CHALMERS

Chalmers EnergiCentrum – CEC

Towards a Sustainable Oil Refinery

Pre-study for larger co-operation projects

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Report - CEC 2008:1
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Förord

Chalmers EnergiCentrum (CEC) redovisar i denna rapport resultat från en förstudie på uppdrag av Preem om effektiv produktion av framtidens fordonsbränslen.

Förstudien omfattar tre delstudier med inriktning på dels energieffektivisering, tillvaratagande av spillvärme och koldioxidavskiljning, dels bioraffinering avseende förgasning och hydrering av vegetabiliska oljor. En gemensam utgångspunkt för studierna har varit aktuella förhållanden vid Preems raffinaderier i Göteborg och Lysekil där mätdata har hämtats.

Rapporten sammanfattar kunskapsläget från aktuell forskning inom resp. teknikområde. Resultaten visar på intressanta framtida möjligheter för utveckling av en hållbar produktion av framtidens fordonsbränslen. Kapitlen ser lite olika ut beroende på att de aktuella områdena är olika och skrivna av olika författare. Rapporten utmynnar i gemensamma slutsatser och ett antal frågeställningar som föreslås kunna ingå och besvaras i en kommande större huvudstudie som ett led i ett utvecklat forskningssamarbete mellan Preem och Chalmers. Preliminära resultat från arbetet har behandlats tillsammans med beställaren vid workshops den 1 oktober och den 29 november 2007. Rapporten är skriven på engelska med en utvidgad sammanfattning på svenska med förslag på en framtida huvudstudie. Förord och avsnittet 2 ”Uppdrag” är skrivna på svenska och engelska.

Studien har genomförts av Chalmers EnergiCentrum (CEC) i samverkan med ett antal forskare inom CEC:s nätverk, där insatser gjorts av Thore Berntsson, Jessica Algehed, Erik Hektor och Lennart Persson Elmeroth samtliga Värmeteknik och maskinlära, Börje Gevert, Teknisk ytkemi, Tobias Richards, Skogsindustriell kemiteknik, Filip Johnsson och Anders Lyngfelt, Energiteknik samt Per-Åke Franck och Anders Åsblad, CIT Industriell Energianalys AB. Beställaren Preem har representerats av Bengt Ahlén, Sören Eriksson, Johan Jervehed, Bertil Karlsson, Gunnar Olsson, Ulf Kuylenstierna, Stefan Nyström, Martin Sjöberg and Thomas Ögren.

Tobias Richards har svarat för sammanställning av rapporten och Bertil Pettersson har varit projektledare.

Göteborg den 22 januari 2008

Bertil Pettersson
Chef för CEC

Foreword

In this report, the Chalmers EnergiCentrum (CEC) presents the results of a pre-study commissioned by Preem relating to the effective production of future vehicle fuels.

This pre-study was made up of three studies focusing on energy streamlining, the utilisation of waste heat and carbon-dioxide separation and biorefinement relating to the gasification and hydration of vegetable oils. One of the common starting points for these studies was the current situation at the Preem refineries in Göteborg and Lysekil from where the measurement data were obtained and analysed.

The report summarises the knowledge situation based on current research in the individual technical fields. The results present some interesting future opportunities for developing the sustainable production of future vehicle fuels. The sections vary, as the areas that have been examined differ and the sections have been written by different people. The reports ends with some joint conclusions and a number of questions which could be included and answered in a more extensive future main study, as part of a developed research partnership between Preem and the Chalmers University of Technology. The preliminary results of this work were analysed with the client at workshops on 1 October and 29 November 2007. The report is written in English combined with an extensive summary in Swedish including a proposal on a future main study.

The study was conducted by the Chalmers EnergiCentrum (CEC), in collaboration with a number of researchers in the CEC's network. They included Thore Berntsson, Jessica Algehed, Erik Hektor and Lennart Persson Elmeroth, all from Heat and Power Technology, Börje Gevert, Chemical and Biological Engineering, Tobias Richards, Forest Products and Chemical Engineering, Filip Johnsson and Anders Lyngfelt, Energy Technology, and Per-Åke Franck and Anders Åsblad, CIT Industriell Energianalys AB. The client, Preem, was represented by Bengt Ahlén, Sören Eriksson, Johan Jervehed, Bertil Karlsson, Gunnar Olsson, Ulf Kuylenstierna, Stefan Nyström, Martin Sjöberg and Thomas Ögren.

Tobias Richards was responsible for compiling the report and Bertil Pettersson was the project manager.

Göteborg, 22 January 2008

Bertil Pettersson
Head of the CEC

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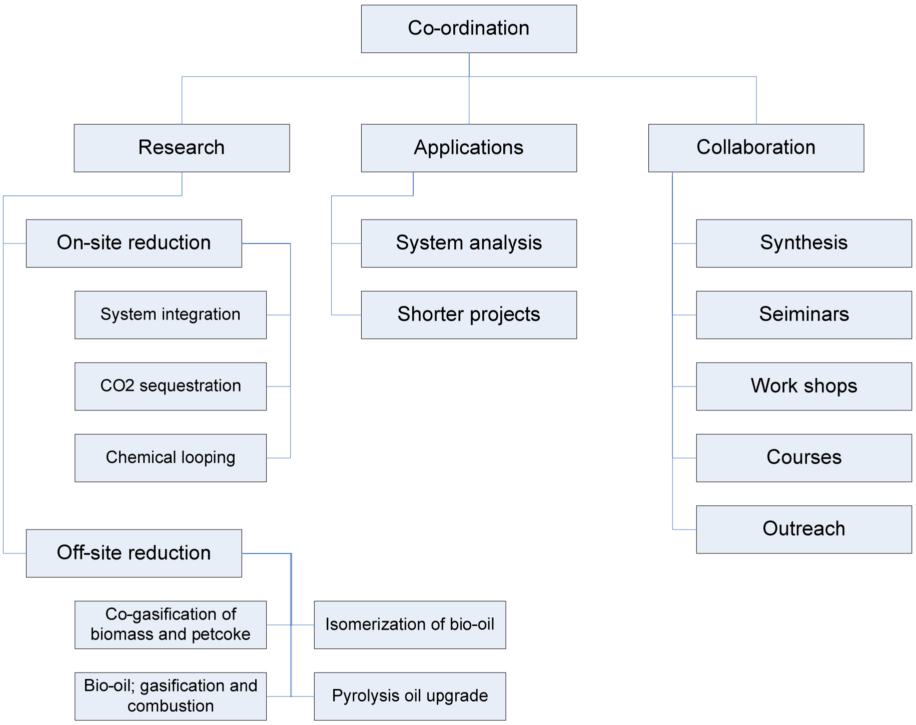
1 Sammanfattning

Idag står vi inför en enorm utmaning att dels minska våra utsläpp av växthusgaser som koldioxid och dels kunna hantera att de fossila resurserna minskar. Speciellt viktigt blir detta för en industri som nu är baserad på fossila råvaror och vars produkter till största delen ska användas för att generera värme eller kraft (antingen som el-generering eller som drivmedel) genom förbränning. Utmaningen blir att maximalt utnyttja den traditionella råvara som tas in och samtidigt öka andelen förnyelsebar råvara. Detta öppnar på samma gång upp för nya möjligheter. I denna förstudie har möjliga sätt att möta dessa utmaningar belysts för en raffinaderiindustri och resulterat i ett förslag till en fortsatt huvudstudie där både forskning och tillämpning står i fokus.

Förstudien har både berört process- och produktrelaterade områden. Med processrelaterat innebär effektivisering på plats med bland annat systemintegration eller avskiljning av koldioxid. Med produktrelaterat innefattas områden som alternativa drivmedel och produktion av vätgas som används inom befintlig process (vätgasen blir därför integrerad i produkten men har förnyelsebart ursprung).

Förstudien är uppdelad i fem områden. Den första delen behandlar energieffektivisering och systemintegration med hjälp av pinchanalys och kunde redan under denna studie generera en första kartläggning av de huvudsakliga energiströmmarna på Preem´s raffinaderi i Göteborg. Nästa del innebär effektiv användning av spillvärme och visar på olika möjligheter som finns att utnyttja och uppgradera det som benämns spillvärme och ofta inte används. I den tredje delen, koldioxidavskiljning, behandlas olika möjligheter att minska på utsläpp av växthusgasen koldioxid från raffinaderiet genom olika metoder för separation och hur det sedan påverkar det omgivande energisystemet. Som specifika exempel är medtaget förbränning i kvävefri miljö, s.k. oxyfuel combustion, och vätgasproduktion från naturgas med hjälp av chemical looping. Detta följs sedan upp i del fyra och fem där möjligheter att tillverka en mer miljöneutral produkt, drivmedel, baserad på förnyelsevara råvaror tas upp. Den fjärde delen har som fokus att tillverka vätgas från biomassa genom förgasning och hur den sedan integreras i processen. Den femte och sista delen har i stället fokus på bio-oljor och hur dessa ska processas för att ge ett drivmedel med minst lika bra förbränningsegenskaper som idag.

Resultatet av förstudien i helhet är ett förslag på huvudstudie som är baserad på de undersökningar och delresultat som erhållits i respektive delområde. Strukturen på programmet kan ses i nedanstående figur. Programmet leds av en koordinator och är sedan uppdelat i de tre områdena forskning, tillämpning och samarbete. Forskningen är i sin tur uppdelad i två delar. Dessa är process- respektive produktrelaterade utsläpp och syftar på var någonstans den huvudsakliga minskningen av utsläpp eller effektiviseringen sker, antingen på plats i raffinaderiet eller vid användandet av produkten. Tillämpningen har två delar vilka i olika grad syftar till att föra över resultat från forskningen för användning. Först är det *system analysis* som innebär den möjlighet att utföra viss konsultverksamhet inom detta område och sedan kommer kortare projekt i den mån det är möjligt och nödvändigt för att säkerhetsställa inriktningen. Området samarbete innefattar de sammankomster såsom seminarier, möten, work shops, eventuell gemensam kursverksamhet och möjligheter för extern kommunikation av forskningsresultaten tillsammans med en kontinuerlig dialog för att överföra forskningsresultat och fortlöpande syntesarbete.



Figur 1-1. Övergripande bild av programstrukturen.

För att klara av detta så föreslås åtta stycken olika projekt. Sju av dessa är forskningsprojekt och innefattar: Systemintegration av nya processer, systemaspekter vid koldioxidavskiljning, produktion av vätgas från naturgas vid samtidig koldioxidavskiljning genom chemical looping, förgasning av biomassa och petcoke för tillverkning av vätgas, användning av olja från biomassa för värmeproduktion och vätgasframställning, isomerisering av bio-olja samt uppgradering av pyrolysolja till drivmedel. Det åttonde projektet är ett projekt som syftar till att hantera och ta fram nödvändiga data på energiströmmar för forskningen samtidigt som mindre projekt direkt mot Preem kan hanteras separat. Ansvariga för de åtta projekten tillsammans med koordinatorn utgör Chalmers del i samarbetsgruppen som vid komplettering med personal från Preem säkerhetsställer en bra samverkan och maximal nytta av resultaten.

2 Uppdraget

Inom ramen för ett inledande samarbete mellan Preem och Chalmers om drivmedels-teknisk forskning har Chalmers EnergiCentrum (CEC) genomfört ett antal förstudier på uppdrag av Preem. Studierna har inriktats på tekniker för energieffektivisering, uppgradering av spillvärme och separation av CO_2 samt bioraffinering enligt uppdraget från Preem.

Följande delar ingår i studierna:
- Energisituationen vid Preem:s raffinaderier i Göteborg och Lysekil
  Ansvarig: Per-Åke Franck, CIT Industriell Energianalys AB
- *Energieffektivisering, Uppgradering av spillvärme och Separation av* CO_2
  Ansvarig: Thore Berntsson, Värmeteknik och maskinlära
- *Bioraffinering – Förgasning*
  Ansvarig: Tobias Richards, Skogsindustriell kemiteknik
- *Bioraffinering - Hydrering av vegetabiliska oljor*
  Ansvarig: Börje Gevert, Teknisk ytkemi

Gemensamt för studierna är att de är beroende av en adekvat beskrivning av processerna och energisituationen vid Preems raffinaderier i Göteborg och Lysekil, som har analyserats med hjälp av mätdata från befintliga förhållanden på raffinaderierna. Avsikten är att förstudierna ska leda till huvudstudier inom respektive område. Arbetet har genomförts enligt en arbetsfördelning som beskrivs i projektplanen.

Det långsiktiga målet med forskningssamarbetet inom dessa teknikområden är att utveckla vetenskapsområdet, initiera nya tillämpningar av de aktuella teknikerna samt utbilda teknologer och doktorander för framtida kompetensförsörjning. De sammantagna vetenskapliga kompetenserna, kunskaperna och erfarenheterna om tillämpningar av alternativa drivmedel utgör basen för samarbetet. Merparten av forskningsarbetet avses utgöra led i utbildningen av doktorander vid Chalmers och bidra till den framtida nödvändiga kompetensförsörjningen inom området. Samarbetet inleds med ett antal förstudier så som de anges och avgränsas i projektplanen.

Projektstarten skedde i samband med att samarbetsavtalet mellan Preem och Chalmers undertecknades 2007-06-18. Förberedande arbete genomfördes under våren 2007 bl.a. i form av gemensamma workshops. Tidplanen för respektive delprojekt som anges i planen har dock förskjutits i motsvarande grad som beslut om projektstarten försenades. Slutrapportering skulle enligt planen ske 2007-12-31 men pga. förseningar i projekt har sluttiden justerats till 2008-01-22 då förslag till slutrapport överlämnas. Tyvärr försenades leverans av mätdata från Lysekil pga. driftstopp och dessa data kan därför inte integreras i denna rapport utan kommer att kompletteras senare i en särskild rapport.

Chalmers EnergiCentrum (CEC) har varit anslagsmottagare och svarat för projektets koordinering och genomförande i samråd med berörda forskare inom Chalmers och med företrädare för Preem.

The Assignment

Within the framework of an introductory research partnership between Preem and the Chalmers University of Technology relating to research on fuel technology, the Chalmers EnergiCentrum (CEC) conducted a number of pre-studies on behalf of Preem. These studies focused on techniques for energy efficiency, upgrading waste heat and separation of CO_2 and biorefinement in accordance with the assignment from Preem.

These studies comprised the following parts:

- *The energy situation at Preem's refineries Göteborg and Lysekil*
  Responsible: Per-Åke Franck, CIT Industriell Energianalys AB
- *Energy Efficiency, Upgrading waste heat and separation of* CO_2
  Responsible: Thore Berntsson, Heat and Power Technology
- *Biorefinement – gasification*
  Responsible: Tobias Richards, Forest Products and Chemical Engineering
- *Biorefinement – the hydration of vegetable oils*
  Responsible: Börje Gevert, Chemical and Biological Engineering

One common denominator for all these studies is that they are dependent on an effective definition of the processes and energy situation at the Preem refineries in Göteborg and Lysekil, which have been analysed using measurement data relating to the current situation at these refineries. The plain is that these pre-studies will lead to main studies in the individual areas. The work has been conducted according to the division of labour specified in the project plan.

The long-term objective of this research partnership in these technological areas is to develop the scientific field, initiate new applications for the technologies in question and educate undergraduates and postgraduates to ensure the future supply of skills and expertise. The combined scientific skills, knowledge and experience of applications for alternative fuels constitute the basis of this partnership. Most of the research work is expected to form part of the education of postgraduates at the Chalmers University of Technology and to contribute to the necessary future supply of skills and expertise in this field. The partnership began with a number of pre-studies, as described and specified in the project plan.

The project began in conjunction with a partnership agreement between Preem and the Chalmers University of Technology, which was signed on 18 June 2007. The preparatory work took place during the spring of 2007 in the form of joint workshops, among other things. The time schedule for the individual sub-projects, which was specified in the plan, was, however, delayed to match the delayed decision to initiate the project. According to the plan, the final report was due on 31 December 2007, but, as a result of delays to the project, this date was amended to 22 January 2008, when a proposal for the final report was due to be presented. Unfortunately, the delivery of measurement data from Lysekil was delayed as a result of stoppages and it was therefore impossible to integrate these data in this report. They will be added at a later date in a separate report.

The Chalmers EnergiCentrum (CEC) was the recipient of grants and was responsible for co-ordinating and running the project, in collaboration with the researchers at the Chalmers University of Technology and CIT who were involved in the project and representatives from Preem.

3 Energy efficiency, Process Integration

3.1 Introduction

In this chapter, process integration as a concept as well as experiences and possible use in a future cooperation between Chalmers and Preem are discussed. First, the concepts are presented very briefly based on “A Process Integration PRIMER” (Gundersen, 2000), in chapter 3.6 developments and applications of process integration at Heat and Power Technology, Chalmers, are discussed and in chapter 3.8 experiences in the refinery industry as well as suggestions for further cooperation activities are presented.

3.2 Definition of Process Integration

Process Integration is a fairly new term that emerged in the 80's and has been extensively used in the 90's to describe certain Systems oriented activities related primarily to Process Design. It has incorrectly been interpreted as Heat Integration by a lot of people, probably caused by the fact that Heat Recovery studies inspired by the Pinch Concept initiated the field and are still core elements of Process Integration. It appears to be a rather dynamic field, with new methods and application areas emerging constantly. The ***definition*** used in this context is the one used by the IEA since 1993:

> *"Systematic and General Methods for Designing Integrated Production Systems, ranging from Individual Processes to Total Sites, with special emphasis on the Efficient Use of Energy and reducing Environmental Effects".*

This definition brings Process Integration very close to Process Synthesis, which is another Systems oriented technology. Process Integration and Synthesis belong to Process Systems Engineering (Figure 3-1), which is Systems Engineering principles applied to Processes.

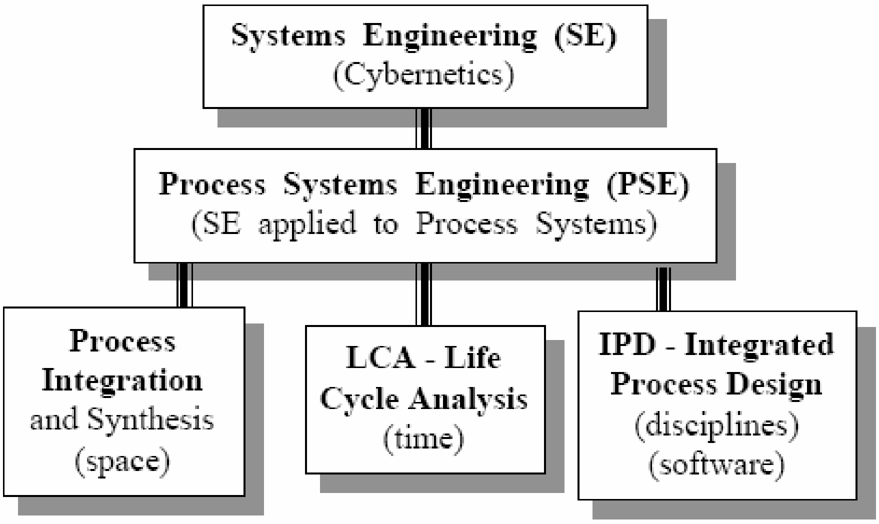


Figure 3-1. ***Process Integration among similar Terms***

While Process Integration and Synthesis are Systems approaches in ***space*** (the whole plant, the entire site, and sometimes even the whole region including domestic needs), Life Cycle Analysis is a Systems oriented methodology in ***time***, and Integrated Process Design is a

Systems view across scientific ***disciplines*** and ***software*** systems.
When using the term Process Integration, we both refer to certain industrial tasks and to classes of methods to address these tasks.

3.3 Process Integration and the Pinch Concept

The single most important concept and the one that originally gave birth to the field of Process Integration is the ***Heat Recovery Pinch***, discovered by, among others, Linnhoff et al. (78-79). It was Linnhoff's group at UMIST in Manchester, that developed this concept into an industrial technology in the 80's. The concept has later been expanded into new areas by using various analogies.

The most obvious analogy is between heat transfer and mass transfer. In heat transfer, heat is transferred with temperature difference as the driving force. Similarly, in mass transfer, mass (or certain components) is transferred with concentration difference as the driving force. The corresponding ***Mass Pinch***, developed by El-Halwagi and Manousiouthakis (89-90), has a number of industrial applications whenever process streams are exchanging mass in a number of mass transfer units, such as absorbers, extractors, etc.

One specific application of the Mass Pinch is in the area of Wastewater Minimization, where optimal use of water and wastewater is achieved through reuse, regeneration and possibly recycling. The corresponding ***Water Pinch***, developed by Wang and Smith (94), can also be applied for design of Distributed Effluent Treatment processes.

The most recent extension is the ***Hydrogen Pinch*** technology, developed by Towler and Alves (96-99). Oil refineries experience these days an increasing need for hydrogen to meet new product specifications (for example on diesel and gasoline). The Hydrogen Pinch method is a tool to optimize the hydrogen distribution system and to evaluate the scope for introducing purification units (such as PSA, membranes and cryogenic units).

In summary, the Pinch concept is a Systems tool since it provides critical information on a total plant or even site level. The concept is also (as shown above) generally applicable in other areas than heat recovery. Actually, whenever an amount (heat or mass) has a quality (temperature or concentration), the concept of ***Composite Curves*** provides a Systems view of the problem concerning efficient recovery (or re-use) of resources. The ***"Pinch"*** then shows the location on these curves where there is an accumulated deficit of an amount above a certain quality. Figure 3-2 shows Composite Curves for a Heat Recovery problem (left) and a Wastewater Minimization application (right).

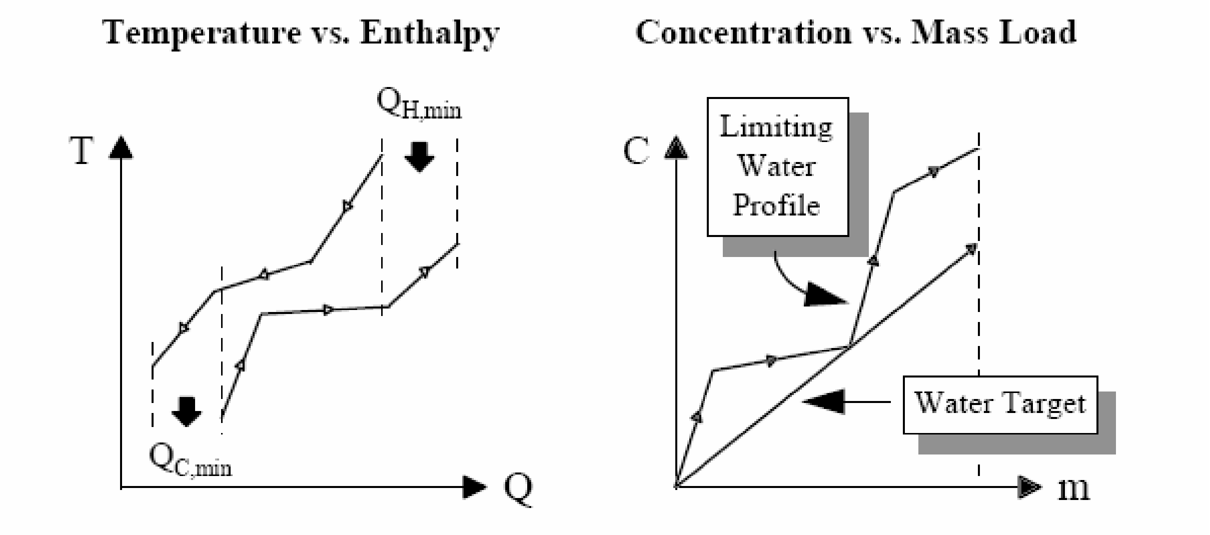


Figure 3-2. ***The General Concept of Composite Curves applied to Heat and Mass Transfer***

It can be concluded that the Composite Curves represent a concept that is general and fundamental in Process Engineering. Another important concept from "early days" Pinch Technology is the idea of establishing objective performance ***targets before*** going into the ***design*** phase. Examples of such targets in the area of heat recovery are figures for minimum energy consumption, fewest numbers of heat transfer equipment, minimum total heat transfer area, and minimum total annual cost. While some of these targets are based on thermodynamics (such as energy), others are based on heuristic rules (such as the fewest number of heat exchangers). Finally, some targets are actually only estimates of the best performance (such as heat transfer area and total annual cost).

Examples of other targets in Process Integration include minimum wastewater, minimum shaftwork in low temperature processes, minimum emissions, maximum power production for total sites, etc. All these and previously mentioned targets have two important features:

1) Any design can be objectively compared with the "best possible".
2) The way some targets are calculated also provides guidelines for design.

In his text book on Chemical Process Design, Smith (1995) puts strong emphasis on the idea of establishing Performance Targets prior to Design.

3.4 Schools of Methods of Process Integration

The three major features of Process Integration methods are the use ***heuristics*** (insight), about design and economy, the use of ***thermodynamics*** and the use of ***optimization*** techniques. There is significant overlap between the various methods and the trend today is strongly towards methods using all three features mentioned above. The large number of structural alternatives in Process Design (and Integration) is significantly reduced by the use of insight, heuristics and thermodynamics, and it then becomes feasible to address the remaining problem and its multiple economic trade-offs with optimization techniques.

Despite the merging trend mentioned above, it is still valid to say that ***Pinch Analysis*** and ***Exergy Analysis*** are methods with a particular focus on Thermodynamics. ***Hierarchical Analysis*** and ***Knowledge Based Systems*** are rule-based approaches with the ability to handle qualitative (or fuzzy) knowledge. Finally, ***Optimization*** techniques can be divided into deterministic (Mathematical Programming) and non-deterministic methods (stochastic search methods such as Simulated Annealing and Genetic Algorithms).

One possible ***classification*** of Process Integration methods is to use the two-dimensional (automatic vs. interactive and quantitative vs. qualitative) representation in Figure 3-3.

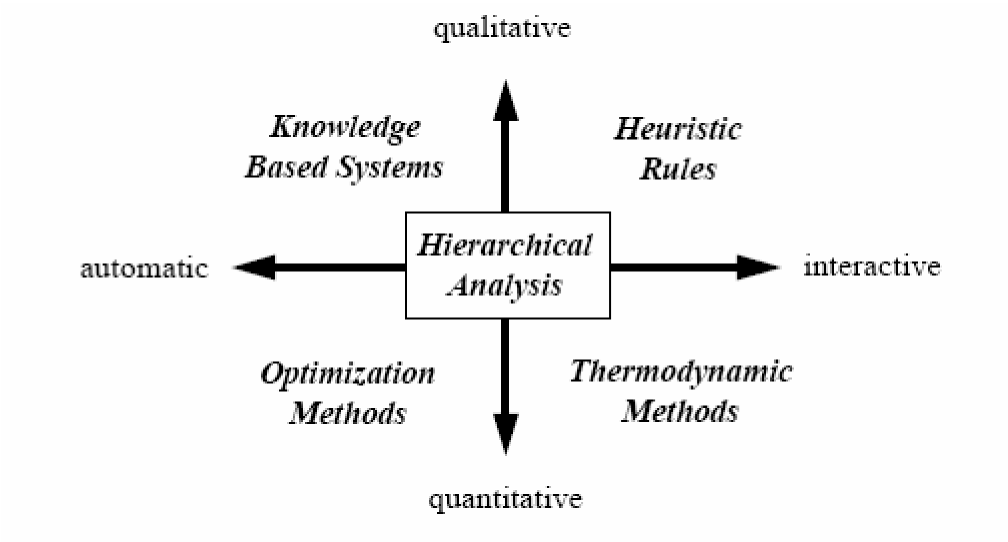


Figure 3-3. ***One possible Classification of Process Integration Methods***

Hierarchical Analysis is placed in the middle of the figure to indicate that all sensible design methods are (or should be) based on this idea in order to make the complete design problem tractable by systematic methods.

3.5 Process Integration Application Areas

The following list of keywords and activities indicate typical ***application areas*** of Process Integration for a large number of industrial branches:

- Planning, Design and Operation of Processes and Utility Systems
- Short Term (Scheduling) and Long Term Planning (including Strategic Planning)
- New Designs and various Retrofit Projects
- Improving Efficiency (Energy and Raw Material) and Productivity (Debottlenecking)
- Continuous, Semi-Continuous and Batch Processes
- All aspects of Processes, such as Reactors, Separators and Heat Exchanger Networks
- Integration between the Process and the Utility System
- Integration between Processes w.r.t. Material Streams and Energy Streams
- Integration between Industrial Sites, Power Stations and District Heating/Cooling
- Operability Issues (Flexibility, Controllability and Switchability)
- Waste and Wastewater Minimization
- Various aspects of Emissions Reduction

3.6 Process Integration Activities at Chalmers and Experiences

3.6.1 Introduction

Heat and power technology at Chalmers is the leading R&D group in Sweden in the area of process integration. From this group stems CIT, IE (Chalmers Industriteknik, Industriell Energianalys), which is a company within CIT. At CIT, IE, many applied and/or commercial process integration projects have been carried out. There is a close link between the research activities at Heat and power technology and the applied/commercial ones at CIT, IE, for the benefit of both groups. When planning possible further cooperation between Preem and Chalmers in this area, a good distribution of work between these two groups should be considered.

In the following the major activities, results and experiences from Heat and power technology and CIT, IE will be described briefly. The purpose of this is to give an understanding of our resources and methods/tools in what types of problems process integration could be used.

We have carried out studies in or in cooperation with several types of industry, including pulp and paper, refineries, petrochemistry, chemistry, iron and steel and food. The studies have included both projects for identifying energy saving opportunities in existing plants and process integration opportunities (energy efficiency, debottlenecking, investment cost reduction, CO_2 mitigation opportunities) at major changes in a plant, e.g. major retrofilling or introduction of new process equipment. In recent years studies have also included process integration between existing plants and different biorefinery concepts or CO_2 separation.

The majority of the studies have been carried out in connection with the pulp and paper industry, obvious in the following sections, but all major methodology developments and experiences should be applicable also to a refinery.

3.6.2 R&D Activities at Chalmers

Heat and power technology has been the most active group in the national research programme Processintegration since its start in 1997. Other major national programmes in which we are/have been active are:

- KAM (Den kretsloppsanpassade massafabriken, finished in 2002)
- FRAM (the future resource adapted pulp mill, ongoing)
- Program Energisystem (the largest R&D programme at the Swedish Energy Agency, ongoing)

In all these programmes most R&D projects have been in cooperation with industry. This is especially true for KAM and FRAM, in which industrial financing is high.

Some examples of projects are:

- Energy saving opportunities in a Greenfield pulp mill

Process integration methods were used to identify economically viable opportunities for energy saving in addition to BAT (best available technology) and best practice standard consultant solutions. Savings of 15-30% compared with BAT were identified.

Process integrated evaporation

A new concept for system integration of the evaporation plant in a pulp mill has been developed at Heat and power technology. By rearranging the heat exchanger network in the secondary heat system, medium temperature heat can be made available for evaporation, thereby decreasing the need for live steam. In this way 20-50% of the evaporation steam, i.e. 8-20% of the total mill steam, can be saved.

Process integration of heat pumps

Heat pumps in process industries will probably be of increasing interest in the future due to their low specific investment costs and high COP:s. A method for identifying heat pump opportunities in complex industrial systems and how to integrate them in the existing process has been developed.

Energy saving through process integration and lignin precipitation

Modern pulp mills can have an excess of heat. If this excess can be increased through process integration, lignin can be extracted as a surplus (i.e. a biorefinery) for energy saving and/or investment cost reduction (the latter case applies to an increased capacity situation, where the cost of a new or upgraded recovery boiler can be avoided. Our studies have shown that the heat excess in an average mill can be 15-25% of the total one. This has been confirmed in case studies in real mills.

Process integration of a biomass or black liquor gasification plant

The introduction of a gasification plant into a process industry has been analyzed and different ways for integration and different mixes of products (e.g. methanol, hydrogen, electricity) have been evaluated technically and economically. In a continuation of this research area process integration aspects of biomass gasification and methanisation are studied in cooperation with Gothenburg Energy (On the BoBiGas project).

Process integration of CO_2 separation technologies

Due to the potentially high interest for this area at Preem, this research area is presented in more detail in chapter 5.

Process integration of ethanol production in a pulp mill

In the project system and integration aspects for ethanol production instead of pulp in an existing pulp mill are studied. In this project alkaline pre-treatment is assumed. Results so far indicate that in this way a bio refinery can be developed in which ethanol possibly could be produced at a lower cost than competing technologies.

Optimization of process integration under future uncertainties

As has been indicated above, with the use of systematic process integration, methods and tools considerably higher energy saving opportunities than traditionally can be identified. In most cases these opportunities have been discussed with and evaluated by the industrial and/or consultant company experts in the projects and have been found to be both technically and economically viable.

3.6.3 Tools and methods

Pinch analysis is the main process integration method used in our group. Also mathematical programming has been used in some projects but to much lower degree. We have incorporated and applied general pinch analysis tools, as described in chapter 3. At CIT, IE, a general pinch analysis tool, ProPi, has been developed and this tool is used in most process integration R&D projects at Heat and power technology.

Generally speaking, there has been a lack of good pinch analysis tools in retrofilling situations. Therefore our group has developed different types of tools for such situations (being the by far most common ones). These are:

The matrix method

The goal of the matrix method is to include and study the impact of all types of costs concerning retrofit designs. These costs are based on the following parameters:

1 Heat exchanger area
2 Unit cost
3 The physical distance between streams
4 Material requirements
5 The types of heat exchangers
6 Auxiliary equipment (valves)
7 Space requirements
8 Annual pressure drop costs
9 Annual maintenance costs
10 Fouling

All possible heat exchanger placements (matches between hot and cold streams), including existing ones, are automatically investigated and the total annual cost for each possible mach is placed in a matrix (hot streams – cold streams). With the aid of several criteria the best matches are successively chosen and a whole optimized heat exchanger network is identified for a given level of energy saving.

Advanced composite curves

In addition to the traditional composite curves in pinch analysis, we have developed three more types of curves. The background is that the traditional ones reveal no information about where existing heat exchangers, heaters and coolers are placed temperature wise in the network. This has been shown to be of high importance. The advanced curves can be used in retrofit situations to:

- Identify economically feasible heat recovery levels prior to detailed design calculations, which guarantees good system solutions and reduces the problem size
- Identify temperature levels where usable excess heat can be extracted and used by other processes (e.g. biorefineries, district heating, distillation plants, CO_2 separation plants)

Optivap

In pulp and paper mills, evaporation is normally the biggest steam consumer, System optimization and rational use of excess heat from other parts of the mill are therefore important aspects. With the Optivap programme system optimization designs can be performed. Some principles developed in this work should be of interest also for e.g. distillation system optimization in the oil refinery industry.

One of the most time consuming parts of a process integration project is stream data acquisition and quality proofing. In this part of the work we use in many cases commercially available simulation tools, such as Aspen +/Hysis or WinGems. We have also developed our own, Excel based, tools for e.g. energy and material balances.

3.6.4 General experiences

Process integration studies have been carried at Heat and power technology and CIT, IE in both research and applied/commercial projects. A general experience is that pinch analysis gives a better understanding of opportunities for energy savings, investment cost reduction and/or environmental opportunities than traditionally, due to its systematic way of approaching problems. This is true both for "targeting", i.e. identification of theoretical opportunities, and for conceptual design aspects. We have used process integration methods for e.g.:

- Energy savings through improved heat exchanger networks
- Process integration of e.g. heat pumps combined heat and power plants and district heating systems
- Process integration of new process equipment (evaporation, distillation, dryers, CO_2 separation plants, etc.)
- Process integration of new, biorefinery type, of processes (gasification, fermentation, biomass upgrading)
- As tool in energy system oriented industrial R&D projects/programmes

In projects for improved energy efficiency (without major equipment changes), our general findings are that 15-20% can be saved through more process integration and of these more than half can be saved at economically attractive conditions. In studies involving new equipment or biorefinery concepts somewhat higher levels of energy savings can normally be identified. This is also the case for research oriented projects.

Although high savings and improvements ca be identified theoretically, our experience is that there are sometimes difficulties to implement these findings. In order to overcome implementation problems, it is important that:

- The study of energy opportunities should normally be performed when larger process changes, retrofillings, etc are planned, so that the energy consequences can be identified already at the conceptual design stage. (It is difficult to implement large changes in e.g. the heat exchanger network if there are no other incentives for production stops.)
- The energy system studies should be performed already at an early stage of the planning, before decisions on type of process equipment and system layouts. In many cases such decision will have a high influence on the energy and environmental opportunities.
- The organisational aspects are taken seriously. There must be a good communication between different departments of a process industry (the lack of this gives in many cases suboptimized solutions). There should also be a good organization for communication/cooperation between the process expert, process integration experts, equipment manufacturers and traditional consultants.

3.7 *Efficient energy usage*

3.7.1 Pinch technology in the refinery sector – a literature survey

In this chapter we briefly describe what has been reported in scientific papers about pinch technology in the refinery sector. The main search has been done using Scopus, one of the larger databases of scientific publications. Many pinch technology studies have been preformed by commercial actors and are not reported in scientific papers. Despite this, major trends and state of the art is likely to have been covered, since many of the examples given are based on two large European and US BAT – (Best Available Technology) reports (Worell 2005 and European IPPC Bureau at the Institute for Prospective Technological Studies, 2003).

3.7.2 Total site analysis and pinch analysis of selected parts of a plant

Pinch analysis can be performed for parts of a plant or an entire site, the later is normally referred to as ”Total site analysis” (Linhoff March 2000). Total site studies has been preformed at some 40 larger refineries world wide, often also including an analysis of the technical potential for integration of an heat and power plant into the refinery (Worell 2005). Large refineries that have conducted total site studies are among others: Amoco, Agip (Italy), BP, Chevron, Exxon (in the Netherlands and Great Britain) and Shell (several plants in Europe). In these analyses technical potentials for energy savings of round 20-30 % has been identified, of which 10-15 % has been possible to implement when also taking economics into account.

There a many examples in literature where pinch studies have been performed on selected parts of a refinery, e.g. distillation columns and crackers. The pay back periods reported for the savings identified are normally between 2-6 years, but depends naturally on location and what year they where performed.

Below are examples of pinch analyses described by Worrell and Galitsky in “Energy Efficiency Improvement and Cost Saving Opportunities for Petroleum Refineries - An ENERGY STAR® Guide for Energy and Plant Managers” are given:

Process Integration - Hot Rundown

Typically process integration studies focus on the integration of steam flows within processes and between processes. Sometimes it is possible to improve the efficiency by retaining the heat in intermediate process flows from one unit to another unit. This reduces the need for cooling or quenching in one unit and reheating in the other unit. Such an integration of two processes can be achieved through automated process controls linking the process flows between both processes. An audit of the Equilon refinery in Martinez, California, identified annual savings of $4.3 million (U.S. DOE-OIT, 2002b). However, the audit results did not include an assessment of investments and payback.

Crude Distillation Unit (CDU)

The CDU process all the incoming crude and, hence, is a major energy user in all refinery layouts (except for those refineries that receive intermediates by pipeline from other refineries). In fact, it is estimated that the CDU is the largest energy consuming process of all refinery processes. Energy use and products of the CDU depend on the type of crude processed. New CDUs are supplied by a number of global companies such as ABB Lummus, Kellog Brown & Root, Shell Global Solutions, Stone & Webster, Technip/Elf, and UOP. An overview of available process designs is published as Hydrocarbon Processing’s Refining Processes (HCP, 2000). Process integration is especially important in the CDU, as it is a large energy consumer processing all incoming crude oil. Older process integration studies show reductions in fuel use between 10 and 19% for the CDU (Clayton, 1986; Sunden, 1988; Lee, 1989) with payback periods less than 2 years. An interesting opportunity is the integration of the CDU and VDU, which can lead to fuel savings from 10-20% (Clayton, 1986; Petrick and Pellegrino, 1999) compared to non-integrated units, at relatively short paybacks. The actual payback period will depend heavily on the layout of the refinery, needed changes in the heat exchanger network and the fuel prices.

The CDU at BP's Kwinana (Australia) refinery was already performing well with limited opportunities for further economic process integration. An analysis of the CDU identified a significant potential for reduction but with a payback of around 6 years. However, integration with the residue cracking unit offered significant opportunities to reduce the combined heating demand by 35-40% with a simple payback period of 1.6 years (Querzoli, 2002).

Fluid Catalytic Cracker (FCC)
The FCC is a considerable energy consumer in a modern refiner. In this Energy Guide, the FCC energy use is estimated at 6% of total energy use. Depending on the design and product mix of a particular refinery, FCC energy use can be higher than 6%. There are a large number of FCC designs in use, and many were originally built in the 1970s. Today, more energy efficient designs are being marketed by a number of suppliers. The designs vary in reactor design, type of catalyst used and degree of heat integration. An overview of available process designs is published as Hydrocarbon Processing's Refining Processes (HCP, 2000). The major suppliers are ABB Lummus, Kellog Brown & Root, Shell Global Solutions, Stone & Webster, and UOP. The optimal design will be based on the type of feed processed and desired product mix and quality. Hence selecting a new FCC, process energy efficiency should be an integral part of the selection process.

In existing FCC units, energy efficiency can be improved by increasing heat integration and recovery, process flow scheme changes, and power recovery. A FCC has a multitude of flows that need to be heated (sink) and cooled (source). The better the integration of the heat sinks and sources, the lower the energy consumption of an FCC will be. Older FCC designs often do not have an optimized heat exchange setup, which may especially lead to wasted low-temperature heat, which could be used to preheat boiler feed water or cold feed. However, by better integrating the sources and sinks, following the principles of pinch technology (see above), through improved combinations of temperature levels and heating/cooling loads energy use is lowered. Various authors have reported on the application of pinch analysis and process optimization of FCCs (Hall et al., 1995; Golden and Fulton, 2000). The appropriate combination will depend on the feed processed and output produced. Furthermore, economics for the installation of heat exchangers may determine the need for less efficient combinations.

Al-Riyami et al. (2001) studied the opportunities for process integration of a FCC unit in a refinery in Romania. The FCC unit was originally built by UOP and is used to convert vacuum gas oil and atmospheric gas oil. Several design options were identified to reduce utility consumption. The study of the FCC identified a reduction in utilities of 27% at a payback of 19 months. However, the calculation for the payback period only includes the heat exchangers, and, depending on the design of the FCC and layout of the plant, the payback period may be longer for other plant designs.

At a refinery in the United Kingdom, a site analysis of energy efficiency opportunities was conducted. The audit identified additional opportunities for heat recovery in the FCC by installing a waste heat boiler before the electrostatic precipitator, resulting in savings of $210,000/year at a payback of 2 years (Venkatesan and Iordanova, 2003).

FCC-Process Flow Changes
The product quality demands and feeds of FCCs may change over time. The process design should remain optimized for this change. Increasing or changing the number of pumparounds can improve energy efficiency of the FCC, as it allows increased heat recovery (Golden and Fulton, 2000). A change in pumparounds may affect the potential combinations of heat sinks and sources. New design and operational tools enable the optimization of FCC operating conditions to enhance product yields. Petrick and Pellegrino (1999) cite studies that have shown that optimization of the FCC-unit with appropriate modifications of equipment and operating conditions can increase the yield of high octane gasoline and alkylate from 3% to 7% per barrel of crude oil. This would result in energy savings.

Reformer
At a refinery in the United Kingdom, a site analysis of energy efficiency opportunities was conducted. The audit identified opportunities to improve the performance of the economizer in the waste heat boilers of two reformer furnaces. The changes would result in annual savings of $140,000 in each reformer at a payback period of 2 years (Venkatesan and Iordanova, 2003).

Coker
A simulation and optimization of a coker of Jinling Petrochemical Corp.'s Nanjing refinery (China) in 1999 identified a more efficient way to integrate the heat flows in the process. By changing the diesel pumparound, they achieved an energy cost reduction of $100,000/year (Zhang, 2001). Unfortunately, there is insufficient data to estimate the savings for U.S. refineries or to evaluate the economics of the project under U.S. conditions.

3.7.3 Water pinch and hydrogen pinch

The Pinch concept is a systems tool since it provides critical information on a total plant or even site level. The concept is also generally applicable in other areas than heat recovery. Actually, whenever an amount (heat or mass) has a quality (temperature or concentration), the concept of Composite Curves provides a systems view of the problem concerning efficient recovery (or re-use) of resources. The "Pinch" then shows the location on these curves where there is an accumulated deficit above a certain quality.

Pinch technology has therefore later been expanded into new areas by using various analogies. The most obvious analogy is between heat transfer and mass transfer. In heat transfer, heat is transferred with temperature difference as the driving force. Similarly, in mass transfer, mass (or certain components) is transferred with concentration difference as the driving force. The corresponding Mass Pinch, developed by El-Halwagi and Manousiouthakis (89-90), has a number of industrial applications whenever process streams are exchanging mass in mass transfer units, such as absorbers, extractors, etc. One specific application of the Mass Pinch is in the area of Wastewater Minimization, where optimal use of water and wastewater is achieved through reuse, regeneration and possibly recycling. The corresponding Water Pinch, developed by Wang and Smith (94), can also be applied for design of Distributed Effluent Treatment processes. Water pinch has been used successfully in food industry and in chemical industry. (Hallale, 2001, Wu, 2000, Polley and Polley, 2000, Dunn and Bush, 2001) To our knowledge, the use of water pinch in the refinery industry has however not been documented.

The most recent extension is the ***Hydrogen Pinch*** technology, specially developed for the refinery industry by UMIST in Manchester in collaboration with an industrial consortium. Due to changes in the market as well as new environmental regulations for gasoline and diesel, many refineries experience a shift from a hydrogen surplus situation (where hydrogen is sent to the fuel gas system) to a situation where hydrogen as a chemical becomes limiting.

In order to avoid the investment in a new Hydrogen plant (a steam reformer), there is a need for refineries to look into the optimal use, recovery and upgrading of hydrogen rich streams in the plant. While the first publications in this field (e.g. Towler et al., 1996) focused on Cost and Added Value (so-called Value Composites) based on interactions with the refinery LP model for operational planning, a more fundamental approach was taken by Alves, 1999. In his thesis, two important new graphical diagrams were presented, see Figure 3-4 and Figure 3-5. The Purity Profile shows Hydrogen Sources and Sinks drawn as Composite Curves in a purity versus gas flowrate diagram. Based on the Purity Profile, a Grand Composite Curve type diagram referred to as the Hydrogen Surplus Diagram can be constructed. The Hydrogen Surplus Diagram indicates the location (purity) of the Hydrogen Pinch, and the diagram can be used to investigate "appropriate placement" of hydrogen recovery processes such as Pressure Swing Absorption (PSA), membranes and cryogenic processes.

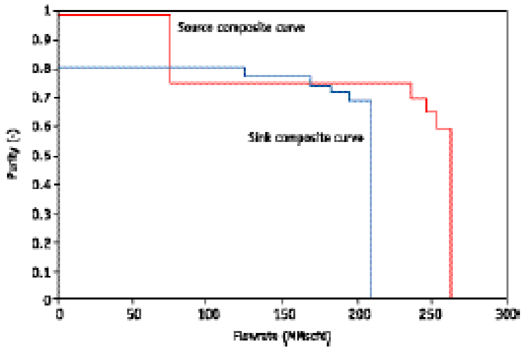


Figure 3-4. Hydrogen composite curves are a useful way of visualising the flows and purities of sources and sinks in a refinery hydrogen network.

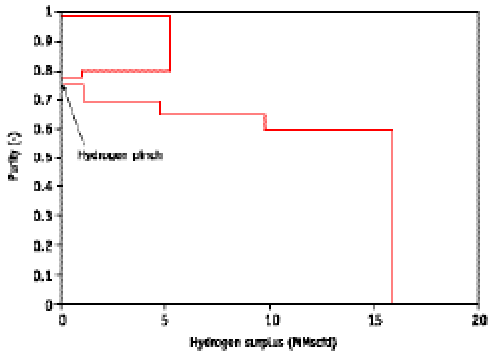


Figure 3-5. The hydrogen surplus diagram identifies the hydrogen pinch and also sets targets for hydrogen re-use, recycling and utility requirements.

Hydrogen pinch can, as traditional pinch technology, be used for both green field designs and retrofit. Even though the technology has been developed recently, applications in the refinery industry are already described in literature. The cost savings identified are relatively large (4-6 MUSD/year) and several of the suggestions have been implemented (especially in California where environmental legislations force refineries to invest in sulphur purification plants which increases hydrogen demands), in some cases even without having to invest in new equipment or extra piping. (Khorram and Swaty, 2002, Zagoria and Huycke, 2003).

There are limitations to the hydrogen pinch methodology however. First it does not handle technical and economical constrains and secondly it does not handle binary mixtures. The latter becomes a problem when optimizing not only hydrogen, but also other chemicals that might be mixed with the hydrogen. Aspen technology have developed a hydrogen pinch tool that takes some of the above mentioned constraints into account, e.g. costs and piping, and optimizes the hydrogen network design. The tool can be used as a complement or combined with other Aspen simulation and optimisation tools. (Hallale 2003)

3.8 The energy situation of Preem's refineries in Göteborg and Lysekil

3.8.1 Aim

Within the research cooperation program between Preem and Chalmers, there have been several projects based on the current situation at the Preem refineries in Göteborg and Lysekil. Their common aspect is that they are based on an adequate description of the processes from an energy perspective. In this subproject, the energy data required for these projects has been determined.

3.8.2 Implementation

The energy data needed to describe the processes from an energy system perspective are the heating and cooling demands at different temperatures of the subprocesses. In order to get the complete picture, it is also necessary to gain knowledge of how the energy is supplied - and removed from the processes by the utility systems.

The possible time variation of different demands, due to e.g. production level, product mix and season, also have to be specified in order to get a good picture. Additionally, it is of interest to see which restrictions apply to increased process integration, such as geographical distance and forbidden heat exchanger matches.

With the heating and cooling demands known, the so called background curve of the process can be constructed, which can be seen as a fingerprint of the process at the actual demand temperatures. Knowing the shape of the background process, different system alternatives can be studied effectively, using process integration tools such as pinch analysis.

However, in this project, due to limited resources, it has not been possible to survey the heating- and cooling demands completely. Thus simplified surveys have been carried out by identifying only the current cooling demand and the potential heat content in the flue gases. This simplification means that the current process design is accepted and not further analyzed. Therefore, the surveys show only available excess heat at different temperatures with current process design. Whether this heat is truly waste heat cannot be concluded from the survey. To determine this, a complete survey and analysis is needed.

The cooling demands have been computed based on logged data, mostly mass flows and temperatures. The sizes of the demands have been computed from these and from physical data on the flowing medium. In most cases, the cooling demands have been computed based on data of the process flows (the hot side), but in some cases data from the cooling side (the cold side) have been used. The actual temperature levels of the cooling demands have been identified using the temperature on the hot side, also for the cases where demands have been calculated from the cold side.

The cooling demands have been calculated down to a minimum temperature determined from discussions with Preem representatives. These target temperatures have been determined based on lowest possible temperature with regards to further processing and pumpability.

3.8.3 Results

The result of the surveys consists of the identified individual cooling demands and where they are found on the site. Below the total cooling demands are discussed.

Göteborg

In this plant, heat from the process is used in the Göteborg city (GEAB) and Volvo district heating systems. In addition to this there are air coolers, which are used when there is not sufficient district heating demand and when lower temperatures than those possible to obtain by cooling with the district heating water are required.

A stream data reference case, representing high throughput, have been derived from logged data (mainly from 2007-04-01 and 2007-10-12).

In Figure 3-6, the total cooling demand (excess heat) of the plant at the above assumptions is shown. The excess heat is 140 MW, out of which 25 MW is located at temperatures above 150°C.

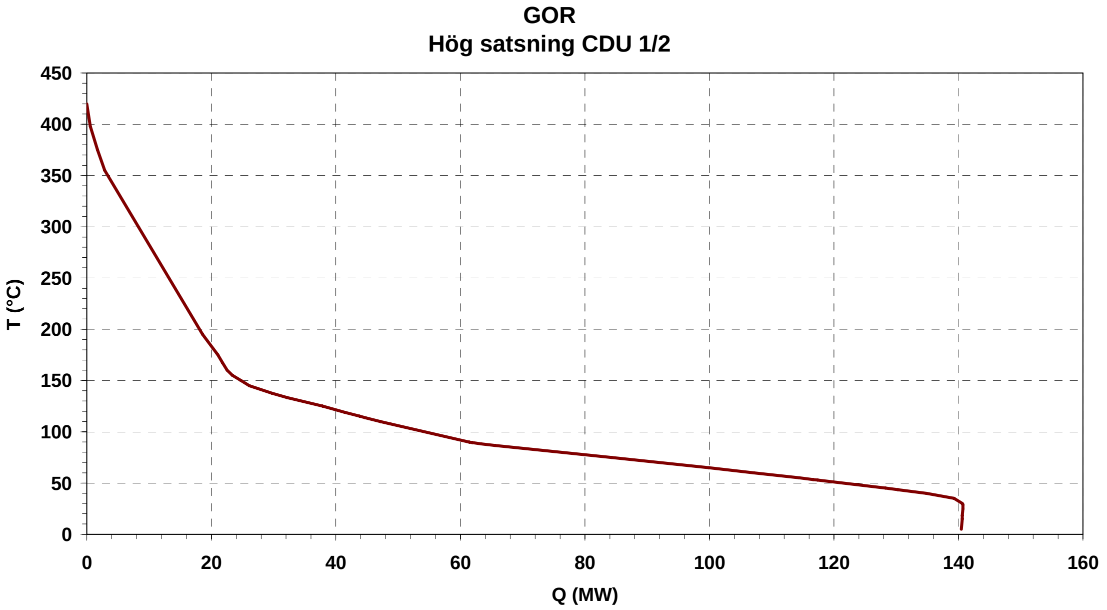


Figure 3-6. Total cooling demand of the Göteborg plant.

The district heat to GEAB and Volvo are delivered from two separate systems. The distribution between these two systems is shown in Figure 3-7. It can be seen that the cooling demand in the GEAB system is 83 MW, but only 7 MW at a temperature exceeding 150°C. The corresponding figures for the Volvo system is 57 MW and 17 MW, respectively. Now it is interesting to see whether the excess heat really is sufficient to satisfy the district heating demand.

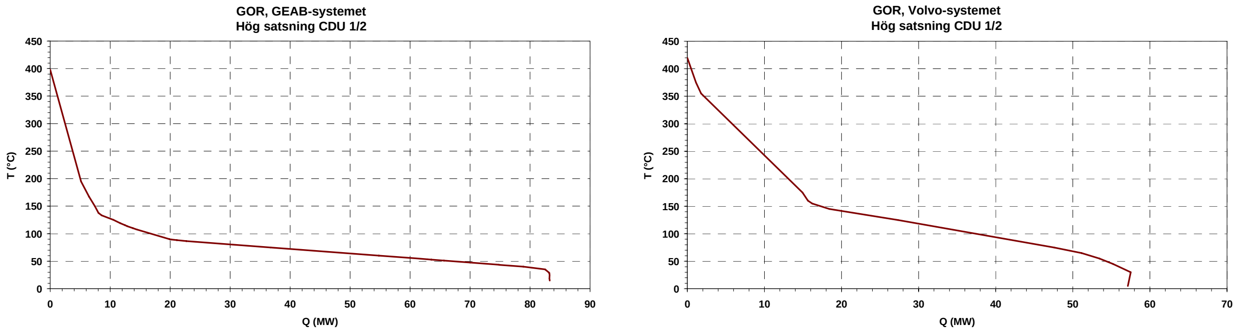


Figure 3-7. The excess heat in the Volvo and GEAB systems.

In Figure 3-8, a district heating demand of 60 MW has been added to each system. In the Volvo case, the supply temperature is 140°C, while the GEAB system has a supply temperature of 90°C. It can be seen from the figure that the excess heat in the Volvo system is insufficient for delivering the required heat; 20.5 MW of primary heat is required to satisfy the demand! In the GEAB case though, there is sufficient amount of excess heat, and no primary heat is required.

However, it is possible to drastically lower the need for primary heat to approximately 7 MW. This can be achieved by arranging the heat exchange to the two district heating systems in a more optimal way and not, as in the current case, in two separate systems.

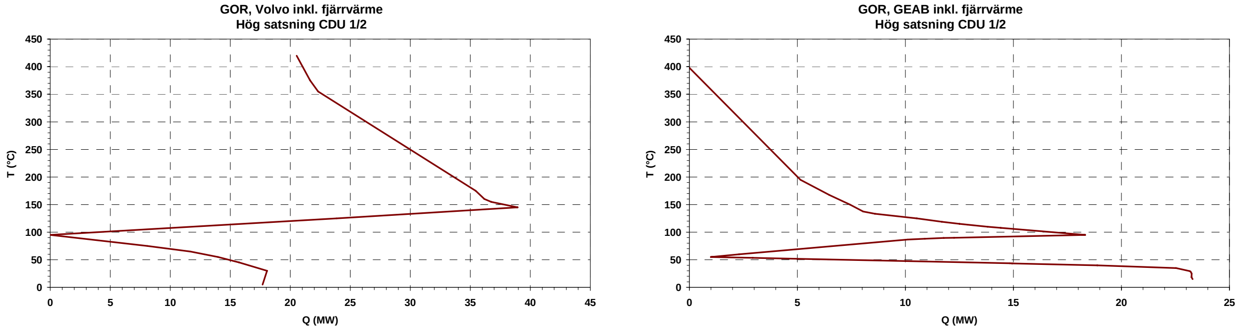


Figure 3-8. Net heating- and cooling demands from the Volvo and GEAB systems with delivered district heat included.

Lysekil

A major turnaround at Preemraff Lysekil, and related start-up problems, delayed the data collection substantially. To get some momentum, it was decided to concentrate only on one case; winter season and a crude oil with high sulphur content (HSW).

Preem personnel have been responsible for the data collection. The aim was to collect data for:

1. cooling of products to tank
2. QW-system (which supplies heat to Lysekil's district heating system)
3. air coolers on distillation columns (condensers)
4. flue gases to atmosphere

According to Preem, the flue gas stack temperatures were near the minimum as specified by the environmental permit for all studied objects except one; the FCC waste heat boiler with a stack temperature of about 260°C. With only one potential heat source it was decided to exclude item 4 from further analysis in this phase of the project. Item 3 was also excluded. Primarily due to lack of time, but also since Preem personal had a hunch that there were few untapped resources amongst the distillation condensers.

Product cooling

Products and intermediate products are cooled before tank storage. Process areas included were; crude distillation unit (CDU), fluid catalytic cracker (FCC), mild hydrocracker (MHC), SynSat unit (SSU), catalytic reforming unit (CRU), isomerisation unit (ISO), and hydrocracker (ICR).

The target temperatures are set by Preem and depend on pumpability, further processing, and flash point. The supply temperatures are based on 24-hour measurements. On-line measurements were not possible in some positions, and those temperatures are based on manual readings from another day with similar production.

The cooling demand for the products is shown in 3-9. The total cooling demand is about 60 MW. The amount of excess heat above 150°C is about 6 MW. Above 100°C the excess heat amounts to about 20 MW.

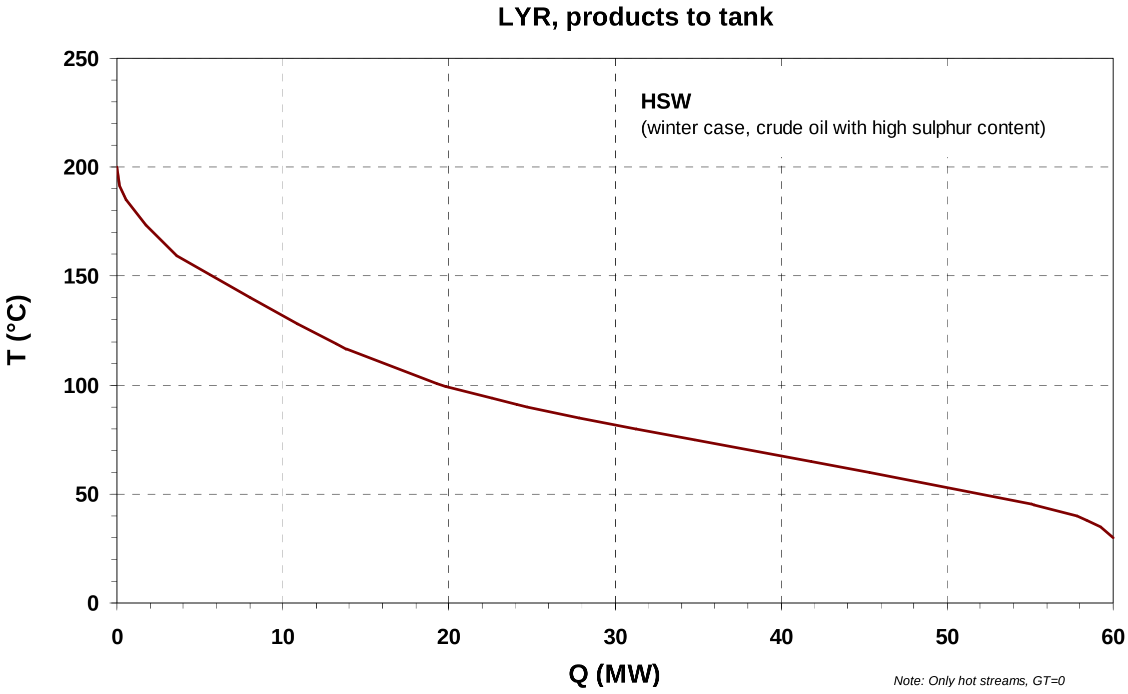


Figure 3-9. Cooling demand of products to tank. Data from 2007-01-13.

QW-system

The QW-system is an indirect cooling system with circulating cooling water. Heat from this system supplies Lysekil with district heating. Processes connected to the QW-system are; crude distillation unit (CDU), vacuum distillation unit (VDU), and visbreaker unit (VBU).

The target temperatures are set by Preem. The supply temperatures are based on 24-hour measurements. On-line measurements were not possible in some positions, and those temperatures are estimated.

The cooling demand is shown in 3-10. The total cooling demand is about 35 MW. The amount of excess heat above 150°C is about 10 MW, and above 100°C it amounts to about 28 MW.

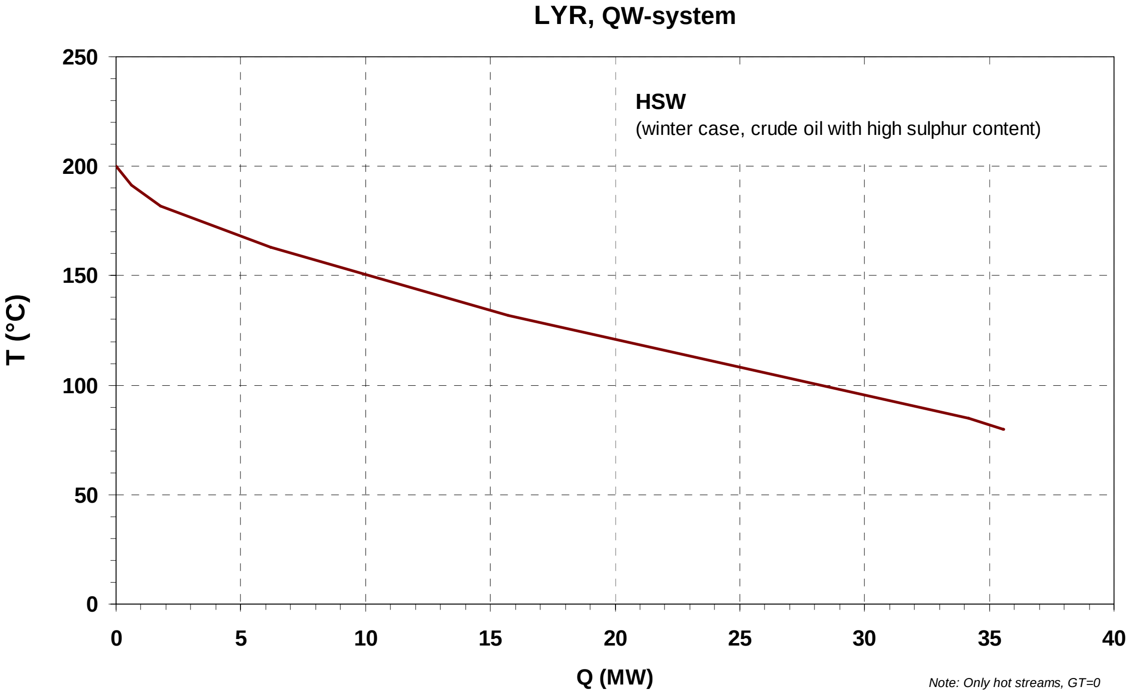


Figure 3-10. Cooling demand of streams connected to the QW-system. Data from 2007-01-13.

The refinery has a commitment to deliver up to 18 MW heat to Lysekil. This heat is taken from the QW-system. The normal load is estimated to be 10 MW.

In 3-11, district heat deliveries of 18 MW are included in the figure. The supply and return temperatures are assumed to be 110°C and 60°C respectively. With careful design of the heat exchanger system, the excess heat (the net cooling demand of 17.6 MW) can be extracted at temperatures of about 120°C and above.

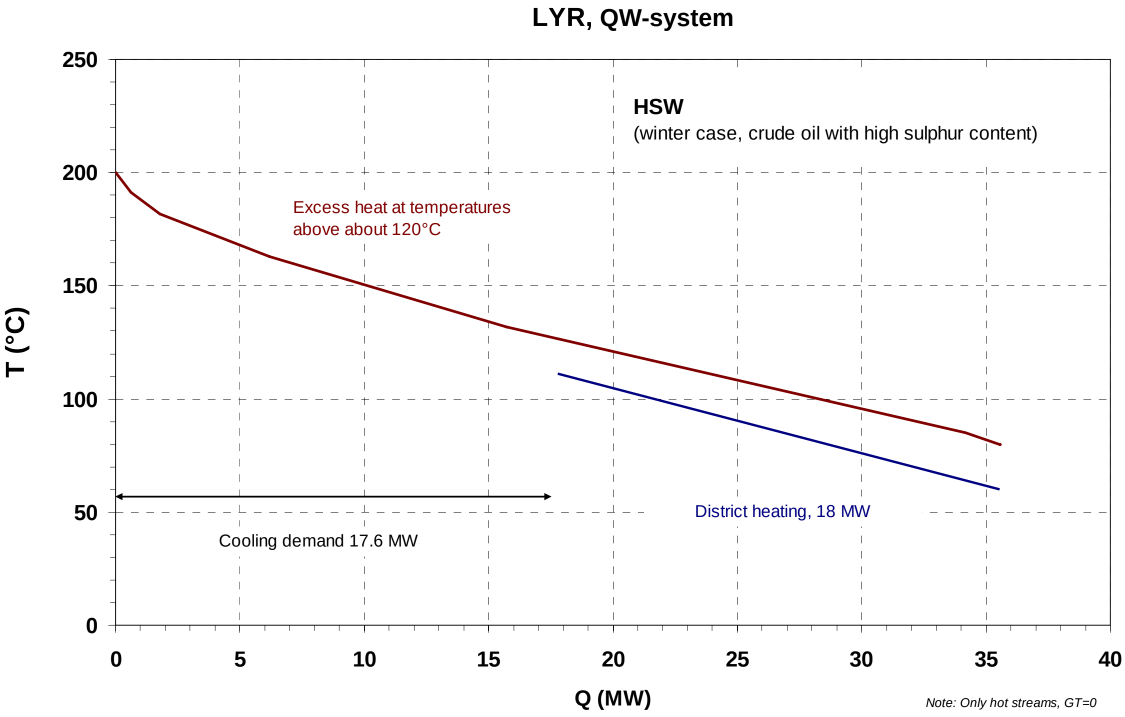


Figure 3-11. Net cooling demand with district heat deliveries of 18 MW. (Assumed supply and return temperatures for the district heating system are 110°C and 60°C respectively.)

Total cooling demand at Lysekil refinery

In 3-12, product cooling to tank and QW-system are combined in one figure, and in 3-13 heat delivery to the district heating network is "subtracted". Figure thus shows the net cooling demand. (A minimum temperature difference of 15°C is assumed in heat exchangers.) Excess heat above 100°C amounts to nearly 40 MW and 16 MW above 150°C.

The total cooling demand shown in 3-12 is just below 100 MW. This is far from the cooling demand of the whole refinery[1], but is believed that most high temperature sources are included in the figure. However, it should be stressed the present analysis is based on as is basis. Retrofitting of the internal heat recovery system could lead to substantially different results. This has been outside of scope of the present study.

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[1] Previously, Preem has suggested that Preemraff Lysekil should deliver district heat to both Uddevalla (400 GWh/y) and Trollhättan (300 GWh/y). The concept was to utilize excess heat below 120°C.

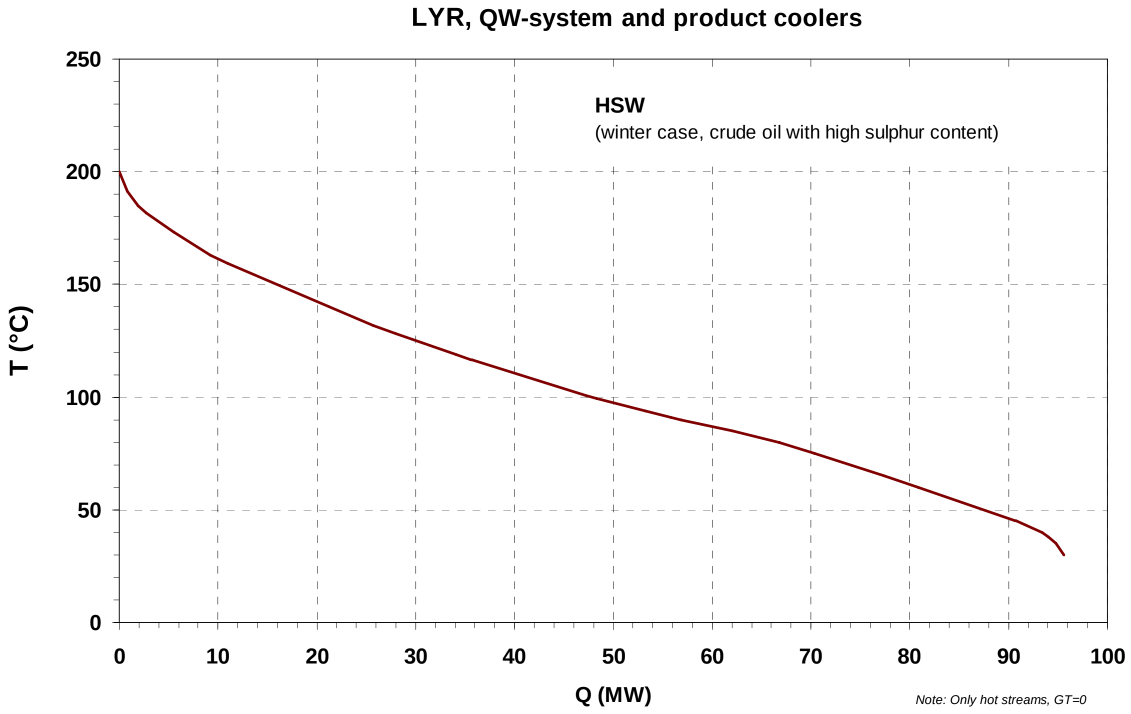

Figure 3-12. Combined cooling demand for product cooling and QW-system.

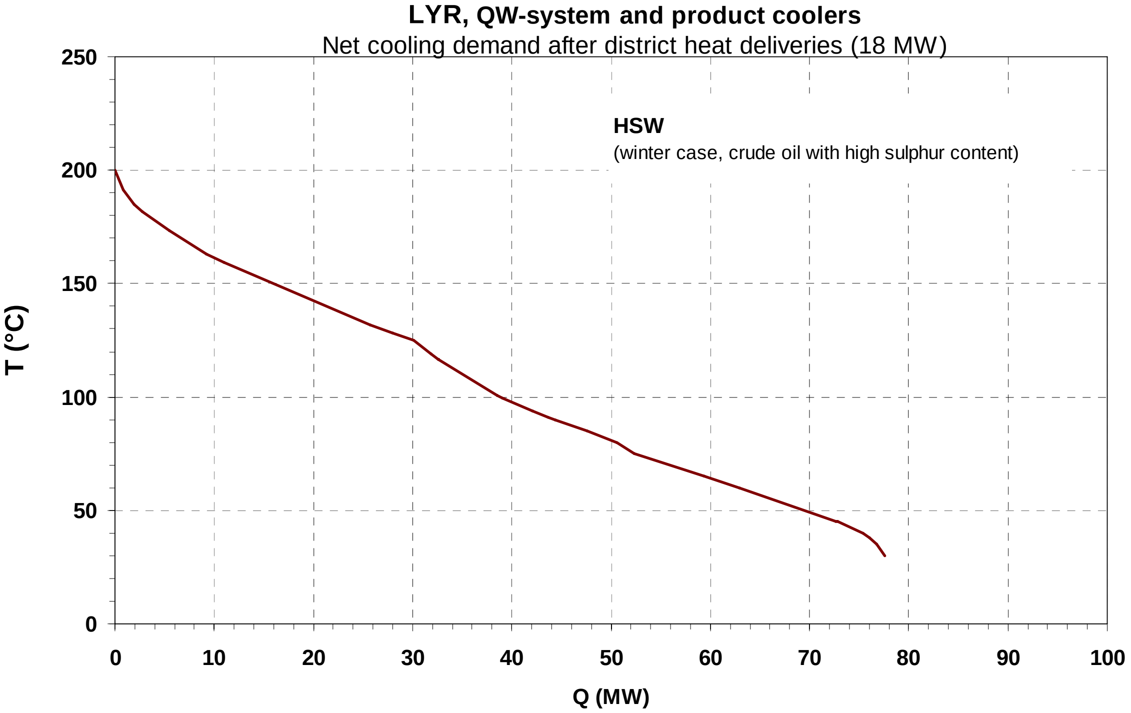

Figure 3-13. Net cooling demand for product cooling and QW-system.

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4 Upgrading excess heat via electricity production

4.1 Introduction

In an industrial system, there is often no way of using low-temperature excess heat and, as a result, upgrading this heat in a heat pump, possibly in the form of a heat transformer (absorption machine), or converting the heat to electrical energy in a thermal power plant are interesting alternatives. In the latter case, the thermal power plant can benefit from using an Organic Rankine Cycle (ORC). On the other hand, the maximum temperature in heat pumps is limited and, as a result, the ORC is an effective technique for basic load purposes in the 150 to 250°C temperature range.

The Rankine Cycle is a thermodynamic cycle that is used to produce electricity in the thermal power plant and it represents the practical implementation of the Carnot Cycle. Superheated steam is generated by a steam generator, usually a fired steam boiler, and it expands in a steam turbine. The turbine powers an electrical generator which converts the work into electrical energy. The excess steam from the turbine is condensed and returned as feed water to the steam generator. One disadvantage when water is used as the working medium is that the steam has to be superheated. Otherwise, the moisture content is too high and this could result in erosion on the turbine blades. An organic medium can be used instead of water as the working medium. The main advantage is that these fluids can be used under 400°C and do not need to be superheated, even if superheating can increase efficiency. This cycle is known as the Organic Rankine Cycle (ORC).

Depending on the organic substance that is used, the temperature of the excess heat, which can be as low as 70-80°C, can be used in an ORC. At these low temperatures, a water-based cycle would not be cost effective, because of the enormous volumes of steam that are created during expansion at low pressure and are required for a reasonable condensation temperature. The investment cost would be too high. The ORC actually achieves higher efficiency at these low temperatures.

Many organic compounds have been used in the ORC to suit waste heat temperatures of 70 to approximately 500°C. Examples of chemical compounds include fluoridated hydrocarbons, isopentane, toluene, ammonia and silicone oil. The organic compounds usually have a higher molecular weight and this results in low volumetric flow-rates and compact systems, thereby enabling a high turbine efficiency level (up to 80%). Another advantage when it comes to organic substances is that they do not need to be superheated, so no drops of liquid are formed during expansion from saturated vapour in the turbine, thereby preventing erosion.

When it comes to operation, the ORC requires little maintenance, it can be run automatically without any staff, its part-load characteristics are good and commissioning is straightforward. Availability is normally high and the thermal efficiency can be estimated at between 10 and 20%, depending on the temperature levels in the evaporator and condenser. Higher evaporation temperatures and lower condensation temperatures produce higher efficiency. The theoretical potential for producing electricity comes from the available waste heat, while the practical potential is determined by the possible use of excess heat for other purposes (such as process integration) or heat pumping. To minimise the cost and energy losses, the ORC should be placed near the heat source, which should be large (> 5 MW), stable and resilient (approx. 8,000 hours/year). Cooling water should be available on the plant site to condense the working medium.

ORC´s can be used to upgrade low-temperature waste heat, improve the efficiency of thermal power plants or recover geothermal energy and solar energy. Small-scale ORC´s have been used commercially or on a pilot scale for the past 20 years. It is estimated that, before 1984, some 30 commercial ORC systems had been built with a minimum output of 100 kW. In different parts of the world, there are currently a number of systems utilising ORC technology. These systems have a relatively low output, 0.5-2 MW. The Italian company Turboden has around 50 systems in operation. They are almost exclusively based on the combustion of wood chips, after which the heat for the ORC process is taken from the flue gases. Most of these systems are based in Austria and Germany. The US company Ormat also has a number of systems in operation in most of the areas in which ORC technology can be applied. The use of ORC´s focuses on the US market, but there are systems in operation throughout the world. The two above-mentioned companies must be regarded as the leading players, but there are also a number of new, smaller companies. The construction of a very large solar-heat-powered ORC system is currently being planned in a desert area in the USA. Its estimated electrical output is 50 MW.

The standard systems are designed for liquid heat sources, often water or heat-transfer oil. Condensing steam calls for special solutions. Some products require high heat-source temperatures (> 150°C), such as waste heat from flue gases or concentrated solar heat, while the Swedish product, for example, require low temperatures (< 120°C). According to the economic evaluations, the specific costs of OCR technology decline as the output increases.

4.2 ORC

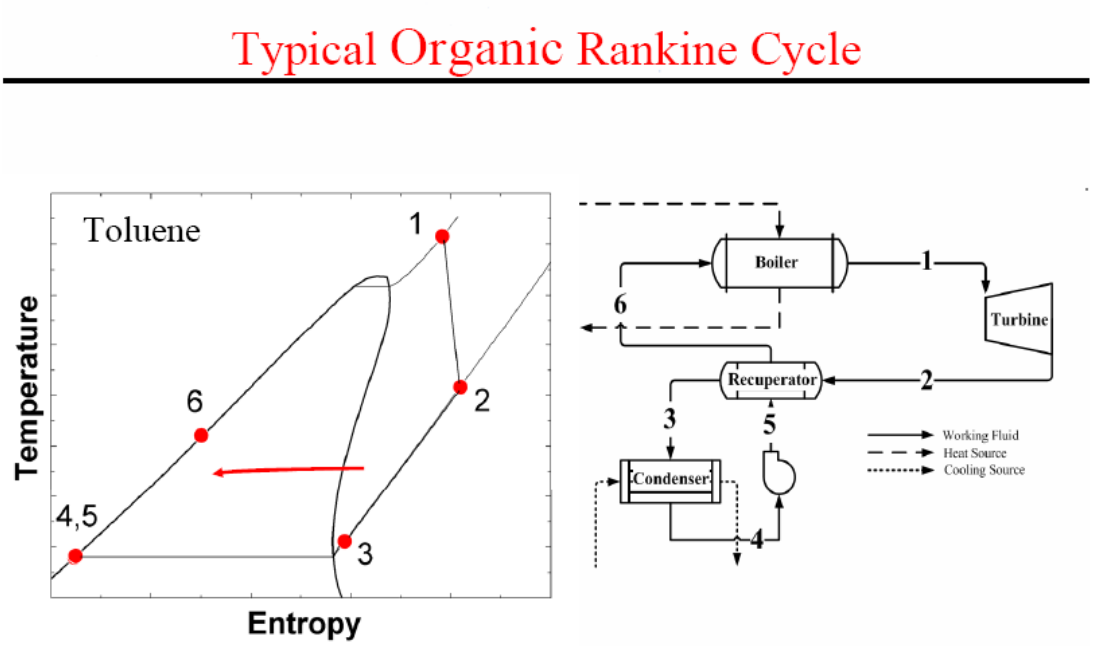


Figure 4-1. Schematic view of a typical Organic Rankine Cycle

The thermodynamic and process design of an ORC with superheating and internal heat exchange (regenerative cycle) can be seen in Figure 4-1. In the expander (in this case, the turbine), the working medium is expanded irreversibly, adiabatically from condition 1 (superheated vapour) to condition 2 (still superheated vapour). The gas is cooled in a heat exchanger to condition 3 (almost saturated vapour) using a cold condensate (red arrow). The gas is cooled under condensation in the condenser to condition 4 (saturated liquid), using an external heat sink (such as cooling water). A fluid feed pump increases the pressure of the condensate to condition 5 and the condensate is now called the feed fluid. The fluid is heated regeneratively in the above-mentioned heat exchanger to condition 6 (liquid). The fluid is heated still further, evaporated and superheated in a vapour generator using an external heat source (such as a waste heat) to condition 1. Like superheating, re-heating can take place in a separate heat exchanger. In many cases, the superheating is excluded. There is always a large need for heating surfaces when cooling low-density gas. A regenerative heat exchanger or a separate gas cooler should therefore always be questioned. The latter can always be replaced by condensate injection for the necessary elimination of superheating. The former can easily be avoided if the exterior heat source contains a flow of fluid with a relatively low temperature.

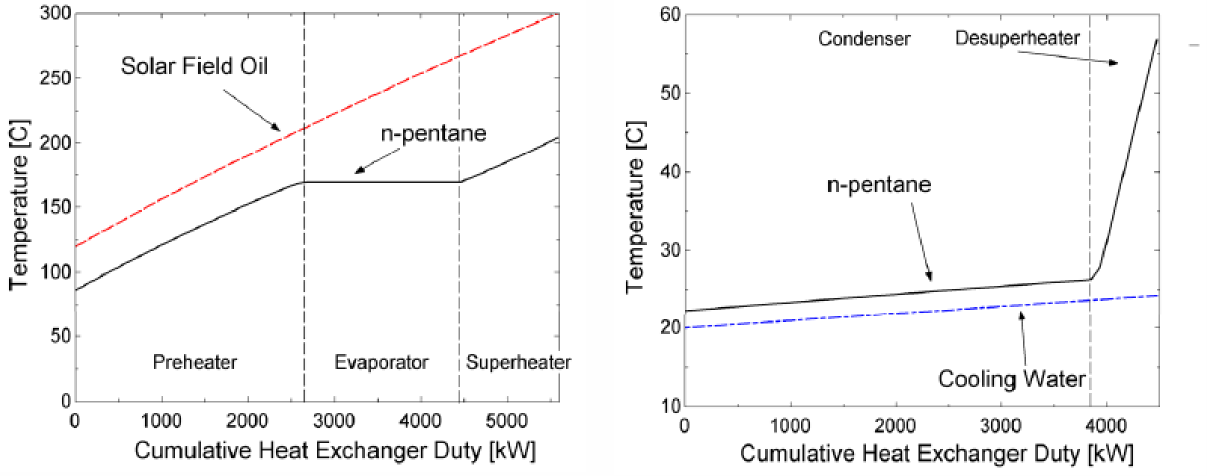


Figure 4-2. Case study (reference case)

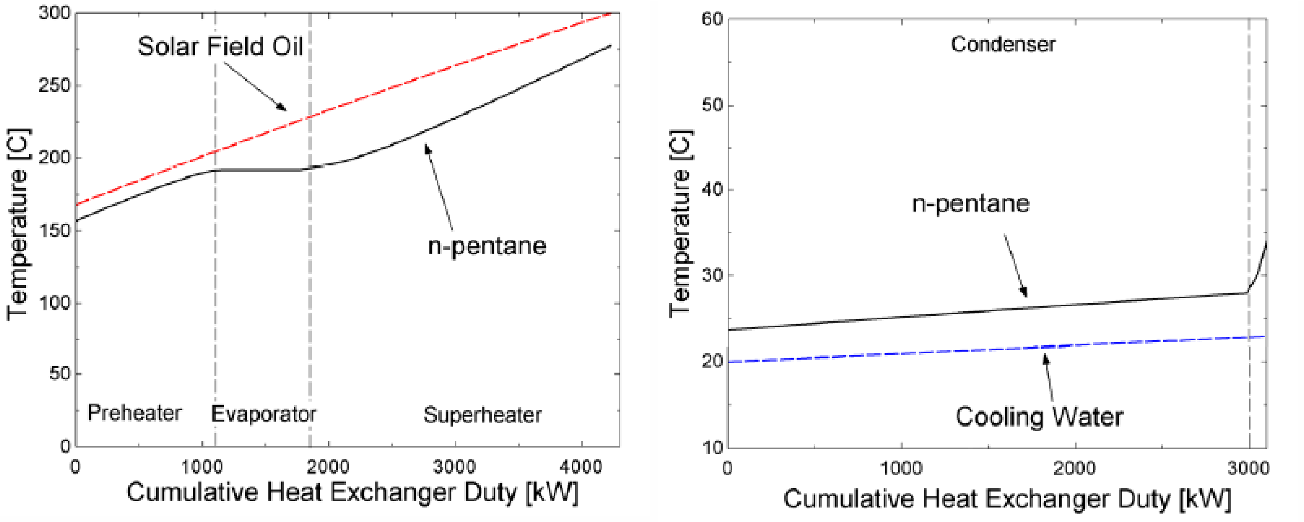


Figure 4-3. Case study (optimised case)

The temperature-entropy diagram (T-s) shows that evaporation takes place near the critical point – in this case, unusually near – and, as a result, there is an abnormal shift towards pre-heating in the distribution between energy requirements for pre-heating and evaporation. The exterior heat source, which can contain several sub-flows of waste heat, should then display a clear gradient.

The temperature characteristics of the evaporator and condenser for a cycle using the working medium of n-pentane are shown in Figure 4-2 and Figure 4-3. The heat source is a circulating flow of heat-transfer oil (from solar panels). In the condenser, a fall in pressure produces a temperature gradient in the working medium. In this case, evaporation takes place at a lower, reduced temperature, far from the critical point. In Fig. 3, there is a shift in the distribution between the different energy requirements towards less, external pre-heating and more superheating compared with Fig. 2. The regenerative heat exchange is also extensive and this is further promoted by the high minimum temperature of the exterior heat source. There is no low-grade waste heat.

4.2.1 ORC in a refinery

In a refinery which does not deliver its waste heat to a district heating system or nearby industry, the heat source for a central ORC system is a temperature spectrum of sub-sources. Without any retrofit of the heat-exchanger network, these sub-sources are all process flows which, as things stand, are cooled by air coolers or in water coolers. Some of these flows are potential sources, due to new opportunities to final cooling of the flows and this also applies to flue gases, for example. A central ORC system, which basically comprises one cycle, requires either a evaporator (or just a pre-heater) for each sub-source or a large vaposteam generator including the collection of the excess heat using a heat carrier (such as water or heat-transfer oil). A central system is placed outside the process area, thereby reducing the danger of fire. Existing coolers normally supplement the process cooling and offer security to operations in the event of problems with the ORC system.

A preliminary analysis of the potential for ORC at Preemraff, Lysekil, is presented in Table 4-1.

The prerequisites are as follows.

- The working medium is pentane (boiling point 36°C)
- No internal heat exchange (access to low-grade waste heat in the fluid flows)
- Access to waste heat at sufficient temperatures for all heat supply
- One (or two) collection system for the excess heat
- Condensation temperature 20°C
- Condensate injection in the exhaust steam from the turbine for gas cooling
- The isentropic efficiency of the expander (such as a turbine) is 75% (relatively low)
- The evaporation temperature (t_{boil}) is 100°C or 140°C
- The total, exterior heat supply (Q_1) is 90 MW

The following calculations are made:

- Turbine output (P) (the electrical output is 3-5% lower)
- Thermal efficiency (η_t)
- Carnot efficiency (η_{tC}) (the average temperature is used for gradient heating)
- Percentage of evaporation heat (Q_{boil}/Q_1)

The turbine output can easily be re-calculated for a lower, total heat supply.

Table 4-1. ORC possibilities at Preem, Lysekil

T_{boil} (°C)	P (MW)	Q_{boil}/Q_1	η_t	η_{tC}
100	12.0	0.596	0.133	0.187
140	14.8	0.432	0.164	0.237

The pump energy for the collection system can probably be offset against the reduction in electrical energy in the fan cooler. The pump output for the cooling water system can be estimated at approximately 400 W for a temperature increase of 5 K in the condenser.

4.2.2 Pilot case at the Lysekil refinery

Within the framework of a master thesis project at the Division of Heat and Power Technology, a pilot case relating to OCR technology has been studied. This project, which was conducted by Erik Cleverstam, began in June 2007 and has now been virtually concluded. The pilot case is based on process flows in the SynSat plant and, using simulations in HYSYS and calculations in Matlab, it has revealed the capacity these flows have for electricity production in different conditions. The thermal energy in the process flow is transferred directly to the ORC system. Interest has focused on demonstrating the effect of the choice of working medium, together with the way different process solutions can be designed and the way they influence the cycle. When it came to the economic evaluation, a number of companies specialising in this sector were contacted with a view to using their combined data to evaluate the profitability of investing in ORC technology.

The choice of working medium and process solution has a major impact on the performance of ORC technology. This study revealed that, in the best case scenario, the flows that were studied can produce a net electrical output of 1,200 kW. Unfortunately, the cost of converting the refinery in order to connect waste heat in process streams and cooling water, plus the cost of EX-classified electrical installations, is high and this therefore contributes to the high total investment cost. If, optimistically speaking, an additional charge of just 30%, including assembly on site, was added to the investment cost, this study reveals the following economic picture (Figure 4-4) for small systems of this kind that are available on the market.

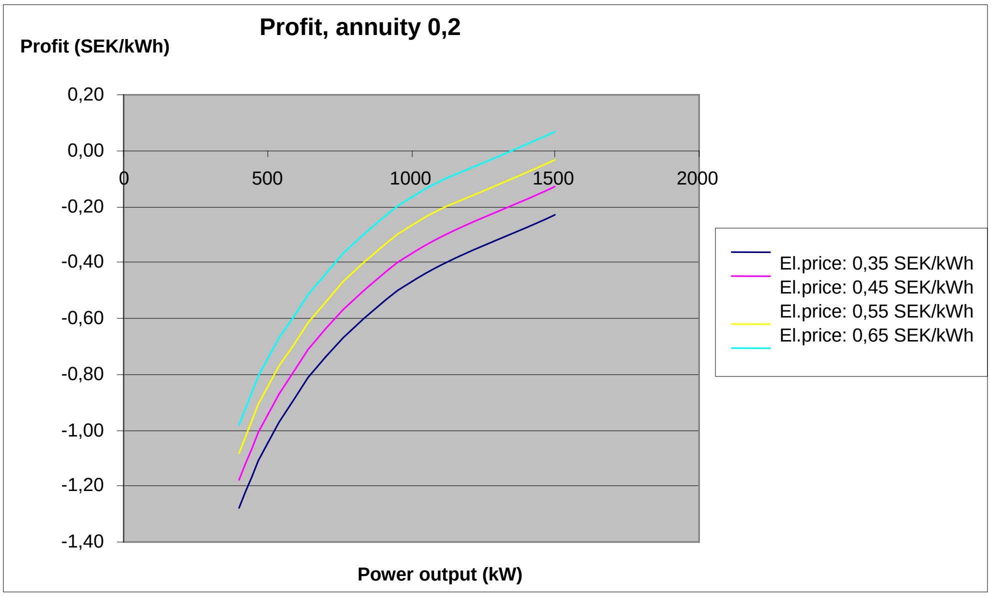


Figure 4-4. Economy of a small OCR system

With current electricity prices, the sale of the electricity that would be produced would not offset the cost an investment would involve. If the income from possible green electricity certificates is taken into account, i.e. if a production subsidy of SEK 0.18/kWh was granted, the situation would improve. The prerequisites are low annuity, a high electricity price (including production subsidies of approximately SEK 0.065/kWh and an installed output of at least 1,500 kW, i.e. more than in the pilot case.

4.3 Heat Pumps

A heat pump is a machine in which heat is lifted from a low-temperature level (heat source) to a higher temperature level (heat sink) with the aid of some type of primary energy. The coefficient of performance (COP) is defined as:

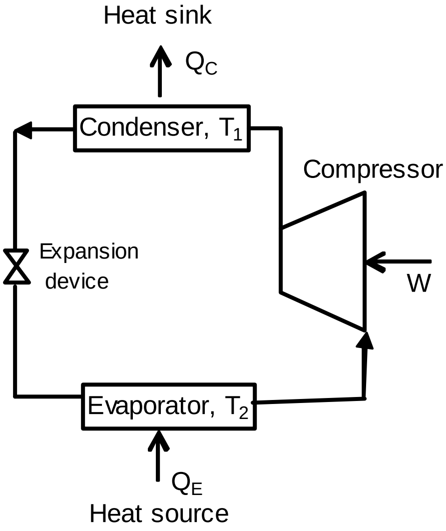
$$\mathrm{COP} = \frac{\text{Heat transferred from the heat pump to the heat sink}}{\text{Primery energy consumption}}$$

A number of different heat pump cycles are possible to use in industrial applications. These cycles can be categorized in various ways, for example as mechanical- or heat-driven cycles, compression or absorption cycles, closed or open cycles. The most important ones are:

- Closed compression cycle
- Mechanical vapour recompression[2] (MVR)
- Thermal vapour recompression[3] (TVR)
- Absorption cycles

All heat pumps include the three different processes shown in Figure 4-5 for a simple closed compression cycle:

- Receive heat from the source (waste heat)
- Temperature increase
- Release heat to the sink at an elevated temperature



$$\boxed{\mathrm{COP} = \frac{Q_C}{W} \approx \frac{Q_C}{Q_C - Q_E}}$$

Figure 4-5. Simple Closed Compression Cycle (The ‘approximately equal’ sign is used in the COP equation since losses are not included in the equation.)

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[2] Also known as mechanical vapour compression (MVC)

[3] Also known as thermal vapour compression (TVC)

The closed compression cycles are based on the ideal Carnot cycle operating between the temperatures T_1 and T_2. The COP for the Carnot cycle is defined as:

$$COP_{Carnot} = \frac{T_1}{T_1 - T_2}$$

The temperature lift is the temperature difference between condenser and evaporator temperatures. As seen from the equation above, the COP decreases with increasing temperature lift.

The COP of the real cycle is often expressed as

$$COP = \eta_C \cdot COP_{Carnot}$$

where η_C is called the Carnot efficiency. For a specified design of a cycle the Carnot efficiency can often be regarded as a constant with varying T_1 and T_2 if these variations are moderate. The Carnot efficiency for a well-designed heat pump is normally in the range of 65 to 75%.

The most common heat pump in industrial applications is mechanical vapour recompression (MVR) and it will be discussed in more detail below.

4.3.1 Mechanical Vapour Recompression

Mechanical vapour recompression is the technique of increasing the pressure and thus the temperature of waste gases, thereby allowing their heat to be reused. The most common type of vapour compressed by MVR is steam, but other process vapours are also used in the (petro-) chemical industry, for example in heat pump assisted distillation.

There are several possible system configurations. The most common is a semi-open type in which the vapour is compressed directly (also referred to as a direct system). After compression, the vapour condenses in a heat exchanger where heat is delivered to the heat sink, see Figure 4-6. This type of MVR system is common in evaporation applications and also used in distillation systems where the overhead vapours are compressed and condensed in the reboiler.

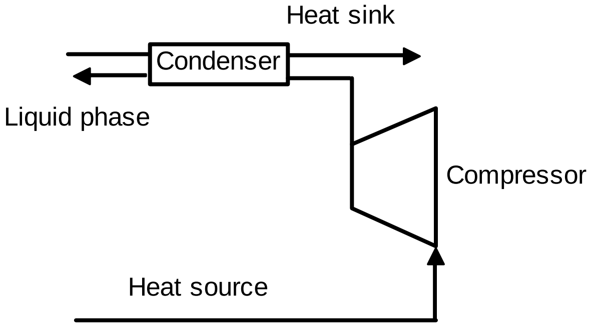

Figure 4-6 Semi-open MVR-system

The other type of semi-open system lacks the condenser, but is equipped with an evaporator. This is type is common in system there the waste vapour is ‘dirty’ and therefore cannot be used directly. Instead, the waste vapour is condensed in a reboiler generating clean steam that can be fed to a compressor. The compressed steam is then distributed to heat consumers.

Examples of this type can be found in heat recovery systems in thermomechanical pulping mills.

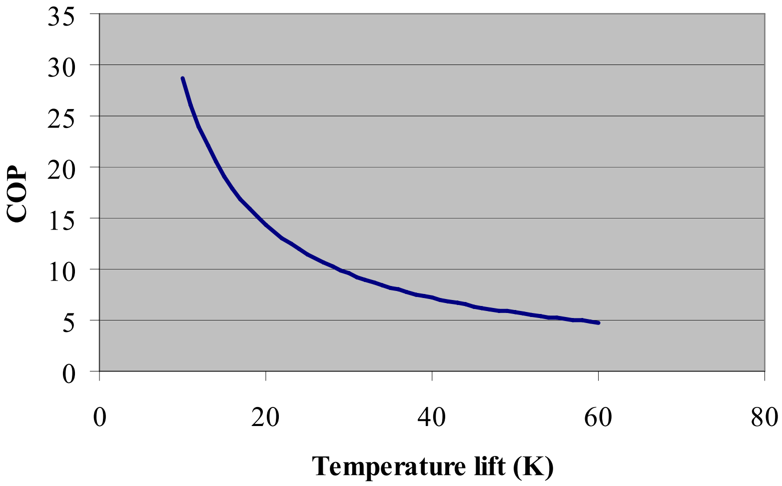

Figure 4-7 COP versus temperature lift for an MVR-system (η_C=70%, steam is compressed to 2.3 barg corresponding to a heat sink temperature of about 135°C)

From Figure 4-7 it can be deduced that MVR systems can give very high COPs. It can also be seen that the COP is very dependent on the temperature lift. Careful design is necessary to achieve the benefits of high COP, without incurring high investment costs for the equipment surrounding the compressor.

By far the most important design issue in MVR systems is the choice of compressor type. Compressors for MVR systems are of two main types: turbo and positive displacement compressors. In turbo compressors, the pressure rise is accomplished by increasing the velocity of the fluid and then converting its dynamic pressure into static pressure. In a positive displacement compressor, the pressure is increased by decreasing the volume of the fluid.

Turbo compressors are suitable for high and medium-high flows. The radial cornpressor is the most common type in MVR systems. Pressure ratios up to 2 are standard, though higher ratios are possible when using advanced materials. High superheating temperatures are controlled by water injection. Turbo compressors are usually equipped with a mist eliminator in the suction line. Typical isentropic efficiencies are 0.7 to 0.8

Screw compressors operate at higher pressure ratios (2-6), and normally at lower flow rates than turbo compressors. Cooling of the compressor can be accomplished by the injection of water, which also serves to seal and lubricate the compressor. Screw compressors are not sensitive to liquid drops in the vapour, so no separator is necessary. Typical isentropic efficiencies are 0.7-0.9.

4.3.2 Basic process considerations

When considering the process in which the heat pump will be used, pinch technology has proved to be a very powerful tool. One of the most important features of pinch technology is that it is possible to identify a temperature (the pinch) in a process which divides the stream system into two separate parts. In the part above the pinch there is a net heat deficit, and heat must be added to the system by a hot utility. If a cold utility is applied above the pinch it follows that the demand for the hot utility will increase by the same amount. Thus, valuable heat is just removed by cooling. On the other hand, in the part below the pinch there is an excess of heat that must be removed from the system by a cold utility. Any heat added below the pinch must also be removed. Hence, in a well designed process no cold utility should be used above the pinch and no hot utility below the pinch. These rules are illustrated in Figure 4-8.

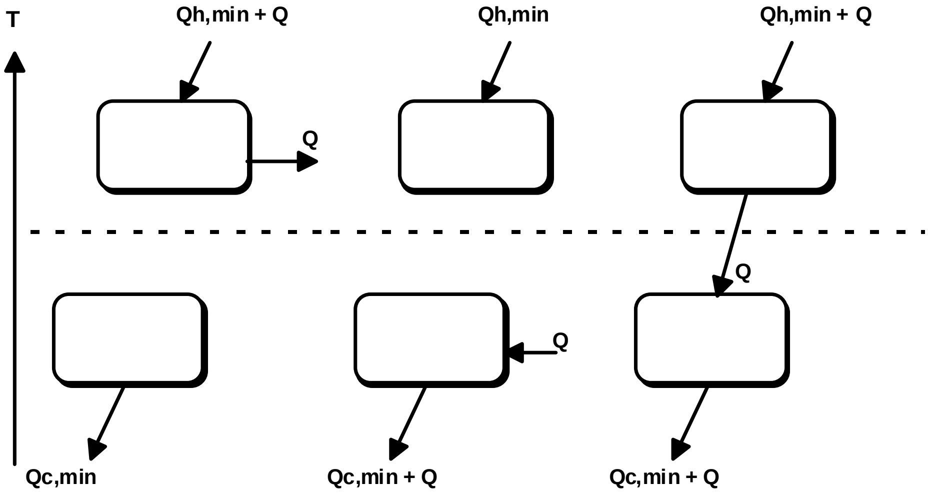

Figure 4-8 "Pinch rules"

It is clear that a heat pump can be placed in three different locations: below, above, or across the pinch.

Placing the heat pump *below the pinch* does not result in any external utility saving because, if no hot utility is used below the pinch, heat is simply pumped around within that part of the system. Indeed, the cold utility will even increase by the drive energy put into the heat pump. Placing the heat pump *above the pinch* will not save any external utility either. By placing the heat pump *across the pinch*, heat is extracted from a system where there is an excess of heat, and delivered to a system where there is a heat deficit. In this way, the demand for both the hot and cold utilities is reduced. Thus, placing a heat pump across the pinch is the best way of integrating it into a process, see

Figure 4-9.

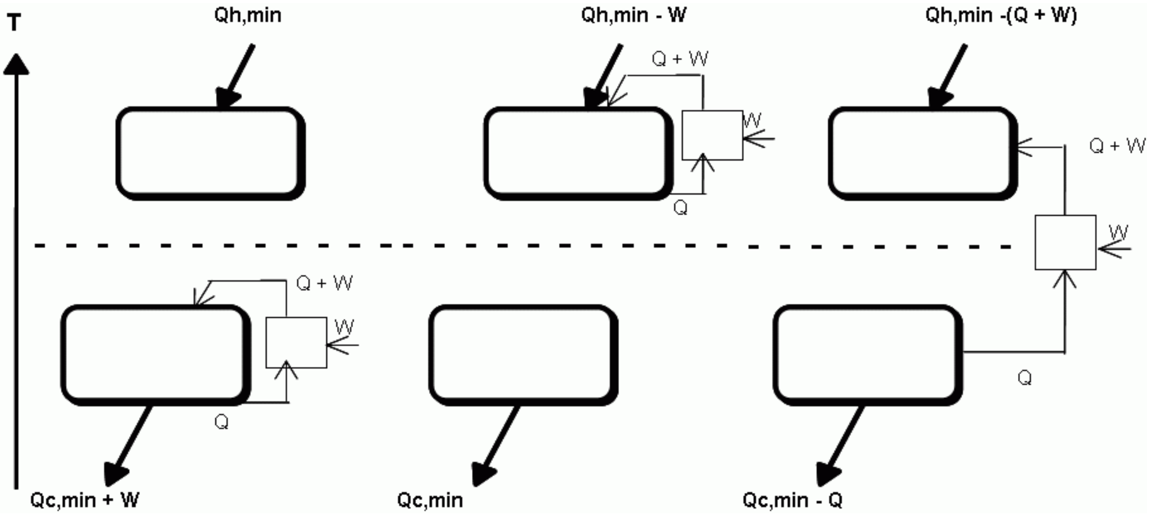

Figure 4-9 Heat pump placement relative the pinch

4.3.3 Heat pumps at Preem's Refineries

A detailed assessment of heat pump possibilities at the refineries in Göteborg and Lysekil has not been within the scope of the present pre-study. However, calculations with reasonable technical and economical data show that heat pumps may be an interesting option. The assumptions for two cases are presented in Table 4-2. The number of full load operating hours is assumed limited to 5 000 hours per year due to plant steam imbalance.

Table 4-2. Technical and economical assumptions used in the evaluation

	Production of LP-steam	Production of MP-steam
Heat source temperature	100°C	130°C
Number of compressor stages	3	3
Pressure ratio per stage	1.7	1.6
Compressor cooling and desuperheating	water injection	water injection
Heat delivered	20 MW	20 MW
Steam price (given by Preem)	249 kr/tonne	254 kr/tonne
Operating hours	5 000 per year	5 000 per year

In Figure 4-10, COP versus isentropic compressor efficiency is shown for the two cases. Reasonable isentropic compressor efficiencies are about 0.75, which gives COP between 5 and 6. The corresponding Carnot efficiency is about 72%. Since COP for the two cases are about the same and the steam prices are similar, only results for LP-steam production are shown in the following.

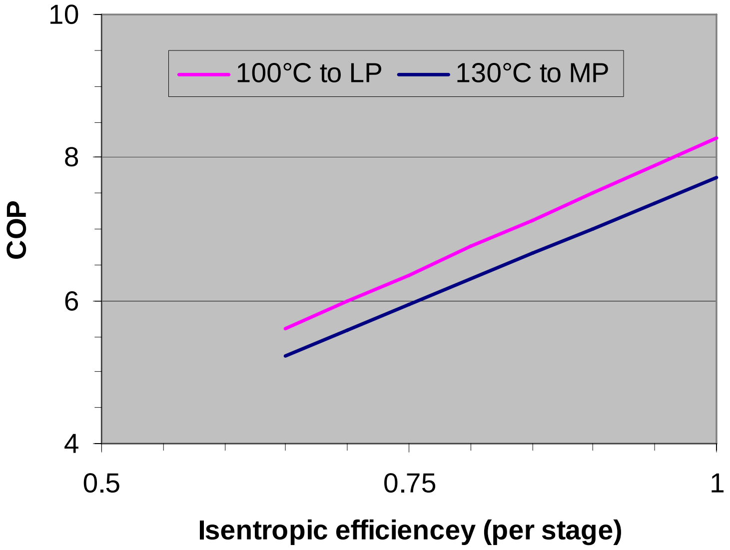

Figure 4-10 COP versus isentropic efficiency for a 3-stage MVR-compressor

In

Figure 4-11, the simple payback period is shown versus the price ratio electricity-to-steam. The steam price is fixed at 249 SEK/tonne. The investment cost, 45 million SEK, is taken from a 15 MW MVR-installation at Stora Enso's Nymölla mill. Since many factors influencing the investment cost depend on local conditions (for example piping), the figures given here are indicative only.

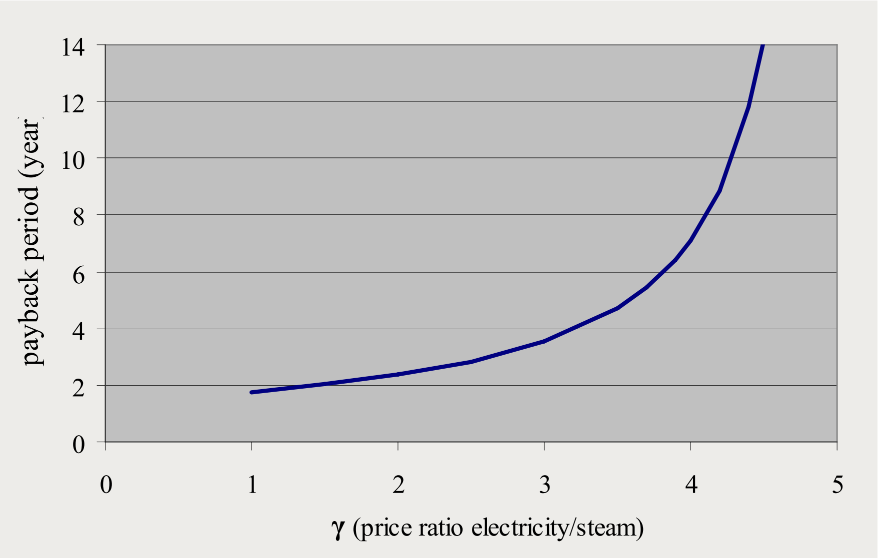

Figure 4-11 Simple payback period versus electricity-to-steam price ratio. (COP = 5, Steam price = 249 SEK/tonne, specific investment cost = 3 000 000 SEK/MW heat delivered, operating hours per year = 5000)

The payback period is directly proportional to the investment cost as shown in Figure 4-12 for two different electricity-to-steam price ratios.

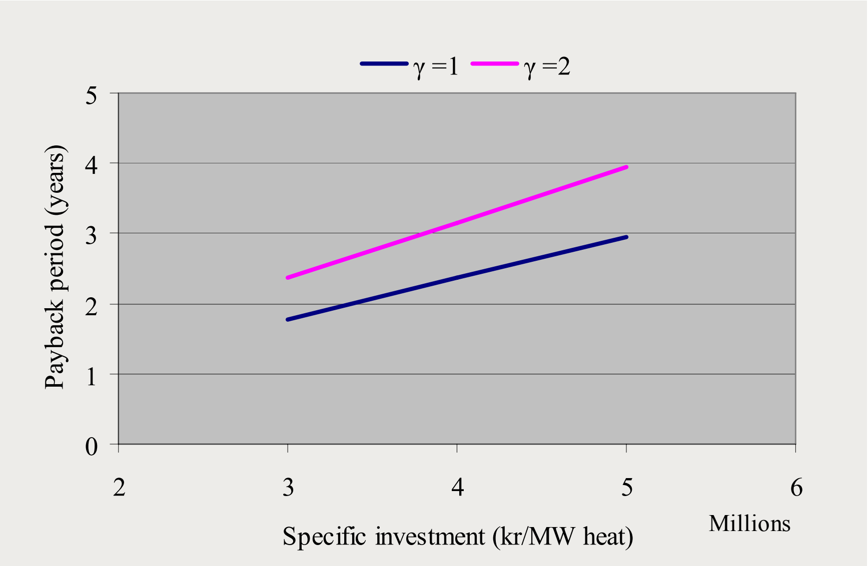

Figure 4-12 Simple payback period versus specific investment cost. (COP = 5, Steam price = 249 SEK/tonne, operating hours per year = 5000)

The figures above show that depending on process conditions, such as amount and temperature of available excess heat, heat pumps can be an interesting upgrading option.

4.3.4 Conclusions

Upgrading excess heat to low-pressure or medium pressure steam can be an economical alternative for Preem and should be evaluated more thoroughly. Payback periods between 2 to 4 years seem realistic under good technical and process conditions.

The present evaluation does not take into account the actual process conditions at the refineries, which of course are crucial. However, the amount of excess heat above 100°C in the Göteborg refinery is about 50 MW according to the pre-study.

Another crucial factor is the electricity-to-steam price ratio. So far, only an electrical engine has been evaluated but to get more realistic estimation, the steam turbine case should also be considered.

4.4 References

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5 CO_2 sequestration

CO_2 capture and storage involves the separation of CO_2 produced during fuel use, its transport and its storage, eg. in geological media. All parts of the chain have been implemented before but never together, (IEA, 2004).

5.1 CO_2 capture

CO_2 capture can be divided into four main processes:

- Post-combustion
- Pre-combustion
- Oxy-combustion
- Chemical-looping combustion (unmixed combustion)

The four processes will be described in following sections.

5.1.1 Post-combustion

When separating CO_2 after the combustion, the CO_2 is removed from the flue gases. Several methods for doing this are available. The composition and properties of the flue gases decides what is the best method. These parameters are in turn dependent on the fuel and combustion process used. The post-combustion process can be applied to all combustion plants and is the only method available for retrofit, (Elforsk, 2005).

The most common method for post-combustion is chemical absorption, since it can handle low partial pressures of CO_2. This regenerative process has rather high separation efficiency, above 85 %, and produces an almost pure CO_2 stream. The CO_2 is then compressed and cooled down to liquid state. The process requires energy for the regeneration of the solvent, (Svendsen et al, 2001). New more energy efficient solvents are under development, more about this in the section “Solvents for absorption”.

5.1.2 Pre-combustion

When the coal is removed from the fuel before combustion a H_2 rich stream and a CO_2 rich stream are formed. The concept can be used for power, heat and hydrogen production.

In the first step a syngas is formed (CO and H_2). For natural gas this is done through high temperature reforming and for other fuels through gasification. The syngas is then shifted with water producing CO_2 and H_2. The mixture is then separated through absorption. The difference compared to post-combustion is that the CO_2 concentration is higher and the efficiency can thereby be higher, (Kvamsdal et al, 2007). Membranes of different kinds are being developed as an alternative to absorption. The CO_2 is compressed and liquefied as before and the hydrogen used as a product or fuel.

5.1.3 Oxy-combustion

Another way of producing almost pure CO_2 is removing the nitrogen from the combustion process. The flue gases then contains CO_2, H_2O and contaminants. This means that almost pure oxygen, produced in an air separation unit, with recirculated CO_2 is used as an oxidizing agent. The flue gases are cleaned from contaminants in the regular way and the steam is removed in a condensing flue gas cooler, (Andersson et al, 2006). The remaining CO_2 is compressed and liquefied as above.

For large-scale air separation, cryogenic distillation is the only commercially available method. It is an expensive technique regarding energy demand and capital cost. Membranes that can produce oxygen enriched air at a lower cost are unde development, (Elforsk, 2005).

5.1.4 Chemical-looping combustion

The concept of chemical-looping combustion (CLC) is based on the use of an oxygen carrier material. The carrier's purpose is to transfer oxygen from the combustion air to the fuel. In this way any costly separation of nitrogen is avoided, since the uptake of oxygen from the air is achieved by a simple solid-gas phase reaction, see chapter 5.9. The advantage compared to normal combustion is that CO2 from the fuel reactor is only diluted with steam in this process. Steam can be condensed and in this way CO2 is achieved in a separate stream. In principle, the fuel could be in gaseous, liquid or solid form, although the most likely initial application will be for gaseous fuels, such as syngas from gasification of coal, refinery gas or natural gas. Expected temperature range are between 800-1200 °C and the combustor could be either pressurized or atmospheric. The concept of CLC can be adapted to hydrogen production with carbon capture, see chapter 5.9.

5.2 CO_2 transportation

Transporting the CO_2 from the emission point to the storage site requires an infrastructure for this purpose. The transportation will probably take place as supercritical CO_2 in high-pressure pipelines or by tankers, (IEA, 2002).

Pipelines for CO_2 transport is an established technology. The advantage with pipeline transportation is the ability to have a continuous flow of CO_2. When using tankers, the advantage is the flexibility. However, there is a need for intermediate storage at the emission point and storage site, (Svensson et al, 2004).

The total cost for transporting the CO_2 in larger networks with several emission points and storage sites is roughly 2 EUR/ton. For a small system with local storage the cost is about 1 EUR/ton, while the cost for the first 10 million tons will be around 6 EUR/ton CO_2, (Svensson et al, 2004).

5.3 CO_2 storage

CO_2 storage can be divided into three main groups; geological formations, mineralization and ocean storage. The three groups will be presented briefly below.

There are four ways of storing CO_2 in geological formations. The first one is emptied gas- and oil fields. These fields have a proven storage potential. This is also valid when pumping the CO_2 into oil fields that are still in operation, in order to enhance the oil recovery. A third option is to use geological formations filled with water, so called saline aquifers. The fourth possibility to use the CO_2, is to recover methane that is bound in coal beds. The cost for handling the CO_2 at the storage site is around 2-4 EUR/ton CO_2 on-shore and 4-7 EUR/ton offshore, (Elforsk, 2005).

Research is also going on with minerals to store the CO_2. These minerals contain magnesium and calcium carbonates that react with the CO_2 (olivines and serpentines), (Zevenhoven et al, 2001). However, it is costly and it creates carbonates, four times as much as the amount of coal that is combusted.

In other parts of the world, especially in Japan, it is studied how CO_2 can be stored in the ocean. CO_2 has a higher density than seawater below a depth of 1500 m, and will form a pool of CO_2 on the bottom of the ocean. However, it is criticized for having a drastic effect on the ecosystem, (Elforsk, 2005).

5.4 Suitable techniques for refineries

In a refinery there are several possibilities for CO_2 capture. Here follows a description of the main possibilities.

CO_2 can be separated from the flue gases from the heaters in the refinery. The challenge is that they are distributed around the refinery. By having separate local absorber for each heater stack the size of the flue gas ducts can be minimized. The regeneration and CO_2 handling is done at a central location. The solvent can readily be circulated back-and-forth between the absorbers and the desorption unit. By separating these activities reduces both the cost and required space, (IEA, 2000).

The regeneration is a process with a considerable energy demand. The energy demand depends on which solvent is used. In process industries with large amounts of excess heat, there is also a possibility to use the excess heat for the regeneration. How the excess heat can be used depends on the temperature level of the excess heat and the temperature level of the regeneration, which varies from solvent to solvent.

Oxy-combustion is also a possibility in the heaters. When using O_2 as the oxidizing agent the volume of the flue gases is reduced by 75 % to 85 %. This makes it possible to have flue gas ducts from the heaters to a central location where the CO_2 can be purified and compressed. (IEA, 2000)

It is also possible to use a H_2 rich fuel in the heaters. This is especially advantageous when there is a demand for H_2 elsewhere in the processes and there exists a plant for this purpose. The hydrogen can then be produced from gasified fuel, including biofuel, with simultaneous CO_2 capture. As an alternative, natural gas can be reformed to CO_2 and H_2. In both cases the CO_2 can be captured at a relatively low extra cost.

Hydrogen production from natural gas or refinery gas with CO_2 capture could be performed using chemical-looping reforming. This technology offers very important characteristics because it can significantly reduce efforts and costs for gas separation. Two processes have been identified as promising: i) an autothermal chemical looping reforming to produce N_2-free syngas without penalties of an air-separation unit and ii) an integrated chemical looping reformer, using a fluidized bed heat exchanger reformer (FBHE/R), and a fuel waste stream from the H_2/CO_2 separation, thus considerably reducing the costs of H_2 separation.

During catalytic cracking the catalyst must be regenerated through combustion. This could be done through oxy-combustion. This would generate a gas flow with high CO_2 concentration. However it is not clear how it would affect the catalyst. (IEA, 2000)

5.5 Solvents for absorption

Here follows a description of suitable solvents for absorption of CO_2.

5.5.1 Amines

Three classes of amines, basically primary, secondary and tertiary, are generally used as organic chemical solvents. Mono-ethanol amines (MEA) are more reactive than secondary amines and hence dominate the CO_2 capture market.

The main concerns with MEA and other amine solvents are corrosion in the presence of O_2 and other impurities, high solvent degradation rates from reactions with SO_2 and NO_2 and the large amounts of energy required for regeneration. (White et al, 2003). These factors generally lead to large equipment, high solvent consumption and large energy losses. New or improved solvents with higher CO_2 absorption capacities, faster CO_2 absorption rates, high degradation resistance and low corrosiveness and energy use for regeneration are needed to reduce equipment sizes and capital and operating costs.

Sterically hindered amines

Sterically hindered amines are amines in which a bulky alkyl group is attached to the amino group. The advantage of sterically hindered amines compared to alkanolamines is that only 1 mol of sterically hindered amine, instead of 2 mol of alkanolamine is required to react with 1 mol of CO_2. Sterically hindered amines can have lower heats of absorption/desorption, (White et al, 2003).

5.5.2 Inorganic solvents

The non-organic based chemical solvents include potassium, sodium carbonate and ammonia. Among these, potassium carbonate has the dominant market share.

One absorption system that shows promising results is chilled ammonia that has been developed by Alstom and EPRI. The absorption takes place at 2 °C and the CO_2/ammonia slurry is compressed to a high pressure. The advantages with this process is that ammonia is relatively cheap, the solvent is stable at the operating conditions, the equipment can be made smaller du to lower flue gas volume, ammonia low heat of absorption and thereby a low steam demand for regeneration and the high pressure regeneration generates a high pressure CO_2 and thus reduces the compression work, (EPRI, 2006).

5.6 Post-combustion – experiences from the pulp and paper industry

Here follows a summary of the work with CO_2 capture from flue gases in the pulp and paper industry that have been performed at the division of Heat and Power Technology. The work is presented in more details in Hektor et al (2005, 2006, 2007).

The calculations in this work are based a fictitious market kraft pulp mill based on the best available technology in Sweden and Finland in the late 1990s (STFI, 1999). A chemical absorption unit is added to the recovery boiler in order to capture the CO_2 from the flue gases.

In order to regenerate the solvent, large quantities of low-pressure (LP) steam are needed for the reboiler in the desorption unit (2880 kJ/kg CO_2) (Möllersten, 2004). In order to satisfy the need for steam demand, a condensing turbine is removed (22 MW LP steam is liberated) and the rest of the steam demand can be satisfied in different ways; by producing more steam in a boiler or combined cycle; by a heat pump or by process integration.

5.6.1 Boiler

In the boiler alternatives, the boiler is installed in order to produce a sufficient amount of steam for the regeneration of the absorbent. The fuel is either biofuel or natural gas. The CO_2 from the biofuel boiler is also captured.

5.6.2 NGCC – CHP

In this alternative, the biofuel boiler is replaced with an NGCC. The NGCC is designed so that the heat recovery steam generator (HRSG) can produce enough steam to capture the CO_2 from the recovery boiler and the NGCC.

5.6.3 Heat pump

The heat pump uses the excess heat from the pulp mill to produce LP steam. The coefficient of performance (COP) value then becomes 4.2. If the temperature levels are elevated the COP value will increase and the investment costs will go down. Therefore a comparison is also made with a fictive absorbent working at higher temperatures compared to MEA. Higher temperature levels will increase the COP value for the heat pump to 4.6. Apart from the working temperatures of the absorbent, the properties and performance are assumed to be the same as for MEA.

5.6.4 Process integration

Another way to save steam in the pulping processes is through thermal process integration (PI) and use this surplus for the capture process. The steam surplus is 2 GJ/ADt, which corresponds to 36 MW (Algehed et al, 2002). This steam is not sufficient for the regeneration of the absorbent. Two alternatives are considered here.

In PI-alternative 1 a biofuel boiler is installed to supply the rest of the steam needed. In PI-alternative 2 the process integration is taken one step further. The CO_2 absorption process is modified and the reboiler use MP steam. Heat from the absorption process is then used to produce LP steam that is needed at the mill. Through these measures there is no need for external fuel, but there is a loss of electricity production since the MP steam is not allowed to expand to LP steam. Since the temperature in the reboiler is increased, MEA cannot be used as an absorbent. In the calculations in this study a fictive absorbent working at higher temperatures is used as for the second heat pump alternative.

5.6.5 Economic evaluation

In order to evaluate the performance of the suggested configurations for capturing the CO_2, the cost of each avoided tonne of CO_2 is calculated. The investment cost, operating and maintenance cost, electricity cost, fuel cost, transportation cost and storage cost are included. The energy market parameters are taken from the energy market scenarios developed by Ådahl et al (2007).

5.6.6 Results

The avoidance cost calculated for the studied configurations are presented in Figure 5-1. The results show that tough CO_2 reduction targets, and thereby a high CO_2 price, are needed for CO_2 capture to be profitable. When the CO_2 capture is profitable, the heat pump and process integration alternatives show the lowest avoidance cost. This is due to the use of excess heat from the pulp mill. This leads to a reduced fuel demand and the fuel demand is a large part of the total cost.

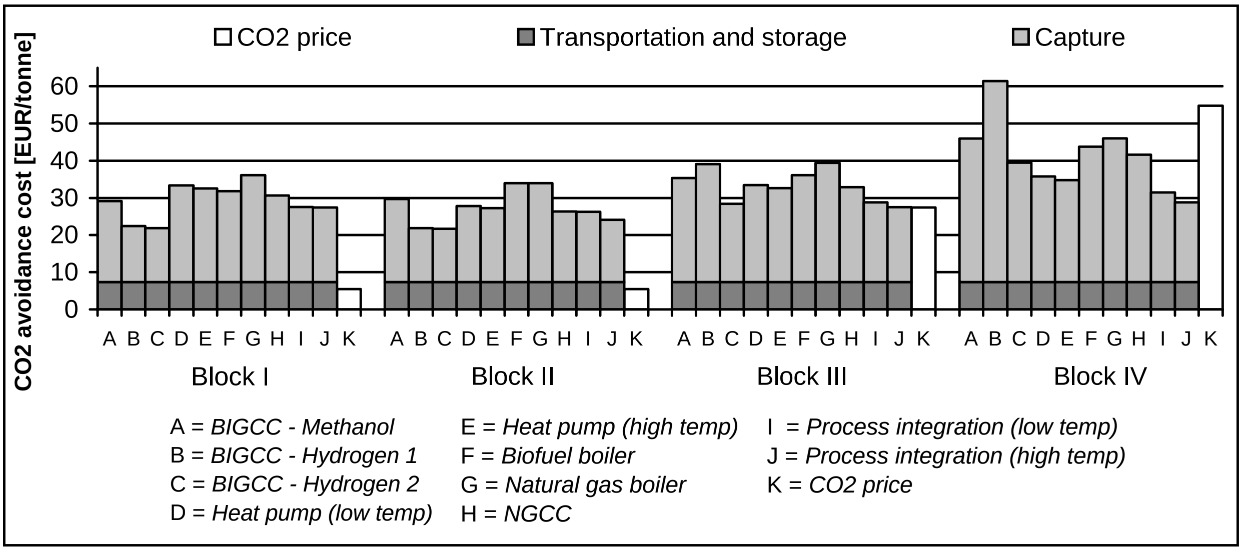

Figure 5-1. ***Avoidance cost for the studied configurations.***

5.7 Pre-combustion – experiences from biofuel based hydrogen production

Here follows a summary of the work with biofuel based hydrogen production that has been performed at the division of Heat and Power Technology. The content is based on Andersson (2007).

There are many process options for gasification of biomass. When producing hydrogen or other fuels, direct oxygen fired or indirectly fired gasifiers must be used, to avoid a diluted product gas (Babu, 2002). Energy input and output data for the complete process from biomass to hydrogen used in is taken from Hamelinck and Faaij (2001).

Dry biomass (pellets), oxygen and steam are fed to the gasifier where the biomass is gasified at a pressure of 3 MPa and a temperature of 850 °C. After the gasifier, there is a high content of methane and a catalytic steam reformer converts the methane into H_2 and CO. To maximize hydrogen production, CO and H_2O can be converted to H_2 and CO_2 in the water gas shift reaction. The shifted gas is cooled to 30 °C and water is condensed out. A pressure swing adsorption (PSA) unit is used to obtain 99.99 % pure hydrogen. The PSA unit includes an adsorption bed for removal of all CO_2 and water prior to separating the hydrogen product.

The technology for hydrogen production considered in the models in this thesis is commercially available technology used in the petrochemical industry today. Given the current strong interest for hydrogen as a possible mainstream energy carrier in the future, there is much research going on to identify better process solutions. Membranes that combine the shift reaction and hydrogen separation in a single unit are also being developed, including membranes where the hydrogen is separated (Kreutz et al, 2002; Jordal et al, 2004) and membranes where CO_2 is separated (Kaggerud et al, 2004) from the gas stream. Membrane technology is expected to offer better separation at lower cost, but so far there are no results for overall performance in full-scale applications.

5.7.1 Studied configurations

Integrated hydrogen production is compared to stand-alone production. Two process integrated hydrogen production configurations are considered: Integration with a pulp mill (gasified black liquor) and integration with an NGCC CHP unit (gasified biomass). Stand-alone production is assumed to adopt the same process technology as the process for production integrated with an NGCC CHP unit. The plant size for the three configurations is selected so as to be able to compare hydrogen production integrated with an NGCC CHP unit with hydrogen production at the pulp mill. As a basis for comparison, the same quantity of biomass input is chosen.

5.7.2 Evaluation

The studied configurations are evaluated with regard to economy CO_2 emissions. Energy market scenarios are used for the evaluation. The Scenarios are based on assumptions regarding possible future fossil fuel price levels and policy instruments for the mid-term future (2020) described in Axelsson et al. (2007).

5.7.3 Results

Figure 5-2 presents CO_2 emissions for the different hydrogen production configurations calculated based on data from energy market Scenarios. The emissions are divided into three categories:

- **Onsite reductions** – reductions achieved by replacing natural gas fired in the gas turbine with waste gas from the hydrogen production process (Bio-H_2 NGCC cases only)
- **Net external effects** – reductions resulting from changes in energy production units in the extended system
- **CCS** – capture and storage of CO_2 from the hydrogen production process

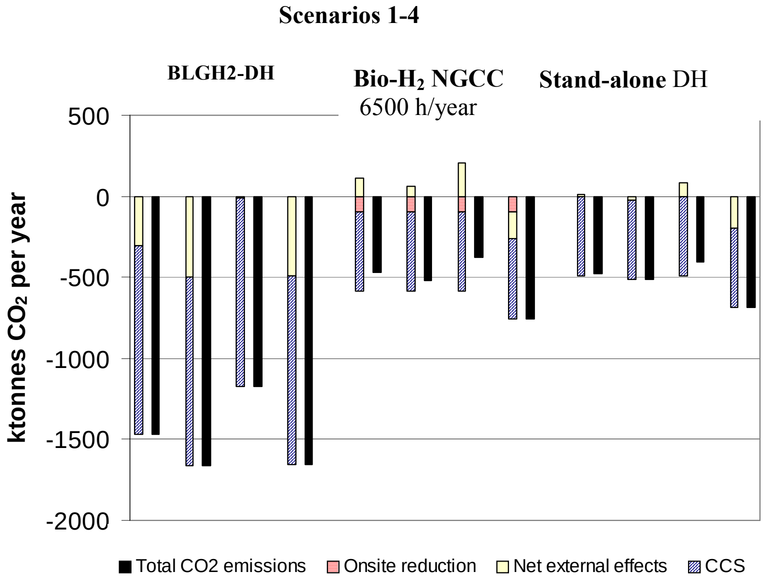

Figure 5-2. ***CO_2 emission balances associated with integrated hydrogen production at a pulp mill (BLGH2) or an NGCC CHP plant (Bio-H2 NGCC); and a Stand-Alone hydrogen production.***

Figure 5-2 shows the resulting change in CO_2 emissions resulting from integration of hydrogen production for three of the studied cases. All configurations evaluated are shown to result in reduction in CO_2 emissions if CO_2 is captured and stored. When hydrogen is produced from gasified biomass (Bio-H2 NGCC and Stand-alone) and no CO_2 is captured in the process, there will be an increase of CO_2 emissions in Scenarios 1 and 3 due to increased CO_2 emissions in external production units included within the expanded system boundary. The annual CO_2 emissions reduction is greatest for the BLGH2 system for all scenarios.

The results of the economic calculations based on the market prices in Scenarios 1-4 are shown in Figure 5-3. Hydrogen production integrated with a pulp mill achieves a substantially lower production cost compared to hydrogen produced integrated with an NGCC CHP unit.

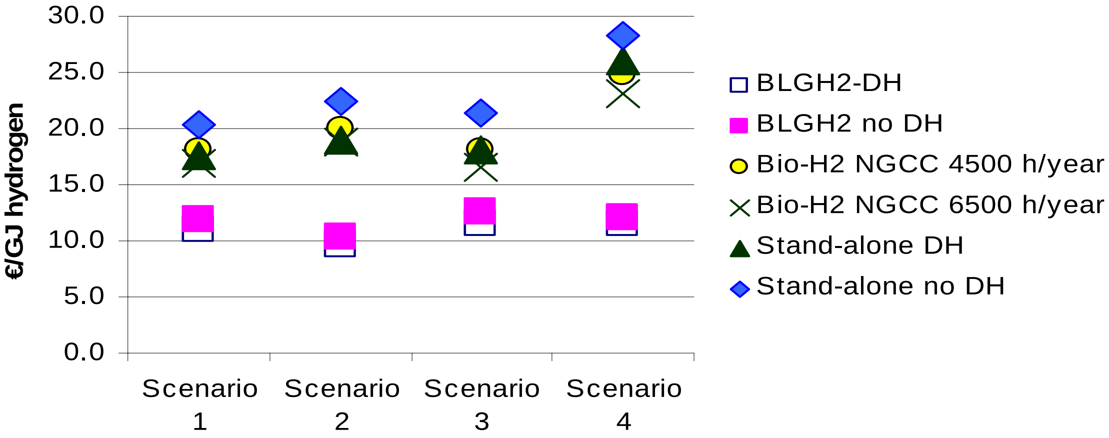

Figure 5-3. ***Hydrogen production cost for production integrated with a pulp mill (BLGH2) or an NGCC CHP plant; or Stand-alone production.***

The hydrogen production costs can be compared to the production cost of hydrogen produced from natural gas with steam-methane reforming or gasification of coal, both including CCS, which are reported in the literature as being around 7 €/GJ H_2 (Williams, 2001). Other studies of hydrogen production from biomass gasification indicate production costs of 7-14 €/GJ H_2 (Hamelinck and Faaij, 2001). These results are however based on market prices for biomass, electricity, coal and natural gas that are less than half of the values proposed in the energy market Scenarios used in this study.

5.8 Oxy-fuel combustion

Chalmers is internationally leading in experimentally based research on oxy-fuel combustion. The oxy-fuel combustion process is studied since it is considered one of the most promising options for carbon dioxide capture in connection to combustion of solid (or gaseous) fuels. The technology is mainly based on commercially known technologies and, thus, is considered a low risk option, especially when it comes to coal as a fuel.

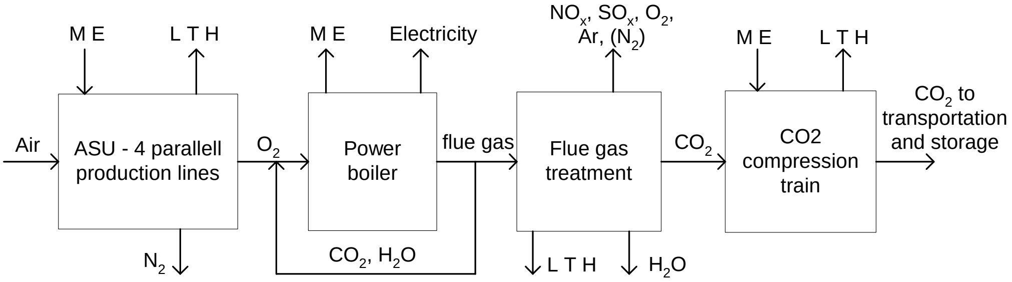

Figure 5-4. Principal process scheme of the lignite-fired O_2/CO_2 process. ME and LTH denote mechanical energy and low temperature heat respectively.

The principle of the oxy-fuel (or O_2/CO_2) process is shown in Figure 5-4. Oxygen in separated in an Air Separation Unit (ASU) and the fuel is burnt in a mixture of oxygen and recirculated flue gas (mainly CO_2). As a result, the flue gas will consist of CO_2 and water (which can be condensated out from the flue gas stream). Yet, significant efforts are required in research and development of this combustion process in order to be able to design and optimize a full scale process. In oxy-fuel combustion, the fuel is burnt with oxygen of high purity instead of air. Typically, a large amount of flue gas is recycled back to the combustion chamber to adjust the flame temperature and heat transfer conditions. As a consequence, the system is in principle free from air borne N_2, whereas the combustion products, such as CO_2, H_2O, NO_x and SO_x, are accumulated to different degree in the system, which has implications on both combustion and heat transfer related processes. This work focuses on the flame and radiation characteristics and the emissions formed during oxy-fuel combustion of both gas and coal. The work is based on experiments carried out in a 100 kW oxy-fuel test facility, which was designed and constructed as a part of this work. In the present work dry recycling conditions were applied to study the effect of CO_2 on the properties mentioned.

The research at Chalmers concerns the conversion of fossil fuels in this novel combustion process and the knowledge and data obtain from the project will serve as a basis for further development of mainly coal-fired oxy-fuel power plants. The work is carried out in a 100kW test unit with full recycling of CO_2 (i.e. the layout is as it would be in a real unit in contrary to laboratory units which often apply CO_2 from bottled to simulate oxyfuel condition). There is now several thousands of hours of operation with the test unit. The research has focussed on flame properties, including radiation properties as well as the formation and destruction of various emissions such as NOx.

There is also the possibility to use oxy-fuel combustion in combination with bio-fuel/waste for production of heat and power. This could also be in terms of co-combustion of coal and bio-fuel. This concept would lead to the interesting possibility to reduce the atmospheric concentration of CO_2. In the oxy-fuel process a significant amount low temperature heat is released, heat which is well suited for a district heating system. Thus, the combination of heat sinks and large bio-fuel resources in Sweden may therefore make this technical alternative interesting in the future. The technology development of a coal-based oxy-fuel process can serve as a basis also for bio-fuelled oxy-fuel technology since both fuels are solid and can be converted in the same type of combustion devices.

Figure 5-5 illustrates the Chalmers test facility in which any solid or liquid fuel can be investigated.

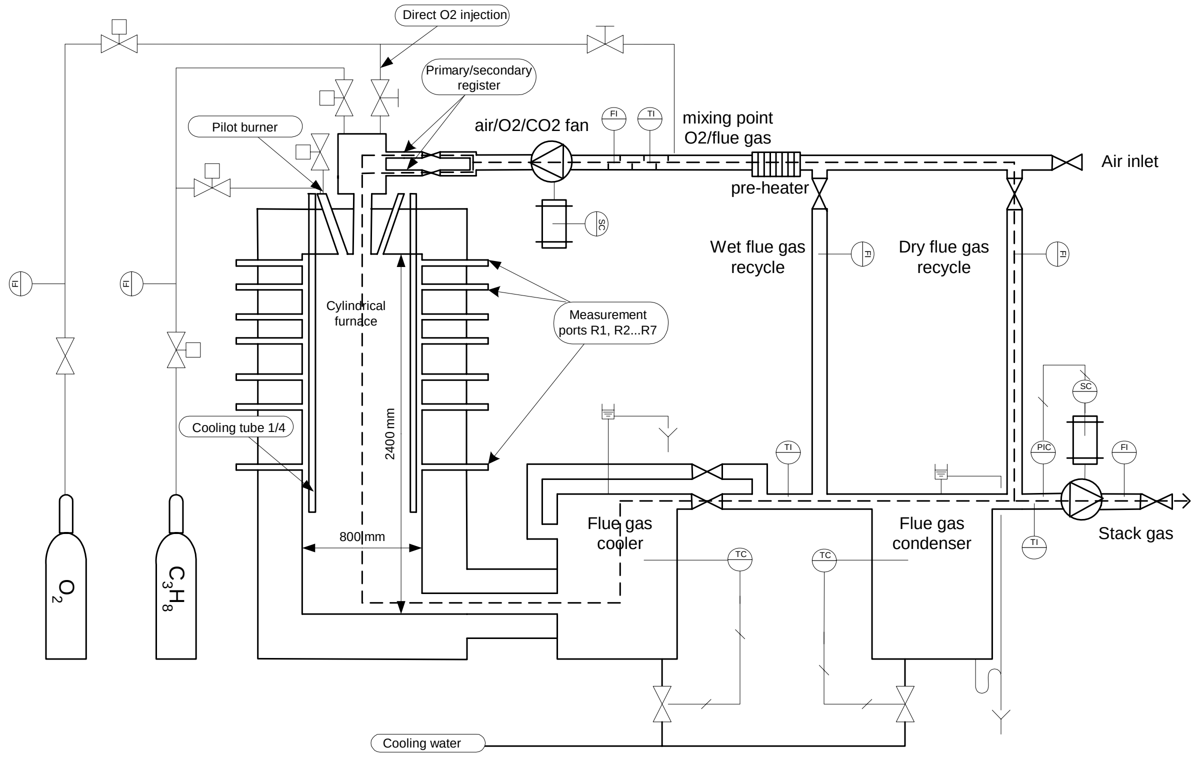

Figure 5-5. The Chalmers 100 kW oxyfuel test unit.

5.8.1 Areas for further research

The test facility at Chalmers is used for intense research in the oxyfuel combustion area. Parts of interest in this context are especially combustion of heavy oil fractions.

5.9 Hydrogen production from natural gas and refinery gas with CO_2 capture using Chemical-looping reforming (CLR)

Chemical looping reforming offers very important advantages for combined hydrogen production and CO_2 capture from natural gas or refinery gas, because it can significantly reduce efforts and costs for gas separation. Two novel and highly innovative chemical looping processes will be studied in this project:

1) an autothermal chemical looping reforming to produce N_2-free syngas without penalties of an air-separation unit, CLR-A.
2) an integrated chemical looping steam reformer, using a fluidized bed heat exchanger reformer (FBHE/R), and a fuel waste stream from the H_2/CO_2 separation, thus considerably reducing the costs of H_2 separation, CLR-S.

5.9.1 Technology status of chemical-looping combustion

Chemical-looping reforming (CLR) is based on chemical-looping combustion (CLC), which is a combustion technology with inherent CO_2 capture, (Lyngfelt et al. 2001; Mattisson and Lyngfelt 2001b; Mattisson and Lyngfelt 2001a; Mattisson et al. 2006b; Mattisson et al. 2006a).

The CLC system is composed of two reactors, an air and a fuel reactor, see Figure 5-6. The fuel is introduced in the fuel reactor, which contains a metal oxide, Me_xO_y. The fuel and the metal oxide react according to:

$$(2n+m)Me_xO_y + C_nH_{2m} \rightarrow (2n+m)Me_xO_{y-1} + mH_2O + nCO_2 \qquad (1)$$

The exit gas stream from the fuel reactor contains CO_2 and H_2O, and a stream of CO_2 is obtained when H_2O is condensed. The reduced metal oxide, Me_xO_{y-1}, is transferred to the air reactor where it is oxidized, reaction (2):

$$Me_xO_{y-1} + \tfrac{1}{2}O_2 \rightarrow Me_xO_y \qquad (2)$$

The air which oxidizes the metal oxide produces a flue gas containing only N_2 and some unused O_2. Depending on the metal oxide and fuel used, reaction (1) is often endothermic, while reaction (2) is exothermic. The total amount of heat evolved from reaction (1) and (2) is the same as for normal combustion, where the oxygen is in direct contact with the fuel. The advantage of chemical-looping combustion compared to normal combustion is that CO_2 is not diluted with N_2 but obtained in a separate stream without any energy or extra equipment needed for the separation.

Several cold-models and hot prototype units have been built and operated. In 2001 Lyngfelt et al. presented a design based on interconnected fluidized beds, see Figure 5-7, (Lyngfelt et al. 2001) and this type of system was also built and operated successfully. (Lyngfelt and Thunman 2005).

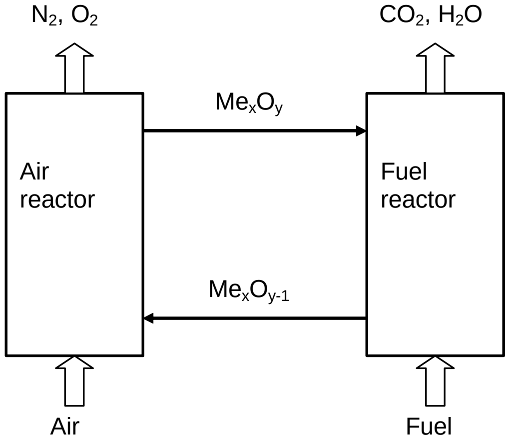

Figure 5-6. Chemical-looping combustion. Me_xO_y/Me_xO_{y-1} denote recirculated oxygen carrier solid material.

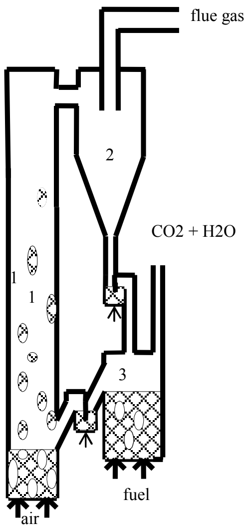

Figure 5-7. Layout of chemical-looping combustion process, with two interconnected fluidized beds. 1) air reactor, 2) cyclone, 3) fuel reactor.

A system based on interconnected fluidised beds has advantages over alternative designs, because the process requires a good contact between gas and solids as well as a significant flow of solid material between the two reactors. The gas velocity in the riser provides the driving force for the circulation of particles between the two beds. Thus, the particles carried away from the riser are recovered by a cyclone and led to the fuel reactor. From the fuel reactor the particles are returned to the air reactor by means of gravity; the fuel reactor bed is at a higher level than the bed of the air reactor. The gas streams of the two reactor systems are separated by fluidised particle locks. Thus, CLC (and CLR) is very similar to circulating fluidised bed combustion of solid fuels, a ***conventional and well established*** **technology** which has been used commercially for decades.

Early in 2002 CLC was a no more than a paper concept; the process as such had never been demonstrated. Since then rapid progress has been accomplished, led by Chalmers University of Technology. Chalmers was first in successfully demonstrating the process in >100 h of actual operation in 2003. Chalmers currently has three working prototype reactors for gas (natural gas, syngas, refinery gas) and solid fuels (coal, petroleum coke). Today, total operational experience at Chalmers is over 1000 hours using oxygen carriers based on nickel-, manganese- and iron oxides, as well as natural ores, showing high conversion as well as high durability of particles. Thus, Chalmers is clearly world leading in this technology development, and the only other actor with any significant operational experience is Chalmers close partner CSIC-ICB in Zaragoza. To reach these results, Chalmers has investigated more than 200 different particle materials in laboratory. From a review on experimental work on oxygen-carriers of >100 papers (Lyngfelt et al, 2008) it appears that Chalmers and its closest partners account for more than ¾ of the materials tested.

Chalmers has worked with chemical-looping technologies for approximately 10 years, and been a leading partner in five different EU-financed projects related to CLC. Three of the EU-projects, GRACE, CLC Gas Power, and Cachet, have been focused on refinery gas /natural gas and performed in close cooperation with the oil and gas industry, through the CCP project, involving the partners BP, Shell, Chevron, Eni, Hydro, Suncor, ConocoPhillips and Petrobras. In four of the EU projects Chalmers work has been working intimately with the development of this technology together with Alstom, one of the leading suppliers of fluidized-bed combustion technology.

5.9.2 Chemical-looping reforming

The experiences gained in chemical looping ***combustion*** (CLC) are highly relevant in the development of Chemical looping ***reforming*** (CLR) . CLR involves hydrogen production, whereas CLC aims at full conversion of the fuel. Two CLR processes have been proposed:

i) autothermal chemical-looping reforming (CLR-a)
ii) steam reforming using chemical-looping combustion (CLR-s), see Figure 5-8.

Autothermal chemical-looping reforming, CLR-a, is similar to CLC, but instead of burning the fuel, it is partially oxidized using a solid oxygen carrier and some steam to produce an undiluted stream of H_2, CO, H_2O and CO_2, see Figure 5-8a. (Ryden and Lyngfelt 2004; Zafar et al. 2005; Ryden et al. 2006a) The actual composition of this mixture depends upon the air ratio, i.e. the fraction of oxygen supplied to the fuel by the oxygen carriers in the fuel reactor to that needed for complete oxidation. This gas could be used as feedstock for chemical manufacture or shifted to contain undiluted CO_2 and H_2 in a low temperature shift reactor. Depending upon the purity of H_2 required and the pressure, the CO_2 can be removed by either absorbtion or adsorbtion processes. The concept has been demonstrated in a continuous CLR reactor using Ni-based oxygen carrier particles, (Ryden et al. 2006a). The work shows that it is possible to achieve a syngas essentially free from methane, and thus no post-reforming unit is needed after the fuel reactor, and the gas can proceed directly to a shift reactor.

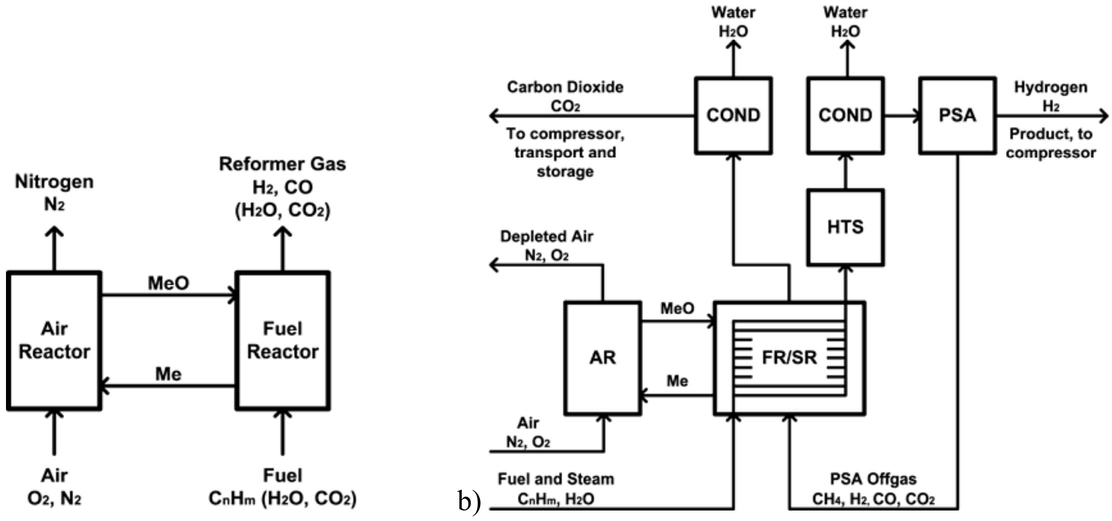

Figure 5-8. a) Autothermal chemical-looping reforming and b) steam reforming with CO_2 capture by chemical-looping combustion:. Air reactor (AR), fuel reactor /steam reformer (FR/SR), high temperature shift (HTS), condenser (COND), pressure swing adsorption (PSA). (Ryden and Lyngfelt 2004; Rydén and Lyngfelt 2005)

Steam reforming with CO_2 capture by chemical-looping combustion, CLR-s, resembles conventional steam reforming but the heat source for the reforming is not a conventional boiler, but a chemical-looping combustor and the fuel is offgas from the hydrogen separation, see Figure 5-8b. (Rydén and Lyngfelt 2005) The steam reformer can possibly be integrated with the fuel reactor as in Figure 5-8b, or placed in a separate fluidized-bed heat exchanger. CLR-s is unique in one sense, CO_2 capture technologies generally show a very significant energy penalty for the CO_2 capture, whereas CLR-s with CO_2 capture shows a potential increase in reforming efficiency compared to conventional steam reforming *without* CO_2 capture. The explanation to this is that the reforming tubes are inside a fluidized bed with efficient heat transfer and temperature control, enabling considerably lower temperatures of the gas leaving air and fuel reactors, compared to a conventional reformer boiler. Thus, heat losses are reduced and more energy can be used in the reforming. (It should be said that in addition to the CO2 capture, there is of course the inevitable penalty of CO_2 compression before storage.)

Chalmers has been working in the development of CLR since 2003, and the work so far involves one on-going EU-project (Cachet), one Nordic project and one project supported by Ångpanneföreningen. The results so far are presented in 14 publications.

The work at Chalmers shows that high steam reforming efficiencies are possible, above 80%, even considering the need of CO_2-free fuel to produce power for CO_2 compression. Even higher efficiencies are expected if possibilities for process integration are included.

5.9.3 Areas for further research

The objective for the project is to develop the two chemical-looping processes for production of hydrogen and conduct sets of dedicated experiments with two bench-scale reactors, a 300 W and 10 kW CLR reactors. In addition, process studies will be conducted in order to obtain an integrated process of hydrogen and heat at a refinery.

The two processes and the major advantages are described briefly below:

- Process 1) Chemical looping for partial oxidation/reforming, involves production of a syngas suitable for shifting and later separation of hydrogen and CO_2. Here chemical looping is combined with autothermal reforming. The major advantage is that the heat needed for converting methane to hydrogen, is supplied without costly oxygen production, without mixing of air with carbon containing fuel gases or without using part of the hydrogen produced in the process, see Figure 5-9 (left).

- Process 2) Integration of chemical-looping combustion with reforming of natural gas, using a fluidized bed heat exchanger reformer. Here the offgas coming from the hydrogen separation is converted to a pure CO_2 stream, at the same time providing heat for the reforming and facilitating the H_2/ CO2 separation process, see Figure 5-9 (right). The heat of reforming can be transferred in an external fluidized bed heat exchanger (FBHE) operating in bubbling regime. The FBHE offers a key advantage by allowing control of the temperature of reforming as well as very high heat transfer coefficient to the reformer tubes. The latter reduces the flue gas outlet temperatures compared to a conventional reformer boiler, thus increasing the reforming efficiency.

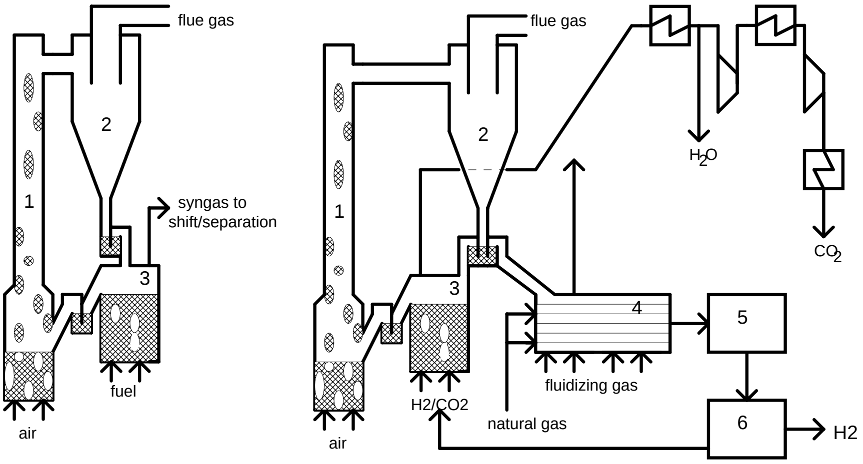

Figure 5-9. CLR process 1 (left) and process 2 (right). 1) air reactor/riser, 2) cyclone, 3) fuel reactor, 4) fluidized bed heat exchanger/reformer (FBHE/R)*, 5) shift reactor 6) hydrogen separation (one pure hydrogen flow, one CO_2/H_2 flow)
*Return of particles from 4 to 1 not shown because of 2-D view. Fluidizing gas for FBHE/R can be gas recycled from fuel reactor outlet.

Costs and difficulties in separation increase rapidly when requirements of gas purity increase. A unique challenge in producing hydrogen together with CO_2 capture is the special requirements on the gas separation, i.e. that ***both*** of the hydrogen and the CO_2 streams are essentially pure. CLR-s offers a solution to this. In conventional reforming without CO_2 recovery there is a need for heat which is supplied by a residual stream of mixed hydrogen/CO_2 used as fuel in the reformer. For simultaneous hydrogen and CO_2 production this is not a good option, since the CO_2 would be diluted with nitrogen from the combustion air. However, using such a residual stream of hydrogen and CO_2 as fuel in a chemical looping reformer would have crucial advantages for the hydrogen CO_2 separation, since it will avoid the need for a high efficiency in the hydrogen separation, as well as eliminate need for additional treatment of the CO_2 stream. Furthermore, the requirements of the efficiency of the shift reactors can be relaxed, since residual CO and CH_4 will be in the H_2/CO_2 stream and thus utilized as fuel for the chemical looping reformer. Thus, this integrated process will offer a large potential for reducing costs in H_2/CO_2 separation, and ultimately the cost of CO_2 capture.

Of major importance is performance testing of oxygen carrier particles with commercial potential, i.e. particulate materials produced by commercially available methods such as spray-drying and using raw materials that are commercially available at competitive prices. Chalmers has significant experience with the up-scaling of particle production using such materials, i.e. in the GRACE projects. Performance testing can be achieved in the Chalmers chemical-looping combustor units, where high performance with respect to gas conversion and long-term durability of particles can be verified.

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6 Bio refinery – Gasification

6.1 Background

Today, there is a huge need of hydrogen in a petroleum refinery in different applications, like the hydro cracker and the desulphurization plant. It would be attractive to produce part of this hydrogen from gasification of biomass on-site and thereby increase the portion of renewables directly into the fuel and also utilize more of the raw material, the petroleum oil, to form a high value product. Preem is going to start a new unit, a coker, at their Lysekil site which will transform the heavy residue that is formed when diesel and lighter hydro carbons are produced. As by-product from this equipment, petroleum coke (petcoke) is formed. This rest could be used in a co-gasification with biomass to produce hydrogen. The co-gasification scenario is attractive because the C:O:H ratio could be optimized for an efficient production. Both petcoke and biomass has a variety of their composition but an estimate can be done for comparisons. Nagpal et al. (2005) has estimated an average composition of petcoke in Table 6-1.

Table 6-1. Average composition of petcoke.

Proximate analysis (wt-%)	
Volitile carbon	9.6
Fixed carbon	80.6
Ash	0.5
Ultimate analysis (wt %)	
C	89.23
H	3.59
N	1.35
O	0.10
S	5.22

Other types of fuels are listed in e.g. Cifernao and Marano (2002), Table 6-2.

Table 6-2. Composition of different fuels.

	Ultimate Analysis (wt% dry basis)						Proximate Analysis (wt% dry basis)			
	C	H	N	O	S	Ash	Moisture	Volatiles	Fixed carbon	HHV (MJ/kg)
Agricultural Residues										
Sawdust	50	6.3	0.8	43	0.03	0.03	7.8	74	25.5	19.3
Bagasse	48	6.0		42		4	1	80	15	17
Corn Cob	49	5.4	0.4	44.6		1	5.8	76.5	15	17
Short Rotation Woody Crop										
Beech wood	50.4	7.2	0.3	41	0	1.0	19	85	14	18.4
Herbaceous Energy Crops										
Switchgrass	43	5.6	0.5	46	0.1	4.5	8.4	73	13.5	15.4
Straw	43.5	4.2	0.6	40.3	0.2	10.1	7.6	68.8	13.5	17
Miscanthus	49	4.6	0.4	46	0.1	1.9	7.9	79	11.5	12
Municipal Solid Waste										
Dry Sewage	20.5	3.2	2.3	17.5	0.6	56	4.7	41.6	2.3	8

Compared to coal, petroleum coke (or pet coke) generally has higher concentration of sulphur and different metals such as vanadium. It is very hard which makes it difficult to grind, has a high ash melting point (the amount of ash is generally lower) and it has very little inherent moisture. Compared with biomass, the oxygen content in petcoke is very small but the amount of hydrogen is rather similar (when compared on a moisture free basis).

6.2 Goal

The purpose is to include biomass in the product (the vehicle fuel) and at the same time have a better utilization of the oil.

6.3 Performance

Three different areas should be investigated. These are:

1) A review of gasification techniques with subsequent cleaning and production of hydrogen.
2) Initial experiments to compare petcoke pyrolysis with biomass pyrolysis to get an estimate of the rection rates.
3) Material, energy and economical considerations for a complete system.

6.4 Results

The section is divided in two parts. First is the description of the different technology possibilities to produce hydrogen through gasification. This is then followed by a description of the experimental procedure and the obtained results from these experiments.

6.4.1 Gasification possibilities

There are several possibilities when gasification of biomass should be performed. If the final product is decided, i.e. hydrogen production in this case, the number of process alternatives decreases. This section will provide a general overview of the gasification route of biomass and in the end some key features regarding hydrogen production will be noticed.

The first process that the incoming biomass encounters,
Figure 6-1, is the pre-treatment process. Here, the biomass is dewatered (mainly by drying) and then sized (milled or crushed) to be suitable for the gasification.

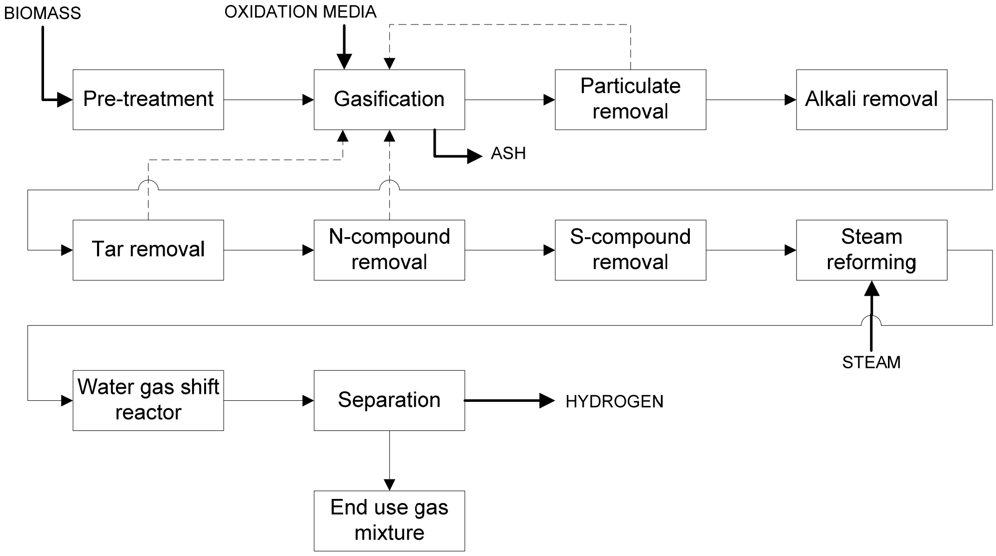


Figure 6-1. ***An overview of the gasification process of biomass to produce hydrogen***

Next step is the gasification reactor. There are several choices regarding reactor type and operation. Most common are the updraft, downdraft and the fluidized bed configurations. The fluidized bed can either bed bubbling or circulating beds and direct or indirect heated. Choices of operation are temperature, oxidizing media (e.g. air, oxygen or water) and pressure. In the gasifier several steps are passed. First, the material is dried, where, primarily, water vapor is leaving the solid material. After that start the pyrolysis reactions, where some of the organic material reacts and form volatile compounds and a char matrix. During pyrolysis, many reactions occur and some of them even occur in parallel. It can be explained from two kinds of reactions: primary reaction and secondary reaction.

The primary reaction is the first reaction and occurs with a sudden increment of heat. The reaction is fast; all products are formed by direct biomass decomposition. To only achieve primary reaction a rapid heating rate with a removal of produced gases by the inert carrier gas is necessary. The thermal decomposition in primary reaction produces primary products as tar, volatile gases (H_2, CO, CO_2, CH_4, HCs, etc) and char.

The secondary reaction or cracking is produced for further reactions due to volatile gases produced in primary reaction and it occurs when the temperature is higher than 700-800 ºC. If the temperature is below 700ºC, it is usually only necessary to consider the primary reaction to calculate kinetic parameters. The importance of secondary reactions increases with the residence time of the volatile compounds in the hot zone of the reactor (Caballero, 1995).

The main reactions, with carbon material, during gasification are:

$$C + O_2 \Leftrightarrow CO_2 \qquad (1)$$

$$C + CO_2 \Leftrightarrow 2CO \qquad (2)$$

$$2C + O_2 \Leftrightarrow 2CO \qquad (3)$$

$$2CO + O_2 \Leftrightarrow 2CO_2 \qquad (4)$$

$$C + H_2O \Leftrightarrow CO + H_2 \qquad (5)$$

$$C + 2H_2O \Leftrightarrow CO_2 + 2H_2 \qquad (6)$$

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \qquad (7)$$

These reactions are equilibrium reactions which mean that they can, during certain circumstances, go in the opposite direction. The equilibrium constants are dependent on both the total pressure and the temperature. In gasification, that main purpose is to achieve a high quality synthesis gas. This means that as much as possible of the carbon should form carbon monoxide (CO) when the reaction occurs with oxygen (to allow for further reactions). If all carbon forms CO then H_2 is formed through reaction (7) when H_2O is added (notice however that reaction (7) is an equilibrium reaction which implies that the conversion of CO to H_2 can not be 100% on a molar basis).

Particular formulation

Depending on temperature and degree of turbulence inside the gasifier, particles may follow the outgoing gas flow. In some gasifier, circulating fluidized bed, this is part of the operational design. The particles could be not fully reacted small particles from the biomass, so-called fly ash originating from the biomass or bed material (either as whole bed particles or torn parts).

Alkali vaporization

Some metals, especially alkali metals, form salts that have a rather low evaporation temperature (700-900°C) and the amount of Na and K in the outgoing gases could not be neglected when further treatment are necessary. These gases starts to condensate again when the temperature goes below 650°C and they will then fall out on existing particles in the flow or form fine particles themselves.

Sulfur reactions

Sulfur present in the biomass feed can react to hydrogen sulfide or sulfur oxide depending on gasification approach (if the biomass feed is very rich in alkali, alkali sulfides may also be formed, this becomes important when the feed is black liquor). Other formed sulfur compounds are carbonyl sulfides. Usually, the content of sulfur is much lower in biomass than in fossil fuels

Hydrocarbon formation

During pyrolysis and gasification many hydrocarbons are formed. They will go from low molecular weight (i.e. methane) up to high molecular weight (condensed tars). If the molecular weight is above the molecular weight of benzene, they are usually called tars. Different compounds are formed depending on temperature; at low temperatures (around 450°C) the tars are dominated by mixed oxygenates and as temperatures increases they will consists of polyaromatic hydrocarbons (at around 900°C), Elliott (1988), see Figure 6-2.

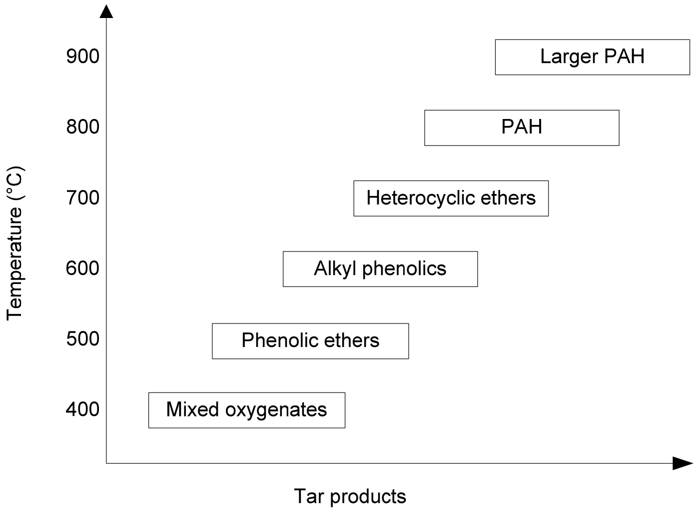


Figure 6-2. ***Different tar products with respect to temperature in gasifier.***

Pre-treatment

The pre-treatment section deals primarily with biomass. Regarding petcoke, the main obstacle is to achieve small enough particles for a high conversion in the gasifier. This is done by grinding and mainly grinding in a suspension.

Dewatering

The pre-treatment is important for the gasification to operate in best possible way. First, the biomass feedstock must be dewatered, either mechanically or by evaporation (drying). The mechanical dewatering is especially attractive when there is a sludge feedstock with very high water content and relatively large particles/conglomerates. In such operation it is possible to achieve dry contents of 60%. Mechanical or hydraulic presses have been used to squeeze water from e.g. extremely wet bark. The drawback is that the moisture content only can be reduced to 55%, Cummer and Brown (2002).

The other alternative is drying, which is more energy consuming (water is evaporated) but can be performed with a low grade heat (low temperature gas in a direct contact method or with low pressure steam in indirect contact methods).

Gases from the drying must be treated since volatile compounds can be found there. These compounds can either come from the biomass as whole compounds (T>100°C) or be thermally degraded compounds (T>200°C), Brammer and Bridgwater (1999). It is possible that some particles follow the gases, but they can easily be removed by cyclones or bag filters. The formed submicron aerosols, blue haze, cannot easily be removed other than using wet electrostatic precipitation or electro-filter beds. It is therefore important to avoid the formation of these compounds.

There is also a potential risk of fire in the drying stage, especially if the temperature is high and oxygen is present is high amount (above 10% are considered dangerous).

The gasification is usually best performed with a moisture content of 10-20% (Brammer and Bridgewater, 1999). A higher content will likely clog the feeding system and if the primarily product is electricity or heat it lowers the heating value. The updraft gasifier may, however tolerate moisture contents of up to 50%.

Sizing

The two most dominant devices for sizing to the gasification operation are knife chippers or hammermills (Cummer and Brown, 2002). A crusher may be needed before, especially the hammermill for best operation (Snow et al, 1997). To ensure proper size of the feedstock it is necessary to follow the sizing with a screen. But sizing by flotation or air classification may also be performed.

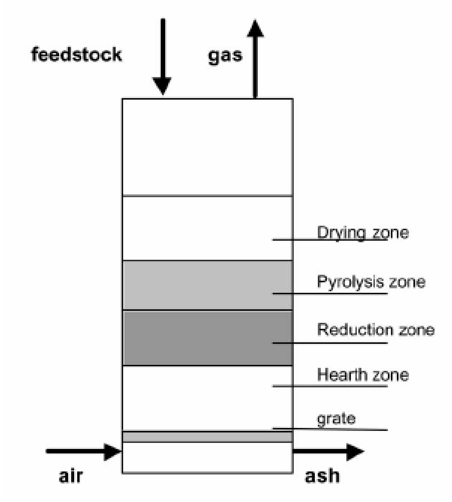
Gasification

The gasification occurs at elevated temperatures and together with some oxidizing media, e.g. air, oxygen or steam. The gasification reactions, especially the pyrolysis reactions, are endothermic, which means that energy must be supplied, either by internal combustion (lose some of the potential of hydrogen production) or by indirect heating.

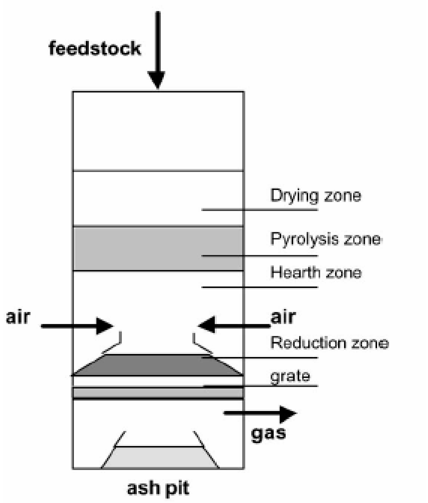
This can be performed in many different ways which have led to several important designs for the gasifier with respect to flow pattern of gas and solid, but also with respect to heat supply.

Different gasifier

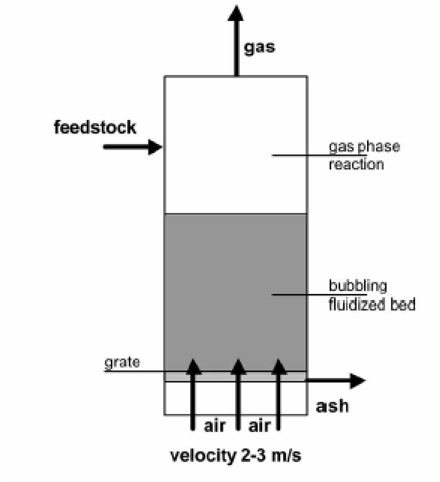
The most used gasifiers today are the fixed bed and the fluidized bed gasifier. The fixed bed gasifiers consist of two types; updraft and downdraft. In the up-flow gasifier, the gas and the solids meet in a counter-current arrangement, with the incoming gasifying media coming from the bottom and the solids enter at top. The downdraft gasifier works in a co-current operation, but have different feed locations of the solids and the gasifying media (the gas is fed further down in the gasifier). The fluidized bed configuration may differ. It is the bubble bed configuration (where the bed material stays in the gasifier main body) or circulating bed configuration (where the bed material goes out with the gases and are separated by cyclones for return). There is also a difference in the heating method. If the gasifier is heated by partial combustion, then the produced syngas will have a lower heating value (even lower if air is used as gasifying media due to the dilution) compared to a system with indirect heating. The indirect heating may be by heating the recirculating bed material (e.g. SilvaGas process or the FICFB process) or by combustion in tubes (e.g. MTCI process).



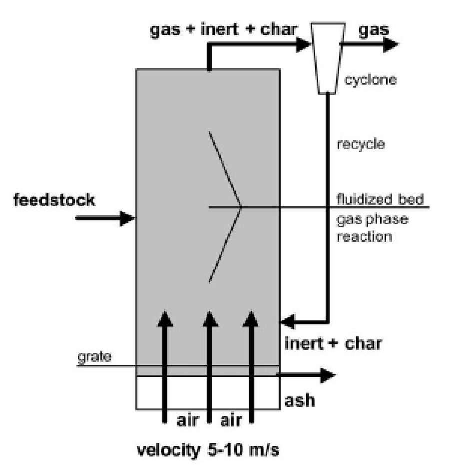
Updraft gasifier



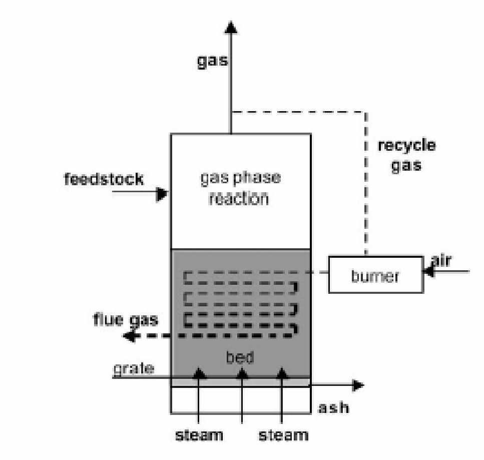
Downdraft gasifier



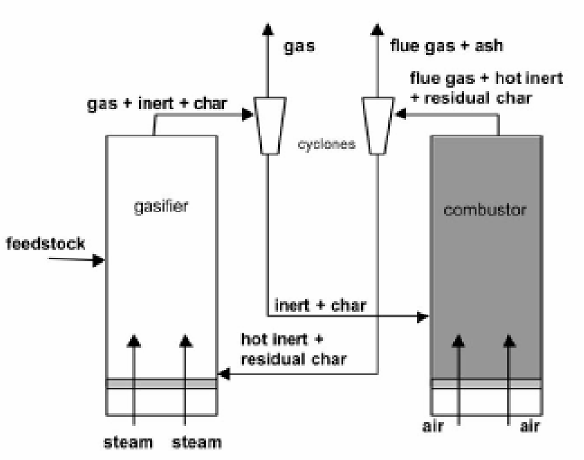
Bubble fluidized bed gasifier



Circulating fluidized bed



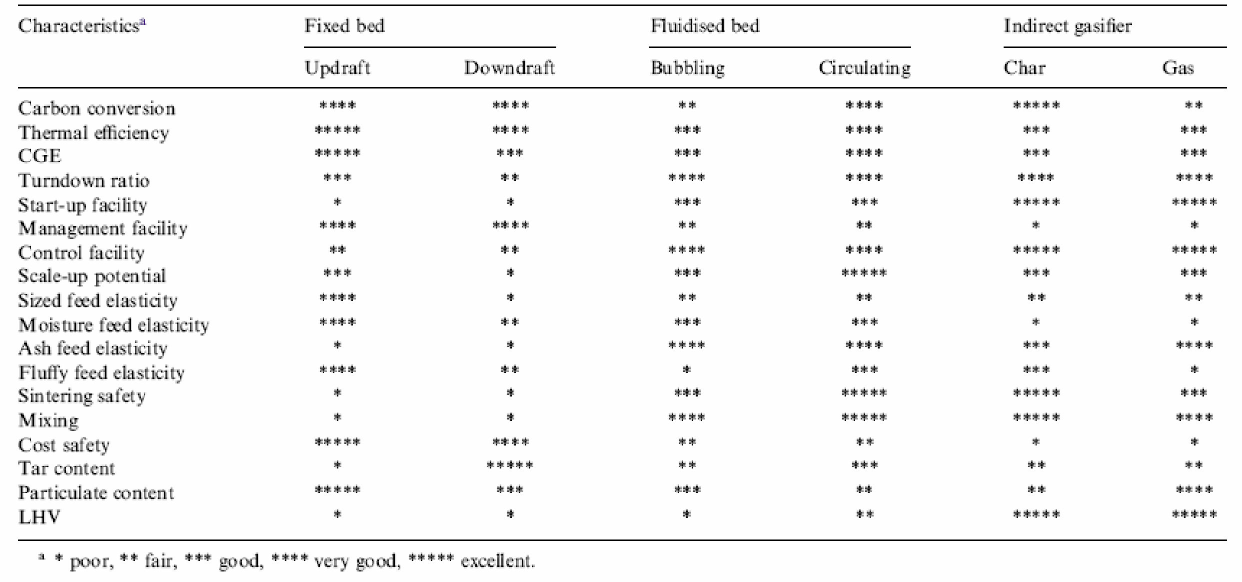
Gas indirect heated fluidized bed



Char indirect heated fluidized bed

As previously mentioned, the different types of gasifier have different operability according to Belgiorno et al (2003), Table 6-3.

Table 6-3. Characteristics of different types of gasifiers.



Characteristics[a]	Fixed bed		Fluidised bed		Indirect gasifier	
	Updraft	Downdraft	Bubbling	Circulating	Char	Gas
Carbon conversion	****	****	**	****	*****	**
Thermal efficiency	*****	****	***	****	***	***
CGE	*****	***	***	****	***	***
Turndown ratio	***	**	****	****	****	****
Start-up facility	*	*	***	***	*****	*****
Management facility	****	****	**	**	*	*
Control facility	**	**	****	****	*****	*****
Scale-up potential	***	*	***	*****	***	***
Sized feed elasticity	****	*	**	**	**	**
Moisture feed elasticity	****	**	***	***	*	*
Ash feed elasticity	*	*	****	****	***	****
Fluffy feed elasticity	****	**	*	***	***	*
Sintering safety	*	*	***	*****	*****	***
Mixing	*	*	****	*****	*****	****
Cost safety	*****	****	**	**	*	*
Tar content	*	*****	**	***	**	**
Particulate content	*****	***	***	**	**	****
LHV	*	*	*	**	*****	*****

[a] * poor, ** fair, *** good, **** very good, ***** excellent.

Beside of these reactors, there are more possibilities found. One such reactor is the entrained flow reactor that can be used for liquid feed, e.g. the Chemrec gasifier using black liquor, or a slurry, e.g. the E-gas technology using petcoke and water. These gasifiers need to operate at a high temperature and with a small particle (droplet) size in order to have high conversion in a short time (to keep the reactor size small). Benefits with the entrained gasifiers are the high conversion and low tar production. The main drawback is the interior material that must withstand high temperatures and at the same time be resistant to the corrosive attack from the formed smelt when especially biomass is used.

Cleaning

The formed syngas include some impurities and must, therefore be cleaned. The amount of cleaning depends on the use of the gas, and according to Ciferno and Marano (2002) the syngas should have the following charateristics when the purpose is hydrogen production.

H_2/CO	High
CO_2	Not important (must be separated from the final product)
Hydrocarbons	Low (recycling may be needed to have a high efficiency)
N_2	Low
H_2O	High (required for the WGS reaction)
Contaminants	<1 ppm Sulfur and low in particulates
Pressure	around 28 bar
Temperature	100-200°C

Particular removal

The different gasifiers form different amount of particles. The ones operating with fixed bed have usually lower amount of particulates compared to the ones with fluidizing bed. Table 6-4 is from Stevens (2001).

Table 6-4. Amount of particles in synthesis gas from different gasifiers.

Gasifier type	Particulate loading (g/Nm^3)		
	Low	High	Representative range
Fixed bed			
Downdraft	0.01	10	0.1-0.2
Updraft	0.1	3	0.1-1.0
Moving bed			
Fluidized bed	1	100	2-20
Circulating fluidized bed	8	100	10-35

There are different kinds of systems to remove particulates. Among the most used are: cyclone filters (low pressure drop but inefficient on small particles), barrier filters (can handle small particle but to a cost of high pressure drop and is also sensitive to temperature), electrostatic filters (effective but associated with a high installation and operation cost) and wet scrubbers (need low temperature and may have a high pressure drop to achieve a good mixing between the gas and the liquid).

Alkali removal

The vaporized alkali compounds starts to condensate around 650°C (Stevens, 2001). It can then condensate either as small droplets/particles (less than 5 μm) or on surfaces and cause corrosion. The formation of small particles means that it is not effective to use cyclones for the removal. It can further be concluded that ceramic and metal barrier filters can corrode due the alkali condensation. Therefore, the best way is to cool the gas temperature enough so that electrostatic filters, bag filters or wet scrubbers can be used.

Sulfur removal

When producing synthesis gas or gas for fuel cells it is necessary to remove the sulfur even from the low containing biomass. The demand in fuel cells are 1 ppm and for synthesis gas 0.1 mg/Nm^3. The different sulfur compounds are usually (Spath and Dayton, 2003) converted to H_2S which then can be adsorbed by a metal oxide or goes with the water when gas temperatures are cooled below 100°C. Several metal oxides are available. Iron oxide is the first used commercially and can handle low concentrations of H_2S. Another oxide is ZnO where it has previously not been possible to regenerate the formed ZnS without forming $ZnSO_4$ (that doesn't react further). New research has, however, showed that at high temperature this might be possible to perform (being the earliest used and ZnO the most promising for high temperature processes (Siriwardane, 2004).

Tar removal

The formed tars can condense onto surfaces or form small aerosols. The most important issue for processes with low tolerance of tars is to have as low production as possible. This means that the design of the gasifier must be optimized (operating method and conditions). Two major ways of handle the tars are: physical removal and tar cracking.

Physical removal of tars

In order to physically remove the tars, the gas temperature must be cooled enough for the condensation to occur. Most common and widely used are the wet scrubbing method, but it is also possible to use electrostatic precipitators, barrier filters and cyclone filters for some applications. The major problem is that the gas temperature of the outlet must be around 60°C in order to have an effective separation. The captured tars are burned to yield some heat back for the system. One problem though is that when wet methods are used, the moisture content is high and therefore, the formed gas temperature is not as high as desired.

Catalytic and thermal destruction

If the temperature is above 1200°C, the tar decomposes to form gases and, sometimes, char. But if catalysts are used, the minimum temperature is 750°C, which is much easier to achieve. In the early 1980s, research begun on in situ destruction inside the gasifier with catalysts. This means that they had to use low-cost catalysts (e.g. dolomites) which could be disposed with the bed material. Test from the Värnamo gasifier showed that even though there was an effect inside the gasifier tars still were coming out. Most research has been performed on a separate reactor for tars destruction, to have a better temperature control and better use of the catalysts.

Nitrogen compound removal

It is mainly the formation of ammonia that is the concern. This compound can be removed either by catalytic cracking or by wet scrubbing. Fortunately, it is possible to use the same catalysts as for tars destruction, e.g. dolomite, which means that the ammonia destruction occurs simultaneously as the tars destruction. The wet scrubbing method is only feasible to use when the temperature is low enough, but has the possibility of recirculate the ammonia into the gasifier and thereby decrease the NOx formation.

Hydrocarbon reduction

The light hydrocarbon compounds still in the syngas, mainly methane and ethane, may cause trouble in the following methanol synthesis or hydrogen use and must, therefore, be removed or destroyed. This can be done by Co/Mo catalysts at 700-900°C (Stevens, 2001) which also is tolerant to sulfur.

Steam reformer

The conventional steam reforming catalysts are 10-33 wt% NiO on a mineral support of e.g. alumina, cement or magnesium (Spath and Dayton, 2003). The reforming catalysts are sensitive to sulfur compounds. It can deactivate already at concentrations on 0.1 ppm. According to Leiby (1994) it is necessary to have the sulfur concentration below 0.5 ppm in order to maintain a 3-year lifetime of the catalyst.

Water gas shift reactor

The HTS reactor operate with an iron oxide/chromium oxide based catalyst at 300-450°C (Spath and Dayton, 2003) while the LTS reactor operate with cupper oxide catalyst (often in combination with zinc oxide) at 180-270°C. The HTS catalyst can stand sulfur concentration of several hundreds ppm but its activity will eventually decline. The LTS catalysts is, however, much more sensitive. The latter is also sensitive to chlorides. Other catalysts that are more sulfur tolerant have been investigated. These consist of cobalt and molybdenum.

Gasification processes to produce hydrogen

There are a number of different processes that are made for gasification; however, not all of them are suitable for hydrogen production. Among the possible options, when biomass is used, are (Babu, 2002): BIOSYN, FERCO SilvaGas, MTCI, Renugas, FICFB, Chemrec and SVZ Scharze Pumpe GmbH. However, the same gasifiers are not fully applicable when other fuels are used. For example, Holt (2004) states that the best technology to produce hydrogen from coal is by one-stage entrained flow reactors. The reason is that the high temperature gives low production of methane and tars and it will be easier to remove the CO_2 by physical absorption (which means less energy demanding compare to absorption). Due to the low reaction kinetics of petcoke, high temperatures are preferable and thus, entrained flow reactors are the primarily choice.

6.4.2 Experimental work

The Laminar entrained flow reactor (LEFR) used in this study is a laboratory-scale reactor that works at atmospheric pressure and in a temperature range between 600 and 1100ºC. Additional operational parameters are given in Table 6-5. The five-zone heating element provides flexibility and high heating rates of 4000-13000ºC/s.

Table 6-5. Operating conditions in the used LEFR.

Temperature	600 - 1100 ºC
Pressure	1 bar
Flow rate	0.1 – 2 g/min
Primary gas flow rate	0.1 – 1.2 l/min
Secondary gas flow rate	2 – 40 l/min
Quench gas flow rate	1 – 30 l/min
Main gas flow rate	1 – 30 l/min

The figure below, Figure 6-3, shows the main system of the LEFR operating with a downward flowing gas stream. The primary flow was injected at the top of the reactor together with the raw material. The secondary flow was preheated to the reactor temperature and injected through a flow straightener coaxially with the primary gas flow. The feeder system, consisting of a screw feeder and a hopper, located at the top of the reactor, controlled the particle flow rate into the reactor.

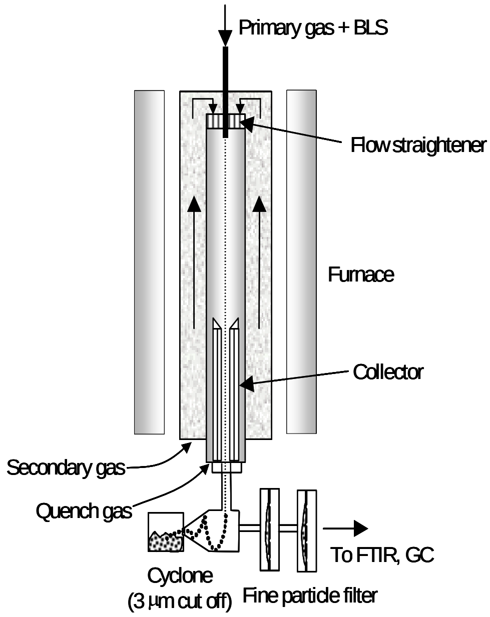


Figure 6-3. Chalmers *Laminar Entrained Flow Reactor.*

When entering the reactor, the particles were rapidly heated up by the secondary flow and the hot walls. The reaction zone length can be varied between 0.2 and 1.2 meters. The inner tube diameter is 70 mm.

After the reaction zone, the particles and gases were quenched with nitrogen in a water-cooled collector tube to stop the reactions. Then, large particles were removed by a cyclone in the bottom part of the reactor and collected in a char bin. Fine particles were removed from the product gas by a glass fibre filter.

The detected gases were CO, CO_2, CH_4, and SO_2. When the exhaust gases were expected to have higher concentrations than the maximum ranges of the analyzer, a diluting gas flow was added before allowing the product gas to enter the gas analyzer.

Methodology

Experiments were conducted in the Chalmers Laminar Entrained Flow Reactor at temperatures between 800 and 1000ºC and estimated residence times around 1.0 s.

Nitrogen was used in the primary, secondary, main and quench flows. The gas flow conditions were recalculated for each run, in order to keep the velocity constant when changing the temperature.

The duration of each run varied from 3-6 minutes depending on the stability during the runs. At the end of each run, the cyclone, particle filter holder and char bin were sealed and removed to a nitrogen purged glove box in order to prevent the reactive char residue from oxidizing or combusting spontaneously on exposure to air. The contents were then weighed and the char was analyzed with respect to calcium (to perform mass balances). During the run, CO_2, CO and CH_4 were analyzed continuously.

As material, either petcoke or washed precipitated lignin was used. The reason to compare with the washed lignin is to have a comparison with a biomass based material without the catalytic effect.

Results

The gas analyses from the experiments are shown below in Figure 6-4 – 6-6.

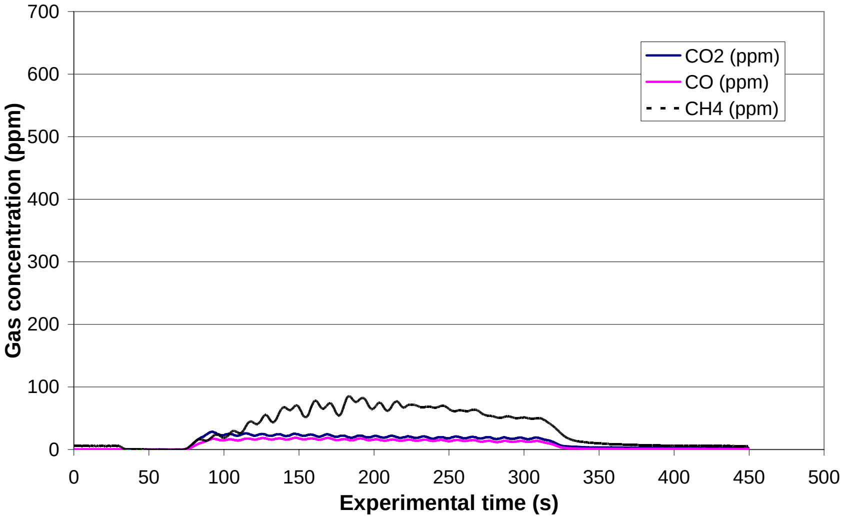


Figure 6-4. ***Gas production from pyrolysis of petcoke at 800°C during approximate 1 s residence time.***

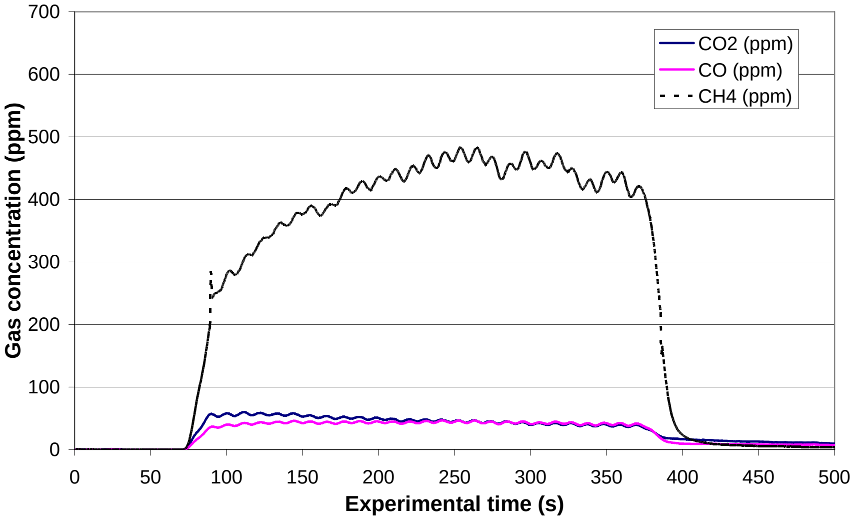


Figure 6-5. ***Gas production from pyrolysis of petcoke at 900°C during approximate 1 s residence time.***

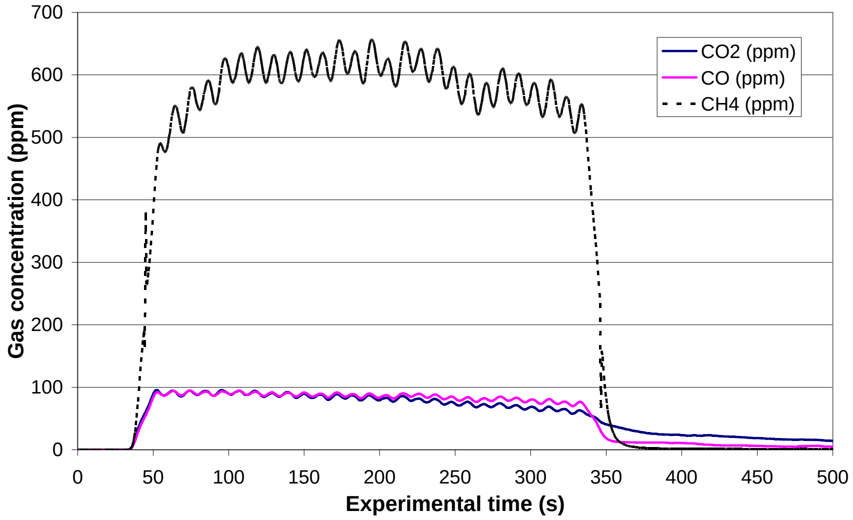


Figure 6-6. ***Gas production from pyrolysis of petcoke at 1000°C during approximate 1 s residence time.***

The experiments were all performed using technical grade nitrogen in the LEFR. This means that there could be a small amount of oxygen present in the gas and this will then explain why there is a formation of CO_2 and CO even though the initial content of oxygen is low in the petcoke. The condition is thus not completely pyrolysis but very close. The oscillation comes from the screw feeder that has a certain frequency. It is clear that the reaction goes faster at higher temperatures, indicated by the higher concentration of produced gases in the outlet gas stream.

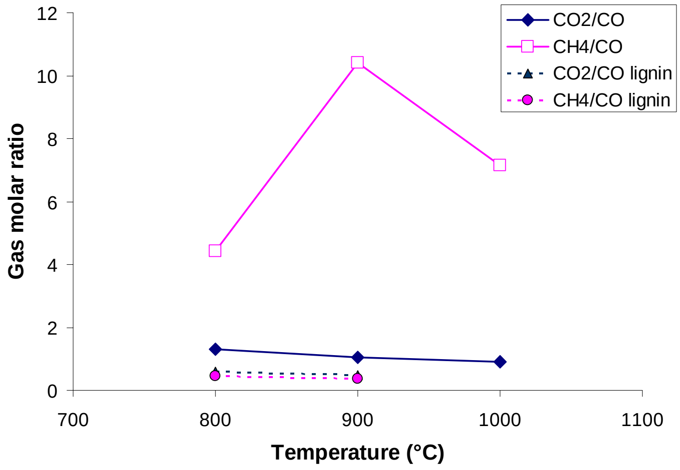


Figure 6-7. ***Molar gas ratios of CO_2 and CO and CH_4 and CO at different temperatures with both petcoke and washed precipitated lignin as fed material.***

The figure above, Figure 6-7, shows the molar ratio of CO_2 and CO and CH_4 and CO in the gas phase during the experiments. As a comparison, also the ratios when washed precipitated lignin was used are seen. It is clear that especially the amount of CH_4 is much higher compared to CO in case of petcoke. This is expected since petcoke is virtually free of oxygen and should therefore not form oxygenated compounds.

6.4.3 Material, energy and economical considerations

The total need of hydrogen at the Lysekil site is about 350 tons/day (this site is used because it is here the production of petcoke will be). A rough estimate would give about 6.5 g hydrogen per kg of biomass. Biomass, on a dry basis, has about 6 wt-% hydrogen from start and with the steam reformer and water gas shift reactor most of the carbon (roughly 50 wt-%) could be producing hydrogen on a 1:6 weight basis. One mol carbon (after formation of CO) could, according to the WGS reaction, form one mol of hydrogen gas (H_2). Thus, totally 14.5 g H_2 could be formed and using a global efficiency of about 45% gives 6.5 g H_2 per kg of dry biomass (which is in accordance with e.g. Orecchini and Bocci, 2007). Regarding a 6.5 % efficiency 5400 ton dry biomass is needed for the necessary production. The amount of oxygen is about more than 40 wt-% which gives the molar ratio of carbon to oxygen to 1.5 (a ratio of 1:1 would, if the reactions occur stoichiometrically, give formation of only CO). A dry content of 50 wt-% (mass of dry material divided by the total mass) would change the carbon to oxygen ratio to 0.5 indicating that no extra steam needs to be added if the reactions occur according to the stoichiometry (each carbon utilizes two oxygen molecules to form CO_2). Therefore, more than 10,000 ton of biomass would be needed each day (as comparison a typical pulp mill uses 2000 ton/day of dry wood). Important to keep in mind is that additional oxygen is usually added make the temperature increase (heating up the material and also evaporate water) and start the reactions (indirect heated gasifiers use another approach) and that the reaction does not occur as one-way reaction but more like equilibrium reactions and thus further decrease the efficiency. It is therefore beneficial to add a material with lower oxygen content to keep a good ratio between C:O:H.

The high heating value of biomass is around 20 MJ/kg and for petcoke it is about 30 MJ/kg. A production of 350 ton H_2/day correspond to 42,000 GJ using a biomass input of 108,000 GJ (1 GJ = 0.28 MWh), thus the energy integration of this process is crucial (notice that this is a low estimate since only the biomass has been addressed).

A price of 7.5 EUR/MWh of biomass at the collection centre would give a total cost of about 10 EUR/MWh on site and a cost of pyrolysis oil of about 19 EUR/MWh (e.g. Kurkela and MacKeough, 2005). The biomass cost would therefore be 120,000 EUR each day for solid biomass. A cost estimate was performed (Spath et al, 2003) for three different gasification methods to produce hydrogen from biomass in the USA; gasification of pyrolysis oil, low pressure gasifiation and high pressure gasification of solid biomass. It was then clear that the current biomass price and utilization of pyrolysis oil products makes the gasification of bio-oil the cheapest production of hydrogen. However, it is necessary to keep in mind that this will demand about 80% more biomass and it will also generate a substantial amount of by-product which must be utilized (the actual feed of bio-oil to the process site is equal to the amount of dry biomass in the gasification cases). The production price (IRR = 0%) was found to be around \$8.9/GJ for the gasification of solid biomass compared to \$5.3/GJ for the gasification of bio-oil (the production rate was 76 ton H_2/day). If an IRR of 15% was used, the prices became \$15.4-17.6/GJ and \$8.7/GJ, respectively. It shall also be stressed that the comparison used three fluidized bed reactors operating at temperatures around 800°C.

6.5 Conclusions

- there exist today several processes to handle gasification of either petcoke or biomass
- regarding biomass no fully commercial system is running to produce synthesis gas
- no information has been found regarding co-gasification of petcoke and biomass

- petcoke as starting material has a low ash content and high energy content. The drawbacks are slow kinetics and a total dominance of carbon compared to hydrogen.
- Petcoke is difficult to grind and the commercial systems using petcoke today mainly grind it in a slurry with water that is then gasified.
- Biomass as starting material has relative high ash content (with a comparable low melting point) but has a high reaction rate. The molecular structure has more oxygen than preferred which gives a lower quality synthesis gas (has more CO_2 in it).
- Using bio-oil instead of grinded biomass takes away the difficulties with the ash (it has already been separated). Further examinations must however be done regarding reaction rates and temperatures inside the gasifier.
- It is not feasible to produce all necessary hydrogen from biomass.
- A system using bio-oil can be cheaper than a system using solid biomass but has a substantial higher usage of biomass may generate many by-products.

6.6 Areas for further research

The pre study has showed that there is a difference between the two studied raw materials; biomass and petcoke. The main purpose would be to utilize the best properties of both materials and be able to combine them for best efficiency. For example, petcoke has a higher heating value, and lower ash content compared to biomass but has a lower reaction rate and is not renewable. The two materials have also different ratio of C, O and H which could be mixed for best performance when producing hydrogen. Regarding biomass, there are two option of how to perform the gasification, either with powder material or as a bio-oil. Therefore, three studies are proposed:

1. **Co-gasification of biomass and petcoke as a powder**
   This concept has the highest potential of producing most hydrogen from a given amount of biomass but the gasification could be technically difficult to perform. Included in this study are potential benefits with a co-gasification both theoretical and experimentally observed, the syngas composition and reaction rate together with a preliminary design of a gasification system. The formed ashes are also considered with respect to composition and possible usages.

2. **Gasification of bio-oil and petcoke**
   To take the benefits from an easy handling and mixing of the two materials, this study focus on the co-gasification of biomass pyrolysis oil and petcoke. Included in this study are potential benefits with a co-gasification both theoretical and experimentally observed, the syngas composition and reaction rate together with a preliminary design of a gasification system where especially the temperature levels are important to follow.

3. **Pre-treatment and availability**
   The source of biomass and its availability are studied. There is also a consideration using experimental and theoretical work about possible raw material (where different types of biomass are studied and also possibilities of using other material like waste). Focus in this study will be mixing properties and methods of the two materials both as powder but also as slurry. The grinding possibilities of petcoke are analyzed from an energy consumption point of view for both cases (in the slurry case, a determination of hydrodynamic properties of the bio-oil is necessary).

6.7 References

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7 Hydroprocessing of vegetable oil

Development of alternative fuel for fossil fuel application is initiated in full research momentum by two reason, first as a necessary to use less polluting oil due to 21% emission resulting in greenhouse gases by transportation account and secondly, the need to guarantee the security of energy supplies by diversifying fuel sources in availability and price fluctuation [1]. Vegetable oils are triglycerides, i.e. three fatty acid chains connected via the carboxyl group to a glycerol backbone, as shown in Figure 7-1 [2].

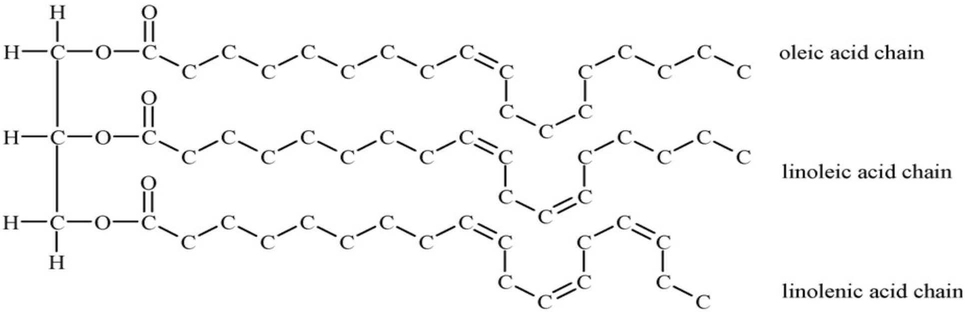

Figure 7-1 Molecular structure of a vegetable oil (example applies for rapeseed oil). All double bonds are in the *cis*-configuration [2].

The cultivation of rape began in Asia, where it was used as fuel for lamps. Its cultivation in Europe began in Holland in the 13th century. Then, it pass to Belgium and France and later, in the 16th century, to Germany. The great development of rape is closely linked to the shipbuilding industry, as its oil shows a greater adherence to metallic surfaces than other vegetable oils. This ensured its expansion to countries such as Canada, currently the world's largest rape producer. Canada is also working on improving the rapeseed, as shown by the nutritional properties of the ''cake'' sub-product for human consumption after the Second World War.

The main criteria in evaluating vegetable oil to fuel are,

- The intrinsic chemical quality (degree of humidity, impurities, impossible to saponify, peroxides, inevitable fraction, fatty acid polymers, strange or toxic substances) particularly emission.
- Enthalpy potential and hydrocarbon composition (energy content, percentage of triglycerides, composition and richness in essential fatty acids, etc).
- Different applications and
- Economic feasibility.

In this chapter the focus is given to the basic idea for rapeseed oil into alternative fuel in different approach on scientific research. Also, the latest achievement by research work to get efficient fuel.

7.1 Rape seed oil composition

Most of the vegetable oil has C12 to C24 hydrocarbon chain in glycerolised formation. As European main source depends on rape seed oil, the variation of carbon number is C14 to C22 in glycerolise appropriate cetane number to get diesel derivatives. One importance's to avoid rape seed oil from cooking insists of other vegetable oil is the presents of erucic acid;

monounsaturated omega-9 fatty acid also known as *cis* 13-docosenic acid, which is also present in wallflower and mustered seed. The C18 cetane combination for diesel oil is well suited, as shown in Table 7-1, in rape seed oil, but presents of unsaturated carbons and carboxylic group are the main focus by researcher to deal with reaction engineering.

Table 7-1.Chemical composition of rapeseed oil, data provided by KOIPE S.A. factory Andu´ jar (Jaen) [3].

Fatty acid profile and characteristics		Refined Rapeseed oil (%)	Raw Rapeseed oil (%)
	C<14	–	–
Myristic	C 14:0	0.06	0.05
Palmitic	C 16:0	4.72	4.32
Palmitoleic	C 16:1	0.24	0.23
Estearic	C 18:0	3.01	2.77
Oleic	C 18:1	54.62	60.27
Linoleic	C 18:2	27.2	19.58
Linolenic	C 18:3	7.14	9.19
	C>19	3.01	3.59

7.2 Trans-esterification

To become an ester, the oils or fats must be heated and mixed with a combination of methanol and sodium hydroxide. The conversion process is called trans-esterification or alcoholysis which is shown in Figure 7-2.Trans-esterification of triglycerides. Trans-esterification or alcoholysis is the displacement of alcohol from an ester by another in a process similar to hydrolysis, except than alcohol is used instead of water. The presence of a catalyst (a strong acid or base) accelerates the conversion. At present, this process is succeeded only for converting vegetable oil [4].

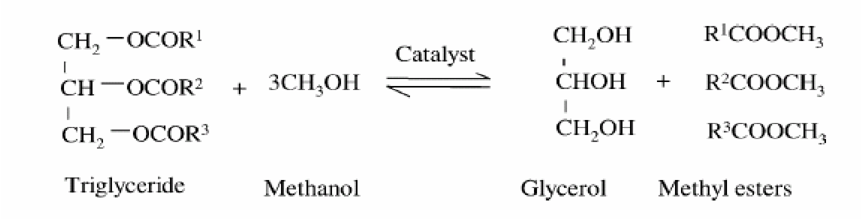

Figure 7-2.Trans-esterification of triglycerides

7.2.1 Trans-esterification disadvantages

- The conversion of bio-diesel gets affect if Free Fatty Acids is greater than 3 wt%.
- Increasing in water reduces the conversion of bio-diesel production, so the catalyst and alkaline should present in anhydrous state. The water content should be reduced below 9% from waste stream to use this technology.
- Higher the acidity of the entering oil, smaller the conversion of bio-diesel conversion.
- The by-product with bio diesel is tending to form soaps, increase the formation of gels, which make it more difficult to produce a high yield of bio diesel fuel.
- Prolonged air contact will affect the efficiency of catalyst. So the system should be under nitrogen atmosphere.
- Poor cold flow properties due to precipitation at low temperatures.

7.3 Partial Hydrogenation

The hydrogenation of rape seed oil can be done by thermal and catalytic conversion. Cracking of rape oil can be done at >400°C, but it doesn't show-up good cetane compound. Actual need to get diesel in appropriate cetane number needs some control over reaction mechanism. Perhaps more detail of thermal conversion of rape oil will be seen later part of sections. Nowadays catalytic conversion of rapeseed oil is preferred most for product yield and better selectivity. Indeed, hydrogenation of carboxylic group through catalyst is more concentrated in research work.

More catalyst on transition metals of VIII groups are, particularly mono and bimetallic of copper, palladium, ruthenium, rhodium, rhenium and nickel, studied on selective hydrogenation for ester to alcohols. But different saturated and unsaturated hydrocarbon chain in glycerol makes tough estimation of reaction mechanism. To understand more on this reaction, initially, Palladium has been the catalyst under lot of research in 1990s. Partial hydrogenation is effective through palladium, but hard in breaking of carboxylic group. E. Santacesaria et al suggested trienic and with some extend of dienic is more adsorbed in Pd surface which hydrogenate to give monoenic compound [5]. Through low thermal condition, the hydrogenation of sunflower oil shows stable trans-monoene, which is originates of saturated compound, is formed. Ferreira also confirmed the Lewis acidic – basic sites for Pd need excess hydrogen to get rid of cis-monoene formation [6]. But still, there is high activation energy, indeed, need to break into aliphatic compounds.

7.4 Cracking and Pyrolysis

Cracking of vegetable oil above 425°C leads to formation of hydrocarbons shorter than diesel fraction. Dupain et al cracked the rapeseed oil through fluid catalytic cracking (FCC) condition under zeolite (ZSM-5) catalyst, identified there is increased aromatics formation with unsaturated bond proportion with lower thermal condition below 585°C. Obviously, products support reasonable diesel, gasoline and rich hydrocarbon gases with majority of oxygen removed as water with none COx. [19]

7.5 Hydrogenation of triglycerides

Addition of hydrogen through particular thermal and/or pressure condition leads to hydrogenate triglycerides into alkane which has close cetane number proportional to diesel. The hydrogenation of triglycerides might have different path way, Decarboxylation, Decarbonylation and Hydrodeoxyenation. Indeed, except Decarboxylation, other two pathways need one or more mole ratio of hydrogen to sustain the desired product [8]. On contrary to the reaction of fatty acids, it is still unknown the exact route of catalysis with which reaction is carried out. The detailed analysis of this literature studies on each pathway is described below.

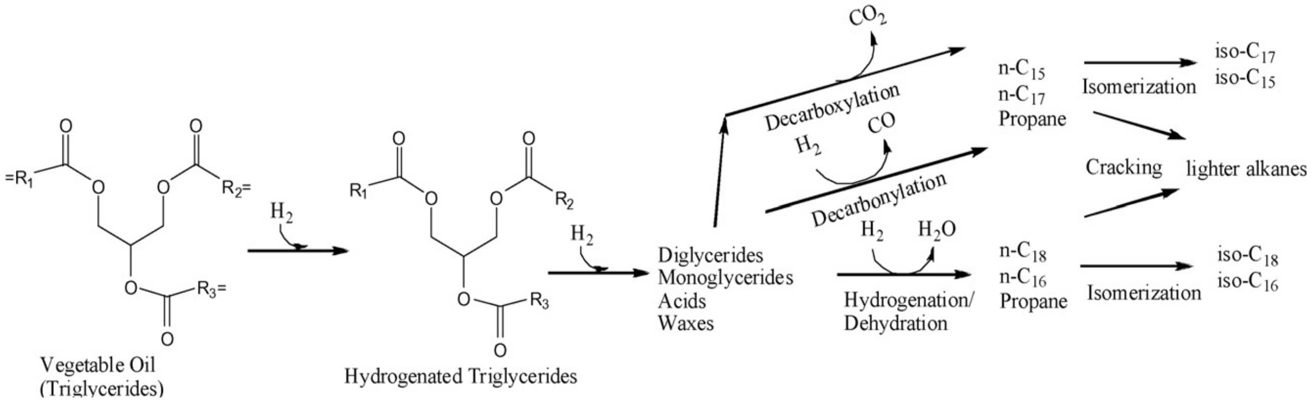

Figure 7-3. Hydrogenation of tri-glycerides into high cetane hydrocarbons.

7.6 Decarboxylation and decarbonylation

Removal of Carboxyl group is a thermal or catalytic reaction through HDO catalysis, but there is so expectation that this might be side reaction in hydrogenation process. Indeed, C=O bond is stronger than C-C and C-H bonding due to configuration stability. Perhaps, to overcome decarboxylation, more controlled reaction condition with in-depth analysis and experimental work is needed. The product has C_{n-1} which loss one mole carbon as CO_2 from its parent reactant of C_n [1]. On decarbonylation, the parental fatty acid loss one mole C as CO and dehydration with limited hydrogen intake gives C_{n-1} compounds. Poulloux et al hydrogenated methyl oleate with Co-Sn catalyst with Al_2O_3, which shows Stearyl alcohol as major product at 270 °C and 8 Mpa condition. Unfortunately, there is no catalyst is effective in decarbonylation and hydrogenation till 2005. Senol et al proved the decarboxylation by methyl heptanoate is satisfying with sulphided Co or Ni -Mo/Al_2O_3 catalyst at 250 °C and 8 Mpa pressure, but formation of esters reduces the conversion efficiency. These carbonyl reductions are mainly achieved by Lewis-acid site. Latest study by Croma et al confirms that the conversion by decarboxylation and decarbonylation has same proportion by Ni-Mo/Al2O3 [2]. Murzin et al tried to understand decarboxy/decarbonyl with Pd/C catalyst, which gives maximum of 55 mol% conversion of heptadecane from stearic acid at 300 °C [3].

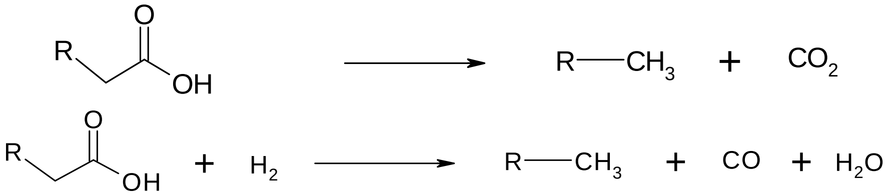

Figure 7-4. Decarboxylation and Decarbonylation of fatty acids

7.7 Hydro-deoxygenation/dehydration

The process of removing oxygen with CO_2 and H_2O from carboxylic group through hydrogen to get hydrocarbon aliphatic compound is called Hydrodeoxyenation (HDO). For HDO, search of catalyst, optimum thermal and pressure condition are in progress to get better yield of diesel quality product. Hark et al understand hydrogenation of FAME under super critical condition is effective to give fatty alcohol under Cu catalyst. Their result gives prominate approach in hydrogenation at continuous reactor with presences of lipids in FAME (Fatty acid methyl ester) hydrogenation at 240-250°C and 150 bars. Indeed, the main motivation to remove oxygen from well established high quality aliphatic hydrocarbon compounds, FAME.

Dehydration, removal of water through hydrogenation, is the best possible idea to get high quality cetane number. In spite of Cu, sulphides hydro treating catalyst like NiMo and CoMO/Al_2O_3, gives better conversion in recent research work. Perhaps, sulphur content in bio diesel (<0.002 wt %) is typically low, so addition of sulphiding agent might be require to maintain the S-level during hydro treating. From this work, Co-Mo HDS catalyst showed good contribution. Viljava et al identified the better reaction stability of HDS catalyst in the presences H_2S, doesn't affect the selectivity on phenol and anisole hydrogenation. HDO conversion reached till 72% at 300°C condition but final product formation is still non-ideal. Y.Pouilloux tried with Co-Sn catalyst for hydrogenation on methyl oleate to stearyl alcohol. He noticed transesterification is more dominate than hydrogenation, which certainly proved unsaturated alcohol formation depends mainly of Sn ratio. Senol investigation under Co & Ni-Mo/Al_2O_3 with H_2S and Water with feed increases ester level. However, addition of H_2S effectively compensated the inhibition by water. Also, shows Ni catalyst better activity and stability than Co. On Comparing CS_2 and H_2S, Senol et al recommends H_2S as promoting hydrogenation sulphiding agent with attributed to acid-catalysed reaction. His result with methyl heptanoate hydrogenation, HDO provides C_7 and C_6 aliphatic compounds by E2 elimination and SN2 nucleophilic substitution mechanism as proposed reaction role.

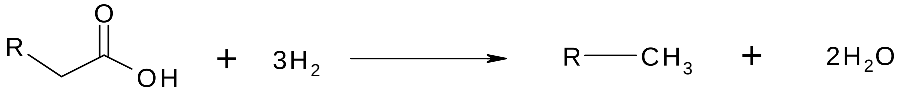

Figure 7-5. Hydro-deoxygenation of fatty acids

7.8 Hydro treating Catalyst

Pd, Co and Ni are the most frequently used metals for this purpose. Pd catalysts are highly active in hydrogenations of double and triple carbon-carbon bonds while they are much less active in hydrogenation of aromatic hydrocarbons and C=O bonds. Resent proposal preferred NiMo/Al_2O_3 and Pd /Zeolite or Active carbon are suitable catalyst for future reaction engineering. Basically, metal hydrides, e.g. $LiAlH_4$–$AlCl_3$, $NaBH_4$–CF_3COOH, $NaCNBH_3$–$BF_3.OEt_2$, Et_3SiH–BF_3, monomeric or dimeric [(C_2H_5)2Ti], are capable to deoxygenate carbonylic compounds, and even Clemmens (acidic) and Wolff-Kizhner (basic) reductions are the oldest procedures enabling the transformation of a carbonyl group of aldehydes to a methyl [17]. Clarke investigation with 5 wt. % of palladium used to investigate the reaction mechanism of benzaldehyde hydro-deoxygenation by large and medium pore zeolite on its structure and their reaction acidity. It observed that the most suitable catalysts for hydro-deoxygenation of benzaldehyde are the catalysts with the large pore zeolite beta as support. The selectivity to toluene is 93.6% after 15 min of the time-on-stream over catalyst Pd/beta and 94% over the catalyst Pd/beta. The selectivity values indicate that the difference in acidity had only a marginal effect on the selectivity in this reaction. Hydro-deoxygenation of benzaldehyde is influenced by acidity of the support over medium pore zeolites, however substantially with a lower diffusivity of reactant and products in 10-membered ring channels of zeolites. Even lower selectivity to toluene at 29.1% over the catalyst Pd/C, which indicates the importance of acidity in this reaction [18]. The incorporation of cobalt or nickel into the MoS_2 structure can significantly increase catalyst activity for hydro treating reactions. Nickel atoms may be present in three forms after sulphidation: as Ni_3S_2 crystallites on the support, as nickel atoms adsorbed on the edges of MoS_2 crystallites (the so-called Ni─Mo─S phase), and as nickel cations at octahedral or tetrahedral sites in the γ-Al_2O_3 lattice. Depending on the relative concentrations of nickel or cobalt and molybdenum and on the pre-treatment conditions, a sulphide catalyst may contain a relatively large amount of either Ni_3O_2 or Co_9S_8

or the Ni─Mo─S (or Co-Mo-S) phase [15]. Cobalt is mainly used in HDS, while Nickel is favorable for HDN. R.Prins (1997) studied that Ni atom perform the real catalytic sites at Ni-Mo/Al_2O_3 catalyst. MoS2 act as secondary support for Ni atoms, in which MoS2 crystalline in turn supported by Al_2O_3. Fully coordinated metal (Mo) atoms in sulfided catalysts unable to adsorb sulfur-containing molecules, and the number of sulfur vacancies may thus be a key measure of the catalytic activity. The detailed atomic structure shown by Byskov (1999), binding energy of sulfur over the metal is the key role in catalytic activity. Their investigation by density functional theory on Co/Ni-Mo-S type edges showed that both bonding and anti-bonding states are well below Fermi level which promote better than MoS2 crystalline. Even compare to other transition metals like Cu and Fe, this metals have much weaker sulfur bonding [16]. The ratio of Co/Ni in the sulphided CoMo/ NiMo catalyst has not been established properly in the literature.

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7.10 Appendix 7-1

Reference. No	CAS regstry	Compounds	Carbon number	Boiling point ^{o}C
1	1731-86-8	Methyl undodecanoate	C11:0	248
1	111-82-0	Methyl laurate	C12:0	262
1	124-10-7	Methyl myristate	C14:0	296
1	112-39-0	Methyl Palmitate	C16:0	415
1	112-61-8	Methyl stearate	C18:0	442
3	112-62-9	Methyl Oleate	C18:1	218 (0.027 bar)
3	1937-62-8	Methyl elaidate (trans)	C18:1	214 (0.02 bar)
3	112-63-0	Methyl linoleate	C18:2	192 (0.005 bar)
2	143-07-7	Lauric acid (dodecanic acid)	C12:0	225
2	544-63-8	Myristic acid	C14:0	250.5
2	57-10-3	Palmitic acid	C16:0	390
2	57-11-4	Stearic acid	C18:0	361 - 386
3	112-80-1	Oleic acid *(cis)*	C18:1	195* (0.001 bar)
3	2197-37-7	Linoleic acid *(cis)*	C18:2	229* (0.021 bar)
3	112-79-8	Elaidic acid (trans)	C:18:1	234 (0.02 bar) & 288 (0.133 bar)
1		Rapeseed ethyl ester		362.24
1		Rapeseed Methyl ester		368.99
3	112-92-5	Stearyl alcohol	C18:0	171 (0.003 bar) & 211 (0.02 bar)
1	143-28-2	Oleyl alcohol	C18:1	360
3	36653-82-4	Palmityl alcohol	C16:0	340

Note: * approximate values

7.10.1 Reference

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8 Pathways – An opportunity to demonstrate the role of Preem and other refineries in the transition toward a sustainable European energy system

8.1 Europe's energy-intensive industry can contribute to a sustainable energy system

Energy-intensive industry comprises about a fourth of the energy use in Europe. This energy use, unlike that in, for example, the engineering industry or the housing sector, is localised in a few large plants or complexes of plants. The refinery sector, which represents 15 % of the energy use by energy-intensive industry, consists of just over 100 plants. Due to its large specific energy use, energy-intensive industry has unique possibilities of contributing to a conversion of Europe’s energy system – by changing fuels, increasing efficiency, investing in new processes, and raising the degree of co-production of electricity, heat and alternative fuels. At the same time, energy-intensive industry operates on global markets and is sensitive to cost increases that deviate from those of competitors, for instance as a result of policy tools in its own and adjacent sectors.

8.2 More knowledge is demanded about the industry’s role in the conversion of Europe's energy system

A properly directed conversion of the energy system should be designable so that the energy-intensive industry decreases its emissions of carbon dioxide and contributes to greater production of electricity, heat, and biofuels, while its competitive power also grows. In order to design such policy tools, however, knowledge about the energy-intensive industry’s energy system must be increased, along with understanding of the interplay between measures in this industry and other sectors.

Energy-intensive industry is capital-intensive and characterized by the fact that most investments are large and have long write-off periods. Decisions made today will influence the industry’s profitability and possibilities of contributing to conversion of the energy system for a long time to come. Thus, decision-makers in industry need to have good insight into what a conversion of Europe’s energy-system means for their own industry’s development. For example, it is necessary to understand how decisions in other sectors affect the industry’s opportunities to act and which investments are economically robust.

8.3 Pathways – a project showing the way to a sustainable energy system

Chalmers has been conducting since 2006, under the direction of Professor Filip Johnsson in its Department of Energy and Environment, a large interdisciplinary research project named Pathways. The project comprises about 100 million Swedish crowns and is a flagship project within the Alliance for Global Sustainability (AGS). AGS is a strategic collaboration for research on sustainable development between Chalmers, the Swiss Federal Institute of Technology, the Massachusetts Institute of Technology (MIT) and Tokyo University, as well as large companies such as Ford, Du Pont and Vattenfall. Some 20 researchers at Chalmers cooperate in Pathways, as do research groups elsewhere – for instance in the Department of Business Economics at Göteborg University, and research institutes in Germany and Holland with competence for general modelling of Europe's energy system. Pathways is financed by, among others, Vattenfall and ABB, the Energy Authority and the EU. The project is still under development, and new research competence and co-financiers are continuously being linked to the project.

8.4 Purpose and goal of Pathways

The purpose of Pathways is to describe ways of achieving a sustainable European energy system. This project is unique in that, while based upon today's technology and European energy system, it describes technological choices and system solutions which can form a bridge from present technologies to a long-term sustainable energy system (Figure 8-1).

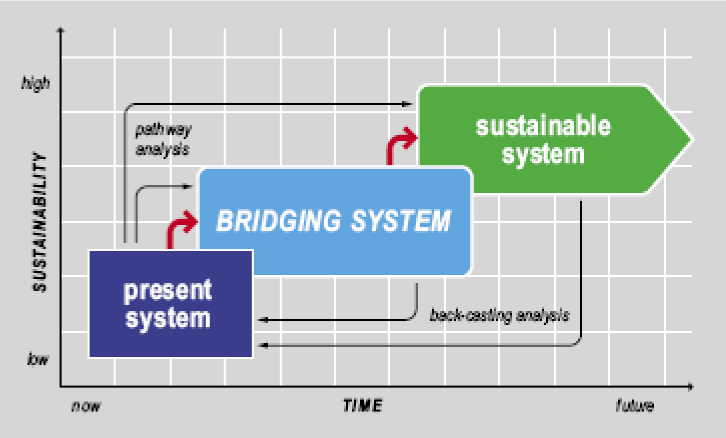

Figure 8-1. *Pathways is unique in being based on today's European energy system and describing technological choices and system solutions that bridge from present-day technologies to a long-term sustainable energy system.*

1. Definition of "pathways"

What are the criteria for definition of "pathways to sustainable energy systems"?

How will the choice of criteria influence the design of the pathways towards a sustainable energy system?

Which are the pathways that do not lead to a sustainable energy system?

2. The current "pathway"

Will the current "pathway" lead to a sustainable energy system?

3. Two-three pathways to sustainable European energy systems

How can pathways to a sustainable energy system be characterized and visualized and what are the consequences of these pathways? ("Pilot scenarios")

4. Key technologies and systems

What are "key" technologies and systems for the identified "pathways"?

Where are the greatest uncertainties in technology choices?

- What is the critical timing for decisions to ensure that a pathway to a sustainable energy system can be followed?
- What role will the stationary systems (such as power systems and district heating) play in the different pathways?
- Where are the critical regions with respect to CO_2 emissions and investments?
- What is the role of renewables and energy efficiency?
- Where and when are the risks for technology lock-in effects?

5. Will a European deregulated market path the way for sustainability?

Are the deregulated energy markets suitable to facilitate a development towards a sustainable energy system?

Are the present market conditions suitable for a development along a pathway towards a sustainable energy system and, if not, can these conditions be changed to facilitate this?

6. Political action and decisions

What kind of political action is necessary?

What can and should the EU and/or the Member States do politically?

What issues have to be addressed at an international level?

7. Acceptance of society?

What possibilities and obstacles can be foreseen?

What are the choices that consumers would like to make which lead to sustainability? How will these affect political decisions, and *vice versa*?

Figure 8-2. *Pathways' research questions include a number of system levels and clarify technological aspects as well as economic, legal and social ones.*

The project's results are to serve as a decision support for both politicians and industrial decision-makers. Great importance is therefore attached to communication of the project's research results. Among other things, Pathways distributes quarterly newsletters and publishes leading results in summary reports which are easier to grasp than, for example, scientific articles and doctoral dissertations.

The goal is that Pathways will illuminate seven different problem areas. These include numerous system levels and clarify technological aspects as well as economic, legal and social ones. The problem areas are described in Figure 8-2.

8.5 Pathways' interdisciplinary toolbox and methodology

To be able to answer the above research questions, Pathways has a comprehensive toolbox and pursues research on several system levels, from engineering research to general research on, for example, energy-system modelling and policy tool analyses. The researchers are divided into different “working groups”. Some are groups that work with general energy-system modelling, resource analyses, and evaluation of policy tools etc. Others are technology-oriented groups that work with the stationary energy sector’s development as well as the three user sectors: housing and services, transport and industry. All research groups work independently with sub-projects within their field. There is also an interdisciplinary compendium to which all the groups contribute as they obtain results in their respective areas. This compendium is to lead gradually to a description of how we can achieve a sustainable energy system in Europe, and will cover four topics:

A. **The present situation**
   This part describes today’s system with the help of existing statistics, and is presented in the form of, for example, databases and trends.
B. **Bridging technologies**
   In this part, technologies and system solutions are identified and described that bridge from today’s energy system to a more sustainable system, including solutions in both the short and long terms.
C. **Contribution to sustainability**
   The third part is to describe how different technologies and system solutions contribute to a sustainable energy system. An important aspect of this work is to develop indicators that coherently describe these diverse contributions. The focus is on trying to describe climate influence, cost efficiency, security of supply, and society’s acceptance for the technology and system.
D. **Pathways**
   In this part all the groups converge with results from the first three parts and propose two or three pathways to a sustainable energy system.

8.6 Industry-related research within Pathways

Pathways’ industry group includes the Chalmers departments of Heat and Power Technology and Physical Resource Theory. Also belonging to the group are consultants from CIT Industriell Energianalys and PROFU, both as expert support and for collection of data and modelling of the energy system. Moreover, the group collaborates from the outset with other researchers on an overall system level and within further disciplines.

The group will describe which possibilities a conversion of the energy system implies for Europe’s energy-intensive industry, and under which conditions the best advantage can be taken of European industry’s opportunity to contribute to a sustainable energy system.

Several energy-intensive branches of industry will be analysed in Pathways. The initial intention is to study the pulp and paper industry. With lessons from this sector it is intended to proceed with analysis of additional industrial branches, starting with for example the refinery and petrochemical sectors.

By joining Pathways, Preem would be able to promote understanding of energy-intensive industry’s importance for the conversion of Europe's energy system. Collaboration between Preem and Pathways would mean that the refinery sector can be viewed in a system perspective, and that the measures proposed within the framework of the research collaboration between Chalmers and Preem can be placed in a system perspective. Cooperation in Pathways also offers Preem a unique opportunity to gain access, at a relatively modest cost, to an extensive research network and a clarification of its own processes through a comprehensive system perspective.

9 Outcome of the pre-study and suggestion of the main study

9.1 Opportunities and need for further research

As is clear from the preceding chapters, there are several opportunities for creating a more sustainable oil refinery. These include the use of biomass as a raw material and/or as energy source, production of alternative transport fuels, savings of heat on site, combined heat and power production and CO_2 separation on site. According to the preceding chapters, the potentials for such measures can be expected to be high. Most of them, however, are linked between each other, i.e. they are either competing or relying on that one or more other new measures are also implemented. Examples are the competition between ORC, heat pumping and CO_2 separation for excess heat use, introduction of gasification and/or hydrogenation processes requires new thinking and new process integration designs and future introduction of CO_2 separation will change the optimal designs and operation of the energy related processes (including gasification) as well as opportunities for combined heat and power production.

The aspects of interactions between different types of measures, discussed above, are new both to industry and research and the knowledge of optimal solutions taking these aspects into account is low. Therefore there is a strong need for further R&D activities, in which there is a close cooperation with researchers from the different disciplines involved in the project. There is also a strong need for coordination between the different players in a possible further work (including "in-house" consultants at Preem). Furthermore there is a need for synthesis and analysis work for clarification of the complex interactions between the different measures and consequences concerning economics and environmental aspects of different future system solutions.

With this background we propose several different research projects in the following of this chapter with the aim to cover all important technological, economic and environmental aspects of different interesting future technologies and systems.

9.2 Program structure

The suggested program has been structured according to Figure 9-1. There is a main co-ordinator and then it is divided in three parts; one directly associated with research, one associated with applications and, finally, one part which includes the collaboration. The research part is also divided in two sections; on-site and off-site reduction which refers to where the main purpose of reduction are taken place. Along the on-site reduction projects are system integration and CO_2 sequestration. Off-site reduction means less impact of the product in the sense that it will be based on renewable material to a larger extent. The suggested project involves hydrogen production from biomass and treatment of bio-oil and pyrolysis oil. Within this second lies the application and included here are the possibility of performing consultant work, mainly in the system analysis area, but also shorter projects. The third area, collaboration, handles the meetings, seminars and work shops. This might result in shorter studies to be performed as well.

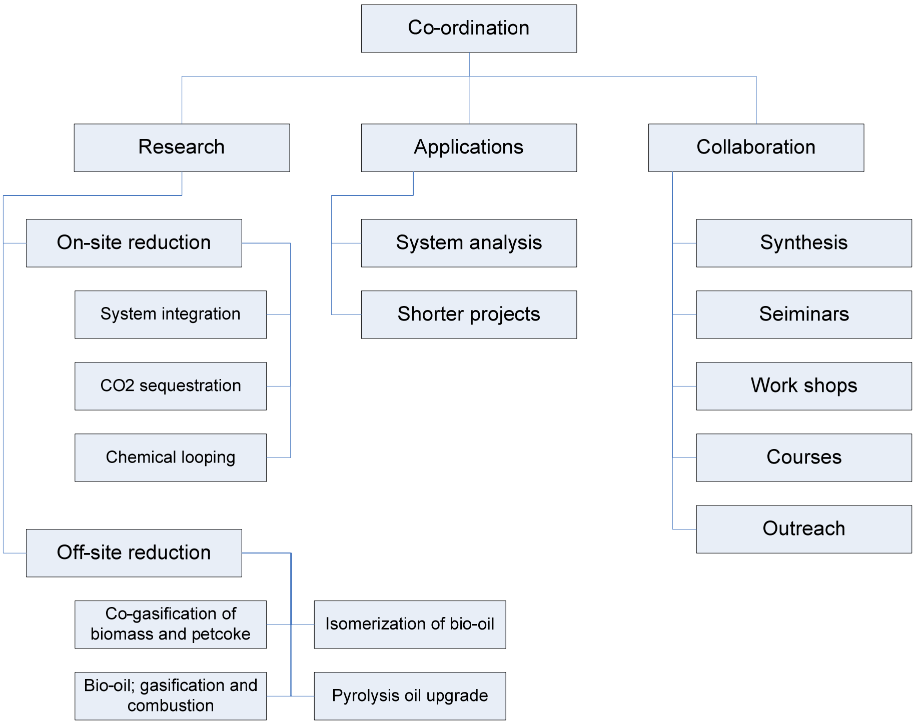

Figure 9-1. Sturure of main study.

Each research project is proposed to be executed by Ph.D. students but has also a substantial amount of supervision included for the principal investigator (PI). The reason is to ensure the quality of the research and to be included in the collaboration and dissemination properly.

The projects proposed below are very much linked to the planned activities in the Pathway project (see Chapter 8). This is especially true for the senior projects. Parts of these could be seen as important analysis and synthesis activities of the kind needed in Pathways and could therefore be seen as parts of the Pathway activities with practically no change in their objectives. If Preem would see an interest to join Pathways and hence have full insight in and information from this programme, it is most probably possible to see the here proposed projects as Preem:s contribution to Pathways.

9.3 Description of suggested projects

9.3.1 Project 1: System integration taking new processes/systems into account

In process industries there are normally rather high economically interesting potentials for energy saving/improved CHP production, even in “good” plants. This is most probably true also for Preem, which is indicated in the pre study for the Gothenburg plant presented in this report. With increasing concerns about higher energy prices and CO_2 costs, the interest for more advanced process integration measures will probably increase considerably. Therefore the competence and methods/tools developed at Heat and power technology at Chalmers will be used in a PhD project to study new energy system solutions and interactions between different processes and evaluate them technically, economically and environmentally at some different future scenarios concerning energy prices, CO_2 costs, etc. In our division we have developed such scenarios for process industries and they will be further developed and adjusted in cooperation with Preem.

In the first part of this chapter the interaction between new technologies and feedstocks, for example gasification and hydrogenation, with the existing process plants was pointed out. An important part of the PhD project suggested here will therefore be to perform process integration studies including such new technologies/processes and identify optimal integration approaches for them as well as opportunities for changes in the traditional process systems in such situations.

9.3.2 Project 2: System aspects of CO_2 separation on site

CO_2 separation in large process industries can be an interesting option for creating considerably more sustainable processes, as has been shown in Chapter 5. This would most probably also be the case at Preem. For further development of this measure both technology and system aspects are of importance. The PhD project suggested here from Heat and power technology will deal with the system oriented parts.

As has been shown in Chapter 5.1, both pre combustion and post combustion techniques could be used. From earlier R&D work it is clear that there is no obvious “winner” concerning these two options. The optimal choice depends on the conditions, both technical and economic ones. In the project these two different principles will be studied and compared technically, economically and environmentally at different future scenarios concerning energy process, CO_2 emission costs, etc. The conditions at Preem refineries concerning geographical distances between CO_2 emission sources, centralised versus decentralised units and other important conditions will be used as an interesting case study.

As shown in Chapter 5 the choice of heating system for the desorption in post combustion techniques is crucial, both economically and environmentally. These aspects will be studied in detail in the project. Normally in process industries there is excess heat from the process, which can be used in the desorber. This is also true at Preem. In earlier comparison works between pre and post combustion techniques, this option has not been included. An important part of the project will therefore be to explore these opportunities and compare solutions with excess heat with other system solutions, both pre and post combustion ones. In order to this, a part of the work will be to identify process integration solutions, which maximise excess heat amounts and temperature levels. This will be done in cooperation with the CIT, IE activities, as described in Project 8.

The use of excess heat for desorption will be compared with other ways for heating, e.g. gas turbine combined cycle (produces also electricity), biomass boiler and heat pump (using low temperature waste heat). The ammonia absorption/desorption cycle will be the main one in the calculations but also other cycles, e g MEA, will be studied.

Excess heat can also be used for electricity production or heat pumping. This must be compared with using it for desorption at different future scenarios. In the CIT, IE project these two options will be studied and compared. In this project the results from CIT, IE will be used in the comparisons and analysis of the most optimal use of excess heat.

Finally, chemical looping and hydrogen production will be studied as a technology. In the project proposed here, these results will be used in system studies and this option will therefore be compared with the other processes for CO_2 separation on site. This part will include opportunities for integration of the waste heat from the chemical looping process.

9.3.3 Project 3: Hydrogen production by chemical-looping reforming with CO_2 capture

Hydrogen production by chemical-looping reforming with CO_2 capture will be studied as a technology. In the project proposed here, these results will be used in system studies and this option will therefore be compared with the other processes for CO_2 separation on site. This part will include opportunities for integration of waste heat from the chemical-looping reforming process.

In the project the following tasks will be addressed:

Task 1: Material selection/development and testing: Chalmers has a world-leading position in oxygen-transfer materials for CLC, and will draw from this in finding the proper materials for the CLR processes, and verify the suitability of these materials in comprehensive testing in two continuous reactors located at Chalmers, a 300 W and 10 kW chemical-looping combustors.

> Task 1.1 CLR process 1 in 300 W unit. Production of selected particles for testing in 300 W unit. Testing of various oxygen-carrier materials in the 300 W unit. Investigation of influence of parameters, e.g. fuel gas composition, temperature, gas flows, air ratio. Testing will be initiated early in the project using previously available materials that could be of interest, also allowing for establishment of the best testing and evaluation procedures.
>
> Task 1.2 Chemical-looping process 2 in 300 W unit. Production of selected particles for testing in 300 W unit. Testing of various oxygen-carrier materials in the 300 W unit. Investigation of influence of parameters.
>
> Task 1.3 Chemical-looping process 1 and 2 in 10 kW unit. From results of Task 1.1 and 1.2, some promising oxygen carriers will be produced and investigated in the Chalmers 10 kW unit. The oxygen carriers will be investigated in continuous operation for more than 100 h in order to validate performance and lifetime.

Task 2: The results obtained will be used in the development of integrated process schemes, sizing and costing for combined H_2/heat production.

9.3.4 Project 4: Co-gasification of biomass and petcoke as a powder to produce hydrogen

Biomass can be incorporated in a petroleum based fuel in many ways. One of these is to produce hydrogen which then is used for e.g. desulfurization and thereby comes into the fuel without changing the fuel properties. It has been shown, as pointed out in chapter 6.4.3, that the most efficient way for this production is by gasifying the biomass. If the biomass is co-gasified with petcoke, the efficiency has a potential of increasing even further. The reasons lay in the different composition (ratio of C:H:O and ash content) together with the high heating value of petcoke. Thereby, petcoke will only be upgraded but also enhances the usage of biomass, i.e. more amount of hydrogen can be produced from a certain amount of biomass.

The project aim at finding a possible route for the gasification and clarify the benefits with the co-gasification of biomass and petcoke. A survey will also be conducted about the available biomass (type and amount) that could be considered (at the research group of Chemical Environmental Science which are close together with the research group of Forest Products and Chemical Engineering, a long tradition has been to investigate different processes and system from a life cycle perspective). These different materials will then be evaluated in the laboratory to investigate the gasification performance. An important aspect is to develop a tool for estimation of the produced syngas composition after the gasifier. It will be collaboration with project 1, regarding the impact on a refinery site.

It is further of high importance to investigate about the necessary pre-treatment methods available and the energy consumption of these to produce the right feedstock properties, like dry content and size fraction.

9.3.5 Project 5: Usage of bio-oil on a refinery site; combustion and gasification.

At a refinery site today, there is an internal need of energy carriers for heating purposes. Some of these carriers, e.g. ethane, propane and butane, are already reined products that instead should be used for other purposes in the petrochemical industry. By introducing biomass for the heating purposes, a better usage of the incoming raw oil is achieved without a higher load for the environment. However, to make this transition as smooth as possible, the used replacement fuel should be a liquid. Therefore, pyrolysis oil, bio-oil, would be the suggested alternative. This project will collaborate with project 8, the CIT project, in order to find the best available positions for such a replacement and also investigate of how to achieve the preliminary product, the pyrolysis oil from bio-mass.

Another part in this project would be more research oriented and aim at finding a suitable way for co-gasification of petcoke and biomass, where the biomass is as pyrolysis oil. The reason for using pyrolysis oil, is the simpler handling of the incoming material (petcoke is generally described as a hard material to crush and therefore much energy would be used in such an operation but a slurry mixture could allow for a more energy efficient pre-treatment) and it also allows for a simpler feeding system into the gasifier. An important task within this project is to characterize the pyrolysis oil with respect to composition and fluid properties, such as viscosity and density, to be able to perform the mixing with petcoke properly as a first step and then to produce the wanted syngas after the gasifier. The project will thus include a study of available biomass for this purpose and an experimental part of how these pyrolysis oils behaves when gasified and especially when co-gasified with petcoke.

9.3.6 Project 6: Upgrading of tar

The high reactivity of the tar makes it impossible for direct refining. A stabilation process and a deoxygenating step is necessary if a diesel product is wanted. If a high aromatic gasoline is wanted there is also a high temperature zeolite (ZSM-5) treatment. But in this case we assume hydrogenation route. It is necessary to start with a light hydroprocessing or reducing stage between 200 and 250 degrees C. The catalyst should be a non acidic and of the sulfided type. In the literature high pressures above 10 MPa have been used and are of interested to develop a process or modified catalyst that can handle this at lower pressures like 5-6 MPa. The actual consumption of hydrogen is also important. Since this step also dries the tar the viscosity it will increase.

In the second stage at a higher temperature it is also important to make development to lower total pressures. In this case the acidity of the catalyst is critical and the promoting amount of Cobalt should be studied. The deoxygenation also reduces the molecular weight of the tar and this reduces the viscosity.

The objective is to convert the tar to a possible feed to the Preem oil refineries. It is likely that there will be only minor amounts of high boiling components. The majority of material should be in the boiling range for gasoline, jet fuel and diesel fuel.

The first part is to adopt the laboratory process for hydro processing a mixture of petroleum and different vegetable oils. Process ability, the effect of selection of process parameters and feed oil will be studied. Especially important is the ratio of decarboxylation and hydro deoxygenation. In this study both vegetable oils like rape seed oil, Fame from different sources and perhaps fat from animal sources like from pig and fish. This first part will be for 18 month. A new longer reactor is also planned.

9.3.7 Project 7: Isomerization of n-alkanes from fatty acids

In this project suitable catalyst has to be prepared and tested. Testing of isomerization catalysts are time consuming since the activity is initially high leading to a long time to get a stable yield before the actual testing can be done. The continues reactor have to be used for this testing.

The goal in this project is to develop a stand alone process which includes a thermal decarboxylation and a second hydro processing. The second step could also be a processing with LLGO or integrated with an isomerization step. The selection of detailed program will be decided later. The main effort in this second part is the isomerization of long alkanes.

The hydroprocessing of pyrolysis oil is going to use a two step approach: With a first reaction at 200-250 degrees and a second reaction above 300 degrees.

9.3.8 Project 8: Process integration at Preem refineries and result dissemination

The proposed research projects from Chalmers are related to the energy situation at the refineries. This project aims at supporting the Chalmers groups and Preem in applied energy related questions. The aims of this project are:

- Support the research groups with accurate energy data describing the refineries.
- In close cooperation with the Chalmers research groups and Preem carry out process integration studies.
- Perform short-term applied process integration studies in cooperation with Preem.
- Perform synthesis analyses based on the result from the Chalmers research groups.
- Support the Chalmers research groups in the dissemination of research results.

Below these subprojects are briefly described. The exact size of each subproject, within the budget frame, should each year be discussed and decided by the cooperation management.

The proposed research projects from the Chalmers groups are dependent of an accurate description, from an energy perspective, of the refinery processes. This description is the basis for the evaluation of the new concepts analyzed in the research projects. These evaluations are important in order to design energy efficient systems and to avoid suboptimizations. The energy situation is very site-dependent and therefore a good local knowledge is crucial. In this subproject energy related data for the processes should be determined and supplied to the research project according to their specific requests. The work should be carried out in close cooperation with appropriate personnel at the refineries. In this way the experience at the refineries can be utilized and practical considerations can be taken into account in an appropriate way. Since the design and operation of the refineries continuously changes energy data must also be upgraded in time intervals.

The concepts analyzed in the research groups should be evaluated in energy terms. Such evaluations include many practical considerations and constraints that must be taken into account in order to present realistic and reliable results. Furthermore these evaluations require a high competence within the field of process integration. Therefore it is suggested that CIT Industriell Energianalys should support these evaluations and together with Preem make sure that they are realistic. One example of such a possible evaluation is the competition between heat pumps and Organic Rankine Cycles when it comes to utilization of excess heat from the process.

It is foreseen that also more short-term and applied questions regarding energy efficiency at the refineries will be of interest for Preem. Therefore it is suggested that process integration competence and experience at CIT Industriell Energianalys should be used to carry out this type of studies together with Preem representatives. These studies could also be seen as internal competence improvement in the field of process integration at Preem.

In each of the proposed research projects concepts are evaluated from various perspectives. To get a complete picture, the concepts need to be compared under consistent economic, technical and environmental conditions. In this syntheses subproject general conclusions should be drawn to identify the most energy efficient alternatives for Preem in the future.

One of the most important issues in large research projects is to disseminate the results to appropriate groups. Researchers have a good tradition in scientific publication but dissemination to other groups is often overlooked. In this subproject it is suggested that CIT Industriell Energianalys should strengthen the dissemination by arranging seminars and prepare short information leaflets.

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Idag står vi inför en stor utmaning att dels minska våra utsläpp av växthusgaser, dels kunna hantera att de fossila resurserna minskar. Speciellt viktigt blir detta för en industri som nu är baserad på fossila råvaror och vars produkter till största delen ska användas för att generera värme eller kraft (antingen som el-generering eller som drivmedel) genom förbränning. Utmaningen blir att maximalt utnyttja den traditionella råvara som tas in och samtidigt öka andelen förnyelsebar råvara. Detta öppnar på samma gång upp för nya möjligheter.

I denna rapport presenteras resultat från en förstudie på uppdrag av Preem om möjliga sätt att möta dessa utmaningar belyst för en raffinaderiindustri. Resultaten visar på intressanta framtida möjligheter för utveckling av en hållbar produktion av framtidens fordonsbränslen.

Förstudien omfattar tre delstudier med inriktning på dels energieffektivisering, tillvaratagande av spillvärme och koldioxidavskiljning, dels bioraffinering avseende förgasning och hydrering av vegetabiliska oljor. En gemensam utgångspunkt för studierna har varit aktuella förhållanden vid Preems raffinaderier i Göteborg och Lysekil där mätdata har hämtats.