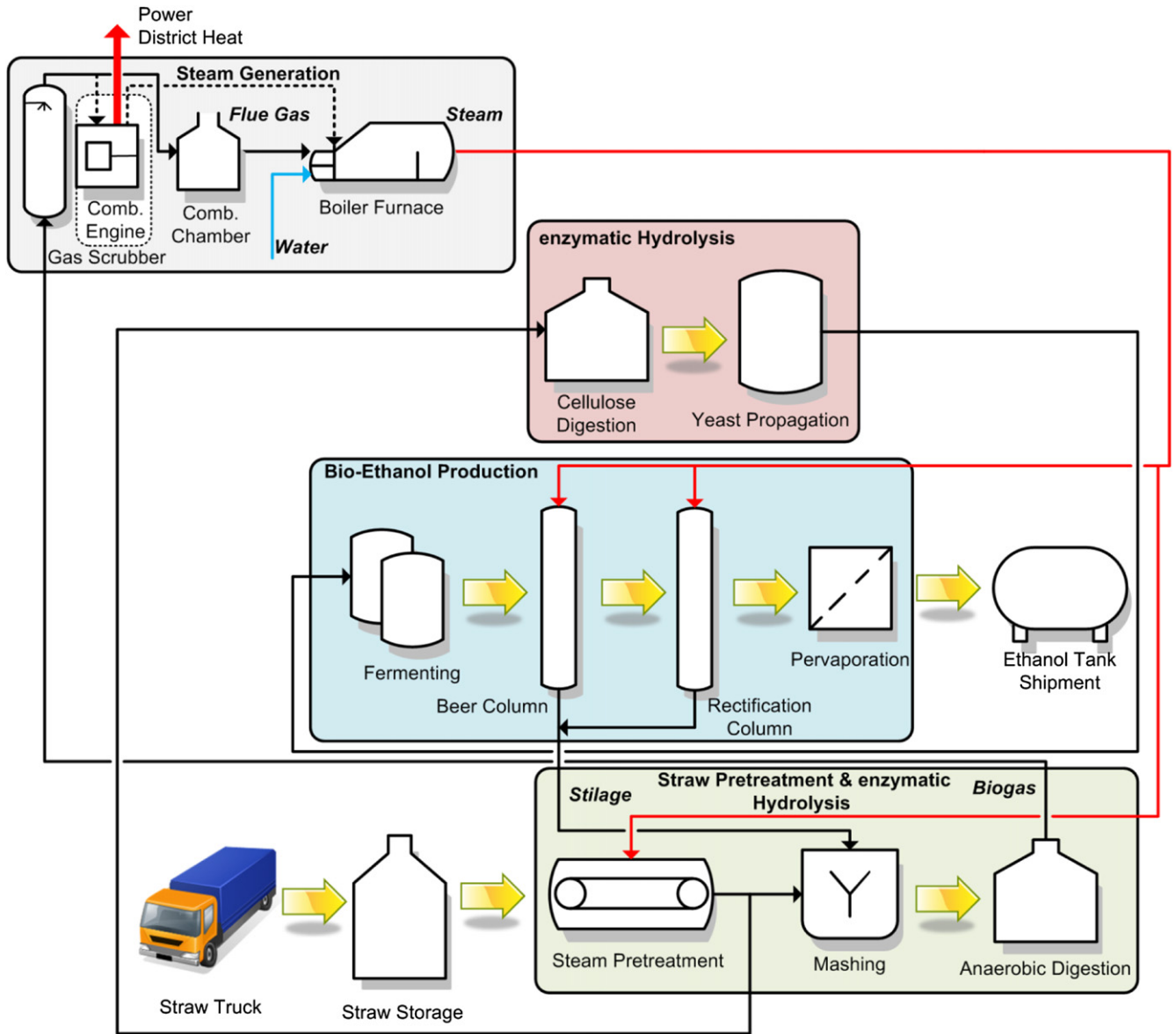
Fig. 3. Process 2 (P2a, P2b), lignocellulose case, ethanol from grain, utilities from stillage and straw via anaerobic fermentation, electricity and district heat not generated in P2a.

The factor β is the ratio of the chemical exergy to the LHV of the organic fraction of biomass. This factor is calculated from statistical correlations developed by Szargut and Styrylska. The following correlations are used:

- Solid organic components (carbohydrates, lignin, protein)

$$\beta = 1.0438 + 0.1882 W_H/W_C + 0.0610 W_O/W_C + 0.0404 W_N/W_C \tag{6}$$

for $W_O/W_C \le 0.5$

$$\beta = [1.0438 + 0.1882 W_H/W_C - 0.2509 W_O/W_C(1 + 0.7256 W_H/W_C) + 0.0383 W_N/W_C]/(1 - 0.3035 W_O/W_C) \tag{7}$$

for $0.5 < W_O/W_C \le 2$

- lipids

$$\beta = 1.0374 + 0.1895 W_H/W_C + 0.0426 W_O/W_C \tag{8}$$

The chemical exergy of ash is determined by its components CaO, K_2O, SO_3 and SiO_2. The chemical exergy of water is 51 kJ/kg [13,23] according to its gibbs energy of formation −237.18 kJ/mol [22]. The chemical exergy is summarized in Table 2.

The sum of the component's chemical exergy weighted by their mass fraction in the biomass

$$Ex_{Chem,Biomass} = \sum Ex_{Chem,i} W_i \tag{9}$$

yields the chemical exergy of the biomass.

2.3.2. Physical exergy

The physical exergy of a solid component in biomass which have a quite constant heat capacity around room temperature is calculated according to its specific heat capacity (see Table 2) as well as the temperature of the mass stream (T_1) in regard to the defined ambient temperature of 293.15 K (T_0).
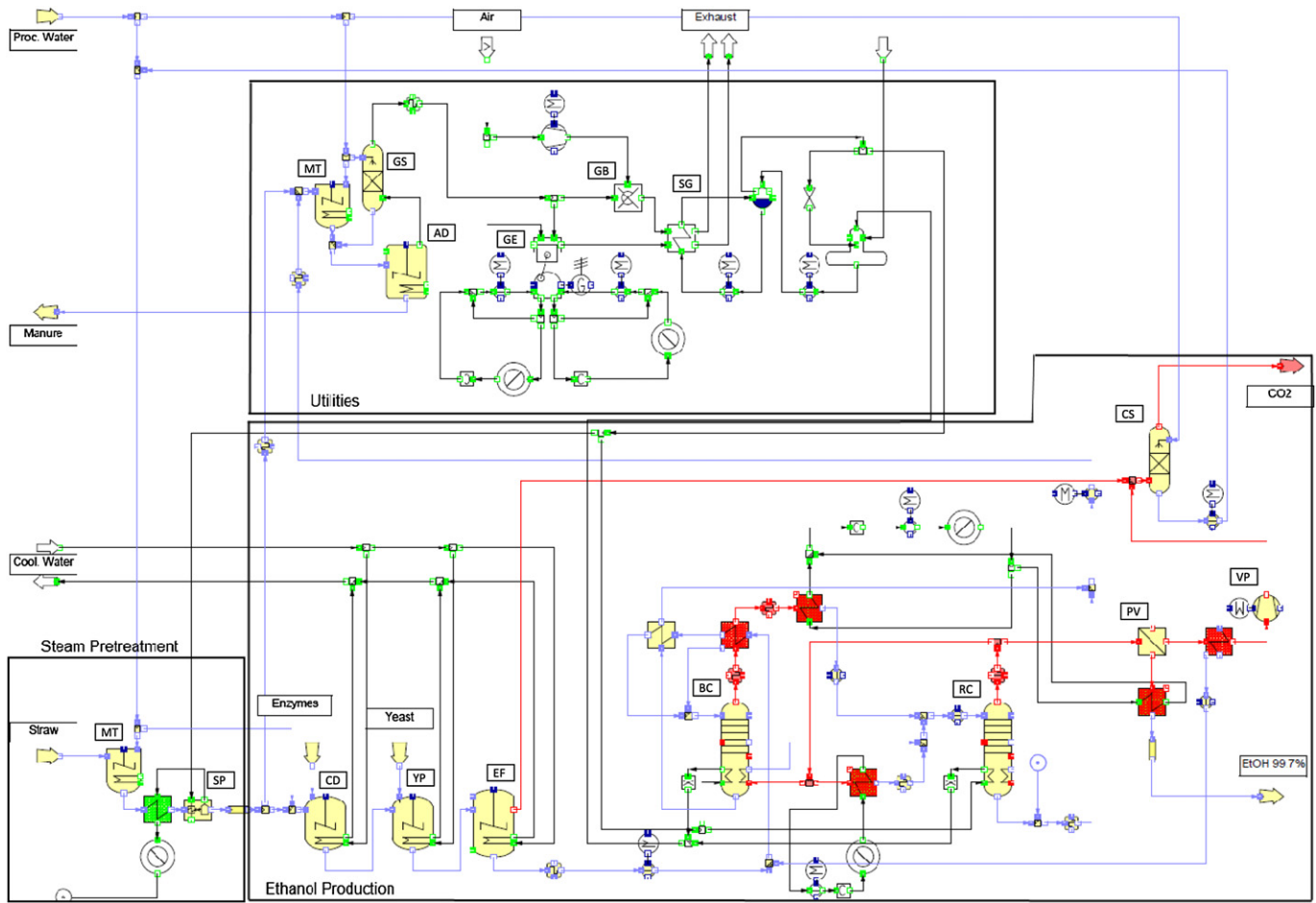
Fig. 4. Representation of Process 2b in IPSEpro. Steam pretreatment, ethanol production and utilities are framed. Mashing Tub (MT), Steam Pretreatment (SP), Cellulose Digestion (CD), Yeast Propagation (YP), Ethanol Fermentation (EF), Beer Column (BC), Rectification Column (RC) Pervaportation Unit (PV), Vacuum Pump (VP), CO$_2$ Scrubber (CS), Anaerobic Digestion (AD), Gas Scrubber (GS), Gas Engine (GE), Gas Boiler (B), Steam Generator (SG).

$$\text{Ex}_{\text{Phys},i} = \text{Cp}[(T_1 - T_0) - T_0\ln(T_1 - T_0)] \tag{10}$$

The sum of the components physical exergy weighted by their mass fraction of the biomass

$$\text{Ex}_{\text{Phys,Biomass}} = \sum \text{Ex}_{\text{Phys},i} W_i \tag{11}$$

yields the physical exergy of the biomass.

2.3.3. Efficiency

Several different factors for efficiency are used to describe the processes and make them comparable based on different grounds.

$$\eta_{\text{General}} = \text{EX}_{\text{Output}}/\text{EX}_{\text{Input}} \tag{12}$$

$$\eta_{\text{Irreversibility}} = \text{Irreversibility}/\text{EX}_{\text{Input}} \tag{13}$$

$$\eta_{\text{Ethanol}} = \text{EX}_{\text{Ethanol}}/\text{EX}_{\text{Input}} \tag{14}$$

$$\eta_{\text{ProductI}} = (\text{EX}_{\text{Ethanol}} + \text{EX}_{\text{Biogas}} + \text{EX}_{\text{Power}})/\text{EX}_{\text{Input}} \tag{15}$$

$$\eta_{\text{ProductII}} = (\text{EX}_{\text{Ethanol}} + \text{EX}_{\text{Biogas}} + \text{EX}_{\text{Power}} + \text{EX}_{\text{DDG}} \\ + \text{EX}_{\text{DistrictHeat}})/\text{EX}_{\text{Input}} \tag{16}$$

$$\eta_{\text{ProductIII}} = (\text{EX}_{\text{Ethanol}} + \text{EX}_{\text{Biogas}} + \text{EX}_{\text{Power}} + \text{EX}_{\text{DDG}} \\ + \text{EX}_{\text{DistrictHeat}} + \text{EX}_{\text{Anaer.Dig.Res.}})/\text{EX}_{\text{Input}} \tag{17}$$

Note: If not explicitly state otherwise specific exergy values (kJ/kg) are always specified as kJ exergy per kg anhydrous ethanol.

3. Results and discussion

3.1. Material streams

The simulation considers a multitude of mass streams. The most significant in terms of exergy are shown in Table 3. Pure methane has an exergy content of 52.1 MJ/kg. In this case biogas has a methane content of 30%w/w, 66%w/w CO$_2$ and 4%w/w H$_2$O yielding 16.0 MJ/kg biogas at the defined ambient temperature. The specific exergy of the dry biomass varies between 18.8 MJ/kg for wheat straw and 21.5 MJ/kg for DDG underlining the high energy content of this product. Since in the process the streams are diluted to a high extend their specific amount of exergy is reduced accordingly with only 1.6 MJ/kg biomass in the case of wheat grain stillage (7.3%w/w DM) or 3.6 MJ/kg biomass with wheat straw stillage (18.5%w/w DM). Depending on the source material of the anaerobic digestion the residue varied in composition and exergy content. The negligible impact of physical exergy streams at the occurring temperature levels of biomass streams in comparison to their chemical exergy is another insight worth noting.

Table 1
Simulation parameters.

Steam pretreatment	Pretreatment straw	$\%DM_{in}$	%w/w	30
		$T_{reaction}$	°C	180
		$p_{reaction}$	Bar	10
Starch-based ethanol	Mashing	T	°C	84
	Liquefaction	T	°C	85
	Saccharification	T	°C	55
		conv. rate $_{Polysacch \rightarrow Hexose}$	%	85
	Yeast propagation	T	°C	35
	Ethanol fermentation	T	°C	35
		conv. rate $_{Hexose \rightarrow EtOH,CO2}$	%	98
		$c_{out, EtOH}$	%w/w	7.6
Lignocellulose-based ethanol	Cellulose digestion	T	°C	50
		conv. rate $_{Cellulose \rightarrow Hexose}$	%	76
	Yeast propagation	T	°C	35
	Fermentation	T	°C	35
		conv. rate $_{Hexose \rightarrow EtOH}$	%	88
		$c_{out, EtOH}$	%w/w	4.5
Distillation and dehydration	Beer column	p_{column}	bar	1.0
		$c_{out, EtOH}$	%w/w	82.6
	Rectification column	p_{column}	bar	4
		$c_{out, EtOH}$	%w/w	94.1
	Pervaporation	Permeability$_{EtOH}$	kg/(m³barh)	0.03
		Permeability$_{H2O}$	kg/(m³barh)	1.29
Utilities	Biogas production	T_{mash}	°C	37
	Combustion chamber	λ		1.6
		$T_{flue\ gas}$	°C	1339
	Gas engine	λ		1.5
		$T_{flue\ gas}$	°C	451
		η_{engine}		0.967
DDG	Separation	$\%DM_{out}$	%w/w	86
	Drying	p	bar	1.02
		$T_{air,in}$	°C	72
		$T_{air,out}$	°C	75

3.2. Process comparison

The Sankey diagrams shown in (Figs. 5—9) give an overview of the level of exergy flows throughout the process. The central process step is the ethanol process supplied by raw materials and utilities yielding ethanol and stillage that is further processed depending on the applied scheme.

The yield of the investigated starch-based ethanol process is 0.316 kg ethanol/kg grain. The exergy uptake of the reference case (anhydrous ethanol and DDG) is 21.2 MJ/kg ethanol including inputs from methane that originates from fossil sources and electric power. When compared to data published by Shapouri et al. the reference case is found to produce 10.5% less ethanol per kg grain and consumes 12% more exergy per kg ethanol [14]. Economy of scale effects can describe this discrepancy since the plants surveyed by Shapouri et al. were at least 40 times larger based on total ethanol output.

The specific exergy inputs (per kg anhydrous ethanol produced) of straw, grain, methane and electric power are given in Table 4. It was found that the reference (P0) and interim case (P1a, P1b) require 56.7 MJ/kg of exergy input originating from wheat grain. In comparison the lignocellulose case that processes wheat straw as feed for the ethanol process (P2a, P2b) requires 111.6 MJ/kg.

Cellulosic material has a lower C6 sugar content than grain that results in a lower specific conversion yield from raw material to ethanol. The C5 sugars are not metabolized in the ethanol fermentation step but are input for the biogas production. The lignin fraction of the lignocellulose is considered inert in the ethanol as well as the biogas fermentation. In contrast to Process 0 that provides its steam utilities by combusting non-renewable methane, the other processes supply their heat requirement themselves by facilitating the biogas. Process 0 has a power consumption of 2.4 MJ/kg. Process 1a and Process 2a have a higher demand since the biogas fermentation requires stirring. The remaining processes (1b and 2b) need only be supplied with grain and/or wheat since both steam utilities and electric power are generated by the process.

Table 2
Chemical exergy of biomass components.

Component	Cp [kJ/kgK]	LHV [kJ/kg]	β [−]	$EX_{Chem,i}$[kJ/kg]
Carbohydrate polymer	1.28	16,340	1.15	18,808
Carbohydrate monomer	1.15	14,140	1.18	16,687
Lignin	1.29	23,380	1.10	25,648
Protein	1.30	22,230	1.10	24,488
Lipids	2.06	39,140	1.07	41,954
Ash	0.70			1006

Table 3
Chemical exergy of wet biomass.

Process stream	Moisture [kg/kg biomass]	$Ex_{Chem,DM}$[kJ/kg DM]	$Ex_{Chem,Biomass}$[kJ/kg biomass]
Wheat grain	9.0%	20,787	17,929
Wheat straw	7.6%	18,784	17,360
Pretreated wheat straw	69.9%	18,784	5689
Wheat grain stillage	92.7%	21,524	1618
Wheat straw stillage	81.5%	18,883	3552
DDG	14.0%	21,524	18,518
Ethanol	0.3%	29,621	29,532
Biogas	4.0%	16,735	16,068
Anaerobic Dig. Res. Pro1	97.8%[a]/90.6%[b]	10,594/12249	285/1191
Anaerobic Dig. Res. Pro2	89.6%[a]/88.8%[b]	15,108/14560	1617/1669

[a] Without power generation.
[b] With power generation.
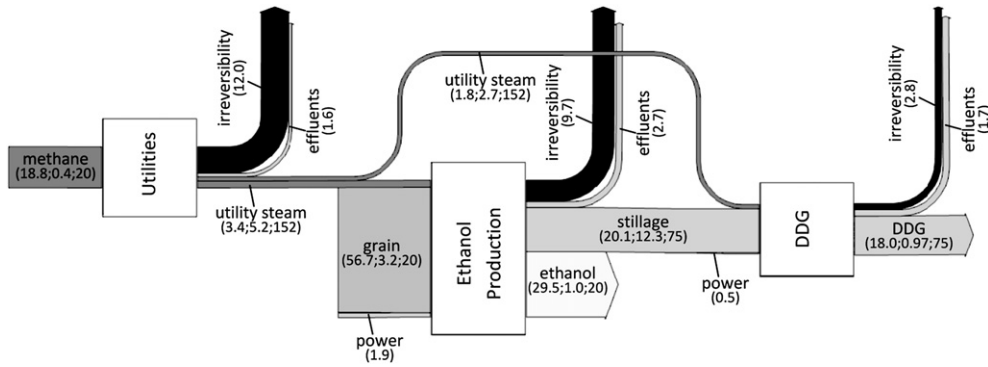
Fig. 5. Process 0, ethanol from grain, DDG from stillage, methane supplies utilities, no power generated; (specific exergy [MJ exergy/kg ethanol]; specific mass [kg mass/kg ethanol], temperature [°C]).
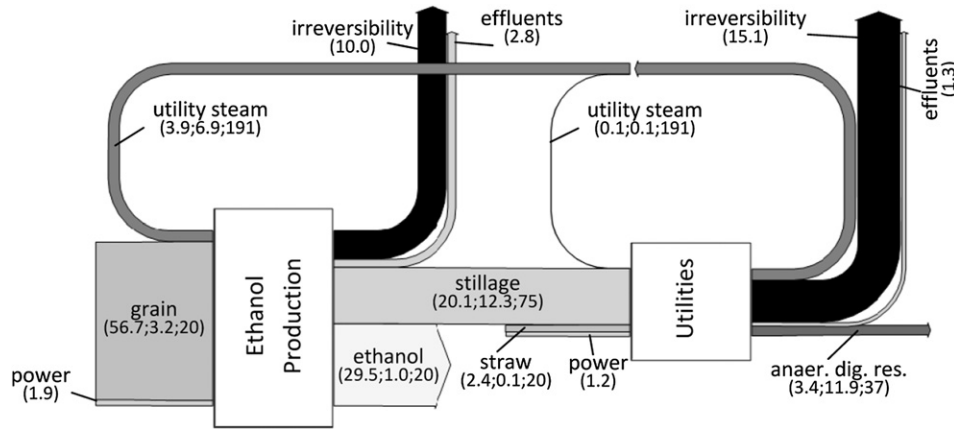
Fig. 6. Process 1a, ethanol from grain, utilities from stillage and straw via anaerobic fermentation, no power generated; (specific exergy [MJ exergy/kg ethanol]; specific mass [kg mass/kg ethanol], temperature [°C]).

The inputs are processed to yield besides ethanol various forms of exergy. A summary of all output streams is shown in Table 5.

All plants are specified to have the same ethanol output of 29.5 MJ/kg. The reference case produces additionally 18.0 MJ/kg of DDG from the stillage. In Process 1a this stillage is used to produce process heat reducing the required amount of exergy input. The scenarios that include combustion engines feed 11.9 MJ/kg electricity into the grid and provide 1.4 MJ/kg district heat. Since

Fig. 7. Process 1b, ethanol from grain, utilities from stillage and straw via anaerobic fermentation, power generated, district heat; (specific exergy [MJ exergy/kg ethanol]; specific mass [kg mass/kg ethanol], temperature [°C]).
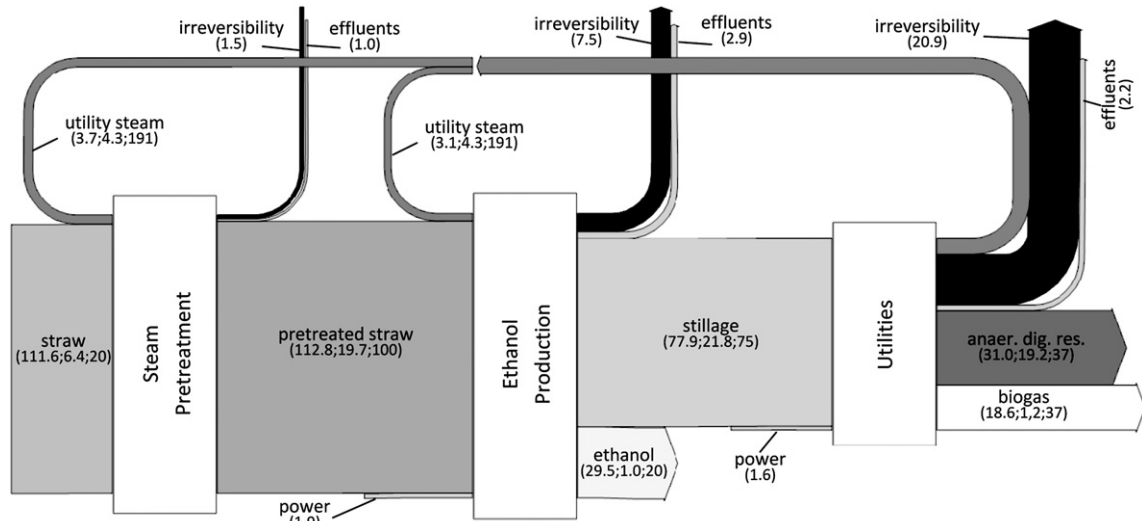
Fig. 8. Process 2a, ethanol from pretreated straw, utilities from stillage via anaerobic fermentation, no power generated, residual biogas; (specific exergy [MJ exergy/kg ethanol]; specific mass [kg mass/kg ethanol], temperature [°C]).

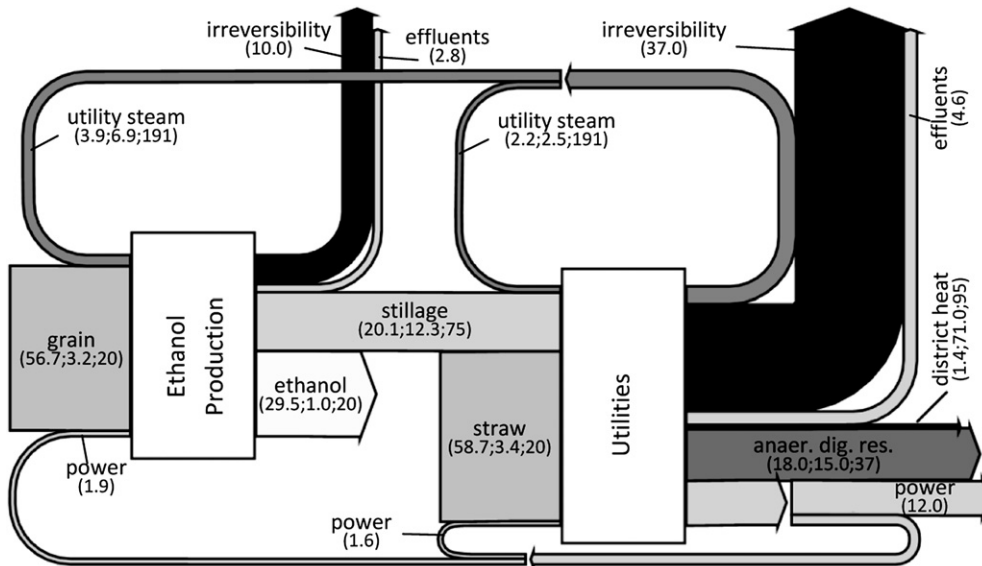Process 2a does not facilitate the full amount of biogas produced, 18.6 MJ/kg are available to be either upgraded and fed into the distribution grid according to approach presented in [15] or utilized elsewhere.

Since the lignin fraction of the wheat straw is not processed a significant amount − the same magnitude as ethanol in terms of exergy − stays unutilized throughout the process. This is one of the largest untapped potentials of all reviewed scenarios processing wheat straw. Lignin is often used as fuel for incineration but after biogas fermentation the anaerobic digestion residue is highly diluted and the melting point of the ash low, resulting in an unfavorable source material for combustion processes [16]. Further processing would suggest itself if lignin or products derived thereof could supply a ready market. For the proposed scenarios the lignin is leaving the process as part of the anaerobic digestion residue. When recycled to the field, were the material originates, it has

a favorable impact on the soil quality and a nutritional value that substitutes mineral fertilizer synthesized from fossil gas.

The absolute amount of irreversibility produced are the highest with the scenarios including gas engines for power production (P1b, P2b). This is consistent with the input requirements. Process 2a stands out in this regard since there is an excess of biogas not further processed and therefore not contributing to the irreversibility that much.

To evaluate the performance of the processes efficiency factors were introduced and summarized for all scenarios in Table 6. $\eta_{General}$ characterizes the overall exergy yield of the process regardless of the outputs nature or value. Not the reference or the interim but the lignocellulose case without power generation (P2a) has the highest general efficiency with 74.0%. This can be accounted to the high amount of unprocessed exergy in the form of lignin as well as the only partial utilization of the obtained biogas. Process 1a

Fig. 9. Process 2b, ethanol from pretreated straw, utilities from stillage and pretreated straw via anaerobic fermentation, power generated, district heat; (specific exergy [MJ exergy/kg ethanol]; specific mass [kg mass/kg ethanol], temperature [°C]).
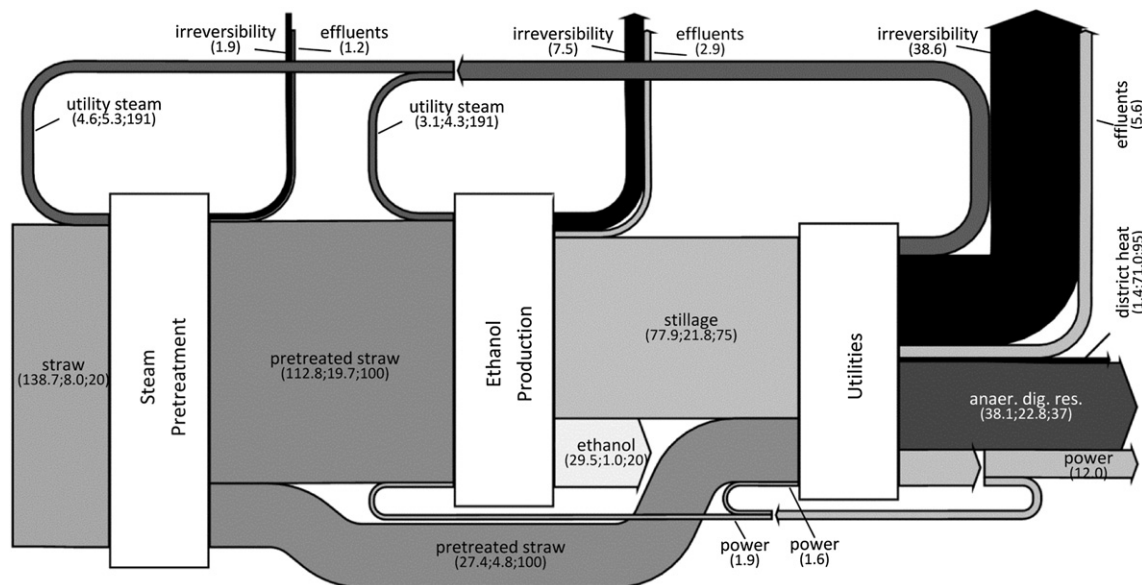
Table 4
Specific exergy of input.

Ex_Input [kJ/kg ethanol]	Process 0	Process 1a	Process 1b	Process 2a	Process 2b
Straw	0	2443	58,687	111,593	138,651
Grain	56,723	56,723	56,723	0	0
Methane	18,790	0	0	0	0
Power	2434	3097	0	3540	0
Sum (Ex_Input)	77,947	62,264	115,410	115,132	138,651

Table 5
Specific exergy of output.

Ex_Output [kJ/kg ethanol]	Process 0	Process 1a	Process 1b	Process 2a	Process 2b
Ethanol	29,532	29,532	29,532	29,532	29,532
Power	0	0	11,947	0	11,947
Biogas	0	0	0	18,593	0
DDG	17,966	0	0	0	0
District heat	0	0	1404	0	1404
Anaer.Dig.Res	0	3394	17,953	31,001	38,080
Effluents	5965	4137	7467	6098	9737
Irreversibility	24,485	25,201	47,107	29,909	47,951
Sum (Ex_Output)	77,947	62,264	115,410	115,132	138,651

and 1b have the lowest $\eta_{General}$ with 59.5% and 59.2%. This accommodates the high degree of raw material utilization including self supply with steam utilities (both) and power (P1b) in conjunction with comparable small amounts of lignin processed. Although the reference case realizes all input streams the production of ethanol and DDG creates less irreversibility then for example electricity. Therefore Process 0 with 68.6% comes in second in terms of general efficiency after Process 2a. $\eta_{Irreversibility}$ mirrors the findings for $\eta_{General}$. Processes with highly processed product streams like electric power or steam utilities have in general a higher amount of irreversibility. The Sankey diagrams show that the units responsible for the highest levels of irreversibility in the facility are not the fermentation processes (neither ethanol nor biogas) but the thermal utilization of the biogas in either a combustion chamber or an engine as shown in Figs. 5–9.

Since the process schemes originate from ethanol production the conversion efficiency for this product stream is closely monitored with $\eta_{Ethanol}$. In regard to the exergy input per kg ethanol the interim cases without power generation has the highest specific ethanol output with 47.4%. Almost half of the exergy that was put into this process was recovered in form of ethanol. Since the reference case is dependent on additional exergy input $\eta_{Ethanol}$ drops to 37.9%. Process 1b and 2a yield about ¼th of exergy in form of ethanol and with Process 2b about $\frac{1}{5}$ th of the exergy remains as ethanol. The low ethanol yields must not be seen as a flaw or drawback but as an intrinsic property of polygeneration. This becomes obvious when the remaining efficiency factors are examined. Besides exergy for ethanol $\eta_{ProductI}$ also accounts for outputs in the form of electric power and biogas. The exergy yield dramatically increases to 35.9% (P1b), 41.8% (P2a) and 29.9% (P2b).

Table 6
Efficiency analysis of exergy flows.

Efficiency factor [%]	Process 0	Process 1a	Process 1b	Process 2a	Process 2b
$\eta_{General}$	68.6%	59.5%	59.2%	74.0%	65.4%
$\eta_{Irreversibility}$	31.4%	40.5%	40.8%	26.0%	34.6%
$\eta_{Ethanol}$	37.9%	47.4%	25.6%	25.7%	21.3%
$\eta_{ProductI}$	37.9%	47.4%	35.9%	41.8%	29.9%
$\eta_{ProductII}$	60.9%	47.4%	37.2%	41.8%	30.9%
$\eta_{ProductIII}$	60.9%	52.9%	52.7%	68.7%	58.4%

$\eta_{ProductII}$ accounts for DDG and district heat over $\eta_{ProductI}$. Although the amount of low temperature enthalpy is in the same range as the electric power the exergy contained in this product stream is small thereby points out a major asset of exergy analysis. By adding the exergy of DDG ($\eta_{ProductII}$) the reference case takes the lead in terms of exergy yield (60.9%). $\eta_{ProductIII}$ is the most complete factor taking into account the anaerobic digestion residue. Process 2a reaches a conversion yield of 68.7%. This is for the lignin and combustion process issues discussed earlier in regard to $\eta_{General}$ (lignin, combustion). An efficient solution for abundant lignin is necessary to achieve an economic viable lignocellulose process since no process can afford to have significant idle energy potentials.

4. Conclusion

The main questions this work tried to answer is how the usage of wheat straw influences the efficiency of ethanol processes and what process combination is closest to the maximal exergy output.

Polygeneration processes for production of ethanol (2500 t/y, anhydrous), electric power and district heat from wheat (grain and straw) were evaluated in terms of exergy analysis and compared with a standard ethanol process that yields DDG as a supplementary product.

Exergy analysis was found to be a very valuable tool for process evaluation since it allowed for an objective comparison of product streams as different as anaerobic digestion residue and electric power.

The reference case based on traditional large scale ethanol production showed a good facilitation of the provided exergy but relies on non-renewable input streams (methane, electricity). In terms of ethanol efficiency the interim case that utilizes starch for ethanol production and the stillage in conjunction with wheat straw for biogas production performed better. Schemes with wheat straw as single source material performed below its potential since neither the ethanol nor the biogas fermentation facilitated the lignin fraction. Fractionation and utilization thereof early in the process would improve the outcome considerably. Power generation is a viable option to increase the economy of the process when subsidies for renewable electricity are in place as they are in Austria and other European countries.

By design the analysis was limited to the process. A thorough life cycle analysis of the processes is suggested as scope for future work.

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7. CONCLUSIONS

7.1. CONCLUSIONS OF BIOHYDROGEN PRODUCTION

Exergy analysis gives useful insights to a novel biohydrogen production process (Hyvolution), pointing out options for process improvement and optimization of raw materials use. To calculate the exergy content of the process streams, a Mathematica-based program was developed which uses a chemical exergy data base and thermodynamic data provided by simulation software.

The obtained results from the exergy program need a careful interpretation in view of different possible definitions of exergy efficiency.

The **first** paper studied the impact of raw materials, substrate conversion in PHF, heat integration and recirculation of effluents as well as impact of residues and by-products on the process performance from exergetic point of view.

The process option based on feedstock thick juice shows the highest rational exergy efficiency (28.5%) followed within narrow margins by feedstock wheat (24.8%) compared to the process option based on feedstock PSP (14.8%). Thick juice consists almost of sugar and water, with only few other components hardly leading to material losses in form of non-fermentables. Therefore, the use of sugar thick juice produces less waste than the use of starchy materials PSP and wheat needing pretreatment and showing a lower ratio of fermentables to nonfermentables.

Comparing Base Case and Engineering Case, thus process options with 80% and 60% hydrogen yield in PHF, respectively, show rational exergy efficiency is considerably decreased for the Engineering Case which clearly reflects the larger amount of feedstock and utility demand of the process due to lower hydrogen yield in the Engineering Case.

Heat integration based on the pinch analysis only slightly contributes to an improvement of exergy efficiency of the Hyvolution process. Depending on the reduction of the heat demand and the temperature level in the process, heat integration measures could even decrease exergy efficiency due to additional exergy losses caused by the introduced heat exchanger

cycles. Nevertheless, process and heat integration reduce the relative irreversibilities of the process operated with PSP from 11.4% to 6.8%.

The level of increasing efficiency depends on the amount of recirculated effluent. The larger the amount of recirculated effluent, and thus the reduction of the demand of fresh water, the higher is the value of exergy efficiency. The reason is that reuse of the effluent exiting from PHF provides the possibility to consume further materials which would leave the process unused without effluent recirculation (e.g. the rational and chemical exergy efficiency improvement from 24.2% to 41.3% and from 36.5% to 44.3%, respectively, based on the recirculation of effluents and feedstock thick juice).

The use of hydrogen in tail-gas only gives a modest improvement of rational exergy efficiency (13.9% and 27.5% based on feedstocks thick juice and PSP, respectively). The internal use of solid residues exiting from pre-treatment in case of feedstock PSP increases rational and exergy efficiency of the process by more than double (50.4%), as a result of the low ratio of fermentable starch to non-fermentables in this feedstock option. Considering the low content of non-fermentables and the missing pre-treatment step for thick juice an improvement of exergy efficiency is not observed here. Nevertheless, for both feedstock options also the cell mass produced in both fermentors could be used to further increase the rational exergy efficiency of the process.

The **second** paper introduced the impact of gas-upgrading technologies and gas stripping on exergy efficiencies. The results show that the highest efficiency is achieved for the process option without stripping and applying gas-upgrading by MEA. Compared to the process options with MEA, rational and chemical exergy efficiency are considerably lower for cases applying VSA. Main reasons are the high hydrogen losses during regeneration of VSA and the connected higher feedstock demand to obtain 60 kg/h pure hydrogen.

Most important contribution to an increase of exergy efficiency comes from (re-) use of produced cell mass and non-fermentables as well as effluent from process as feedstock or nutrient, for heat and power generation or fertilizer, respectively.

In the **third** paper, exergy analysis was performed for starch based feedstock (wheat) at two different concentration of glucose in the THF feed for a plant size of 50 kg/hr produced

hydrogen. Gas-upgrading unit was not included to this analysis. Furthermore no effluents recirculation and heat-integration are considered. This study shows that rational exergy efficiency increases with increasing concentration of glucose from 25% to 28% for 50g/l glucose and 10g/l glucose respectively.

The **forth** paper discussed the effect of substrate concentration and preheating of process water for diluting THF feed on process performance for the production of 60 kg/h of pure hydrogen (99.7 vol.%) corresponding to approximately 2MW of thermal power without considering heat integration and recirculation of effluents within the process. Glucose concentration was varied from 10-200 g/l. Substrate concentration to PHF was kept constant at 100 mM acetic acid. This study shows that heat flow for preheating THF feed can be decreased below 25 kW and the use of preheated dilution water contributes to the decrease of necessary heat flow for temperature adjustment of THF-feed. But it becomes also clear that without measures towards increase of acetic acid concentration in PHF feed total heat flow to operate fermentation steps will lie at approx. 500 kW.

7.2. CONCLUSIONS OF BIOETHANOL PRODUCTION

Polygeneration process for production of ethanol from straw, biomethane and heat as well as electricity was analyzed from exergetic and thermodynamic point of view to improve the design of production processes.

In the **fifth** paper, the exergy and pinch analysis were started with a base case flowsheet model of the bioethanol production process derived from the literature.
The results show that the rational exergy efficiency of bioethanol process, in which bioethanol, liquid fraction of stillage and dried solids are products, is higher (79.3%) than biomethane (53.4%) and CHP process (38.8%). In biomethane process a part of exergy is lost in the form of sludge and in CHP process the flue gas leaving system demonstrates waste exergy stream. Exergy efficiency of biomethane process can be increased if sludge-derived fertilizer is produced or sludge is incinerated. Irreversibility of bioethanol, biomethane and

CHP process are about 12%, 16% and 42% of input exergy attributed to heat losses and non reacting unknown materials, respectively.

The pinch analysis of bioethanol and biomethane production process based on the composite curves shows that around 66MW of heat could be integrated between hot and cold process streams if the process is optimal integrated. To reach the maximum heat integration between hot and cold process streams, a well-designed heat exchanger network has to be structured.

A heat exchanger network considering some forbidden matches between streams because of technical/safety reasons was introduced by means of HENS program in which total HEN annual cost involving operation and capital costs, was minimized.

It shows that around 45MW would be saved by utilization of heat released during the steam explosion treatment, drying and bioethanol cooling for mash preheating before introducing it into the distillation columns, feed and stripper heating.

Some process streams such as slurry and liquids fed to anaerobic digester (AD) consist of the large amounts of insoluble and soluble solids which limit heat recovery of these process streams by commonly used heat exchangers (22.6 MW). Hence, after implementation of heat transfer limitation between process streams thermal integrated process needs around 65MW hot utility and 67MW cold utility. That means thermal integration between process streams reduces steam and cooling water consumption up to 40% which leads to the significant utilities cost reduction.

Integrated grand composite curves show that a maximum of 25 MW electricity can be generated by steam turbine in CHP plant in which 70 MW secondary steam at two pressure levels are co-generated to cover bioethanol production process heat demands.

In the **sixth** paper, some different cases are analyzed for handling stillage waste from ethanol production. Parametric studies show the influence of the proper selection of cases and product definition as well as process integration measures on exergy efficiency. Internal use of waste streams for providing process heat and electricity as well as generation of some useful by-products such as animal feed and pellets using additional steps could increase exergy efficiency. It is recommended to produce electricity by combustion of residuals to use the chemical exergy of solids (bioethanol and electricity as products with a rational exergy efficiency of 35.5%). Most important contribution to an increase of rational exergy efficiency

comes from (re-) use of C_5 sugars and pellets for heat and power generation or for sale (65.9%).

In the **seventh** paper studying the ethanol production from straw, the pinch analysis shows that the base case has a potential for 52MW or 50% of heat recovery. The design modifications of the distillation and evaporation sections were implemented to create an improved design of the process. To be specific, the two sections were integrated by reducing the number of stages and shifting the heat loads to different temperature levels. The thermal analysis showed that the total heat demand of bioethanol production plant (113MW) can be provided by utilizing only 51% of residues, without any need of external utilities.

The **eighth** paper focuses on the polygeneration processes for production of ethanol, electrical power, and district heat from wheat straw and wheat grain. Some scenarios are defined to evaluate the impact of different feed materials and process configurations with regard to exergy efficiencies. The reference case is a conventional wheat grain to ethanol process in which the stillage is dried to become DDG. The reference case yielded a rational exergy efficiency of 37.9% for ethanol and 60.9% for products (ethanol and DDG). In the interim case (wheat grain and wheat straw as feedstock), the stillage from ethanol separation and additional pretreated wheat straw are fed to the anaerobic digestion unit to produce biogas. The biogas is fed to a combustion engine or chamber to generate (electricity and steam) or only steam, respectively (interim case with or without power generation). The interim case without power generation was found to be more efficient producing ethanol (47.4% for ethanol) compare to the interim case with power generation (37.2% for ethanol and electricity). The lignocellulose case uses wheat straw to produce ethanol. The stillage and biogas are further processed as in the interim case The lignocelluloses case without power generation yielded an higher exergy efficiency (41.8% for ethanol and biogas) than case with power generation (30.9% for ethanol and electricity). This analysis demonstrated that the irreversibility produced is the highest with the scenarios including gas engines for power production.

Further development and optimization of novel production concepts are possible through the methods and programs developed for exergy calculation and heat exchanger network optimization, as mentioned in the above process improvement case studies. An optimization of new process configurations can be achieved using these approaches.

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2010-2013 (36 Monate)   Energieoptimierung von Industriestandorten
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2013   (6 Monate)   Energierückgewinnung im Zementwerk
(**Lafarge GmbH & Bilfinger**)

Sprachkenntnisse

Deutsch   (gut)
Englisch   (gut)
Persisch   (Muttersprache)
Arabisch   (Grundkenntnisse)

Publikationen

2004

A. Modarresi, M. Sadrameli:
"Modeling and simulation of a phase change regenerator system"; Heat Transfer
Engineering, 25 (2004), S. 45 - 53.

2008

A. Modarresi, W. Wukovits, A. Friedl:
"Exergy Analysis of biological hydrogen production"; Computer Aided Chemical
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"Effect of process integration on the exergy balance of a two-stage process for fermentative hydrogen production"; J. of Cleaner Production, 18 (2010), S. 63 - 71.

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"Application of exergy balances for evaluation of process configurations for biological hydrogen production"; Applied Thermal Engineering, 30 (2010), S. 70 - 76.

2011

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2012

A. Modarresi, P. Kravanja, A. Friedl:
"Pinch and exergy analysis of lignocellulosic ethanol, biomethane, heat and power production from straw"; Applied Thermal Engineering, 43 (2012), S. 20 - 28.

P. Bösch, **A. Modarresi**, A. Friedl:
"Comparison of combined ethanol and biogas polygeneration facilities using exergy analysis"; Applied Thermal Engineering, 37 (2012), S. 19 - 29.

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S. Riepl, B. Adler, A. Friedl, **A. Modarresi**:
"Mit wenig Energie mehr Wärme - Hochtemperaturwärmepumpe für den Einsatz in der Prozesstechnik"; Process, 3 (2013), S. 78 - 79.

Vorträge & Poster-Präsentationen

2008

A. Modarresi, **W. Wukovits**, A. Friedl:
"Exergy analysis of biological hydrogen production"; **Poster**: Escape 18, Lyon.

W. Wukovits, **A. Modarresi**, A. Friedl:
"Application of mass-, energy- and exergy- balances for evaluation of process configurations for biological hydrogen production"; **Vortrag**: PRES 2008, Prag.

W. Wukovits, A. Modarresi, A. Friedl:
"Evaluation of process configurations for biological hydrogen production applying mass-energy- and exergy-balances"; **Poster**: 16th European Biomass Conference&Exhibition, Valencia.

2009

A. Modarresi, W. Wukovits, A. Friedl:
"Effect of process integration on the exergy balance of a process for biological hydrogen production"; **Poster**: PRES 2009, Rom.

W. Wukovits, A. Modarresi, A. Friedl:
"Beitrag der Exergieanalyse zur Effizienzsteigerung eines Prozesses zur biologischen Produktion von Wasserstoff"; **Poster**: ProcessNet 2009, Mannheim.

2010

A. Modarresi, A. Miltner, A. Friedl, M. Wiesinger:
"Reduktion des fossilen Energiebedarfs von Industriestandorten durch Optimierung der Wärmetauschernetzwerke"; **Vortrag**: ProcessNet 2010, Aachen.

2011

A. Friedl, **A. Modarresi**:
"Analyse industrieller Standorte durch Einsatz von Pinch-Technology und Optimierung mit HEN (Heat Exchanger Network) - Tools"; **Vortrag**: Energy Master 2011, Berlin.

A. Modarresi, P. Kravanja, A. Friedl:
"Exergy Analysis of the Production of lignocellulosic Ethanol"; **Poster**: PRES 2011, Florenz.

W. Wukovits, D. Foglia, A. Modarresi, A. Friedl:
"HYVOLUTION - Biological Production of Hydrogen from Biomasses: Process Balances and Process Integration"; **Vortrag**: 8th European Congress of Chemical Engineering, Berlin.

2012

A. Modarresi, A. Friedl, B. Zauner, A. Bauer, W. Reindl, F. Hatzl:
"Potenzialanalyse für solarthermische Anlagen an vier Standorten der Zellstoff- und Faserindustrie"; **Poster**: ProcessNet 2012, Karlsruhe.

2013

A. Drljo, A. Modarresi, F. Weinwurm, W. Wukovits, A. Friedl:
"Integration of an organosolv process applying pinch and exery analysis"; **Poster**: ICEEM07, Wien

Verleihungen

1998   Jahrgangsbester Bachalorstudium TU Teheran
2002   Jahrgangsbester Masterstudium TU Tarbiat-Modarres

IKT-Kenntnisse

Wolfram Mathematica
EES (Engineering Equation Solver)
Aspen Plus
TRNSYS (Solarthermie, Geothermie, Wärmepumpe und Absorptionskältemaschine)
LateX (Texmaker)
MS Visual Studio
MS Office

Interessen

Tennis, Wandern, Laufen, Radfahren, Musik hören, Malen und Reisen

Referenzen

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Diplomarbeit

"Exergy analysis of non-thermal biological hydrogen production from Biomass", Betreuer/in(nen): A. Friedl, W. Wukovits; Institut für Verfahrenstechnik, Umwelttechnik und Technische Biowissenschaften, 2007.

Diplomarbeit (mitbetreuer)

A. del Pozo Hijano, "Evaluation of applicability of solar absorption cooling plants in industrial processes", Betreuer/in(nen): A. Friedl, A. Modarresi, Bericht für Institut für Verfahrenstechnik, Umwelttechnik und Technische Biowissenschaften, 2011.