

# Een Kennisbank voor Alternatieve Warmteprocessen

A.K. Wemmers A. Motelica

ECN-E--10-059

Juli 2010

## Verantwoording

Deze studie is tot stand gekomen in opdracht van AgentschapNL. De studie is uitgevoerd onder ECN projectnummer 6.00005.

## Abstract

The purpose of this study is to design a knowledge base containing information relevant to the detection of increased energy efficiency in industrial processes. This information must be stored and made accessible to those involved in energy efficiency in industry.

What information is relevant is detected by going through the imaginary phases of an energy audit and to determine for each phase which information is needed, resulting in the following categories.

- 1. Energy use and production volumes of sectors;
- 2. Existing processes, divided into sub-processes, with the specific energy use, energy and exergybalances and exergy efficiency of sub processes;
- 3. Newly designed processes, divided into sub-processes, with the specific energy use, energy and exergy balances and exergy efficiency of sub processes;
- 4. Technology Descriptions.

Finally, as an example, the developed system is applied to the following processes: milk powder production, ammonia production and asphalt production.

## Keywords

Energy, Industrial Processes, Specific Energy Consumption, Database.

## Inhoud

Lijst va	an tabe	llen	4			
Lijst va	Lijst van figuren					
Samer	Samenvatting					
1.	Inleidir	ng	7			
2.	De ker 2.1 2.2	Inisbank Selectie van relevantie informatie Definitie van kengetallen 2.2.1 Het specifieke energiegebruik 2.2.2 Exergie rendement De structuur van de kennisbank	8 9 9 10			
3.	Het en	ergiegebruik van sectoren	15			
4.	Het en 4.1 4.2 4.3 4.4 4.5 4.6 4.7 4.8 4.9	ergiegebruik van processen Factsheet melkpoeder productie, 'referentieproces' Factsheet melkpoeder productie 'deelproces indamper' Factsheet melkpoeder productie 'gasturbine' Factsheet melkpoeder productie 'mechanische damprecompressie' Factsheet melkpoeder productie 'gasturbine en mechanische damprecompressie' Factsheet ammoniak productie 'referentieproces' Factsheet ammoniak productie 'membraanscheidingsproces' Factsheet asfaltproductie 'proces 1' Factsheet asfaltproductie 'proces 2'	16 16 17 17 18 19 20 21 22 23			
5.	Techn	ologie beschrijvingen	25			
6.	De wa	arde van de Kennisbank	26			
Refere	Referenties					
Bijlage A Analyses van het melkpoeder proces PM						
Bijlage	Bijlage B Analyse van het ammoniak proces					
Bijlage C		Voorbeeld van een technologiebeschrijving afkomstig uit 'PI-scans'				

## Lijst van tabellen

Tabel 3.1	Overzicht warmtegebruikende	processen in de Nederlandse	industrie
14001 5.1	oversient warmiegebraikenae	processen in de riederidnuse	<i>inuusini</i>

## Lijst van figuren

Figuur 2.1	Schematische weergave van een productieproces	10
Figuur 2.2	Een proces opgesplitst in deelprocessen en technologieën	11
Figuur 2.3	Exergie stromen door een deelproces of technologie	12
Figuur 2.4	Schematische weergave van de Kennisbank	13
Figuur 4.1	Voorbeeld van de factsheet van een 'bestaand' melkpoeder proces	16
Figuur 4.2	Voorbeeld van de factsheet van een 6-effect indamper in het 'bestaande'	
-	melkpoeder proces	17
Figuur 4.3	Factsheet van een melkpoederproces met gasturbine	18
Figuur 4.4	Factsheet van een melkpoederproces met indamper met mechanische	
	damprecompressie	19
Figuur 4.5	Factsheet van een melkpoederproces met indamper met mechanische	
-	damprecompressie en voorgeschakelde gasturbine	20
Figuur 4.6	Factsheet van het ammoniaksynthese proces	21
Figuur 4.7	Factsheet van een alternatief ammoniaksynthese proces	22
Figuur 4.8	Factsheet van een asfaltproductieproces	23
Figuur 4.9	Factsheet van een lage temperatuur asfaltproductieproces	24

## Samenvatting

Het doel van deze studie is het ontwerpen van een kennisbank waarin informatie die relevant is voor het opsporen van energie-efficiency verhoging in industriële processen op te slaan en toegankelijk te maken voor partijen die betrokken zijn bij energie-efficiency in de industrie.

Welke informatie relevant is wordt opgespoord door denkbeeldig de fasen van een energetische procesdoorlichting te doorlopen en voor iedere fase vast te stellen aan welke informatie behoefte is, resulterend in de volgende categorieën.

- 1. Het energiegebruik en de productievolumes van sectoren;
- 2. Bestaande processen, opgedeeld in deelprocessen, met het specifiek energiegebruik, de energie- en exergiebalansen en het exergierendement van deelprocessen;
- 3. Nieuw ontworpen processen, opgedeeld in deelprocessen, met het specifiek energiegebruik, de energie- en exergiebalansen en het exergierendement van deelprocessen;
- 4. Technologiebeschrijvingen.

Ten slotte wordt als voorbeeld de ontwikkelde systematiek toegepast op de processen melkpoederproductie, ammoniakproductie en asfaltproductie.

## 1. Inleiding

In Nederland worden sinds de jaren '90 tussen de overheid en de industrie op vrijwillige basis afspraken gemaakt met betrekking tot het verhogen van de energie-efficiency van industriële productie. De afspraken worden per sector gemaakt en vastgelegd in convenanten: de zogenoemde Meerjarenafspraken (MJA's). Op dit moment wordt de derde ronde (de MJA3) vormgegeven.

In de eerste twee MJA's is flinke vooruitgang geboekt met het verhogen van de energieefficiency. Voor de MJA3 ontstaat daardoor de behoefte aan een meer diepgravend instrumentarium om de mogelijkheden voor verdergaande energie-efficiency te identificeren. Dit meer diepgravende instrumentarium wordt door AgentschapNL vormgegeven in de *integrale aanpak*. De *integrale aanpak* kent twee instrumenten: de warmtescan en de kennisbank.

In de warmtescan wordt de energiehuishouding van processen of procesonderdelen diepgravend doorgelicht gebruikmakend van een breed assortiment thermodynamische analyse technieken zoals Pinch analyses, exergieanalyses, etc.

In de kennisbank wordt een deel van de informatie, die tijdens de warmtescans wordt verzameld, opgeslagen met als doel deze toegankelijk te maken voor partijen die warmtescans uitvoeren. De kennisbank wordt daarmee een levend onderdeel van de *integrale aanpak* waarin zowel informatie uit de warmtescans wordt toegevoegd en van waaruit informatie naar de warmtescans toevloeit. Dit rapport beschrijft de vormgeving van het technische deel van de kennisbank. Het draait hierbij om de vraag:

Hoe ziet een kennisbank eruit waarin relevante informatie over de energie-efficiency van industriële processen kan worden verzameld en toegankelijk gemaakt?

Andere aspecten zoals economische, juridische of vertrouwelijkheid van bedrijfsspecifieke informatie zijn geen onderdeel van dit rapport. In hoofdstuk 2 wordt het ontwerp van de kennisbank uitgelegd en worden de energetische kengetallen gedefinieerd die in de kennisbank worden opgenomen. In hoofdstuk 3 wordt op basis van informatie van het Centraal Bureau voor de Statistiek de kennisbank voor een deel gevuld met informatie over sectoren en enkele van de grootste energiegebruikende deelsectoren. In hoofdstuk 4 en verder worden voor enkele energie intensieve processen de energetische kengetallen, die in de kennisbank worden opgenomen, berekend.

## 2. De kennisbank

De behoefte om informatie te verzamelen die betrekking heeft op het energiegebruik van industriële processen is niet nieuw. Het Centraal Bureau voor de Statistiek (CBS) houdt bijvoorbeeld informatie over het verbruik van primaire energiedragers van productielocaties bij. In het verleden zijn productieprocessen al eens beschreven in de Spin documenten (RIVM) en in de NEEDIS documenten (Stichting NEEDIS). Door de Universiteit van Utrecht is een database met technologieën en hun effect op het energiegebruik (ICARUS) ontwikkeld.

Kenmerkend voor de *integrale aanpak* is dat statistische energie-informatie, energie-informatie van specifieke processen en technologieën in de Kennisbank moeten worden verzameld, zodanig dat die energie-informatie ondersteunend wordt aan het opsporen van energiebesparingen. De informatie van het CBS zegt alleen iets over productielocaties, niet over de productieprocessen. De systematiek zoals gebruikt in de SPIN en NEEDIS documentatie zijn te beschrijvend en te generiek. De ICARUS database is te veel op alleen technologieën en te weinig op de processen georiënteerd. Voor de Kennisbank wordt daarom een nieuwe informatiestructuur met bijbehorende energiekengetallen ontworpen. De eisen die daarbij aan de verzamelde informatie worden gesteld is dat zij:

- 1. Ondersteunend is bij het opsporen van energiebesparingen in industriële processen;
- 2. Iets zegt over het besparingspotentieel van alternatieve processen en alternatieve technologieën.

#### 2.1 Selectie van relevantie informatie

Om te achterhalen welke informatie voldoet aan de bovengestelde eisen wordt een warmtescan van een proces denkbeeldig doorlopen. Onder een proces wordt hier verstaan een serie bewerkingen (deelprocessen) die, gebruik makend van grondstoffen en energiedragers, één of meerdere producten oplevert. De verschillende fasen die bij het uitvoeren van een warmtescan worden doorlopen worden in onderstaande paragrafen beschreven. Van iedere fase kan zodoende worden vastgesteld welke informatie relevant is voor de kennisbank.

#### Oriënterende fase

Bij een doorlichting wordt als eerste informatie verzameld van het verbruik van primaire energiedragers en elektriciteit en de productievolumes. Op basis van deze getallen kan het specifieke primaire energiegebruik worden berekend.

Binnen een sector wordt over het algemeen hetzelfde product met meerdere productieprocessen vervaardigd. Gebruik makend van het specifieke energiegebruik van een bepaald proces kan door onderling vergelijk binnen de sector verbetering van de energie-efficiency worden opgespoord.

Door het specifieke energiegebruik te vermenigvuldigen met de productievolumes ontstaat een beeld van het totale besparingpotentieel van de alternatieve processen binnen de sector.

Het energiegebruik, de productievolumes en het hieruit berekende specifieke energiegebruik van sectoren is relevante informatie om in de Kennisbank op te nemen. Het ligt voor de hand om hierin de sector indeling van het CBS te volgen.

#### Analyse fase, het opstellen van massa-, energie- en exergiebalansen

Om het energiegebruik van een proces te analyseren wordt het proces opgedeeld in deelprocessen. Een deelproces vervult een functie binnen het totale proces, bijvoorbeeld drogen, scheiden, reageren, etcetera. Van het proces en de deelprocessen worden de massa-, energie- en exergiebalansen bepaald. Gebruikmakend van de resultaten uit de massa-, energie en exergiebalansen wordt van het proces het specifieke energiegebruik berekend en van de deelprocessen het exergierendement.

Er ontstaat nu een beeld in welke mate het specifieke primaire energiegebruik wordt bepaald door het proces ontwerp, bijvoorbeeld doordat meerdere processen op een productielocatie met elkaar zijn geïntegreerd, of door de gebruikte deelprocessen. Daarnaast worden eventuele alternatieve deelprocessen met een hoger exergierendement dan de deelprocessen in het huidige proces gevonden.

De energie- en exergiebalansen van het proces en van de deelprocessen is revelante informatie om in de Kennisbank op te nemen. Processen worden gekenmerkt door het specifieke energiegebruik, deelprocessen door het exergierendement.

#### Fase van proces herontwerp

Gebruikmakend van de massa- en energiebalansen en de eventueel gevonden alternatieve deelprocessen wordt door procesherontwerp het besparingspotentieel opgespoord. Doordat aanpassingen in een proces elkaar onderling beïnvloeden moet het effect op het primaire energiegebruik voor iedere aanpassing en iedere combinatie van aanpassingen worden berekend.

De energie- en exergiebalansen van de nieuw ontworpen processen is revelatie informatie om in de kennisbak op te nemen. Nieuw ontworpen processen worden gekenmerkt door het specifieke energiegebruik.

#### Herontwerp van deelprocessen

Analoog aan de werkwijze van proces herontwerp kunnen deelprocessen worden herontworpen. Hierbij wordt gebruik gemaakt van technologieën die in de Kennisbank zijn opgenomen.

Beschrijvingen van technologieën is revelatie informatie om in de Kennisbank op te nemen. Het exergierendement van een technologie is onderdeel van de beschrijving.

#### Resumé

Samenvattend is de relevante informatie in te delen in de volgende categorieën.

- 1. Het energiegebruik en de productievolumes van sectoren;
- 2. Bestaande processen, opgedeeld in deelprocessen, met het specifiek energiegebruik, de energie en exergiebalansen en het exergierendement van deelprocessen;
- 3. Nieuw ontworpen processen, opgedeeld in deelprocessen, met het specifiek energiegebruik, de energie en exergiebalansen en het exergierendement van deelprocessen;
- 4. Technologiebeschrijvingen.

#### 2.2 Definitie van kengetallen

In hoofdstuk 2.1 worden 2 kengetallen als maat voor de efficiency van het energiegebruik genoemd: het specifieke energiegebruik [GJ/ton<sub>product</sub>] en het exergierendement. In onderstaande hoofdstukken 2.2.1 en 2.2.2 wordt gedefinieerd hoe deze kengetallen worden berekend.

#### 2.2.1 Het specifieke energiegebruik

In de meest eenvoudige vorm kan een proces volgens onderstaande figuur worden weergegeven.



Figuur 2.1 Schematische weergave van een productieproces

#### Eén product, product en grondstoffen hebben dezelfde chemische samenstelling.

In het eenvoudigste geval wordt één product gemaakt uit één grondstof waarbij chemische energie-inhoud van de grondstof en het product hetzelfde zijn, bijvoorbeeld bij de productie van papier uit cellulose of oud papier. Het energiegebruik van het proces wordt uitgedrukt in de hoeveelheid primaire energie (olie, kolen, aardgas, etc) per ton product. Door het energiegebruik van het proces uit te drukken in primaire energie worden de energieconversie processen tot het proces gerekend. De energieconversie kan plaatsvinden bij het proces bijvoorbeeld stoomopwekking in een ketel of daarbuiten, bijvoorbeeld elektriciteitsopwekking in een centrale. Het primaire energiegebruik van elektriciteit wordt berekend met behulp van het gemiddelde centralerendement van 41%.

#### Eén product, product en grondstoffen hebben verschillende chemische samenstelling.

In sommige productieprocessen (staal, plastics, brandstoffen) wordt een deel van de grondstoffen energetisch gebruikt. Het energetische gebruik wordt bepaald door het verschil tussen de energie-inhoud van de grondstoffen en de energie-inhoud van het product of de producten. Het totale energiegebruik wordt dan [primaire energiedragers + (energie-inhoud grondstoffen energie-inhoud product(en) )] / tonnen product(en).

#### Meerdere producten uit één proces

In sommige productieprocessen worden meerdere producten gemaakt. Het energiegebruik wordt aan afzonderlijke producten toegekend naar rato van de chemische exergiewaarde van de producten.

### 2.2.2 Exergie rendement

Door het proces op te splitsen in deelprocessen en technologieën ontstaan functionele eenheden waar processtromen doorheen lopen en secundaire energiedragers aan worden toegevoerd. Deze opsplitsing wordt in Figuur 2.2 schematisch weergegeven.



Figuur 2.2 Een proces opgesplitst in deelprocessen en technologieën

Het effect op het specifieke primaire energiegebruik van deelprocessen of technologieën is alleen te bepalen door het deelproces of de technologie in het proces op te nemen en de gevolgen te berekenen. Dit komt omdat de eerste hoofdwet van de thermodynamica, de wet van behoud van energie, geen onderscheid maakt naar de aard van de energiestromen. Op basis van een energiebalans kan daardoor geen uitspraak kan worden gedaan over de energetische effectiviteit van het beschouwde proces. De toegevoerde energie is immers altijd gelijk aan de afgevoerde energie.

Het specifieke energiegebruik wordt bepaald door de alleen de primaire energiedragers en het energetische deel in de grondstoffen te selecteren en te bepalen hoeveel van deze geselecteerde energiedragers nodig zijn om het product of de producten te maken. Kennelijk hebben niet alle energiestromen in de energiebalans dezelfde waarde.

Om een uitspraak te kunnen over de effectiviteit van het energiegebruik van een deelproces moet een generieke maat voor de waarde van processtromen en (secondaire) energiedragers worden gezocht. In de thermodynamica is deze generieke maat het vermogen van een processtroom of energiedrager om *arbeid* te verrichten.

#### Exergie

De exergie van een materiaal of een energiedrager is de maximale hoeveelheid arbeid die kan worden verkregen door het materiaal of de energiedrager via een omkeerbaar proces naar een inerte referentietoestand te brengen (Van Gool).

De mate waarin exergie in een proces verloren gaat zegt daardoor iets over de effectiviteit van het energiegebruik van dat proces. Het saldo van de exergie van alle ingaande en uitgaande processtromen en energiedragers van een deelproces of een technologie, het exergieverlies of de irreversibiliteit (I), is de hoeveelheid arbeid die minimaal nodig is om het proces te laten plaatsvinden. Vanwege het feit dat de exergie van primaire energiedragers als olie, kolen en gas vrijwel gelijk is aan de stookwaarde, is de exergie tevens een maat voor de hoeveelheid primaire energiedragers die minimaal nodig zijn om het proces te laten plaatsvinden.

#### Exergie rendement

In Figuur 2.3 wordt een deelproces met in- en uitgaande exergiestromen schematisch voorgesteld.



Figuur 2.3 Exergie stromen door een deelproces of technologie

Een rendement is het quotiënt van de nuttige opbrengst en het verbruik. Bij het bepalen van het exergierendement van een deelproces of technologie wordt de nuttige exergetische opbrengst bepaald door de functie van het deelproces of de technologie. De nuttige exergie van een stoomketel is bijvoorbeeld het verschil van de exergie van de stoom en de exergie van het voedingswater. De verbruikte exergie is het saldo van de overige proces- en energiestromen. In het geval van de stoomketel de brandstof, rookgasverliezen, spuiverliezen, etc.

In formulevorm wordt exergierendement  $(\eta_{ex})$  van het deelproces of de technologie uit Figuur 2.3 geschreven als:

$$\eta_{ex} = \frac{nuttige \ exergie \ verandering}{gebruikte \ exergie} = \frac{exergie_{uir;1} - exergie_{in;1}}{exergie_{in;2} + exergie_{in;3} - exergie_{uir;2}}$$
(I)

Met behulp van de irreversibiliteit (I), in formulevorm geschreven als:

$$I = \sum exergie_{in} - \sum exergie_{uit}$$
(II)

Kan als alternatief voor (I) het exergierendement geschreven kan worden als:

$$\eta_{ex} = \frac{nuttige \ exergie \ verandering}{I + nuttige \ exergie \ verandering} \tag{III}$$

De hier gebruikte definitie van exergierendement wordt het rationele exergierendement genoemd. In de literatuur wordt ook het simpele exergierendement gebruikt. Het simpele exergierendement is het quotiënt van in- en uitgaande exergiestromen. Het gebruik van het rationele exergierendement verdient de voorkeur omdat het wordt gebaseerd op functie die het deelproces of de technologie vervult in plaats van op alle uitgaande stromen.

#### Vormen van exergie

De exergie van materialen en energiedragers wordt in 2 hoofdcategorieën ingedeeld: de fysische exergie en de chemische exergie. De fysische exergie is het arbeidspotentieel wat samenhangt met de fysische grootheden van het materiaal of de energiedrager zoals de druk, de kinetische energie, de temperatuur etcetera. De chemische exergie is het arbeidspotentieel van een chemische verbinding. Voor de berekening van exergie wordt verwezen naar de literatuur zoals (Van Gool), (Kotas), (Dincer, Rosen), (Cornelissen).

## 2.3 De structuur van de kennisbank

De informatie die in de kennisbank moet worden opgenomen kan denkbeeldig worden gestructureerd in een driedimensionale matrix. Deze drie dimensionale matrix wordt weergegeven in Figuur 2.4.



Figuur 2.4 Schematische weergave van de Kennisbank

In Figuur 2.4 wordt 1 proces, opgebouwd uit deelprocessen, weergegeven. Dit proces kan bijvoorbeeld zijn de vervaardiging van papier en karton voor verpakking (SBI- 2008 17.12.2). Dit proces komt in 8 fabrieken VNP) in Nederland voor. Door het specifieke energiegebruik van deze processen naast elkaar in de Kennisbank op te nemen worden onderlinge verschillen zichtbaar en kunnen potentiële verbeteringen worden opgespoord.

Door vermenigvuldiging van het specifieke energiegebruik van een proces met het productie volume uit de CBS gegevens ontstaat een beeld van de prestatie van dat proces ten opzichte van het (productievolume gewogen) gemiddelde van de sector volgens de CBS gegevens. Door

vermenigvuldiging van het proces met het laagste specifieke energiegebruik met het productievolume ontstaat een beeld van het besparingspotentieel.

Gebruikmakend van de exergierendementen van alternatieve deelprocessen die in de kennisbank zijn opgenomen kunnen potentieel efficiëntere deelprocessen worden opgespoord. Door toepassing van het deelproces in het proces ontstaat een beeld van mate waarin procesherontwerp nodig is en het besparingspotentieel van het alternatieve deelproces.

Gebruikmakend van de exergierendementen van technologieën die in de kennisbank zijn opgenomen kunnen potentieel efficiëntere technologieën worden opgespoord. Door toepassing van een technologie in een deelproces ontstaat een beeld van mate waarin het exergierendement van deelprocessen kan worden verbeterd.

## 3. Het energiegebruik van sectoren

Informatie over sectoren wordt uit de statistieken van het CBS gehaald. Vanwege de grote rol die warmte speelt in industrie heeft ECN, gebruik makend van CBS gegevens en de ECN database chemische industrie, een overzicht gemaakt van de warmtegebruikende processen in Nederland.

Aan de hand van dit overzicht wordt een indruk verkregen van het warmtegebruik in de Nederlandse industrie. Mede op basis van dit overzicht is gekozen voor melkpoeder- en ammoniakproductie als voorbeelden voor uitwerking in hoofdstuk 4.

Door PDC en TUE is een energiestudie bij Ooms Avenhorn Asfaltcentrale in Schagen uitgevoerd. Van deze analyse zijn op verzoek van AgentschapNL twee opties geselecteerd en als factsheets opgenomen.

	warmte [PJ/a]		
	sector	proces	
Voedings- en genotmiddelen	61		
Suiker		6,2	
Zuivel		9,1	
Bakkerijen		9,6	
Papier en karton	16,7	16,7	
Anorchanische baisischemie	18		
Organische basischemie*	207		
Ethyleen/propyleen		79,8	
Stryreen		42,6	
Ammonia		22,4	
Waterstof		7,7	
Propyleen oxide		7,6	
Benzeen		6,4	
Caprolactam		6,2	
Polyethyleen		5,2	
Overige basischemie	34,8		
Raffinage	110	110	
Bouwmaterialen	23,6		
glas		7,9	
keramiek		7,0	
Metaal	57,8		
basismetaal		35	
Overig	47,1		
totalen	576	379	

 Tabel 3.1
 Overzicht warmtegebruikende processen in de Nederlandse industrie

\*NB onderverdeling organische basischemie op basis van het totale energiegebruik, niet alleen het warmtegebruik

## 4. Het energiegebruik van processen

Het energiegebruik van processen en deelprocessen wordt verzameld op factsheets. ECN heeft op basis van de openbare literatuur en aangenomen procesdata voor melkpoeder productie en voor ammoniak productie een procesanalyse gemaakt en de procesdata opgenomen in factsheets. De gedetailleerde analyses zijn als bijlagen opgenomen.

### 4.1 Factsheet melkpoeder productie, 'referentieproces'

Het referentieproces is het proces zodat bij het uitvoeren van een Warmtescan wordt aangetroffen. In figuur 4.1 wordt de factsheet van dit proces weergegeven. Details van de berekeningen zijn in Bijlage A opgenomen.



Figuur 4.1 Voorbeeld van de factsheet van een 'bestaand' melkpoeder proces

## 4.2 Factsheet melkpoeder productie 'deelproces indamper'

Van het deelproces '6 effect indamper' wordt in een factsheet 'indampen' gedetailleerde informatie van dit type indamper opgenomen.



Figuur 4.2 Voorbeeld van de factsheet van een 6-effect indamper in het 'bestaande' melkpoeder proces

#### Zoeken op functie

Door het analyseresultaat van de indamper uit de Warmtescans als deelproces 'indampen' in de kennisbank op te nemen wordt het mogelijk informatie over de toepassing van indampers in verschillende processen in alle sectoren op te sporen. Daarnaast wordt informatie gevonden over welke types indampers er bestaan, hoe ze functioneren, in welke processen ze worden toegepast en welke technologieën worden gebruikt.

### 4.3 Factsheet melkpoeder productie 'gasturbine'

In Figuur 4.1 is te zien dat het exergierendement van het verwarmen van de drooglucht laag 0,16 bedraagt. Door voorschakeling van een gasturbine en gedeeltelijk herontwerp van het proces kan het exergierendement worden verhoogd naar 0,35. De resultaten zijn opgenomen in de factsheet van Figuur 4.3.



Figuur 4.3 Factsheet van een melkpoederproces met gasturbine

Door dit alternatieve proces in de Kennisbank op te nemen komt het idee van de combinatie van een gasturbine en een luchtverhitter beschikbaar voor Warmtescans bij andere bedrijven.

### 4.4 Factsheet melkpoeder productie 'mechanische damprecompressie'

In plaats van een thermisch aangedreven verdamper kan ook met mechanische damprecompressie worden gewerkt. Dit alternatief is uitgewerkt en in onderstaande factsheet weergegeven in Figuur 4.4.



Figuur 4.4 Factsheet van een melkpoederproces met indamper met mechanische damprecompressie

# 4.5 Factsheet melkpoeder productie 'gasturbine en mechanische damprecompressie'

Tenslotte zijn de gasturbine en de mechanische damprecompressie gecombineerd, het resultaat wordt in onderstaande factsheet weergeven in Figuur 4.5.



Figuur 4.5 Factsheet van een melkpoederproces met indamper met mechanische damprecompressie en voorgeschakelde gasturbine

## 4.6 Factsheet ammoniak productie 'referentieproces'

Ammoniak kan uit verschillende grondstoffen worden geproduceerd. In het factsheet (Figuur 4.5) is het deelproces 'synthese' opgenomen. Details van de berekeningen zijn in Bijlage B opgenomen.



Figuur 4.6 Factsheet van het ammoniaksynthese proces

### 4.7 Factsheet ammoniak productie 'membraanscheidingsproces'

In plaats van de ammoniak door middel van koeling en condensatie uit het mengsel van ammoniak, waterstof en stikstof te scheiden kan de ammoniak ook met behulp van een membraan worden gescheiden. Het factsheet voor het membraanscheidingsproces wordt in Figuur 4.7 weergegeven.



Figuur 4.7 Factsheet van een alternatief ammoniaksynthese proces

## 4.8 Factsheet asfaltproductie 'proces 1'

Door het Proces Design Centre (PDC) is een warmtescan van de productie van asfalt uit gerecycled asfalt opgesteld. Gebruikmakend van deze informatie zijn twee factsheets opgesteld, één voor een generiek standaard proces en één voor een generiek lage temperatuurproces. Voor een goede samenhang tussen de Warmtescan en de Kennisbank is het aan te bevelen om factsheets van de geanalyseerde processen en de gevonden alternatieven een deliverable van een warmtescan te maken.



Figuur 4.8 Factsheet van een asfaltproductieproces

## 4.9 Factsheet asfaltproductie 'proces 2'

Eén van de door PDC onderzocht verbeteropties is een lage temperatuur proces. Het factsheet van dit proces wordt onderstaand weergegeven.



Figuur 4.9 Factsheet van een lage temperatuur asfaltproductieproces

## 5. Technologie beschrijvingen

Technologieën, zoals warmtewisselaars, pompen, reactoren, ventilatoren, etcetera zijn de kleinste bouwstenen van een proces. Technologieën worden zeer veel toegepast. Door voor ieder proces en voor ieder herontworpen proces informatie van een technologie in de kennisbank op te nemen wordt de Kennisbank belast met een grote hoeveelheid gegevens. Daar komt bij dat al deze gegevens ten opzichte van elkaar nauwelijks nieuwe informatie bevatten. Voor informatie over technologieën wordt in de Kennisbank daarom de technologie, en niet langer het proces of het deelproces, centraal gesteld.

Door de technologie centraal te stellen wordt in de technologiebeschrijvingen op één plaats gedetailleerde informatie over die technologie gegeven. Als format is bijvoorbeeld het format zoals dat is gebruikt voor de PI-scans goed geschikt. Het format van de PI-scans is als bijlage C toegevoegd.

Door technologieën centraal te stellen ontbreekt de procesinformatie waarmee het exergierendement kan worden berekend. In de Kennisbank wordt als alternatief een uitgewerkte definitie van het exergierendement opgenomen. Uitgewerkte definities van het exergierendement van technologieën worden in de literatuur onder anderen gegeven in [Cornelissen, Dincer, Kotas].

## 6. De waarde van de Kennisbank

De kennisbank is bedoeld als onderdeel van de *Integrale aanpak* die bestaat uit Warmtescans en de Kennisbank. De functie van de kennisbank is om relevante informatie uit Warmtescans te verzamelen en beschikbaar te maken voor volgende Warmtescans. In hoeverre de hier ontworpen Kennisbank in deze functie voorziet wordt nagegaan aan de hand van de belangrijkste kenmerken van de Kennisbank.

In de kennisbank wordt informatie verzameld van:

- 1. Het CBS over het specifieke energiegebruik van sectoren. Met behulp van deze informatie kan worden bepaald hoe groot het verbeterpotentieel van bestaande of nieuw ontworpen processen is;
- 2. Het ontwerp van bestaande en nieuw ontworpen processen in de vorm van factsheets met het specifieke energiegebruik. Met behulp van deze informatie kan gericht worden gezocht naar verbeteringen binnen sectoren.
- 3. Het ontwerp van functionele eenheden in processen, de deelprocessen, in de vorm van factsheets met het rationele exergie rendement. Met behulp van deze informatie kan, over sectoren heen, gericht worden gezocht naar alternatieve deelprocessen met een betere prestatie.
- 4. Technologieën. Technologiebeschrijvingen ondersteunen het herontwerpen van (deel)processen.

Geconcludeerd kan worden dat de voorgestelde Kennisbank voldoet een de eisen die de *integrale aanpak* er aan stelt.

#### Kanttekening bij het exergierendement

In de kennisbank is er, in overleg met AgentschapNL en CCS B.V., voor gekozen om het rationele exergierendement als maat voor de prestatie van deelprocessen en technologieën te kiezen. Van doorslaggevend belang voor de betekenis van het rendementsgetal is de keuze van de nuttige prestatie. De functie van een droog- of indampinstallatie is het verwijderen van water. Voor droog- en indampprocessen wordt hier daarom in navolging van Dincer [6] de exergie van de waterdamp (drogen) of het water (indampen) als de nuttige prestatie gekozen. Zoals in de case van het sproeidrogen is te zien is het rendementsgetal voor de sproeidroger hoger dan voor de indamper. Dit zou kunnen leiden tot de foute conclusie dat de sproeidroger beter presteert dan de indamper.

De keuze van Dincer voor de uitgaande waterdamp wordt niet gemotiveerd maar komt vermoedelijk voort uit het feit dat de meng exergie in vloeistoffen over het algemeen klein is ten opzichte van de chemische en fysische exergie. Wordt voor een droogproces het ontmengen als de nuttige functie gekozen dan is het rendementsgetal ongeveer nul. De meer zuivere keuze van de nuttige functie, het ontmengen, leidt daardoor tot rendementsgetallen die weinig betekenis meer hebben.

Als alternatief is zou de afstand tot het thermodynamisch minimum als maat kunnen worden genomen bijvoorbeeld door de irreversibiliteit van een droogproces te delen door de (ont)meng exergie.

#### Referenties

- Alsema, E.A., Nieuwlaar, E., *ICARUS-4 A database for energy efficiency measures in the Netherlands* 1995 – 2020, ISBN 90-73958-70-9, September 2001.
- Cornelissen, R. et al., *Equations and structure used in OptiJoule versie 1.3*, Intern document CCS, Postbus 780, 7400 AT DEVENTER, 2010.
- Dincer, I., Rosen M.A. Exergy, Elsevier, ISBN 978-0-08-0044529-8, 2007.
- Gool, W. van, *Energie en exergie*, Van Gool ESE Consultancy, ISBN 90-804468-1-5, Driebergen, 1989.
- Koninklijke Vereniging van Nederlandse Papier- en kartonfabrieken, VNP., *Papiersoorten*, Postbus 731, 2130 AS Hoofddorp.
- Kotas, T.J., *The exergy method of thermal plant design*, Krieger Publishing Company Florida, 1985.
- RIVM, Samenwerking Procesbeschrijving Industrie Nederland (SPIN)., PO Box 1, 3720 BA Bilthoven.
- Stichting NEEDIS, Nationaal Energie-efficiency Data Informatie Systeem (NEEDIS)., Postbus 1, 1755 ZG Petten
- Universiteit van Utrecht, ICARUS is a database of technological options for energy efficiency measures, inventoried for all economic sectors in the Netherlands., Utrecht Centre for Energy Research, Van Unnikgebouw, Heidelberglaan 2.
- Vleeming, H. et al. *Integrale aanpak procesverbetering*. *Prépilot bij een asfaltcentrale*. *Versie* 3.2, 29 oktober 2010. PDC Postbus 7052 4800- GB Breda.

Bijlage A Analyses van het melkpoeder proces PM













Gronings gas HHV 35,10 MJ/m3 LHV 31,67 MJ/m3 luchtbehoefte 8,528 m3/m3 luchtovermaat 1,2 dichtheid 0,833 kg/m

ketel

gewenste exergieverandering is het maken van stoom uit condensaat

- exergie condensaat 0,03
- exergie stoom 0,87
- nuttige verandering 0,84
  - Irreversibiliteit 1,82
    - η<sub>i</sub> 0,32

Wa	armte G	J		exergie	e [GJ]
	in	uit		in	uit
aardgas	2,53		aardgas	2,65	
conden. 1	0,32		conden. 1	0,03	
rookgas		0,20	rookgas		0,00
10 bar stoom		2,65	10 bar stoom		0,87
=	2,85	2,85	-	2,69	0,87



#### Vacuümindamper 6-effecten





GJ ηi 5,11 0,32 6,47 0,28 8,52 0,25

#### Melkpoeder productie MDR indamper en gasturbine voor de toren



sproeitoren				exerg	jie [GJ]				
	mass	a ton	warm	te GJ		in	uit	gewenste exergieverandering is veplaatsen water	
	in	uit	in	uit	dikmelk	. ####		uit dikmelk naar water in de lucht	exergie water in de dikmelk #####
dik melk	2,10		0,28		aardgas	7,36			exergie water in de lucht ######
lucht toren	19,11	20,22	0,45	4,64	lucht torenverhitte	r 0,00			nuttige exergie drogen ######
aardgas			7,1		lucht fluidized bec	0,00			
elektriciteit				1,51	rookgas	5	#####		geleverde elektriciteit 1,51
rookgas				1,55	torenluch		#####		
lucht fluidized bed	2,01	2,01	0,14	0,15	melkpoede	r	#####		totaal nuttige exergie ######
melkpoeder		1,00		0,10	elektriciteit		1,51		
-	23,22	23,22	7,94	7,94		####	#####		Irreversibiliteit #####
									ŋ, #####
								luchtverhitter/GT combinatie	
					warmte GJ		exergie	[GJ]	

gewenste exergieverandering is opwarmen van de lucht elektriciteitopwekking_	1,04 1,51
=	2,54
Irreversibiliteit	4,81
η	0,346

```
        warmte GJ
        exergie [GJ]

        in
        uit
        in
        uit

        lucht 0,45 4,48
        lucht 0,40
        aardgas 7,36
        elefcriciteit 1,51
        lucht 1.04

        rookgas
        1,55
        rookgas ####
        1,51
        rookgas ####

        7,53
        7,53
        elek
        1,7,36
        ####
```


#### Melkpoeder productie MDR indamper en gasturbine voor de toren

	MDR ind	amper	
	massa ton	energie GJ	exergie GJ
	in uit	in uit	in uit
melk 1	9,70	0,23	0,00
stoom	0,20	0,55	######
dikmelk	2,11	0,37	0,02
condensaat	7,59	0,51	0,00
condensaat	0,20	0,15	#####
elektriciteit		0,25	0,25
=	9,90 9,90	1,03 1,03	###### ######

gewenste exergieverandering is het verplaatsen van water uit de melk naar condensaat

exergie water in de melk 0,00

exergie water in de condensaten 0,00

Irreversibiliteit #####

η<sub>i</sub> #####



m	assa ton	war	rmte GJ				exergi	e [GJ]			
	in	uit	in	uit			in	uit	gewenste exergieverandering is veplaatsen water		
dik melk	2,11		0,37			dikmelk	0,02		uit dikmelk naar water in de lucht exergie water in de dikr	ielk	0,02
lucht toren	18,50	19,61	0,43	4,59		aardgas	6,27		exergie water in de l	icht #	<b>V###</b>
aardgas			6,27		luch	t torenverhitter	0,00		nuttige exe	gie #	<b>V###</b>
rookgas				2,37	luch	nt fluidized bed	0,01				
lucht fluidized bed	2,01	2,01	0,14	0,15		rookgas		*****	Irreversibi	teit	5,82
melkpoeder		1,00		0,10		torenlucht		*****		η,##	<i><b>4</b>###</i>
-	22,62	22,62	7,20	7,20		melkpoeder		*****			
					luch	t fluidized bed		*****			
							6.30	#####			
								luch	itverhitter		
		war	rmte GJ			exergie (GJ)					
			in	uit		in uit			gewenste exergieverandering is opwarmen van de lucht 1.01		
		lucht	0,43		lucht	0,00			Irreversibiliteit 5,47		
	aa	rdgas	6,27		aardgas	6,52			n, 0,155		
		lucht		4,33	lucht	1,01					
	roo	okgas		2,37	rookgas	*****					
			6 70	6 70		6.52 #####					
			-,	-,							
									toren		
		war	rmte GJ			exergie [GJ]			gewenste exergieverandering is		
			in	uit		in uit			gewenste exergieverandering is veplaatsen water exergie water in de dikr	ielk	0,02
		lucht	4,33		lucht	1,01			uit dikmelk naar water in de lucht exergie water in de l	icht #	<i><b><i><b>W</b>MM</i></b></i>
	dił	kmelk	0,37		dikmelk	0,02			nuttige exe	gie #	<i><b>4</b>###</i>
		lucht		4,59	lucht	*****					
	рое	der 1		0,11	poeder 1	######			Irreversibi	teit #	<i><b>4</b>###</i>
		-	4,70	4,70	-	1,03 #####				η; #	<i></i>

#### Melkpoeder productie MDR indamper en gasturbine voor de toren



	s	proeito	ren				exe	gie [GJ	]		
	mass	a ton	warm	te GJ			ir	n uî		gewenste exergieverandering is veplaatsen water	
	in	uit	in	uit			dikmelk 0,02	2		uit dikmelk naar water in de lucht	exergie water in de dikmelk 0,02
dik melk	2,11		0,37				aardgas 7,13	3			exergie water in de lucht ######
lucht toren	18,50	19,61	0,43	4,59	lu	cht tore	enverhitter 0,00	)			nuttige exergie drogen #####
aardgas			6,9		l.	ucht flui	dized bed 0,00	)			
elektriciteit				1,46			rookgas	#####			geleverde elektriciteit 1,46
rookgas				1,50		;	torenlucht	#####			
lucht fluidized bed	2,01	2,01	0,14	0,15		m	elkpoeder	#####			totaal nuttige exergie ######
melkpoeder		1,00		0,10		e	ektriciteit	1,46			
	22.62	22.62	7.79	7.79			7.1	5 ####	-		Irreversibiliteit #####
											ŋ, #####
										luchtverhitter/GT combinatie	
					warmte	GJ		exerg	ie [GJ]		
					in	uit		ir	uit	gewenste exergieverandering is opwarmen van de lucht 1,0	l .
				1	ucht 0,43	4,33	luch	t 0,00		elektriciteitopwekking 1,4	3
				aar	dgas 6,85		aardga	s 7,13		2,4	3
				electri	citeit	1.46	luch	t í	1.01		
				roo	kgas	1,50	rookga	s	####	Irreversibiliteit 4,6	5
					7.29	7.29	elek		1 46	n. 0.34	1
								-			

uit		in	uit	gewenste exergieverandering is opwarmen van de lucht 1,0	1
33	lucht	0,00		elektriciteitopwekking 1,48	ô
	aardgas	7,13		2,44	ô
46	lucht		1,01		
50	rookgas		###	Irreversibiliteit 4,65	ō
29	elek		1,46	η, 0,34	ô
	-	7,13	###		

Bijlage B Analyse van het ammoniak proces

Exergy analysis in Ammonia production

## Abstract

In the framework of sustainable development, the process industry is interested in improving and developing more energy efficient processes. This calls for a need of a set of methodologies with which to asses the relative merits of alternative and novel technologies.

This report is meant to describe a methodology of exergy analysis applied to chemical processes. The described methodology is compiled based on open literature sources and many references available in field of exergy analysis. Further, the methodology is used to investigate, as an example, the ammonia synthesis loop that is considered to be one the most energy intensive processes. For this case, two technology routes are analysed: the classical route where the ammonia is removed from the synthesis loop trough refrigeration and a novel route in which ammonia is removed selectively trough membrane. The proposed methodology of exergy analysis shows that membrane separation route is more energy efficient leading in savings of about 22% in terms of primary energy use and 9% reduction in exergy destroyed when compared to refrigeration, if the membrane is 100 % selective for the ammonia. The analysis also shows that the most of exergy (~ 75%) is destroyed in reactor unit in both processes.

### Keywords

Exergy, methodology, exergy analysis, process analysis, energy efficiency, exergy efficiency, rational efficiency

## Contents

List c	of tables		4
List c	of figures	3	4
List c	of notatic	ons	5
1.	Introd 1.1 1.2 1.3	uction Scope of this study Concept of exergy Energy intensive processes	6 6 7 8
2.	Exerg 2.1	y analysis methodology Exergy of material stream 2.1.1 Chemical exergy 2.1.2 Physical exergy 2.1.3 Exergy change of mixing	9 9 9 10 11
	2.2 2.3	Exergy of other streams Exergy efficiency and balance 2.3.1 Energy efficiency 2.3.2 Simple exergy efficiency 2.3.3 Rational efficiency	12 13 13 13 13
	2.4	Analysis of simple process units 2.4.1 Material stream mixers 2.4.2 Material flow splitters	15 15 15
	2.5	Analysis of pressure changers 2.5.1 Valves 2.5.2 Compressors 2.5.3 Turbinos	16 16 16
	2.6	Analysis of heat transfer equipments 2.6.1 Coolers 2.6.2 Heaters 2.6.3 Heat exchangers	18 18 18 18 19
	2.7	Analysis of separation systems 2.7.1 Flash separation 2.7.2 Membranes 2.7.3 Distillations column	20 20 20 21
	2.8	Reactors 2.8.1 Adiabatic reactors	22 22 22
2	2.9 Evere		22
з.	3.1	Synthesis loop with refrigeration system (Process A) 3.1.1 Process description 3.1.2 Exergy analysis per unit operation 3.1.3 Overview of the results	23 23 23 24 26
	3.2	Synthesis loop with membrane system (Process B) 3.2.1 Process description 3.2.2 Exergy analysis per unit operation 3.2.3 Overview of the results	20 27 27 28 30
4.	Concl	usions	31
5.	Refere	ences	32

## List of tables

Table 2.1	Szargut environment properties	9
Table 2.2	Validation of EXEROM routine	12
Table 2.3	Exergy analysis of material stream mixers	15
Table 2.4	Exergy analysis of material stream splitters	15
Table 2.5	Exergy analysis of valves	16
Table 2.6	Exergy analysis of compressors	16
Table 2.7	Exergy analysis of turbine	16
Table 2.8	Exergy analysis of coolers	18
Table 2.9	Exergy analysis of heaters	18
Table 2.10	Exergy analysis of heat exchangers	19
Table 2.11	Exergy analysis of heat exchangers	20
Table 2.12	Exergy analysis of gas separating membranes with sweep gas	20
Table 2.13	Exergy analysis of distillation columns	21
Table 2.14	Conversion factor from secondary to primary energy type	22
Table 3.1	Stream data of ammonia synthesis loop – Process A	24
Table 3.2	Overview of exergy analysis of process B	26
Table 3.3	Overall exergy balance of process A	26
Table 3.4	Stream data of ammonia synthesis loop – Process B	28
Table 3.5	Overview of exergy analysis of process A	30
Table 3.6	Overall exergy balance of process B	30
Table 4.1	Technology comparison from energy point of view	31

# List of figures

Figure 1.1	Concept of exergy, theoretical minimum and actual process energy (Ozokwelu	
	<i>et al., 2006)</i>	7
Figure 1.2	Classification of exergy (taken from Gundersen, 2009)	7
Figure 1.3	Recoverable energy across chemical technologies and top 10 products by total	
	energy input (,Ozokwelu et al., 2006, 1 trillion Btu/yr is 1.06 PJ/yr)	8
Figure 3.1	PFD of ammonia synthesis loop with refrigeration (process A)	23
Figure 3.2	PFD of ammonia synthesis loop with membrane separation (process $B$ )	27

## List of notations

$Q_{in}$	- energy flow in a control volume, J/s
$Q_{out}$	- energy leaving a control volume, J/s
$Q_{\scriptscriptstyle waste}$	- energy wasted in the control volume, J/s
$\dot{E}x_{in}$	- exergy entering a control volume, J/s
$\dot{E}x_{out}$	- exergy leaving a control volume, J/s
$\dot{E}x_{waste}$	- exergy wasted in control volume J/s
Ėx	- exergy, J/s
1	- exergy destroyed in a control volume, J/s

### Subscripts

in	- denotes that streams flows into system
out	- denotes that a stream is leaving a system
phys	- physical
chem	- chemical

*mix* - mixing

### 1. Introduction

#### 1.1 Scope of this study

In the framework of sustainable development, the process industry is interested in improving and developing more energy efficient processes. This calls for a need of a set of methodologies with which to asses the relative merits of alternative and novel technologies that takes into account the exergy efficiency, environmental impact and depletion of natural resources.

This report is meant to describe a methodology of exergy analysis applied to chemical processes. Even if exergy analysis is considered a traditional method of assessing the way how energy is used in a chemical process, this methodology became more popular in the last decade. The number of publications, on exergy analysis of chemical processes also has increased considerably (e.g. Cornelissen and Hirs, 1998; Kirova-Yordanova, 2004; Kahraman and Cengel, 2005; Ptasinski et al., 2006; Talens et al., 2007; Pellegrini and de Oliveira, 2007; Shudo et al., 2009; Jurascik et al., 2010). However, not many publications are addressing to the methodologies of performing exergy analysis in chemical processes. The work of Hinderink and Cornelissen (e.g. Hinderink et al., 1996a; Hinderink et al., 1996b; Cornelissen, 1997) are one of few papers where is described a consistent methodology of exergy analysis, applied to chemical processes. They also show the possibility of implementation the exergy analysis method in available commercial process simulations programs. Their work will serve as basis for this report.

In addition, in some papers are used different definitions for the exergy efficiencies, which makes difficult to compare processes. Based on the open source information, the author of this report tries to identify and describe a common methodology of exergy analysis that will be used in evaluating the energetic performance of different chemical processes. This methodology will be used further to asses, based on process simulations studies or available data, the primary energy consumption and exergy losses (efficiencies) of chemical processes, which are part of Dutch petrochemical industry. This will help to identify, on common basis, which processes destroys the most of exergy and where exactly this destruction occurs. The results of these studies will help to understand better where to direct the research and technological development in order to reduce the exergy inefficiencies in Dutch petrochemical industry. In addition, the methodology can be used to evaluate different technologies of the same process and classify the technologies based on their overall exergetic efficiency and/or primary energy consumption. A similar study was performed already for U.S. petrochemical industry by Ozokwelu et al., 2006.

An illustrative example, of appliance of this methodology will be shown in this report. Exergy analysis of ammonia synthesis loop will be performed for two different technologies: a classic synthesis loop that uses refrigeration to remove ammonia from the loop and a synthesis loop where membrane is used to remove ammonia from the loop. All required data, process and exergy analysis of both processes are obtained trough process simulation using ASPEN Plus

#### 1.2 Concept of exergy

It is important to understand the difference between exergy and energy in order to avoid confusion with traditional energy-based methods. Exergy is defined as the maximum amount of work that can be extracted from a stream as it flows towards equilibrium. This follows the 2<sup>nd</sup> law of thermodynamics, which states that not all heat energy can be converted to useful work (e.g. shaft power, electricity). The proportion that can be converted to useful work is referred to exergy, while the remainder is called non-exergy input (Ozokwelu et al., 2006).



Figure 1.1 Concept of exergy, theoretical minimum and actual process energy (Ozokwelu et al., 2006)

When exergy analysis applied to a manufacturing plant, the purpose of its application is to identify the places in the processing steps where exergy (useful energy) is lost the most. In manufacturing plant exergy can be lost in two ways: *external exergy losses* - associated with exhaust gases, cooling water outflow, or other utility streams leaving the system and *internal exergy looses*. In this case no energy leaves the system and these losses are associated with 2<sup>nd</sup> law of thermodynamics that states that exergy is lost in every irreversible processing step, which often is the case.

Classification of exergy (useful energy) is depicted in Figure 1.2. As indicated in this figure, exergy can consist from physical and chemical exergy. In many articles, actually only physical exergy (thermo-mechanical) is considered as real exergy of a stream because of convenience and easiness of calculations. However, the chemical exergy can not be neglected especially in multi-component system where many reactions, combustion and separation steps occurs.



Figure 1.2 Classification of exergy (taken from Gundersen, 2009)

In this report both, physical and chemical exergy are considered as part of a stream. The calculation method for both will be shown. The kinetic and potential exergy will be neglected from our calculations, because these exergies, usually, are much smaller than chemical or thermomechanical exergy. If we will compare the enthalpy of a stream with exergy of the same stream then the exergy will be always higher if chemical exergy is included in exergy flow.

### 1.3 Energy intensive processes

The exergy analysis methodology presented in this work will be used to perform analysis of an existing energy intensive process. In Figure 1.3 is shown the list of technologies and top 10 products ranked according to the recoverable energy and total energy input. This diagram was compiled by Ozokwelu et al., and it also based on exergy analysis of presented processes. Based on this diagram and in-house expirence, we will consider ammonia synthesis as a good process candidate to be analysed. The results shown in Figure 1.3, for ammonia technology, are based on analysis of full process starting with natural gas as raw material and finishing with ammonia as product.

In this work, we will consider only the synthesis loop for analysis, hence starting from syngas and finishing with ammonia as product.



Figure 1.3 Recoverable energy across chemical technologies and top 10 products by total energy input (,Ozokwelu et al., 2006, 1 trillion Btu/yr is 1.06 PJ/yr)

### 2. Exergy analysis methodology

#### 2.1 Exergy of material stream

Many industrial processes are basically processes of energy conversion. To perform exergy analysis of them it is necessary to know the exergy of every material stream in addition to exergy of heat or work streams. In this chapter are described the thermodynamic relations and method of exergy calculation of material streams. The methodology described here is based on the article of Hinderink et al., 1996a, who describes a consistent calculation method of exergy for material streams.

For a certain flowing multicomponent material stream, the exergy represent the sum of chemical exergy, physical exergy, exergy change of mixing, potential and kinetic exergy. Usually the last two types of exergy are smaller compared to other, in addition it is difficult to calculate them at the level of process simulation, therefore we neglect these terms in calculation of total exergy of an material stream, which is expressed by relation (2.1).

$$\dot{E}x_{tot} = \dot{E}x_{chem} + \dot{E}x_{phys} + \dot{E}x_{mix}$$
(2.1)

In order to calculate the total exergy properly, each term has to be determined separately and systematically. In addition, a reference environment has to be selected. For the methodology presented below, the considered reference environment is that suggested by Szargut et al., 1988 and it has the properties shown in Table 2.1.

Property name	Value
Temperature	25 °C
Pressure	1.01325 bar
Composition, mol %	
Water	2.2
Nitrogen	75.78
Carbon Dioxide	0.0335
Oxygen	20.39
Argon	0.906

 Table 2.1
 Szargut environment properties

#### 2.1.1 Chemical exergy

Chemical exergy of a material stream represent the difference in chemical potential evaluated at reference conditions  $(T_0, P_0)$  between pure process components and the reference environment components in their environment concentration. For multicomponent fluid streams, chemical exergy is given by relation (2.2).

$$Ex_{chem} = L_0 \sum_{i=1}^{n} \left( x_{0,i} \cdot Ex_{chem,i}^{0L} \right) + V_0 \sum_{i=1}^{n} \left( y_{0,i} \cdot Ex_{chem,i}^{0V} \right) \text{ at } T_0, P_0$$
(2.2)

where:

 $Ex_{chem}$  - specific chemical exergy, J/mol

 $L_0$  - liquid mol fraction at standard conditions

 $\begin{array}{ll} V_0 & - \text{vapour mol fraction at standard conditions} \\ x_{0,i} & - \text{composition in liquid phase at } T_0, P_0 \text{ of specie } i \text{ , mol fr.} \\ y_{0,i} & - \text{composition in vapour phase at } T_0, P_0 \text{ of specie } i \text{ , mol fr.} \\ Ex_{chem,i}^{0L} \text{ - specific chemical exergy of species } i \text{ in liquid phase at } T_0, P_0, \text{ J/mol} \\ Ex_{chem,i}^{0V} \text{ - specific chemical exergy of species } i \text{ in vapour phase at } T_0, P_0, \text{ J/mol} \end{array}$ 

To calculate chemical exergy using relation (2.2), a flash to reference conditions  $(T_0, P_0)$  is needed to obtain the required phase and composition data. Hinderink et al., 1996a, explain in more detail how to calculate chemical exergy of species *i* in liquid and vapour phase, he also exemplify the calculation of chemical exergy with a numerical example for a gaseous mixture.

#### 2.1.2 Physical exergy

The physical exergy of a material stream is the maximum obtainable amount of shaft work (or electrical energy) when this stream is brought from actual conditions (T, P) to reference conditions (T, P) by reversible process and heat being only exchanged with the environment at  $T_0$ . This change of state is accomplished in two rounds. First, the material stream is adiabatically brought to the temperature of the environment  $T_0$ . Secondly, the material stream is isothermally brought to the thermo-mechanical equilibrium with the environment at  $T_0, P_0$ . This is expressed mathematically by equation (2.3), where *exf* here is noted as physical exergy function, which depends on current T and P of the stream.

$$Ex_{phys} = exf_{T,P} - exf_{T_0,P_0}$$
(2.3)

Hinderink et al., 1996a, define the physical exergy function as shown by relation (2.4).

$$exf(T,P) = L\left(\sum_{i=1}^{n} (x_i \cdot H_i^L) - T_0 \sum_{i=1}^{n} (x_i \cdot S_i^L)\right) + V\left(\sum_{i=1}^{n} (y_i \cdot H_i^V) - T_0 \sum_{i=1}^{n} (y_i \cdot S_i^V)\right)$$
(2.4)

where:

- *L* liquid mol fraction of the stream
- *V* vapour mol fraction of the stream
- $x_i$  composition in liquid phase of specie *i*, mol fr.
- $y_i$  composition in vapour rphase of specie *i*, mol fr.

 $H_i^L$  - enthalpy of component *i* in liquid phase at *T*, *P* condition, J/mol

 $H_i^V$  - enthalpy of component *i* in vapour phase at *T*, *P* condition, J/mol

 $S_i^L$  - entropy of component *i* in liquid phase at *T*, *P* condition, J/mol

 $S_i^V$  - entropy of component *i* in vapour phase at *T*, *P* condition, J/mol

 $T_0$  - reference temperature (usually, 298.15 K)

As can be seen from relations (2.3) and (2.4), a flash to reference conditions and pure component enthalpies and entropies at these conditions is necessary, in order to calculate the physical exergy of multicomponent stream. By considering imaginary unmixed material streams in calculation of chemical and physical exergies, mixing effects are excluded. An advantage of this calculation method is that the calculation of thermodynamic properties like enthalpy and entropy of pure components is more accurate that those of a mixture within a large range of thermodynamic conditions.

#### 2.1.3 Exergy change of mixing

So far, the mixture has been treaded as collection of individual components. The final step in calculation of the total exergy of a material stream is calculation of mixing term. This is calculated from isothermal and isobaric mixing of pure process components at actual thermodynamic conditions (T, P). This mixing term, has a negative value relative to the pure components and to calculate it, Hinderink et al., 1996a, is using the concept of "property change of mixing" as given by relation (2.5) written for certain thermodynamic property M.

$$\Delta_{mix}M = M^{\alpha} - \sum_{i=1}^{n} \left( x_i^{\alpha} \cdot M_i^{\alpha} \right)$$
(2.5)

where:

 $M^{\alpha}$  - thermodynamic property of mixture in phase  $\alpha$  $M_i^{\alpha}$  - thermodynamic property of pure component in phase  $\alpha$  $x_i^{\alpha}$  - composition of component *i* in the phase  $\alpha$  of the mixture, mol fr. *n* - number of components

For two phase liquid-vapour) material stream, the general equation (2.5) becomes:

$$\Delta_{mix}M = L\left(M^L - \sum_{i=1}^n \left(x_i^L \cdot M_i^L\right)\right) + V\left(M^V - \sum_{i=1}^n \left(y_i^V \cdot M_i^V\right)\right)$$
(2.6)

By applying relation (2.6) to calculate enthalpy and entropy of mixing, we can calculate the exergy change of mixing as shown by relation

$$Ex_{mix} = \Delta_{mix}H - T_0 \cdot \Delta_{mix}S \tag{2.7}$$

The exergy flow rate (expressed in e.g. in J/s) of chemical exergy, physical exergy and exergy change of mixing at actual conditions, can be calculated by multiplying the specific exergies, calculated with relations (2.2), (2.3) and (2.15) with the total molar flow rate F.

$$\dot{E}x_{chem} = F \cdot Ex_{chem} \tag{2.8}$$

$$\dot{E}x_{phys} = F \cdot Ex_{phys} \tag{2.9}$$

$$\dot{E}x_{mix} = F \cdot Ex_{mix} \tag{2.10}$$

Then the total exergy flow rate of a multicomponent stream is the sum of exergy flow rates as shown by equation (2.1).

By using the presented methodology in calculation the exergy of a material stream, it is not necessary to have complicated physical property models. The physical exergy and exergy change of mixing are based on enthalpy and entropy calculation for pure components and mixtures, together with phase behaviour calculations. These calculations are easy possible with a flowsheet simulator. Chemical exergies can be obtained by determined standard chemical exergy values of the process components with respect to a well-defined reference environment, as for example suggested by Szargut et al., 1988.

This methodology of calculations was implemented as subroutine (known as EXERCOM) in ASPEN plus process simulator. This subroutine was licensed to ECN by Jacobs Consultancy Netherlands and will be used in this study, to calculate the stream exergy and make an exergetic analysis of certain process.

In order to validate the results calculated by the EXERCOM subroutine, it was considered the example given Hinderink et al., 1996a. He has calculated by hand the chemical, physical, mixing and total exergy for the following mixture:  $H_2O-0.22$ , N2 - 0.75,  $CO_2 - 0.02$ , NO - 0.005 and CO - 0.005 mol fr. at 423.15 K and 101.325 kPa. As can be seen in Table 2.2, calculated exergies by Hinderink et al., 1996a are almost the same as those calculated by EXERCOM v2.1. The small difference arises due to slightly different physical properties used by current version of ASPEN Plus..

Table 2.2 Validation of EXEROM routine

Exergy type	Literature data (Himderink et al.,1996)	Computer program (EXERCOM v2.1)
Chemical, kW	3123	3110
Physical, kW	2532	2523
Mixing, kW	-1678	-1683
Total exergy, kW	3977	3950

### 2.2 Exergy of other streams

Besides the material streams, in a chemical processing plant we have other types of exergy inputs and/or outputs, such as electrical power, shaft power or heat flow generated by certain media. To have a complete exergy analysis of a system, it is important to know the exergy value of such stream. Below are presented the relation to calculate these exergies:

*a)* Exergy of heat streams is calculated by the relation (2.11).

$$\dot{E}x_{heat} = \left(1 - \frac{T_0}{T}\right) \cdot Q \tag{2.11}$$

where:

 $T_0$  - reference temperature (298.15 K)

*T* - temperature of the source heat, K

Q - transfere heat, J/s

 $\dot{E}x_{heat}$  - exergy rate of a heat stream, J/s

From relation (2.11) can be seen that depending on the temperature of heat stream, the exergy can be positive or negative. In this case, the sign of the exergy flow will indicate the actual direction of the exergy flow (to the system or from the system).

b) Exergy of shaft work ( $\dot{E}x_{work}$ ) is equal to the actual work:

$$\dot{E}x_{work} = W \tag{2.12}$$

c) Exergy of electricity ( $Ex_{elec}$ ) is equal to the electrical energy

$$\dot{E}x_{elec} = E \tag{2.13}$$

#### 2.3 Exergy efficiency and balance

Exergy efficiency is an efficiency based on  $2^{nd}$  law of thermodynamics. In this section is given the definitions and physical meaning of efficiencies that are the most used in practice. Efficiencies are used frequent to show the performance of a unit operation and/or process, hence it is very important to understand their meaning. The definition of efficiency is based on energy and exergy balance, the general relations of both, for controlled volume, at steady state conditions is given by the relations (2.14) and (2.15).

$$\dot{Q}_{in} = \dot{Q}_{out} + \dot{Q}_{waste} \tag{2.14}$$

$$\dot{E}x_{in} = \dot{E}x_{out} + \dot{E}x_{waste} + \dot{I}$$
(2.15)

In these equations the term with subscript "out" may refer shaft work, electricity, a certain heat transfer, one or more particular exit streams, or some combinations of these. The term with subscript "waste" refers to emission to the surrounding as waste heat and/or stack gases. These relations also express the difference between energy and exergy balance, where in case of exergy an additional term is added (I) - called irreversibility, which accounts for the internal dissipated energy within the control volume, according to the  $2^{nd}$  law of thermodynamics.

#### 2.3.1 Energy efficiency

.

Based on the energy balance relation (2.14) the energy efficiency of certain process or unit operation is defined as ratio between total output energy in the products (e.g. electricity, shaft power, particular material streams, certain heat transfer etc.) and total energy input into the system. This is expressed by the relation (2.16).

$$\eta = \frac{Q_{out}}{Q_{in}} = 1 - \frac{Q_{waste}}{Q_{in}}$$
(2.16)

For unit operations like, reactors, mixers, splitter, valves, membrane units etc., energy efficiency often is considered equal to 1 (or 100%), if it operates under adiabatic regime (no exchange of heat trough the wall with the environment). For units that have rotating parts (pumps, compressors, etc.) this efficiency is below 1 (typically between 0.7-0.98) and for units that uses external heat input (like natural gas, fuel oil, etc.,) this efficiency usually is lower (typically between 0.2 - 0.7). Note that in definition of energy efficiency is not taken into account quality of energy that is wasted or lost in the process.

#### 2.3.2 Simple exergy efficiency

Based on exergy balance given by (2.15) the exergy efficiency of certain process or unit operation is defined as ratio between exergy leaving the system as product (e.g. electricity, shaft power, particular material streams, certain heat transfer etc.) and total incoming exergy into the system. This is expressed by the relation (2.17).

$$\varepsilon = \frac{Ex_{out}}{Ex_{in}} = 1 - \frac{Ex_{waste} + I}{Ex_{in}}$$
(2.17)

From this relation we can see that this efficiency will be always less than 1, even in conditions if it is assumed that no energy waste to the environment occurs. The simple exergy efficiency shows how much of useful energy is destroyed compared to the total exergy input into the system.

#### 2.3.3 Rational efficiency

This form of exergetic efficiency, known also as functional efficiency is defined as ratio of the desired exergy output to the exergy used (Kotas, 1995). This is given by the relation (2.18).

$$\psi = \frac{Ex_{desired output}}{Ex_{used}}$$
(2.18)

The desired exergy output represent the sum of all exergy transfer from the system, which is regarded as desired output, plus any by-product which is produced by the system. Exergy used is the required exergy input for the process to be performed. If exergy used ( $Ex_{used}$ ) and desired exergy output ( $Ex_{desired output}$ ) are correctly identified in relation to a control volume then together they should account for all exergy transfers. In other words, any exergy transfer term should be included in either  $Ex_{used}$  or  $Ex_{desired output}$ . The only exergy transfer term that is not included in these terms is reversibility (I) thus we write the exergy balance as shown by (2.19).

$$Ex_{used} = Ex_{desired \ output} + I \tag{2.19}$$

Based on relation (2.19), rational efficiency given by (2.18) can be rewritten to relation (2.20) or (2.21) as follow:

$$\psi = 1 - \frac{I}{Ex_{used}} \tag{2.20}$$

$$\psi = \frac{Ex_{desired output}}{Ex_{desired output} + I}$$
(2.21)

Rational efficiency can be applied to any system, except to purely dissipative systems, because no desired product can be defined in this case (Cornelissen, 1997).

Based on relation (2.21) we can define the physical meaning of rational efficiency as follow: *rational exergy efficiency show the energy efficiency of certain process in achieving its purpose, this value will be always below 100% because it is related to the total exergy destroyed in the process.* A process that has 100 % rational effiency means that no exergy is destroyed, A process that has rational efficiency close to 100 % means that a big part of the destroyed exergy is used to get the desired output. A process with rational efficiency close to zero means that all the exergy is destroyed in vain.

### 2.4 Analysis of simple process units

### 2.4.1 Material stream mixers

Exergy analysis method	Stream mixer	
Simple exergy efficiency	Rational efficiency	
$\varepsilon = \frac{\dot{E}x_{out}}{\dot{E}x_{in}}$	$\psi = \frac{\dot{E}x_{desired output}}{\dot{E}x_{desired output} + I}$	$ \begin{array}{c} \dot{E}x_{in,1} \\ \dot{E}x_{in,2} \\ \dot{E}x_{out,1} \end{array} $
Desired output: increase in exe	ergy of mixing	
$\dot{E}x_{desired output} = \left  \dot{E}x_{out,1,min} \right $	$\sum_{x}^{N} - \sum_{i=1}^{N} \dot{E} x_{in,i,mix}$	$\dot{E}x_{in,N}$
Exergy to the system:	Exergy out of the system:	$\dot{E}x$ - exerginal flow/stream, kW
$\dot{E}x_{in} = \sum_{i=1}^{N} \dot{E}x_{in,i}$	$\dot{E}x_{out} = Ex_{out,1}$	Subscripts: in - flow to system
Exergy loss (irreversibility):		1.2 N - every stream number
$I = \dot{E}x_{out} - \dot{E}x_{in}$		mix - exergy of mixing

 Table 2.3
 Exergy analysis of material stream mixers

### 2.4.2 Material flow splitters

 Table 2.4
 Exergy analysis of material stream splitters

Exergy analysis method		Stream splitter
Simple exergy efficiency	Rational efficiency	
$\varepsilon = \frac{\dot{E}x_{out}}{\dot{E}x_{in}}$	$\psi = \frac{\dot{E}x_{desired output}}{\dot{E}x_{desired output} + I}$	$\dot{E}x_{out,1}$ $\dot{E}x_{out,2}$ $\dot{E}x_{in,1}$
Desired output: increase in exe	ergy of mixing	
$\dot{E}x_{desired output} = \left  \sum_{i=1}^{N} \dot{E}x_{out,i,mix} - \dot{E}x_{in,1,mix} \right $		$Ex_{out,N}$
Exergy to the system:	Exergy out of the system:	$\dot{E}x$ - exergy flow/stream kW
$\dot{E}x_{in} = Ex_{in,1}$	$\dot{E}x_{out} = \sum_{i=1}^{N} \dot{E}x_{out,i}$	Subscripts: in - flow to system
Exergy loss (irreversibility):		1.2 N - every stream number
$I = \dot{E}x_{out} - \dot{E}x_{in}$		mix - exergy of mixing

## 2.5 Analysis of pressure changers

### 2.5.1 Valves

Exergy analysis method		Adiabatic valve
Simple exergy efficiency	Rational efficiency	
$\varepsilon = \frac{\dot{E}x_{out}}{\dot{E}x_{in}}$	$\psi = \frac{\dot{E}x_{desired output}}{\dot{E}x_{desired output} + I}$	$\dot{E}x_{in,1}$ $\dot{E}x_{out,1}$
Desired output: increase in phy	/sical exergy	
$\dot{E}x_{desired\ output} = \dot{E}x_{in,1,phys} - \dot{E}x_{out,1,phys}$		
Exergy to the system:	Exergy out of the system:	$\dot{E}x$ - exergy flow/stream, kW
$\dot{E}x_{in} = \dot{E}x_{in,1}$	$\dot{E}x_{out} = \dot{E}x_{out,1}$	Subscripts: in, OUt - flow to/from system
Exergy loss (irreversibility):		1,2 - exergy stream number
$I = \dot{E}x_{out} - \dot{E}x_{in}$		phys - physical exergy of the flow

#### Table 2.5Exergy analysis of values

Note: for an adiabatic valve the rational exergy efficiency will be always 50 %

### 2.5.2 Compressors

Exergy analysis method		Stream splitter
Simple exergy efficiency $\varepsilon = \frac{\dot{E}x_{out}}{\dot{E}x_{in}}$ Desired output: <i>increase in phy</i>	Rational efficiency $\psi = \frac{\dot{E}x_{desired output}}{\dot{E}x_{desired output} + I}$ <i>vsical exergy</i>	$ \frac{\dot{E}x_{in,1}}{\dot{E}x_{in,2}} \qquad $
$\dot{E}x_{desired output} = \dot{E}x_{out,1,phys} - \dot{E}x_{in,1,phys}$		──── Material stream ──── Electric stream
Exergy to the system:	Exergy out of the system:	$\dot{E}x$ - exergy flow/stream, kW
$\dot{E}x_{in} = \dot{E}x_{in,1} + \dot{E}x_{in,2} \qquad \dot{E}x_{out} = \dot{E}x_{out,1}$		Subscripts:
Exergy loss (irreversibility):		UII - flow to system OUI - flow from system
$I = \dot{E}x_{out} - \dot{E}x_{in}$		1, 2 - exergy stream number $phys$ - physical exergy of the flow

 Table 2.6
 Exergy analysis of compressors

#### 2.5.3 Turbines

Table 2.7Exergy analysis of turbine

Exergy analysis method		Stream splitter
Simple exergy efficiency $\varepsilon = \frac{\dot{E}x_{out}}{\dot{E}x_{in}}$ Desired output: <i>increase in (sh</i>	Rational efficiency $\psi = \frac{\dot{E}x_{desired output}}{\dot{E}x_{desired output}} + I$ aft) electric power output	$\dot{E}x_{in,1}$ $\dot{E}x_{out,2}$ $\dot{E}x_{uut,2}$
$\dot{E}x_{desired\ output} = \dot{E}x_{out,2}$		Material stream     Electric stream
Exergy to the system:	Exergy out of the system:	$\dot{Ex}$ - exergy flow/stream, kW
$\dot{E}x_{in} = \dot{E}x_{in,1}$	$\dot{E}x_{out} = Ex_{out,1} + Ex_{out,2}$	Subscripts:
Exergy loss (irreversibility):		III - flow to system OUT - flow from system
$I = \dot{E}x_{out} - \dot{E}x_{in}$		1, 2 - exergy stream number

Below are shown other pressure change units widely used in process industry, for which the exergy analysis method is not shown explicitly in this report.

- Pipes
- Pumps
- Fans

However, their analysis does not differ from the analysis of shown units. For example the analysis for pipes will be similar as for valve, and analysis for pumps and fans will be similar as for compressors.

## 2.6 Analysis of heat transfer equipments

### 2.6.1 Coolers

Exergy analysis method		Cooler
Simple exergy efficiency $\mathcal{E} = \frac{\dot{E}x_{out}}{\dot{E}x_{in}}$	Rational efficiency $\psi = \frac{\dot{E}x_{desired output}}{\dot{E}x_{desired output} + I}$	$\dot{Ex}_{in,1}$ $\dot{Ex}_{out,1}$
Desired output: increase in physical exergy $\dot{E}x_{desired output} = \dot{E}x_{in,1,phys} - Ex_{out,1,phys}$		Material stream
Exergy to the system: $\dot{E}x_{in} = \dot{E}x_{in,1}$	Exergy out of the system: $\dot{E}x_{out} = Ex_{out,1} + Ex_{out,2}$	$\dot{E}x$ - exergy flow/stream, kW T - inlet temperature of thermal
Exergy loss (irreversibility): $I = \dot{E}x_{out} - \dot{E}x_{in}$	Exergy of thermal streams $\dot{E}x_{out,2} = \left(1 - \frac{T_0}{T}\right) \cdot Q$	Subscripts: <i>in</i> - flow to system <i>Out</i> - flow from system 1, 2 - exergy stream number <i>phys</i> - physical exergy of the flow

Table 2.8   Exergy analysis of coolers	
--	--

### 2.6.2 Heaters

Table 2.9	Exergy	analysis	of heaters
-----------	--------	----------	------------

Exergy analysis method		Heater
Simple exergy efficiency $\mathcal{E} = \frac{\dot{E}x_{out}}{\dot{E}x_{in}}$	Rational efficiency $\psi = \frac{\dot{E}x_{desired output}}{\dot{E}x_{desired output} + I}$	$\dot{Ex}_{in,1}$ $\dot{Ex}_{out,1}$
Desired output: increase in physical exergy $\dot{E}x_{desired output} = \dot{E}x_{out,1,phys} - Ex_{in,1,phys}$		Exin,2     Material stream     Thermal stream
Exergy to the system: $\dot{E}x_{in} = \dot{E}x_{in,1}$	Exergy out of the system: $\dot{E}x_{out} = Ex_{out,1} + Ex_{out,2}$	$\dot{E}x$ - exergy flow/stream, kW $T$ - inlet temperature of thermal stream
Exergy loss (irreversibility): $I = \dot{E}x_{out} - \dot{E}x_{in}$	Exergy of thermal streams $\dot{E}x_{out,2} = \left(1 - \frac{T_0}{T}\right) \cdot Q$	Subscripts: in, OUt - flow to/out of the system 1, 2 - exergy stream number phys - physical exergy of the flow

### 2.6.3 Heat exchangers

Exergy analysis method		Heat exchanger
Simple exergy efficiency	Rational efficiency	
$\varepsilon = \frac{\dot{E}x_{out}}{\dot{E}x_{in}}$	$\psi = \frac{\dot{E}x_{desired output}}{\dot{E}x_{desired output} + I}$	
Desired output: increase in physic	al exergy	
$\dot{E}x_{desired output} = \dot{E}x_{in,1, phys} + \dot{E}x_{in,2, phys} - \dot{E}x_{out,1, phys} - \dot{E}x_{out,2, phys}$		$\dot{E}x_{out,2}$ $\dot{E}x_{in,2}$
Exergy to the system:	Exergy out of the system:	$\dot{E}x$ - exergy flow/stream, kW
$\dot{E}x_{in} = \dot{E}x_{in,1} + \dot{E}x_{in,2}$	$\dot{E}x_{out} = \dot{E}x_{out,1} + \dot{E}x_{out,2}$	Subscripts: in - flow to system
Exergy loss (irreversibility):		<i>OUL</i> - flow from system
$I = \dot{E}x_{out} - \dot{E}x_{in}$		1, 2 - exergy stream number <i>phys</i> - physical exergy of the flow

Table 2.10 Exergy analysis of heat exchangers

Below are shown other heat transfer equipments that are used in process industry but not covered in this report, for which the exergy analysis method is not shown explicitly in this report.

- furnace
- steam boilers

## 2.7 Analysis of separation systems

#### 2.7.1 Flash separation

Table 2.11 Exergy analysis of heat exchangers



#### 2.7.2 Membranes

	Table 2.12 Exergy	analysis of ga	s separating memb	branes with sweep gas
--	-------------------	----------------	-------------------	-----------------------

Exergy analysis method		Membrane with swep gas
Simple exergy efficiency	Rational efficiency	
$\varepsilon = \frac{\dot{E}x_{out}}{\dot{E}x_{in}} \qquad $		$\dot{E}x_{in,1}$
Desired output: increase in physical exergy		$\dot{Ex}_{out,2}$ $\dot{Ex}_{in,2}$
$\dot{E}x_{desired output} = \dot{E}x_{in,1,phys} +$	$\dot{E}x_{in,2,phys} - \dot{E}x_{out,1,phys} - \dot{E}x_{out,2,phys}$	
Exergy to the system: Exergy out of the system:		$\dot{Ex}$ - exergy flow/stream, kW
$\dot{E}x_{in} = \dot{E}x_{in,1} + \dot{E}x_{in,2} \qquad \dot{E}x_{out} = \dot{E}x_{out,1} + \dot{E}x_{out,2}$		Subscripts: in - flow to system
Exergy loss (irreversibility):		<i>OUL</i> - flow from system
$I = \dot{E}x_{out} - \dot{E}x_{in}$		1, 2 - exergy stream number <i>phys</i> - physical exergy of the flow

#### 2.7.3 Distillations column

 Table 2.13 Exergy analysis of distillation columns

Simple exergy efficiency: $\varepsilon = \frac{\dot{E}x_{out}}{\dot{E}x_{in}}$ $\dot{E}x_{out}$ Rational effiency: $\psi = \frac{\dot{E}x_{desired output}}{\dot{E}x_{desired output} + I}$ $\dot{E}x_{in,1}$ Desired output: increase in chemical exergy $\dot{E}x_{desired output} = \dot{E}x_{out,1,chem} + \dot{E}x_{out,2,chem} - \dot{E}x_{in,1,chem}$ Exergy to the system: $\dot{E}x_{in} = \dot{E}x_{in,1} + \dot{E}x_{in,2}$ $Q_R$ - Added he $Q_C$ - Remov. If $T_R$ - temperatu $T_C$ - temperatu $T_0 = 298.15$ Exergy loss (irreversibility): $I = \dot{E}x_{in} - \dot{E}x_{in}$ $I = \dot{E}x_{in} - \dot{E}x_{in}$	mn
Rational effiency: $\dot{E}x_{desired output}$ $\dot{E}x_{desired output} + I$ $\psi = \frac{\dot{E}x_{desired output}}{\dot{E}x_{desired output} + I}$ $\dot{E}x_{in,1}$ Desired output: increase in chemical exergy $\dot{E}x_{desired output} = \dot{E}x_{out,1,chem} + \dot{E}x_{out,2,chem} - \dot{E}x_{in,1,chem}$ Exergy to the system: $\dot{E}x_{in} = \dot{E}x_{in,1} + \dot{E}x_{in,2}$ Exergy out of the system: $\dot{E}x_{out} = \dot{E}x_{out,1} + \dot{E}x_{out,2} + \dot{E}x_{out,3}$ Exergy loss (irreversibility): $I = \dot{E}x_{n-} - \dot{E}x_{n-}$	
Exergy to the system: $Q_R$ - Added he $\dot{E}x_{in} = \dot{E}x_{in,1} + \dot{E}x_{in,2}$ $Q_C$ - Remove theExergy out of the system: $T_R$ - temperature $\dot{E}x_{out} = \dot{E}x_{out,1} + \dot{E}x_{out,2} + \dot{E}x_{out,3}$ $T_C$ - temperatureExergy loss (irreversibility): $L = \dot{E}x_{out,2} - \dot{E}x_{out,3}$	Ėx <sub>in,2</sub> Ėx <sub>out,2</sub>
Exergy of heat streams: $\dot{E}x_{out,3} = \left(1 - \frac{T_0}{T_c}\right) \cdot Q_R$ $\dot{E}x_{out,3} = \left(1 - \frac{T_0}{T_c}\right) \cdot Q_R$ $\dot{E}x_{out,3} = \left(1 - \frac{T_0}{T_c}\right) \cdot Q_R$ Note: It is assurates in adiabation	eat in reboiler, kW heat in condenser, kW ure in reboiler, K ure in condenser, K 5 K low/stream, kW v to/out of the system gy stream number nical exergy of the flow med that column oper- ic regime.

Below are shown other separation units widely used in process industry, for which the exergy analysis method is not shown explicitly in this report.

- Adsorption column
- Absorption columns
- Extraction columns
- Reactive distillation
- Dividing distillation wall columns
- Batch distillation
- Dryers
- Filters

#### 2.8 Reactors

#### 2.8.1 Adiabatic reactors

Exergy analysis method	Heat exchanger	
Simple exergy efficiency $\varepsilon = \frac{\dot{E}x_{out}}{\dot{E}x_{in}}$ Desired output: Increase in cherr $\dot{E}x_{desired output} = \dot{E}x_{in,1,phys}$	Rational efficiency $\psi = \frac{\dot{E}x_{desired output}}{\dot{E}x_{desired output} + I}$ nical and physical exergy $-\dot{E}x_{out,1,phys} + \dot{E}x_{in,2,chem}\dot{E}x_{out,2,chem}$	<u>Ėx</u> <sub>in,1</sub>
Exergy to the system: $\dot{E}x_{in} = \dot{E}x_{in,1}$	Exergy out of the system: $\dot{E}x_{out} = \dot{E}x_{out,1}$	$\dot{Ex}$ - exergy flow/stream, kW Subscripts: in, OUT - flow to/out of the sys-
Exergy loss (irreversibility):		tem 1, 2 - exergy stream number <i>phys</i> - physical exer. of the flow
$I = \dot{E}x_{out} - \dot{E}x_{in}$		<i>chem</i> - chemical exer. of the flow

For reactor types such as exothermal reactors, endothermic reactors, batch reactors or membrane reactors, the exergy analysis method is not shown explicitly in this report.

### 2.9 Conversions to primary energy use

In Table 2.14 are shown the equivalence factors between primary and secondary energy carriers. This factor show the ratio between amounts of primary energy needed to produce 1 unit of secondary energy. The secondary energy is considered electricity and steam. Other secondary energy as refrigerant, heating oil, etc., is not included in this table.

Energy type	Equivalence factor	Observations
Natural gas	1	Heating value of natural gas 31.65 MJ/Nm <sup>3</sup>
Electricity	2.38	Power plant effiency 42 %
Steam 100-0.95	1.20	Steam at 100 C, and boiler eff. 95%
Steam 120-0.95	1.25	Steam at 100 C, and boiler eff. 95%
Steam 140-0.95	1.30	Steam at 100 C, and boiler eff. 95%

Table 2.14 Conversion factor from secondary to primary energy type

These factors are purely used to estimated the total primary energy consumption of a process and you should keep in mind that this is a just an estimation. Often such estimation are subject to debate because values of these factors depends on plant location, raw material used, technology used to generate secondary energy etc., However, the author expect that for plants located in the Netherlands, these factors corresponds to reality.

### 3. Exergy analysis of ammonia synthesis loop

#### 3.1 Synthesis loop with refrigeration system (Process A)

#### 3.1.1 Process description

Energy consumption of an ammonia production plant depends strongly on the synthesis loop design. The exergy loss associated only with this part of the process account for 3.1 GJ/ton of ammonia produced which represents about 35 % of total exergy consumed in ammonia production plant (Ozokwelu et al., 2006, p.23). Large exergy consumption is due to the thermodynamically limited degree of conversion of  $H_2$  and  $N_2$  mixture to NH<sub>3</sub>, which impose to design the system by recycling unreacted  $H_2$  and  $N_2$  back to the reactor, after NH<sub>3</sub> is removed from the recycling loop. A big part from total exergy used in synthesis loop, is used to remove NH<sub>3</sub> from recycling loop (it is state of the art method) due required cryogenic temperatures (about -16 °C). In Figure 3.1 is shown the simplified process flow diagram (without heat integration) of this process, which is taken as example for exergy analysis.



Figure 3.1 PFD of ammonia synthesis loop with refrigeration (process A)

In this process, syngas (H<sub>2</sub>:N<sub>2</sub> molar ratio 3:1) enters in the loop at 25 °C and 25 bars. It is compressed to 150 bar and mixed with the reactor outlet stream (which also at 150 bar). The mixture (stream 5) is cooled down to 25 °C (in H100) with cooling water and further cooled down to about -16 °C using a single stage refrigeration system (shown in blue line in Figure 3.1). The considered refrigerant is pure ammonia and water is used as cooling agent (in H102). The temperature of stream 7 (about -16 °C), from deep cooling, is selected such that after flash separation in V100 the composition of NH<sub>3</sub> in vapour phase (stream 1) is 2.5 mol% while pure NH<sub>3</sub> is collected as product in liquid phase. Stream 1 with 3:1 molar ratio of H<sub>2</sub>:N<sub>2</sub> and 2.5 mol% of NH<sub>3</sub> enters to reactor R100 where conversion to ammonia occurs (3H<sub>2</sub> + N<sub>2</sub> = 2NH<sub>3</sub>). Due to

exothermic effect of the reaction, in a real plant, the reactor consists of three catalytic beds with intermediate cooling or with intermediate cold shots between catalytic beds. In this case, the rector is modelled as stoechiometric reactor with specified composition of  $NH_3$  in outlet stream of 16 mol%, which is typical in this process.

### 3.1.2 Exergy analysis per unit operation

The process shown in Figure 3.1 is simulated using ASPEN Plus process simulated, de detailed stream data are presented in Table 3.1. In this table are also shown the chemical, physical and mixing exergy of each stream, which were calculated using EXERCOM subroutine within Aspen Plus. This data are used to make an exergetic analysis of the whole process and for each unit operation in part, by using methodology presented in chapter 2.

Table 3.1 Stream data of ammonia synthesis loop – Process A

Property	SYNGAS	1	2	3	4	5	6	7	8	9	10	11	AMMONIA
Temperature, °C	25	-16.1	40	47.6	95	56.1	25	-16.1	15.5	111.9	25	-23.5	-16.1
Pressure, bar	25	150	140	150	150	150	150	150	1.6	10	10	1.6	150
Vapor fraction	1	1	1	1	1	1	0.97	0.895	1	1	0	0.168	0
Mass Flow, kg/hr	44708	184148	184148	184148	44708	228857	228857	228857	59000	59000	59000	59000	44708
Volume Flow, m <sup>3</sup> /hr	5263	3419	3794	3646	1144	4790	4240	3487	51210	10644	98	7452	68
Enthalpy, MW	-0.014	-15.435	-40.060	-38.772	3.074	-35.699	-46.459	-66.413	-44.576	-41.455	-64.530	-64.530	-50.977
Density, kg/m <sup>3</sup>	8.50	53.87	48.54	50.51	39.07	47.78	53.98	65.64	1.15	5.54	601.63	7.92	655.12
Mole fraction													
H <sub>2</sub>	0.75	0.7520	0.6535	0.6535	0.75	0.6736	0.6736	0.6736	0	0	0	0	0.0041
N <sub>2</sub>	0.25	0.2230	0.1865	0.1865	0.25	0.1997	0.1997	0.1997	0	0	0	0	0.0014
NH <sub>3</sub>	0	0.0250	0.1601	0.1601	0	0.1266	0.1266	0.1266	1	1	1	1	0.9945
WATER	0	0	0	0	0	0	0	0	0	0	0	0	0
TOTEX, MW	268.1	1231.9	1205.6	1206.7	275.1	1481.2	1480.8	1482.2	325.4	330.0	329.6	329.1	250.3
CHEMEX, MW	258.5	1162.8	1150.1	1150.1	258.5	1408.6	1408.6	1408.6	324.3	324.3	324.3	324.3	245.8
PHYSEX, MW	11.6	78.0	64.2	65.2	18.6	83.7	82.8	82.5	1.1	5.7	5.3	4.8	4.5
MIXEX, MW	-2.02	-8.94	-8.71	-8.62	-1.96	-11.11	-10.61	-8.97	0.00	0.00	0.00	0.00	-0.03

Below is tabulated the exergy	analysis around	each unit.
-------------------------------	-----------------	------------

Unit		H100			
Functionality	Cooler				
Process flow rat	е	228857	kg/hr		
Temperature ho	t in	56.1	°C		
Temperature ho	t out	25	°C		
Cooling duty		10.8	MW		
Coolant		Cooling water			
Exergy, MW	in	n out			
Stream	5	6	Thermal		
Chemical	1408.6	1408.6	-		
Physical	83.7	82.8	-		
Mixing	-11.1	-10.6	-		
TOTAL	1481.2	1480.8	0.0		
Total exergy in		1481.2	MW		
Total exergy ou	ıt	1480.8	MW		
Exergy loss		0.4	MW		
Simple exergy e	ffiency	99.97	%		
Rational exergy	effiency	69.19	%		

Unit		V100				
Functionality	Phase se	Phase separator (V-L)				
Feed flow rater		228857	kg/hr			
Vapour flow rate		184149	kg/hr			
Liquid flow rate		44709	kg/hr			
Exergy, MW	in		out			
Stream	7	1	AMMONIA			
Chemical	1408.6	1162.8	245.8			
Physical	82.5	78.0	4.5			
Mixing	-9.0	-8.9	0.0			
TOTAL	1482.2	1231.9	250.3			
Total exergy in		1482.2	MW			
Total exergy out		1482.2	MW			
Exergy loss		0.0	MW			
Simple exergy eff	iency	100.00	%			
Rational exergy e	ffiency	100.00	%			

Unit		H101		
Functionality	He	at exchanger		
Cold flow rate		59000	kg/hr	
Hot flow rate		228857	kg/hr	
Cold temperatur	e in	-23.5	°C	
Cold temperatur	e out	15.5	°C	
Hot temperature	in	25	°C	
Hot temperature	out	-16.1	°C	
Duty		20.0	MW	
Exergy, MW	ir	1	01	ut
Stream	6	11	7	8
Chemical	1408.6	324.3	1408.6	324.3
Physical	82.8	4.8	82.5	1.1
Mixing	-10.6	0.0	-9.0	0.0
TOTAL	1480.8	329.1	1482.2	325.4
Total exergy in		1809.9	MW	
Total exergy ou	t	1807.6	MW	
Exergy loss		2.4	MW	
Simple exergy e	fiency	99.87	%	
Rational exergy	effiency	62.80	%	

l lució		11400		
Unit		H102		
Functionality		Cooler		
Process flow rat	e	59000	kg/hr	
Temperature ho	t in	111.9	°C	
Temperature ho	t out	25	°C	
Cooling duty		23.1	MW	
Coolant		Cooling water		
Exergy, MW	in	0	ut	
Stream	5	6		Thermal
Chemical	324.3	324.3		-
Physical	5.7	5.3		-
TOTAL	330.0	320.6		-
Total exergy in	550.0	330.0	MW	0.0
Total exergy ou	ıt	329.6	MW	
Exergy loss		0.4	MW	
Simple exergy e	ffiency	99.87	%	
Rational exergy	effiency	50.00	%	
	,		, .	
Unit		C100		
Functionality	1 stan	e compressor		
Process flow rat	e	184149	kg/hr	
Isentropic effien	су	0.8	[-]	
Net power		1.3	MW	
Exergy, MW	i	n		out
Stream	2	Shaft		3
Chemical	1150.1	-		1150.1
Physical	64.2	-		65.2
Mixing	-8.7	-		-8.6
TOTAL	1205.7	1.3		1206.7
Total exergy in		1206.9	MW	
Total exergy οι	ıt	1206.7	MW	
Exergy loss		0.2	MW	
Simple exergy e	ffiency	99.98	%	
Rational exergy	effiency	79.90	%	
Unit		VLV1		
Europei en elitere		Mahaa		
Functionality		valve		
Process flow rat	e	59000	kg/hr	
Temperature in		25.0	°C	
Temperature ou	t	-23.5	-C	
Exergy, WW		in 10		out
Stream		10		3
Physical		324.3 E 2		324.3 م ا
Miving		0.0		4.0 0.0
TOTAL		329.6		329.1
Total exergy in	1	329.6	MW	520.1
Total exergy ou	ıt	329.1	MW	
Exergy loss				
		0.4	IVIVV	
Simple exergy e	ffiency	0.4 99.87	MVV %	
Simple exergy e Rational exergy	ffiency effiency	0.4 99.87 50.00	MVV % %	
Simple exergy e Rational exergy	ffiency effiency	0.4 99.87 50.00	MVV % %	
Simple exergy e Rational exergy Unit	ffiency effiency	0.4 99.87 50.00 <b>R100</b>	MVV % %	
Simple exergy e Rational exergy Unit Functionality	ffiency effiency	0.4 99.87 50.00 <b>R100</b> Reaction	MVV % %	
Simple exergy e Rational exergy Unit Functionality Process flow rat	ffiency effiency	0.4 99.87 50.00 <b>R100</b> Reaction	MVV % %	
Simple exergy e Rational exergy Unit Functionality Process flow rat	ffiency effiency eff	0.4 99.87 50.00 R100 Reaction 184149 -16.1	MVV % % kg/hr °C	
Simple exergy e Rational exergy Unit Functionality Process flow rat Temperature on	ffiency effiency e	0.4 99.87 50.00 Reaction 184149 -16.1 40.0	kg/hr °C °C	
Simple exergy e Rational exergy Unit Functionality Process flow rat Temperature ou Exerov. MW	ffiency effiency e t	0.4 99.87 50.00 Reaction 184149 -16.1 40.0 in	MVV % % kg/hr °C °C	out
Simple exergy e Rational exergy Unit Functionality Process flow rat Temperature ou Exergy, MW Stream	ffiency effiency e t	0.4 99.87 50.00 Reaction 184149 -16.1 40.0 <b>in</b> 1	MVV % % kg/hr °C °C	
Simple exergy e Rational exergy Unit Functionality Process flow rat Temperature in Exergy, MW Stream Chemical	ffiency effiency e t	0.4 99.87 50.00 Reaction 184149 -16.1 40.0 in 1 1162.8	MVV % % kg/hr °C °C	out 2 1150.1
Simple exergy e Rational exergy Unit Functionality Process flow rat Temperature ou Exergy, MW Stream Chemical Physical	ffiency effiency e t	0.4 99.87 50.00 Reaction 184149 -16.1 40.0 in 1 1162.8 78.0	MVV % % % kg/hr °C °C	out 2 1150.1 64.2
Simple exergy e Rational exergy Unit Functionality Process flow rat Temperature ou Exergy, MW Stream Chemical Physical Mixing	ffiency effiency e t	0.4 99.87 50.00 Reaction 184149 -16.1 40.0 in 1 1162.8 78.0 -8.9	MVV % % kg/hr °C °C	out 2 1150.1 64.2 -8.7
Simple exergy e Rational exergy Unit Functionality Process flow rat Temperature ou Exergy, MW Stream Chemical Physical Mixing TOTAL	ffiency effiency e t	0.4 99.87 50.00 Reaction 184149 -16.1 40.0 in 1162.8 78.0 -8.9 1231.9	₩₩ % % °C °C	out 2 1150.1 64.2 -8.7 1205.7
Simple exergy e Rational exergy Unit Functionality Process flow rat Temperature on Exergy, MW Stream Chemical Physical Mixing TOTAL Total exergy in	ffiency effiency e t	0.4 99.87 50.00 Reaction 184149 -16.1 40.0 in 1162.8 78.0 -8.9 1231.9 1231.9	MW % % kg/hr °C °C °C MW	out 2 1150.1 64.2 -8.7 1205.7
Simple exergy e Rational exergy Unit Functionality Process flow rat Temperature ou Exergy, MW Stream Chemical Physical Mixing TOTAL Total exergy in	ffiency effiency e t t	0.4 99.87 50.00 Reaction 184149 -16.1 40.0 in 1162.8 78.0 -8.9 1231.9 1231.9 1205.7	MW % % % °C °C MW MW	out 2 1150.1 64.2 -8.7 1205.7

Simple exergy effiency

Rational exergy effiency

97.87 %

50.22 %

Unit		C101			
Functionality	3 stage	compressor			
Process flow rat	e	44708	kg/hr		
Isentropic effien	су	0.8	[-]		
Total cooling du	ty	6.0	MW		
Coolant	Co	ooling water			
Temperature of	thermal strean	25.0	°C		
Total net electric	power	9.1	MW		
Exergy, MW	in			0	ut
Stream	SYNGAS	Shaft		4	Thermal
Chemical	258.5	-		258.5	-
Physical	11.6	-		18.6	-
Mixing	-2.0	-		-2.0	-
TOTAL	268.1	9.1		275.1	0.0
Total exergy in		277.2	MW		
Total exergy ou	it	275.1	MW		
Exergy loss	<i></i>	2.1	MW		
Simple exergy e	ffiency	99.24	%		
Rational exergy	ettiency	76.63	%		
Unit		C102			
Functionality	3 stage	compressor			
Process flow rate	е	59000	kg/hr		
Isentropic effiend	су	0.8	[-]		
Total cooling dut	ty	2.7	MW		
Coolant	Co	oling water			
Temperature of	thermal strean	25.0	°C		
Temperature of Total net electric	thermal strean power	25.0 5.8	°C MW		
Temperature of f Total net electric Exergy, MW	thermal strean power in	25.0 5.8	°C MW	0	ut
Temperature of Total net electric Exergy, MW Stream	thermal strean power in 8	25.0 5.8 Shaft	°C MW	9	ut Thermal
Temperature of Total net electric Exergy, MW Stream Chemical	thermal strean power in 8 324.3	25.0 5.8 Shaft	°C MW	0 9 324.3	ut Thermal -
Temperature of t Total net electric Exergy, MW Stream Chemical Physical	thermal strean power 8 324.3 1.1	25.0 5.8 Shaft - -	°C MW	<b>0</b> <b>9</b> 324.3 5.7	ut Thermal - -
Temperature of i Total net electric Exergy, MW Stream Chemical Physical Mixing	thermal strean power 8 324.3 1.1 0.0 0.0	25.0 5.8 Shaft - - -	°C MW	9 324.3 5.7 0.0	ut Thermal - - -
Temperature of Total net electric Exergy, MW Stream Chemical Physical Mixing TOTAL	thermal strean power 324.3 1.1 0.0 325.4	25.0 5.8 Shaft - - 5.8	°C MW	<b>9</b> 324.3 5.7 0.0 330.0	ut Thermal - - 0.0
Temperature of 1 Total net electric Exergy, MW Stream Chemical Physical Mixing TOTAL Total exergy in	thermal stream power 8 324.3 1.1 0.0 325.4	25.0 5.8 Shaft - - - 5.8 331.2 230.0	°C MW MW	0 9 324.3 5.7 0.0 330.0	ut Thermal - - 0.0
Temperature of 1 Total net electric Exergy, MW Stream Chemical Physical Mixing TOTAL Total exergy ou Total exergy ou	thermal stream : power 8 324.3 1.1 0.0 325.4 t	25.0 5.8 Shaft - - - 5.8 331.2 330.0 1 2	°C MW MW MW	0 9 324.3 5.7 0.0 330.0	ut Thermal - - - 0.0
Temperature of 1 Total net electric Exergy, MW Stream Chemical Physical Mixing TOTAL Total exergy in Total exergy ou Exergy loss	thermal stream : power 8 324.3 1.1 0.0 325.4 t ffioner/	25.0 5.8 Shaft - - - 5.8 331.2 330.0 1.2 0.63	°C MW MW MW MW WW	0 9 324.3 5.7 0.0 330.0	ut Thermal - - - 0.0
Temperature of 1 Total net electric Exergy, MW Stream Chemical Physical Mixing TOTAL Total exergy in Total exergy ou Exergy loss Simple exergy e	thermal stream : power 8 324.3 1.1 0.0 325.4 t ffiency officency	25.0 5.8 Shaft - - 5.8 331.2 330.0 1.2 99.63 78.80	°C MW MW MW MW %	<b>0</b> <b>9</b> 324.3 5.7 0.0 330.0	ut Thermal - - - 0.0
Temperature of 1 Total net electric Exergy, MW Stream Chemical Physical Mixing TOTAL Total exergy in Total exergy ou Exergy loss Simple exergy e Rational exergy	thermal stream : power 324.3 1.1 0.0 325.4 t tfiency effiency	25.0 5.8 Shaft - - - - - - - - - - - - - - - - - - -	°C MW MW MW MW % %	<b>9</b> 324.3 5.7 0.0 330.0	ut Thermal - - - 0.0
Temperature of i Total net electric Exergy, MW Stream Chemical Physical Mixing TOTAL Total exergy ou Exergy loss Simple exergy e Rational exergy Unit	thermal stream : power 8 324.3 1.1 0.0 325.4 t ffiency effiency	25.0 5.8 Shaft - - - - - - - - - - - - - - - - - - -	°C MW MW MW MW % %	0 9 324.3 5.7 0.0 330.0	ut Thermal - - - 0.0
Temperature of 1 Total net electric Exergy, MW Stream Chemical Physical Mixing TOTAL Total exergy in Total exergy ou Exergy loss Simple exergy e Rational exergy Unit Functionality	thermal stream power in 8 324.3 1.1 0.0 325.4 t tfiency effiency	25.0 5.8 Shaft - - 5.8 331.2 330.0 1.2 99.63 78.89 MIX1 Mixing	°C MW MW MW % %	0 9 324.3 5.7 0.0 330.0	ut Thermal - - - 0.0
Temperature of 1 Total net electric Exergy, MW Stream Chemical Physical Mixing TOTAL Total exergy in Total exergy ou Exergy loss Simple exergy e Rational exergy Unit Functionality Process flow rate	thermal stream : power 8 324.3 1.1 0.0 325.4 t ffiency effiency effiency effiency	25.0 5.8 Shaft - - - - - - - - - - - - - - - - - - -	°C MW MW MW % %	0 9 324.3 5.7 0.0 330.0	ut Thermal - - 0.0
Temperature of 1 Total net electric Exergy, MW Stream Chemical Physical Mixing TOTAL Total exergy ou Exergy loss Simple exergy e Rational exergy Unit Functionality Process flow rat	thermal stream : power 1 8 324.3 1.1 0.0 325.4 t ffiency effiency e (3) e (4)	25.0 5.8 Shaft - - - - - - - - - - - - - - - - - - -	°C MW MW MW % %	0 9 324.3 5.7 0.0 330.0	ut Thermal - - 0.0
Temperature of 1 Total net electric Exergy, MW Stream Chemical Physical Mixing TOTAL Total exergy in Total exergy ou Exergy loss Simple exergy e Rational exergy Unit Functionality Process flow rat Process flow rat	thermal stream : power 1 8 324.3 1.1 0.0 325.4 t t ffiency effiency effiency e (3) e (4) e (5)	25.0 5.8 Shaft - - - - - - - - - - - - - - - - - - -	°C MW MW MW % % % kg/hr kg/hr	0 9 324.3 5.7 0.0 330.0	ut Thermal - - 0.0
Temperature of 1 Total net electric Exergy, MW Stream Chemical Physical Mixing TOTAL Total exergy in Total exergy ou Exergy loss Simple exergy ou Exergy loss Simple exergy e Rational exergy Unit Functionality Process flow rat Process flow rat Exergy, MW	thermal stream : power 1 8 324.3 1.1 0.0 325.4 t t ffiency effiency effiency e (3) e (4) e (5) in	25.0 5.8 Shaft - - - - - - - - - - - - - - - - - - -	°C MW MW MW MW % % kg/hr kg/hr	0 9 324.3 5.7 0.0 330.0	ut Thermal - - 0.0
Temperature of 1 Total net electric Exergy, MW Stream Chemical Physical Mixing TOTAL Total exergy in Total exergy ou Exergy loss Simple exergy ou Exergy loss Simple exergy e Rational exergy Unit Functionality Process flow rat Process flow rat Exergy, MW Stream	thermal stream : power 1 8 324.3 1.1 0.0 325.4 t t ffiency effiency effiency e (3) e (4) e (5) in 3 3 3 3 3 3 3 3 3 3 3 3 3	25.0 5.8 Shaft - - - - - - - - - - - - - - - - - - -	°C MW MW MW MW % % %	0 9 324.3 5.7 0.0 330.0 330.0	ut Thermal - - 0.0
Temperature of 1 Total net electric Exergy, MW Stream Chemical Physical Mixing TOTAL Total exergy in Total exergy ou Exergy loss Simple exergy ou Exergy loss Simple exergy e Rational exergy ou Exergy loss Unit Functionality Process flow rat Process flow rat Exergy, MW Stream Chemical	thermal stream power in 8 324.3 1.1 0.0 325.4 t ffiency effiency effiency e (3) e (4) e (5) in 3 1150.1	25.0 5.8 Shaft - - - - - - - - - - - - - - - - - - -	°C MW MW MW MW % %	0 9 324.3 5.7 0.0 330.0 330.0	ut Thermal - - - 0.0
Temperature of 1 Total net electric Exergy, MW Stream Chemical Physical Mixing TOTAL Total exergy in Total exergy ou Exergy loss Simple exergy ou Exergy loss Simple exergy e Rational exergy ou Exergy loss Unit Functionality Process flow rat Process flow rat Process flow rat Process flow rat Exergy, MW Stream Chemical Physical	thermal stream power in 8 324.3 1.1 0.0 325.4 t ffiency effiency effiency e (3) e (4) e (5) in 3 1150.1 65.2	25.0 5.8 Shaft - - - - - - - - - - - - - - - - - - -	°C MW MW MW MW % %	0 9 324.3 5.7 0.0 330.0 330.0 330.0 1408.6 83.7	ut Thermal - - - 0.0
Temperature of 1 Total net electric Exergy, MW Stream Chemical Physical Mixing TOTAL Total exergy ou Exergy loss Simple exergy ou Exergy loss Chemical Physical Physical Mixing	thermal stream : power 324.3 1.1 0.0 325.4 t ffiency effiency e (3) e (4) e (4) e (5) in 3 1150.1 65.2 -8.6	25.0 5.8 Shaft - - - - - - - - - - - - - - - - - - -	°C MW MW MW MW % %	0 9 324.3 5.7 0.0 330.0 330.0 330.0 5 1408.6 83.7 -11.1	ut Thermal - - 0.0
Temperature of 1 Total net electric Exergy, MW Chemical Physical Mixing TOTAL Total exergy ou Exergy loss Simple exergy ou Exergy loss Chemical Physical Mixing TOTAL	thermal stream : power 324.3 1.1 0.0 325.4 t ffiency effiency e (3) e (4) e (4) e (5) in 3 1150.1 65.2 -8.6 1206.7	25.0 5.8 Shaft - - - 5.8 331.2 330.0 1.2 99.63 78.89 MiX1 Mixing 184149 44708.4 228857.1 4 4228857.1 4 228857.1 8.6 -2.0 275.1	°C MW MW MW % % kg/hr kg/hr	0 9 324.3 5.7 0.0 330.0 330.0 330.0 5 1408.6 83.7 -11.1 1481.2	ut Thermal - - 0.0

1481.2 MW

46.19 %

0.6 MW 99.96 %

Total exergy out

Exergy loss Simple exergy effiency

Rational exergy effiency

25

#### 3.1.3 Overview of the results

Process unit	Functionality	Exergy loss	Fraction of exergy loss from total	Rational efficiency
		[MW]	[%]	[%]
H100	Cooler	0.4	1.2	69.2
H101	Heat exchanger	2.4	7.1	62.8
H102	Cooler	0.4	1.2	50.0
C100	3 stage compressor	2.1	6.3	76.6
C102	3 stage compressor	1.2	3.6	78.9
VLV1	Valve	0.4	1.2	50.0
V100	Phase separator (V-L)	0.0	0.0	100.0
R100	Reaction	26.2	77.6	50.2
MIX1	Mixing	0.6	1.8	46.2

Table 3.2Overview of exergy analysis of process B

 Table 3.3
 Overall exergy balance of process A

Functionality		Ammonia synthesis									
Desired output		Increase in chemical and physical exergy									
Exergy, MW		in ou									
Stream	SYNGAS	Power C100	Power C101	Power C102	AMMONIA						
Chemical	258.5	-	-	-	245.8						
Physical	11.6	-	-	-	4.5						
Mixing	-2.0	-	-	-	0.0						
Shaft/Electric	-	9.1	1.3	5.8	-						
TOTAL	268.1	9.1	1.3	5.8	250.3						
Total exergy in		284.3	MW								
Total exergy out		250.3	MW								
Exergy loss		34.1	MW								
Total electricity u	se	1.31	GJ/ton ammonia								
Exergy loss		2.74	GJ/ton ammonia								
Primary energy u	se*	3.11	GJ/ton ammonia								
Simple exergy efficient	ency	88.02	%								
Rational exergy eff	fiency	36.77	%								

Primary energy uses were calculated by considering that energetic efficiency of transformation from primary energy type (natural gas) into secondary (electricity) is 42 %. This number is based on the study performed by Hers et al., 2008. He analyses for Netherlands, the efficiency of transformation the primary energy sources (e.g. natural gas) into electricity. This corresponds to the equivalence factor of 2.38 as shown in Table 2.14.

### 3.2 Synthesis loop with membrane system (Process B)

#### 3.2.1 Process description

Compared with process A, in this process a modification is made in ammonia removal from the synthesis loop. The idea of this process is to avoid refrigeration unit and replace it with an alternative technology that can remove  $NH_3$  from synthesis loop in a more energy efficient manner. Therefore we have considered the option to remove  $NH_3$  from the synthesis loop trough a membrane, which is considered being a more energy efficient separation technique, because no cryogenic temperatures are needed. The process flow diagram, with membrane separation option is depicted in Figure 3.2.



Figure 3.2 PFD of ammonia synthesis loop with membrane separation (process B)

In this process, the original syngas is used as sweep stream in membrane unit M100. The ammonia from stream 6 is passing selectively trough membrane and exists with stream 7 from the membrane unit. Further the stream is compresses in a 3 stage compressor (C101) with intermediate cooling with cooling water. Because of intermediate cooling and high NH<sub>3</sub> composition in this stream, NH<sub>3</sub> is condensing, and can be removed in liquid phase from each compression stage. Therefore NH<sub>3</sub> can be collected as product after each compression-cooling stage. Since we have 3 stage compressor we have two ammonia products that comes after compression stage one (stream P1) and compression stage two (stream P2). The stream (8) leaving the third compression stage is first mixed with the reactor outlet, which is also rich in NH<sub>3</sub>, and further cooled with cooling water to 25 °C and then flashed in V100. The liquid stream, with high purity in NH<sub>3</sub> is collected as product, while the vapour stream is used as feed to the membrane unit, where the remaining ammonia after flash operation, is removed selectively trough membrane. Similar as in process B, it is considered that composition of NH<sub>3</sub> in stream is 2.5 mol%.

In this calculations was assumed that membrane is 100% selective to ammonia and  $NH_3$  permeance trough membrane is  $3.71E-7 \text{ mol}/(Pa \cdot s \cdot m^2)$ .

#### 3.2.2 Exergy analysis per unit operation

The process shown in Figure 3.2 is simulated using ASPEN Plus process simulated, de detailed stream data are presented in Table 3.4. As in previous case, it is shown the chemical, physical and mixing exergy of each stream. This data will be used to make an exergetic analysis of the whole process and for each unit operation in part, by using methodology presented in chapter 2.

Property	SYNGAS	1	2	3	4	5	6	7	8	P1	P2	P3	
Troperty	OTHEAD	•	-	3	-	3	v	•	J	••		10	Annionia
Temperature, °C	25	25	41	48	59	25	25	25	92	25	25	25	26
Pressure, bar	25	150	140	150	150	150	150	25	150	45	83	150	45
Vapor fraction	1	1	1	1	1	0.932346	1	1	1	0	0	0	0.00895895
Mass Flow, kg/hr	44708	164305	164305	164305	225485	225485	195633	76037	61180	588	14269	29852	44708
Volume Flow, m <sup>3</sup> /hr	5263	3971	3805	3656	4967	4265	4215	6947	1310	1	24	51	87
Enthalpy, MW	-0.014	-7.350	-39.731	-38.440	-47.731	-64.396	-32.056	-23.795	-9.291	-0.641	-15.515	-32.341	-48.497
Density, kg/m <sup>3</sup>	8.5	41.4	43.2	44.9	45.4	52.9	46.4	10.9	46.7	598.6	595.5	589.9	512.6
Mole fraction													
H <sub>2</sub>	0.75	0.7856	0.6916	0.6916	0.6776	0.6776	0.7261	0.5554	0.6330	0.0022	0.0044	0.0088	0.0073
N <sub>2</sub>	0.25	0.1893	0.1484	0.1484	0.1633	0.1633	0.1750	0.1851	0.2109	0.0010	0.0020	0.0027	0.0024
NH <sub>3</sub>	0	0.0251	0.1600	0.1600	0.1591	0.1591	0.0989	0.2595	0.1561	0.9968	0.9936	0.9885	0.9902
WATER	0	0	0	0	0.00	0.00	0	0.00	0.00	0	0	0	0
TOTEX, MW	268.1	1280.0	1254.5	1255.5	1622.4	1621.7	1454.6	441.5	367.0	3.3	79.7	167.1	249.9
CHEMEX, MW	258.5	1210.9	1198.2	1198.2	1547.3	1547.3	1383.1	430.7	349.1	3.2	78.4	164.2	245.8
PHYSEX, MW	11.6	77.4	64.2	65.2	85.9	84.3	81.4	15.4	20.8	0.1	1.3	2.9	4.1
MIXEX, MW	-2.02	-8.33	-7.98	-7.89	-10.80	-9.92	-9.89	-4.62	-2.84	0.00	-0.01	-0.04	-0.04

 Table 3.4
 Stream data of ammonia synthesis loop – Process B

The exergy analysis per unit operation is presented consequently in tables below:

Unit				C10	11				
Functionality				3 st	age compressor				
Process flow rate (str	eam 7)		7603	37 kg/ł	nr				
Process flow rate (str	eam P1)		58	38 kg/ł	nr				
Process flow rate (str	eam P2)		1426	59 kg/ł	nr				
Isentropic effiency			0	.8 [-]					
Total cooling duty			13	.0 MW	,				
Coolant		(	Cooling water						
Temperature of thern	nal stream		2	25 °C					
Total net electric pow	ver		11	.4 MW	,				
Exergy, MW	i	n			out			1	
Stream	7	Shaft		8	P1	P2	Thermal	1	
Chemical	430.7	-	349	.1	3.2	78.4	-	1	
Physical	15.4	-	20	.8	0.1	1.3	-		
Mixing	-4.6	-	-2	.8	0.0	0.0	-		
TOTAL	441.5	11.4	367	.0	3.3	79.7	0.0	1	
Total exergy in		452.9	MW					1	
Total exergy out		450.0	MW						
Exergy loss		2.8	MW						
Simple exergy effiend	су	99.37	%						
Rational exergy effier	псу	70.42	%						
Unit		H100		L.	Jnit			C100	
Functionality		Cooler		F	unctionality	1	stage comp	essor	
Process flow rate		225485 kg	/hr	F	Process flow rate		1	64305	kg/hr
Temperature hot in		58.5 °C		1	sentropic effiency			0.8	[-]
Temperature hot out		25 °C		1	Net power			1.3	MW
Cooling duty		16.7 M	W		Exergy, MW		in		
Coolant	r	Cooling water		L	Stream		2	Shaft	
Exergy, MW	in	out			Chemical	1198	3.2	-	
Stream	4	5	Thermal		Physical	64	1.2	-	
Chemical	1547.3	1547.3	-	_  -	Mixing	-8	3.0	-	
Physical	85.9	84.3	-	- E	TOTAL	1254	1.5	1.3	
Mixing	-10.8	-9.9	-		fotal exergy in		1	255.8	MW
Total averav in	1622.4	1621.7 1622.4 M	0.0	!	otal exergy out		1	255.5	MVV
Total every in		1621.7 M	N/			2001		0.2	1VI VV
Exergy loss		07 M	w		Rational exercic off	iency		79 92	/0 %
Simple exergy effiend	CV.	99.96 %		Ľ	tational everyy en	ionoy		10.02	70
Rational exergy effier	ncy	69.67 %							

out 3 1198.2 65.2 -7.9 1255.5

Unit		V100		
Functionality	Phase	separator (V-L)		
Feed flow rater		225485	kg/hr	
Vapour flow rate		195633	kg/hr	
Liquid flow rate		29852	kg/hr	
Exergy, MW	in	in out		
Stream	5	6	P3	
Chemical	1547.3	1383.1	164.2	
Physical	84.3	81.4	2.9	
Mixing	-9.9	-9.9	0.0	
TOTAL	1621.7	1454.6	167.1	
Total exergy in		1621.7	MW	
Total exergy out		1621.7	MW	
Exergy loss 0.0 MW			MW	
Simple exergy effi	ency	100.00	%	
Rational exergy ef	fiency	100.00	%	

Unit		MIX1	
Functionality		Mixing	
Process flow rate	(3)	164305	kg/hr
Process flow rate	(8)	61180	kg/hr
Process flow rate	(4)	225485	kg/hr
Exergy, MW	i	n	out
Stream	3	8	4
Chemical	1198.2	349.1	1547.3
Physical	65.2	20.8	85.9
Mixing	-7.9	-2.8	-10.8
TOTAL	1255.5	367.0	1622.4
Total exergy in		1622.6	MW
Total exergy out		1622.4	MW
Exergy loss		0.2	MW
Simple exergy effi	ency	99.99	%
Rational exergy ef	fiency	30.81	%

Unit		R100	
Functionality		Reaction	
Process flow rate		164305	kg/hr
Temperature in		25.0	°C
Temperature out		40.5	°C
Exergy, MW		in	out
Stream		1	2
Chemical		1210.9	1198.2
Physical		77.4	64.2
Mixing		-8.3	-8.0
TOTAL		1280.0	1254.5
Total exergy in		1280.0	MW
Total exergy out		1254.5	MW
Exergy loss		25.5	MW
Simple exergy efficient	ency	98.01	%
Rational exergy ef	iency	50.34	%

Unit			M100	
Functionality		Separation tr	ough membrane	
Process flow rate	(SYNGAS)		44708	kg/hr
Process flow rate	(6)		195633	kg/hr
Process flow rate	(1)		164305	kg/hr
Process flow rate	(6)		76037	kg/hr
Membrane area			2474	m2
Pressure feed side	Э		150	bar
Pressure permeate	e side		25	bar
Exergy, MW	ir		out	
Stream	SYNGAS	6	1	6
Chemical	258.5	1383.1	1210.9	430.7
Physical	11.6	81.4	77.4	15.4
Mixing	-2.0	-9.9	-8.3	-4.6
TOTAL	268.1	1454.6	1280.0	441.5
Total exergy in		1722.7	MW	
Total exergy out		1721.5	MW	
Exergy loss		1.3	MW	
Simple exergy effi	ency	99.93	%	
Rational exergy ef	fiency	14.43	%	

Unit			MIX2	
Functionality			Mixing	
Process flow rate	(P1)		588	kg/hr
Process flow rate	(P2)		14269	kg/hr
Process flow rate	(P3)		29852	kg/hr
Process flow rate	(Ammonia)		44708	kg/hr
Exergy, MW		in		out
Stream	P1	P2	P3	AMMONIA
Chemical	3.2	78.4	164.2	245.8
Physical	0.1	1.3	2.9	4.1
Mixing	0.0	0.0	0.0	0.0
TOTAL	3.3	79.7	167.1	249.9
Total exergy in		250.1 MW		
Total exergy out		249.9 MW		
Exergy loss		0.2 MW		
Simple exergy effiency		99.92 %		

### 3.2.3 Overview of the results

Process unit	Functionality	Exergy loss	Fraction of exergy loss from total	Rational efficiency
		[MW]	[%]	[%]
H100	Cooler	0.7	2.0	69.7
C100	1 stage compressor	0.2	0.7	79.9
C101	3 stage compressor	2.8	8.4	70.4
V100	Phase separator (V-L)	0.0	0.0	100.0
R100	Reaction	25.5	74.9	50.3
MIX1	Mixing	0.2	0.4	30.8
MIX2	Mixing	0.2	0.6	19.9
M100	Separation trough membrane	1.3	3.7	14.4

Table 3.5Overview of exergy analysis of process A

 Table 3.6
 Overall exergy balance of process B

Functionality		sis			
Desired output	nical and physical e	xergy			
Exergy, MW	in			out	
Stream	SYNGAS	Power C100	Power C101	AMMONIA	
Chemical	258.5	-	-	245.8	
Physical	11.6	-	-	4.1	
Mixing	-2.0	-	-	0.0	
Shaft/Electric	-	1.3	11.4	-	
TOTAL	268.1	1.3	11.4	249.9	
Total exergy in		280.8	MW		
Total exergy out		249.9	MW		
Exergy loss		30.9	MW		
Total electricity use 1.02			GJ/ton ammonia		
Exergy loss		2.49	GJ/ton ammonia		
Primary energy use 2.43			GJ/ton ammonia		
Simple exergy effiency 89.00			%		
Rational exergy eff	iency	39.53	%		

### 4. Conclusions

In this report is presented a methodology of exergy analysis that can be applicable in analysis of various product manufacturing in process industry. The presented methodology is compiled by using existing literature information and it is purely theoretical and it can be applied easily by using process simulation software like Aspen Plus.

In order to show the applicability of the method, an example of energy intensive process is selected. In this work, ammonia synthesis process is taken as case study. Two technologies for this process were analysed:

- synthesis and separation trough refrigeration (process A)
- synthesis and separation trough membrane (process B)

The summary results of this analysis are shown in Table 4.1.

Comparison criteria	Process A	Process B
Absolute exergy loss, MW	34.1	30.9
Specific exergy loss, GJ/ton product	2.74	2.49
Primary energy use, GJ/ton product	3.11	2.43

 Table 4.1
 Technology comparison from energy point of view

Product = Ammonia

From this analysis we can see that process B compared to process A, uses 9% less exergy (useful energy) and about 22% less primary energy (e.g. natural gas). Hence, we can conclude that process B is more energy efficient than process A. The obtained results for this process is in line with the results shown by Ozokwelu et al., 2006, they show that internal exergy loss in ammonia synthesis loop where ammonia is removed from the system trough refrigeration is about 2.5 GJ/ton of ammonia. The small difference that arises may be due to slightly different process configurations and process assumptions used in this study. Please not that in the analysis done in this work, we have no external exergy loss, this is due to the assumptions we have used (reference temperature is considered 25 °C, and temperature of thermal streams leaving the system is also considered 25 °C because it is assumed that this heat is removed from the system with cooling water).

It is notable that in both processes, the reactor is the main exergy consumer. Here is destroyed 77.6 % from total destroyed exergy for process A and 74.9 % for process B. Based on this outcome, it can be concluded that the reactor unit will be next equipment to look at, for further reduction of destroyed exergy in ammonia synthesis loop.

#### 5. References

- Cornelissen, R.L., *Thermodynamics and sustainable development. The use of exergy analysis and the reduction of irreversibility*, PhD thesis, UTwente, (1997)
- Cornelissen, R.L., Hirs, G.G., *Exergy analysis of cryogenic air separation*, Energy Conversion and Management, 39, p.1821-1826, (1998)
- Gundersen, T., An Introduction to The Concept of Exergy and Energy Quality, Department of Energy and Process Engineering of Norwegian Univ. of Sci. and Tech., Public report, (2009)
- Hers, J.S., Wetzels, W., Seebregts, A.J., van der Welle, A.J., Onrendabele top berekeningen voor bestaande WKK 2008, ECN, ECN-E--08-022, (2008)
- Hinderink, A.P., Kerkhof, F.P.J.M., Lie, A.B.K., De Swaan Arons, J., Van Der Kooi, H.J., *Exergy analysis with a flowsheeting simulator--I. Theory; calculating exergies of material streams*, Chemical Engineering Science, 51, p.4693-4700, (1996a)
- Hinderink, A.P., Kerkhof, F.P.J.M., Lie, A.B.K., De Swaan Arons, J., Van Der Kooi, H.J., Exergy analysis with a flowsheeting simulator--II. Application; synthesis gas production from natural gas, Chemical Engineering Science, 51, p.4701-4715, (1996b)
- Jurascik, M., Sues, A., Ptasinski, K.J., *Exergy analysis of synthetic natural gas production method from biomass*, Energy, In Press, Corrected Proof, (2010)
- Kahraman, N., Cengel, Y.A., *Exergy analysis of a MSF distillation plant*, Energy Conversion and Management, 46, p.2625-2636, (2005)
- Kirova-Yordanova, Z., Exergy analysis of industrial ammonia synthesis, Energy, 29, p.2373-2384, (2004)
- Kotas, T.J., *The Exergy Method of Thermal Plant Analysis*, 2nd Ed., Krieger Publishing Company, 328 pages, (1995)
- Ozokwelu, D., Porcelli, J., Akinjiola, P., *Chemical Brandwith Study. Exergy Analysis: A Powerful Tool* for Identifying Process Inefficiencies in the U.S. Chemical Industry, JVP Inernational, Draft Summary report, (2006)
- Pellegrini, L.F., de Oliveira, J., *Exergy analysis of sugarcane bagasse gasification*, Energy, 32, p.314-327, (2007)
- Ptasinski, K.J., Hamelinck, C., Kerkhof, P.J.A.M., *Exergy analysis of methanol from the sewage sludge process*, Energy Conversion and Management, 43, p.1445-1457, (2006)
- Shudo, Y., Ohkubo, T., Hideshima, Y., Akiyama, T., Exergy analysis of the demonstration plant for coproduction of hydrogen and benzene from biogas, International Journal of Hydrogen Energy, 34, p.4500-4508, (2009)
- Szargut, J., Morris, D.R., Steward, F.R., *Exergy Analysis of Thermal Chemical and Metallurgical Proc*esses, Hemisphere Publishing, New York, (1988)
- Talens, L., Villalba, G., Gabarrell, X., *Exergy analysis applied to biodiesel production*, Resources, Conservation and Recycling, 51, p.397-407, (2007)
Bijlage C Voorbeeld van een technologiebeschrijving afkomstig uit 'PI-scans'



# **EUROPEAN ROADMAP OF PROCESS INTENSIFICATION**

# - TECHNOLOGY REPORT -

TECHNOLOGY: ADVANCED PLATE TYPE HEAT EXCHANGERS

TECHNOLOGY CODE: 1.1.1

AUTHOR: Bert Boxma, Heat Transfer ABC B.V., Leiden

Table of contents		
1. Technol	ogy	
1.1.1	-4 Description of technology / working principle	
1.2.1	-4 Types and "versions"	
1.3	Potency for Process Intensification: possible benefits	
1.4	Stage of development	
2. Applicat	ions	
2.1	Existing technology (currently used)	
2.2	Known commercial applications	
2.3	Known demonstration projects	
2.4	Potential applications discussed in literature	
3. What are	e the development and application issues?	
3.1	Technology development issues	
3.2	Challenges in developing processes based on the	
	technology	
4. Where c	an information be found?	
4.1	Key publications	
4.2	Relevant patents and patent holders	
4.3	Institutes/companies working on the technology	
5. Stakeho	Iders	
5.1	Suppliers/developers	
5.2	End-users	
6. Expert's	brief final judgment on the technology	

# 1. Technology

#### 1.1.1 Description of technology / working principle

(Feel free to modify/extend the short technology description below)

Plate exchanger consists of a pack of corrugated metal plates with portholes for the passage of two fluids between which heat transfer will take place.

#### 1.2.1 Types and "versions"

(Describe the most important forms/versions of technology under consideration, including their characteristic features, differences and similarities)

The plate pack is assembled between a pressure plate and a frame plate and compressed by tightening bolts. The plates are fitted with gaskets, which seals the channels and directs the fluids into alternate channels (Fig.A). Basic advantages of the plate heat exchangers are compactness, large heat transfer areas and high heat transfer coefficients. For applications where gaskets are undesirable (high pressure and temperature or very corrosive fluids), semi-welded or totally welded heat exchangers are available. A welded heat exchanger cannot be opened, and fouling will limit the range of application. Originally the first application was agro and now we have many applications in (petro)chemical and heavy duty off-shore. Plate-fin exchanger consists of stacked corrugated sheets (fins) separated by flat plates with openings for the inlet and outlet of fluids (Fig.B) This type also called brazed aluminium are used in cryogenic applications like LNG and air separation processes. Flow direction of each of the fluids relative to one another may be

counter-current, co-current or cross-flow.

In plate-and-shell heat exchangers bundle of plates are inserted in a shell (Fig.C). On the plate side, the fluid flows inside corrugated or embossed channels; on the shell side, the flow is similar to shell and tube heat exchangers, and baffles can be inserted. These exchangers are often used for revamping applications, as the shell can be kept identical as for a bundle of tubes.

Flat tube-and-plate heat exchangers have been developed in the automobile industry for engine cooling and air conditioning. Generally on the air side the surface is finned (plain or louver fins – Fig.D) and on the other side the fluid flows in small diameter channels.

# 

#### **ILLUSTRATIONS:**

Flow pattern in a plate heat exchanger.

#### Figure A







Figure B

Figure C

Figure D

#### **1.1.2 Description of technology / working principle** (Feel free to modify/extend the short technology description below)

Spiral Plate exchanger consists of metal plates spiralised dividing the two heat transfer fluids.

#### 1.2.2 Types and "versions"

(Describe the most important forms/versions of technology under consideration, including their characteristic features, differences and similarities)

In spiral heat exchanger the hot fluid enters at the center of the unit and flows the inside outward. The cold fluid enters at the periphery and flows towards the center. Passages can be either smooth or corrugated general flow configuration can be crossflow (single or multipass) or counterflow depending on the configuration of the inlet and outlet distribution boxes. Compactness is the most important advantage of spiral heat exchangers: 100 m2 of effective surface is contained in a spiral element 1 m in diameter and 1.5 m long. High turbulence, low fouling and easy access are further advantages of the spiral units. Design pressure limit is 20 bar.

#### **ILLUSTRATION:**



#### 1.1.3 Description of technology / working principle

(Feel free to modify/extend the short technology description below)

Plate exchanger consists of a pack of corrugated metal plates with portholes for the passage of multiple fluids between which heat transfer will take place.

#### 1.2.3 Types and "versions"

(Describe the most important forms/versions of technology under consideration, including their characteristic features, differences and similarities)

In multi-stream heat exchangers three or more streams are thermally processed in a single unit. These exchangers have been used in cryogenic plants and in diary industry. In chemical industries they have been rarely applied so far. The multi-stream configuration can easily be achieved in the conventional plate heat exchangers, simply by installation of an intermediate plate on which the ports have not been cut out. Multi-stream units allow for further integration of chemical plants.



**ILLUSTRATION:** 

Scheme of a four-stream plate-and-frame unit

#### 1.1.4 Description of technology / working principle

(Feel free to modify/extend the short technology description below)

Micro-channel Plate exchanger consists of a pack of corrugated metal plates with portholes for the passage of two or multiple fluids between which heat transfer will take place.

#### 1.2.4 Types and "versions"

(Describe the most important forms/versions of technology under consideration, including their characteristic features, differences and similarities)

The channels in the micro heat exchanger plates have sizes around or lower than 1 mm and are fabricated via silicon micromachining, deep x-ray lithography or nonlithographic micromachining (Fig. A, B). The plates are stacked forming 'sandwich' structures. All flow configurations (co-, counter-current and crossflow) are possible. The basic limitations of microchannel heat exchangers are: sensitivity to clogging and pressure drop which is roughly inversely proportional to channel diameter. Matrix heat exchanger consists of a stack of perforated plates made of high thermal conductivity material such as copper or aluminum, alternating with spacers of low thermal conductivity such as plastic of stainless steel. They are used for cryogenic and low temperature applications and for fuels cells, and are suitable for a large range of operating conditions (Fig.C).

**ILLUSTRATIONS:** 



(A) Silicium deep etching micro-channels (CEA)



(B) Components of the plate and frame microchannel heat exchanger for countercurrent flow.



(C)

#### 1.3 Potency for Process Intensification: possible benefits

(In Table 1 describe the most important documented and expected benefits offered by the technology under consideration, focusing primarily on energy;  $CO_2$  emission and costs, providing quantitative data, wherever possible. Add other benefits, if needed).

Table 1: Documented and expected be	enefits resulting from	technology a	pplication
-------------------------------------	------------------------	--------------	------------

Benefit	Magnitude	Remarks
Energy Savings	30 to 50%	All Plate Type Heat exchangers have a tendency to foul much less than shell & tube heat exchangers. Turbulent flow regime is achieved at low flowrate. High convergence ratio heat transfer/pressure drop
Less CO2 emission	30 to 50%	See remarks above, and spiral plate type has embedded a self cleaning mechanism.
Cost Saving	Up to 1000%	All Plate Type Heat Exchangers can be designed with less heat transfer area.
Safety		Plate Type heat exchangers shall be used within their mechanical design limits. Some types are sensitive to cycling operation. Types provided with gasket are sensitive for leaking. Gasket made of special rubber like EPDM or VITON needs to be replaced frequently at least once every 3 years. Smaller inventory of chemical fluid. Lower retention time than Shell & Tube type.
Fouling		Plate Type Heat exchangers do operate much faster in turbulent regime than comparable Shell & Tube types. Normally a higher turbulence works anti-fouling. Wide

	gap plates are recommended are recommend for fiber containing fluids. Spiral Plate type work according a self-cleaning principle. Plate types with too small port holes are sensitive for fouling.
Maintenance	Plate Type exchangers with gasket and Spiral types are easy to maintain. Brazed types and diffusion bonded types can operate safely with clean fluids only.

#### 1.4 Stage of development

All Plate Type heat exchangers are fully matured. Existing profiles like Herringbone structure is challenged to further improve ratio heat transfer/pressure drop.

Different types are entering the market. Vatherus with Plate in Shell is combining the advantages of a shell and tube type together with plate and frame. This is made from circular plates welded together.



# 2. Applications

#### 2.1 Existing technology (currently used)

(Describe technology (-ies) that are conventionally used to perform the same or similar operations as the PI-technology under consideration)

Etched plate technology used by Heatric UK was introduced for heat exchanger application. Now it is being considered to be used as micro-channel reactor.

#### 2.2 Known commercial applications

(Is the technology broadly applied on commercial scale? In which process industry sectors is the technology most often applied: large volume chemicals – specialty chemicals & pharma – consumer products – ingredients based on agro feedstocks? What is the estimated number of existing applications? In Table 2 provide the most prominent examples of realized applications and provide their short characteristics)

All Plate Type Heat Exchanger Types have been broadly applied on commercial scale in various processes.

Table 2. Industrial-scale applications of the Technology (existing and under realization)

Sector	Company - Process/Product name/type	Short characteristic of application	Product ion capacity /Plant size	Year of applica tion	Reported effects
Chemical	Many End Users				•
Petro	Many End Users				
Pharma	Many End Users				
Food	Many End Users				

#### 2.3 Known demonstration projects

(Are there any demonstration projects known related to the technology under consideration? In which process industry sectors are those projects carried out: large volume chemicals – specialty chemicals & pharma – consumer products – ingredients based on agro feedstocks? In Table 3 provide the short characteristics of those projects.)

All mentioned Plate Type Heat exchangers are matured technologies so demonstration projects are covered by numerous life plant examples.

Table 3. Demonstration projects related to the technology (existing and under realization)

Sector	Who is carrying out the project	Short characteristic of application investigated, including product name/type	Aimed year of applicati on	Reported effects
				•

#### 2.4 Potential applications discussed in literature

(Provide a short review, including, wherever possible, the types/examples of products that can be manufactured with this technology)

The literature concerning the potential applications of Plate type heat exchangers is very rich. Petro – Chemical, Utility, Pharma and Food examples are overwhelming. Plate and Frame, Spiral Plate are more often used in heavy duty oil refining application and FPSO's.

Plate Fin type, are being considered to replace large LNG kettles shell tube type of 6 meter diameter 60 meter long. Core in Kettles is the next step to reduce size. However each Plate Type should be applied within their own mechanical pressure and temperature range.

# 3. What are the development and application issues?

#### 3.1 Technology development issues

(In Table 4 list and characterize the essential development issues, both technical and nontechnical, of the technology under consideration. Pay also attention to "boundary" issues, such as instrumentation and control equipment, models, etc.) Also, provide your opinion on how and by whom these issues should be addressed)

Table 4. Technology development issues

Issue	Description	How and by whom should be addressed?
Engineering & Design	Plate and Frame exchangers are originally used in milk applications. Manufacturers have developed different plate types from washboard, Herringbone to composite structures. Plate Fin type also brazed type aluminium type is used in cryogenic services. Spiral Plate Type is often used in applications like slurry and fouling fluids. Each vendor have developed their own correlations for pressure drop and heat transfer.	Vendors
Modelling	HTRI has developed software (X-PHE) to check-rate different vendor plate and frame types and spiral plate type. HTFS has developed MULE and MUSE software to model different plate fin types.	www.htri.net
Control	Proper control is required to operate plate types. For Plate and Frame type used for cooling high viscous liquids with open cooling water operate in winter condition may lead to local "freezing" effect. For Plate Fin, brazed aluminium types, and etched type like Heatric, are sensitive for temperature shock. Internal leakage is possible after cycling operation. Spiral Plate can be sensitive for cycling operation. Welded studs which ae needed in order to keep the plate distance, can protrude the plate leading to internal leakage. Spiral plate are used as (reflux) top condensers and lead to space and weight reduction.	

#### 3.2 Challenges in developing processes based on the technology

(In Table 5 list and characterize the essential challenges, both technical and non-technical, in developing commercial processes based on the technology under consideration. Also, provide your opinion on how and by whom these challenges should be addressed)

Challenge	Description	How and by whom should the challenge be addressed?
Distribution problem in Plate and Frame Type	Flow distribution for large plate surfaces is a point of concern. Flow needs to be proper distributed from a port hole area to square area.	Various vendors develop different plate shapes to improve the flow distribution
Etched type compact plate type like Heatric	Heatric is being investigated to work as micro reactor	ECN
Plate Fin Type used in HIDIC	C2 splitter applications to reduce column height.	TUD
Plate Fin Type used in Cold	LNG liquefaction process is making use of this type and resulted in compact scale LNG Snohvit	Linde/Statoil

#### Table 5. Challenges in developing processes based on the technology

Box	Core in Kettles.	
Plate & Frame Plate in Shell	The high conversion rate heat transfer / pressure drop this type can be seen as a good static mixer and can keep small bubbles in dispersion.	Vendors

# 4. Where can information be found?

**4.1 Key publications** (Provide the list of key publications in Table 6)

Table 6. Key	publications	on the technology
--------------	--------------	-------------------

Publication	Publication type (research paper/review/book/ report)	Remarks
K. M. Bailey. Understand spiral heat exchangers. <i>Chemical Engineering Progress</i> 1994 (May):59- 63, 1994.	Paper	
K. M. Bailey. Plate heat exchangers- A compact Heat Exchanger Technology. Anonymous. Anonymous. 1997.	Paper	
S. Deshpande. Spiral Heat Exchangers. <i>CEW</i> XXVIII (2):81, 2007.	Paper	
A. Heierle. Static Mixer-Heat Exchanger. <i>CAV</i> 1989, 1989.	Paper	
M. Picón-Núñez and R. Flow Passage Arrangement and Surface Selection in Multistream Plate-Fin Heat Exchangers. <i>Heat</i> <i>Transfer Engineering</i> 26 (9):5-14, 2005.	Paper	
S. K. Ramesh. Advances in Science and Technology of Compact Heat Exchangers'. <i>Heat</i> <i>Transfer Engineering</i> 27 (5):3-22, 2006.	Paper	
R. K. Shah. Advances in Science and Technology of Compact Heat Exchangers. <i>Heat</i> <i>Transfer Engineering</i> 27 (5):3-22, 2006.	Paper	
P. Stehlík and W. Different Strategies to Improve Industrial Heat Exchange. <i>Heat Transfer</i> <i>Engineering</i> 23 (6):36-48, 2007.	Paper	
B. Thonon and P. Tochon. Compact multifunctional heat exchangers: A Pathway to Process Intensification. In: <i>Reengineering the</i> <i>chemical plant - Process Intensification</i> , edited by A. Stankiewicz and J. A. Moulijn, New York - Basel:Marcel Dekker, 2004,	Paper	
B. Thonon and P. Tochon. Compact multifunctional heat exchangers: A Pathway to Process Intensification. In: <i>Reengineering the</i> <i>chemical plant - Process Intensification</i> , edited by A. Stankiewicz and J. A. Moulijn, New York - Basel:Marcel Dekker, 2004,	Paper	
J. van Reisen, P. J. T. Verheijen, and G. T. Polley. Potential benefits of using compact multi- stream heat exchangers in integrated process plants. BHR Group Conference Series Publication. Anonymous. Anonymous. 83-93, 1995.	Paper	
V. V. Wadeker, Compact heat exchangers, CEP	Book	

2000 (december), 2000.		
J. H. Wang. Use of plate heat exchangers in refinery and petrochemical plants. 2007.	Paper	
L. Wang and S. Design Methodology for Multistream Plate-Fin Heat Exchangers in Heat Exchanger Networks. <i>Heat Transfer Engineering</i> 22 (6):3-11, 2001.	Paper	

**4.2 Relevant patents and patent holders** (Provide the list of relevant patents in Table 7. Under "remarks" provide, where applicable, the names/types of products targeted by the given patent.)

Table 7. Relevant	patents
-------------------	---------

Patent	Patent holder	Remarks, including names/types of products targeted by the patent
WQ2006087E20	BP Exploration	
VVO200007520	Operating Co Ltd	
WO9967587,US6289693	Chart Industries Inc.	
WO9967587,US6289693	Process Systems Int. Inc.	
JP2006015277	Kobe Steel Ltd.	
EP1477761,DE10322406,JP2004340569	API Scmidt-Bretten	
CA2465599,US2004251003,US7055588	GmbH & Co KG	
CN1482057,CN123143C	Henan Yuguang Gold & Lead Co Ltd.	
JP2003320213	Mitsubishi Kasei Eng.KK	
DE10135714,WO03011850,EP1412345, KR20040018494,AU20023555636, US2004182692,CN1535269, JP2005506968T,CN1250537C	BASF AG	
CN1236730,CN1085187C	UNIV East-China SCI & Eng.	
FR2780772	Packinox	
DE10000288, EP1114975	Renzmann & Gruenewald GmbH	
DE10023684	Gea Canzler GmbH	
DE10133958	Canzler GmbH	
DE19519270	Rainer B	
DE19810186	Renzmann & Gruenewald GmbH	
EP1050570, US6413414	Bechtel Corp.	
US2001006104,JP2001194077	Nippon	
US6736200	Shokubai Co Ltd.	

#### 4.3 Institutes/companies working on the technology

(Provide the list of most important research centers and companies in Table 8)

#### Table 8. Institutes and companies working on the technology

Institute/Company	Country	Remarks
Alfa Laval	Sweden	
Gea Canzler GmbH	Germany	
CERT	France	
Heatric	UK	
ECN	The Netherlands	
Kobe Steel Ltd	Japan	

## 5. Stakeholders

#### 5.1 Suppliers and developers

(Provide the list of key suppliers/developers in Table 9)

|--|

Institute/Company	Country	Remarks
Alfa Laval	Sweden	
Gea Canzler GmbH	Germany	
Heatric	UK	
Marston	UK	
Linde	Germany	
Tranter	USA	
Schmidt Bretten	Germany	
Vatherus	Finland	
APV	UK	
Alfa Laval/Packinox	France	
Renzmann & Gruenewald GmbH	Germany	
Kobe Steel Ltd.	Japan	

#### 5.2 End users

(Describe the existing and potential end-users, other than those already listed in Table 2)

Aviation Industry

### 6. Expert's brief final judgment on the technology

(maximum 5 sentences)

The use of Plate Type Heat Exchangers has grown the last decennia exponential. Compactness and low CAPEX were the key sales drivers. However once you have decided to install a compact it will be forever compact. A way back to conventional Shell & Tube is often very difficult due to space limitations. Heat exchanger type selection must be "right the first time".