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Thesis

Second generation biodiesel synthesis and its innovative utilization in order to improve biomass gasification process

Settore Scientifico Disciplinare ING-IND/27 – Chimica Industriale e Tecnologica

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Introduction

Currently in our country, the exploitation of biomass for power generation is very limited: according to the statistics on renewable energy sources by the national Energy Services Provider (GSE), in Italy a power capacity from crops and agro-industrial wastes of about 450 MW was in fact installed in 2008 with a annual electrical energy generation around 2700 GWh, equivalent to less than 1% of the total national production. Among the technologies for biomass into electrical energy conversion, combustion is the prevailing one. In particular, almost all operating systems are based on the Rankine cycle steam turbine mainly combined to a mobile grate boiler (in a lesser degree to a fluidized bed boiler).

Biomass combustion is a simple and established process, but its efficiency is rather low. In fact, the ratio between produced electrical electricity and consumed energy in the form of biomass does not exceed 25% for plants with a significant size (capacities starting from 10 MW are considered as significant for biomass powered systems) and decreases dramatically for smaller size systems.

Furthermore, as plant capacity increases, supplying and storage of the fuel become more and more complex, since, according to the aforementioned values of efficiency, an average of 1-1.5 kg of biomass per kWh of generated electricity is needed. As a result, with the exception of particularly advantageous cases, the optimal plant capacity for electricity generation from biomass tends to be rather small (around 1 MW). In effect, even for values close to 10 MW, the supply chain of fuel can be very expensive.

On the other hand, gasification is a technology that has a great potential in terms of efficiency of biomass into electricity conversion. Actually, by transforming a solid fuel into a gaseous one, it makes to be possible the use of biomass to power a high-performance system, allowing the achievement of overall conversion efficiency much higher (in principle approaching 40%).

About this kind of applications, currently the main expectations are placed upon the development of systems (known as IGCC, Integrated Gasification Combined Cycle) obtained through the combination of a fluidized bed gasifier, which will be used preferably oxygen and / or steam which gasification agent, with a gas-steam combined cycle.

However, the technical and economic feasibility of these systems requires the installation of significantly power plant (from 20 MW). Therefore, also in the hypothesis of *a favorable development of technology, the problems, which we mentioned earlier, associated with the retrieval, transport and storage of large quantities of biomass required would persist.*

Moreover, the development of advanced gasification technologies, such as steam or just oxygen steam, allows producing a gas with relatively high hydrogen content, from 30 to over 45% by volume. Therefore, there is an increasing interest in the possibility of producing hydrogen, which many experts will be the energy carrier of the future, from renewable sources and, in particular, biomass. As it is known, hydrogen can also be used to generate electricity by the use of power fuel cells.

In this respect the present paper examines the possibility of direct coupling between the steam gasifier and fuel cell, which would avoid complex and costly systems for handling and storage of gas produced. Also an integrated gasifier/fuel cell, in addition to environmental benefits, offers in principle a total return at least equal to that obtained with the combined cycle, but, thanks to the modular design of the conversion device, which yield is virtually independent from the size of the plant. So this technology, therefore, is particularly suitable for distributed generation, which is the most promising field of application for the use of biomass energy.

Among the different types available with an adequate level of technological maturity, the molten carbonate fuel cell is best suited to be powered by gas produced by the gasification process. In fact, it accepts as fuel, including carbon monoxide, present in high percentage in the gas, and makes, therefore, not necessarily insertion of a unit of separation of hydrogen or intermediate reforming, which would further complicate the structure of installation.

The very complexity of design, implementation and management is one of the most critical aspects of an integrated gasifier/molten carbonate fuel cell plant.

Specifically, the present work aims to examine some critical aspects of the integration of a dual fluidized bed steam gasification plant and a molten carbonate fuel cell, such as:

1. *conditions to make the gas produced from the gasification actually usable as fuel for the cell;*
2. *the definition of improvements necessary to clean-up section for the matching gasifier /cell and their optimization;*

3. *The optimization of energetic integration needed by the plant for a more efficient running.*

Summary

The necessity of using clean energy sources to meet the growing energy needs of the planet is a topic of strong current especially given the consequences, sometimes even tragic, that climate change brings.

Therefore the development of new low-emission energy sources becomes a must for research. Gasification of biomass, especially considering the significant possibility of future developments, and bio-diesel from waste sources, are certainly among these sources.

The first and second chapter provides a state of the art gasification technologies and processes, describing the differences between the various technologies currently available and the lines of ongoing research.

In the third chapter has been described the biomass gasification platform operating in Enea Research centre of Trisaia.

Chapter four give us a detailed state of arts about gasification producer gas cleaning. The most recent technologies are described divided respect to the most important pollutants presents in the producer gas.

In the fifth chapter was instead described the research work made to develop an innovative cleaning section to remove tars from syngs. In fact, this is the direction my work has concentrated primarily in the development of the process of cleaning the gas produced and optimization of mating gasifier / fuel cell with a view to distributed generation of electricity.

So in the sixth chapter it is described the technology developed in order to remove from syngas acid pollutants and sulphur compounds.

In chapter seven the simulation carried out to optimize the accomplishing between gasification plant and a molten carbonate fuel cell are described.

The chapter eighth provides a detailed state of arts about biodiesel production with a particular focus on the different technology depending in the triglyceride source.

Chapters nine and ten describes the research dedicated to the synthesis of bio-diesel. Hence my research has been directed especially towards the study of innovative catalysts, which enable it to use waste materials as sources for the reaction of trans-esterification, thus lowering the cost of bio-diesel product.

This thesis work was done in collaboration with ENEA (Italian Agency for New Technologies, the Energy el Environment), Department of Technologies for the Energy, Renewable and Energy Saving in particular biomass energy at the Section established Research Center Trisaia.

Introduzione

L'utilizzo delle biomasse per la produzione di energia elettrica è allo stato attuale molto limitato: dalle statistiche sulle fonti rinnovabili del GSE relative all'anno 2008 risulta, infatti, installata una potenza elettrica da colture e scarti agro-industriali di circa 450 MW con una produzione di energia annua intorno ai 2.700 GWh, pari a meno dell'1% della produzione nazionale complessiva.

La tecnologia di conversione energetica pressoché esclusivamente adoperata è la combustione. In particolare la quasi totalità degli impianti si basa sul ciclo Rankine a vapore associato a caldaie a griglia mobile o, in qualche caso, a letto fluido. Si tratta di un processo semplice e consolidato, il quale però offre una modesta efficienza globale di conversione: infatti, il rendimento elettrico netto in genere non supera il 25% per impianti di potenza dell'ordine dei 10 MW elettrici. Tale valore si riduce ulteriormente per sistemi di piccola taglia, salvo che non si ricorra a cicli Rankine a fluido organico, i quali però comportano un notevole incremento del costo d'impianto.

D'altro canto al crescere della potenza installata diventa progressivamente più critico l'approvvigionamento e lo stoccaggio della materia prima, dato che, con i suddetti valori del rendimento, occorrono in media 1÷1,5 kg di biomassa per ogni kWh di energia elettrica prodotto. Ne consegue che, salvo casi particolarmente favorevoli, conviene limitare la potenza degli impianti per la produzione di energia elettrica da biomasse a poche decine di MW, tenendo comunque presente che, per questi valori della taglia, la gestione dei flussi del combustibile può essere complessa e onerosa.

Il processo di gassificazione rappresenta una risposta interessante al problema della bassa efficienza di conversione delle biomasse in energia elettrica. Infatti, la trasformazione del materiale solido di partenza in un combustibile gassoso, ne consente la valorizzazione in un sistema ad alto rendimento (ciclo combinato) con un'efficienza complessiva che secondo le stime può attestarsi sul 40%. Per siffatte applicazioni, bisogna però ricorrere a processi tecnologicamente avanzati, utilizzanti ossigeno e/o vapore quale agente di gassificazione, ed a dimensioni dell'impianto significative. In effetti, il gassificatore a letto fluido, in ossigeno o vapore, abbinato al ciclo combinato è, a giudizio degli esperti, la tecnologia con le più grandi potenzialità, per potenze elettriche installate a partire da 20 MW. In ogni caso tale opzione presenta degli aspetti critici, legati ai *problemi di reperimento, trasporto e stoccaggio della biomassa cui si è accennato in precedenza.*

Peraltro la possibilità di produrre un gas con un'alta frazione d'idrogeno ne consente in linea di principio l'utilizzo in una cella a combustibile. In tal modo, oltre ai notevoli benefici di natura ambientale, è possibile ottenere un elevato rendimento energetico complessivo e, grazie alla struttura modulare del dispositivo di conversione, poco influenzato dalla taglia dell'impianto.

Questa tecnologia si presta quindi molto bene per la generazione distribuita, che costituisce forse il campo di applicazione più promettente per l'utilizzo ai fini energetici delle biomasse. Infatti, gli impianti di piccola potenza (qualche centinaio di kW) che da un lato consentono di attenuare i problemi connessi con la gestione logistica della materia prima e dall'altro, avendo un impatto più ridotto sul territorio, possono risultare più accettabili per le comunità locali.

Una tipologia di cella particolarmente adatta a essere alimentata con il gas prodotto, tra quelle che consentono l'installazione di potenze significative, è quella a carbonati fusi, per il fatto che essa accetta, come combustibile, anche il monossido di carbonio, presente in alta percentuale nel suddetto gas. In tal caso, quindi, non si rendono necessarie unità di separazione dell'idrogeno, che complicherebbero ulteriormente la struttura dell'impianto. Proprio la complessità di progettazione, realizzazione e gestione costituisce uno degli aspetti più critici di un sistema integrato gassificatore/cella a carbonati fusi. In effetti, alle problematiche specifiche delle singole tecnologie coinvolte, ancora in fase di sviluppo, si aggiungono quelle derivanti dal loro accoppiamento. Tra queste grande rilievo assume la necessità di ottenere un gas dall'elevata purezza: il corretto funzionamento della cella, infatti, impone vincoli molto stringenti sul contenuto massimo di contaminanti, quali ad esempio i composti carboniosi condensabili (tars) e quelli acidi.

L'utilizzo di un gas combustibile avente caratteristiche inadeguate potrebbe determinare una drastica riduzione nella vita dello stack, la cui durata, già in condizioni di esercizio ordinarie, è relativamente breve e costituisce uno dei principali svantaggi della pila a carbonati fusi.

Il mio lavoro di ricerca si inserisce nel quadro del miglioramento delle prestazioni del gassificatore, in termini di resa energetica e di sviluppo del sistema di purificazione del gas prodotto, in modo da consentire l'alimentazione di una cella a carbonati fusi con *tale gas ed ottimizzare l'impianto integrato gassificatore/celle a combustibile. In quest'ottica è stato svolto un lavoro di modellazione del sistema di lavaggio del gas attraverso un innovativo scrubber a bio-diesel. Per fare ciò è stata utilizzata una modellazione tramite l'utilizzo di un software commerciale, il ChemCad.*

È stato quindi sviluppato un completo up-grading della sezione di cleaning rivolto all'ottimizzazione dei sistemi di abbattimento dei composti acidi e dei composti dello zolfo.

Sono state infine valutate le prestazioni del sistema integrato gassificatore-cella a combustibile sia da un punto di vista di efficienza energetica che di performance ambientali.

Il secondo filone della ricerca svolta si è così concentrato sullo studio dei processi di produzione del biodiesel e sulla loro ottimizzazione tecnica ed economica. Sono stati studiati nuovi catalizzatori in grado di migliorare la fase di produzione anche partendo da una sorgente di scarto, quali gli oli esausti. Infatti, l'utilizzo, come sorgente, dei trigliceridi degli oli esausti porterebbe, oltre ad un abbattimento sensibile del costo di produzione del bio-diesel stesso (dove l'elemento principale di spesa è proprio il costo della materia prima), anche a un processo di produzione distribuita di questo bio-fuel secondo le crescenti esigenze del mercato.

È stata inoltre analizzata la possibilità di far avvenire la reazione di transesterificazione in continuo in un innovativo reattore PFR in luogo della classica configurazione in batch, in modo da ottimizzare anche questa fase del processo di produzione e renderla quindi più vicina a un'eventuale produzione su larga scala.

Sommario

La necessità di ricorrere a fonti di energia pulita per soddisfare i sempre crescenti bisogni energetici del pianeta è un tema di forte attualità soprattutto di fronte alle conseguenze, talvolta anche drammatiche, che l'alterazione del clima porta con sé.

Di conseguenza lo sviluppo di nuove fonti di energia a basse emissioni diventa un must per la ricerca. La gassificazione delle biomasse, soprattutto considerando la notevole possibilità di sviluppi futuri, e il bio-diesel da fonti di scarto, rientra certamente tra tali fonti.

Il primo e il secondo capitolo forniscono uno stato dell'arte delle tecnologie di gassificazione, dei processi più diffusi industrialmente con una particolare attenzione ai processi di gassificazione termica della biomassa.

Nel terzo capitolo viene data una descrizione degli impianti di gassificazione operanti nel Centro Ricerche ENEA della Trisaia, impianti su cui si è focalizzato questo lavoro di ricerca.

Nel quarto capitolo viene fornito un dettagliato stato dell'arte sui processi di pulizia del gas prodotto da impianti di gassificazione.

Nel quinto capitolo sono descritte le analisi e le simulazioni effettuate nell'ottica dell'abbattimento del tenore di Tars nel gas di sintesi.

Nel sesto capitolo sono riportati risultati relativi agli studi fatti sulla rimozione degli altri composti inquinanti con particolare attenzione ai composti dello zolfo ed ai composti acidi.

Nel settimo capitolo vengono descritti gli studi relativi all'accoppiamento gassificatore-cella a combustibile dal punto di vista dell'efficienza energetica e delle performance ambientali del sistema integrato.

Il capitolo otto fornisce una descrizione dettaglia dei processi di produzione del bio-diesel con particolare attenzione alle diverse materie prime utilizzate come fonti di trigliceridi.

Nel nono capitolo viene rportata l'analisi delle variabili di processo nella sintesi del biodiesel con particolare attenzione allo studio della migliore catlisi da utilizzare al fine di ottimizzare i costi di produzione..

Nel capitolo dieci sono mostrati i risultati dei tests sperimentali di sintesi dei biodiesel effettuati variando la materia prima, variando il tipo di catalizzatore ed a diverse configurazioni reattoristiche.

Questo lavoro di ricerca è stato svolto in collaborazione con l'ENEA – Ente per le Nuove Tecnonologie, l'Energia e l'Ambiente, ed in particolare col dipartimento di Tecnologie per l'energia, le biomasse ed il risparmio del centro Ricerche ENEA della Trisaia.

Chapter 1

The Gasification Process

1. The Gasification Process

1.1 Introduction

A large effort was directed towards the development of advanced biomass gasification technologies in the last decades. The current biomass gasification technology developments are essentially based on coal gasification processes.

During World War II, biomass gasification was widespread. It was used primarily to create a fuel gas e.g. in cars. After the war, however, the gasifier development stagnated for many years, until the first oil crisis. At that time, the re-discovery of the tremendous potential of biomass launched a new age for gasification [1].

Several recently developed biomass gasification plants have reached the pilot scale level, however, only a few technologies have advanced to the commercialization stage so far. The biomass gasification process is quite similar to that of coal gasification, yielding in both cases a mixture of gases with the same main components. However, the distribution of the resulting gases is different for biomass and coal, and the reaction conditions for biomass are milder than for coal gasification, due to the higher reactivity of biomass [2]. As in the case of coal gasification, biomass gasification under increased pressure conditions favors the production of methane and carbon dioxide, whereas increasing the temperature tends to increase the concentration of hydrogen and carbon monoxide. Undesirable by-products and emissions encountered in the product gas, such as particulates and tar, are the main complications for its use in downstream synthesis or electricity production. Steam is often used as the gasification agent for syngas production.

Blended with oxygen or air, it promotes the formation of H2 and CO. Furthermore, steam gasification contributes substantially to the reduction of tar formation. The use of catalysts (e.g. Ni) in connection with steam gasification additionally contributes to increasing the hydrogen content due to the catalytic conversion of tar [2].

Using high-temperature oxygen-blown gasification, the tar content can be reduced to even lower levels. The general purity requirements for synthesis gas suitable for synfuel production are listed in table 1.1.

Tab. 1.1: Permissible particle, tar, alkali and sulphur content of a synthesis gas suitable for a commercial methanol synthesis process [3,4,5]

Component	**Permissible Concentration**
H_2S and other sulphur compounds	< 0,1 mg/Nm^3
Particles	< 0,1 mg/Nm^3
Tar	< 1,0 mg/Nm^3
Alkalis	< 0,25 mg/Nm^3

The general reaction of fuel synthesis is the formation of hydrocarbon chains from synthesis gas as follows:

$$CO + H_2 \rightarrow -(CH_2)- \ + H_2O$$

The reaction is exothermic and needs a catalyst. Process conditions of the main fuel synthesis are listed exemplary in table 2. Most synthesis forming hydrocarbon chains – CH_2- and H_2O need a ratio of the educts H_2/CO of 2/1.

Tab.1. 2: Exemplary process conditions of fuel synthesis and synthesis gas ratio.

	Product	**Pressure**	**Temperature**	**Catalyst**	**H_2/CO**
Methane	CH_4	1-30 bar	300-400 °C	Ni	3/1
Methanol	CH_3OH	50-100 bar	250-280 °C	Cu/ZnO	2/1
Fischer-Tropsch	- CH_2-	3-25 bar	190-240 °C	Co	2/1
Fischer-Tropsch	- CH_2-	3-25 bar	250-300 °C	Fe	2/1

The use of catalysts requires a very clean synthesis gas. Therefore, high-priority research efforts focus on gas cleaning and on technologies with gas cleaning/conditioning (e.g. catalytic and thermal tar cracking), which yield synthesis grade gases. There are several options for gasification available or in development.

However, only a few of them are suitable for biomass applications for producing hydrogen and synthesis gas. Gasifiers can work either with direct heating, in which the biomass is partially oxidized in order to supply the heat for the gasification or with indirect heating, using heat exchangers or heat carriers for the heat supply. For synthesis gas generation from biomass, the indirectly heated reactors or the directly heated, oxygen-blown reactors with partial oxidation are preferred. In both cases, the product gases show low proportions of inert gas (N2) with a relatively high hydrogen concentration. Besides the operation mode of the gasifier - autothermal with direct heating or allothermal with indirect heating - the main classifications of the gasification process are the fluidized, fixed-bed, and entrained flow reactor type.

1.2 Fundamental of Thermo-Chemical conversion

Thermo-chemical conversion covers different processes with interleaved boundaries listed in table 3. The main differences between pyrolysis and gasification are the envisaged products and the process conditions. While biomass pyrolysis starts in a temperature range above 400 °C without air contact or other agent, gasification needs higher temperature and a gasification agent like air, O_2, steam or hydrogen.

Tab. 1.3: Conditions and products of thermo-chemical conversion

Process	**Conditions**	**Products (mass %)**		
		Liquids	**Coke**	**Gas**
Fast Pyrolisis	400-550 °C, short residence time	75%	12%	13%
Carbonation	>500 °C, long residence time	30%	35%	35%
Gasification	>800 °C, gasification agent: air, O2, steam	5%	10%	85%

Pyrolysis and gasification are both endothermic therefore heat transfer to the reactor is necessary. In the case of gasification a distinction in direct (autotherm) and indirect heated gasifiers (allotherm) is established. While direct heated gasifiers use partial oxidation to generate the necessary heat demand, indirect gasifiers are heated from outside mainly over the reactor wall or heat carriers. Heating value, amount and composition of the product gas depends strongly on heat transfer method and gasification agent. Exemplary product gas compositions for different gasification agents are given in table 1.4. Air blown direct heated gasifiers produce a nitrogen diluted low calorific gas. Oxygen blown or indirect heated gasifiers generate a medium calorific gas.

Tab. 1.4: Average product gas compositions (vol. %) with different gasification agents

Gasification agent	**H_2**	**CO**	**CH_4**	**CO_2**	**N_2**	**H_2/CO**
Air	15%	20%	2%	15%	48%	0.75
Oxygen	40%	40%		20%		1
Steam	40%	25%	8%	25%	2%	1.6

1.3 Classification of Gasifier.

Gasifier could be classified on the basis of heat transfer method, gasification agent, thermal capacity and the technical design. The functional principle of common gasifier layouts are shown in figure 1.1.

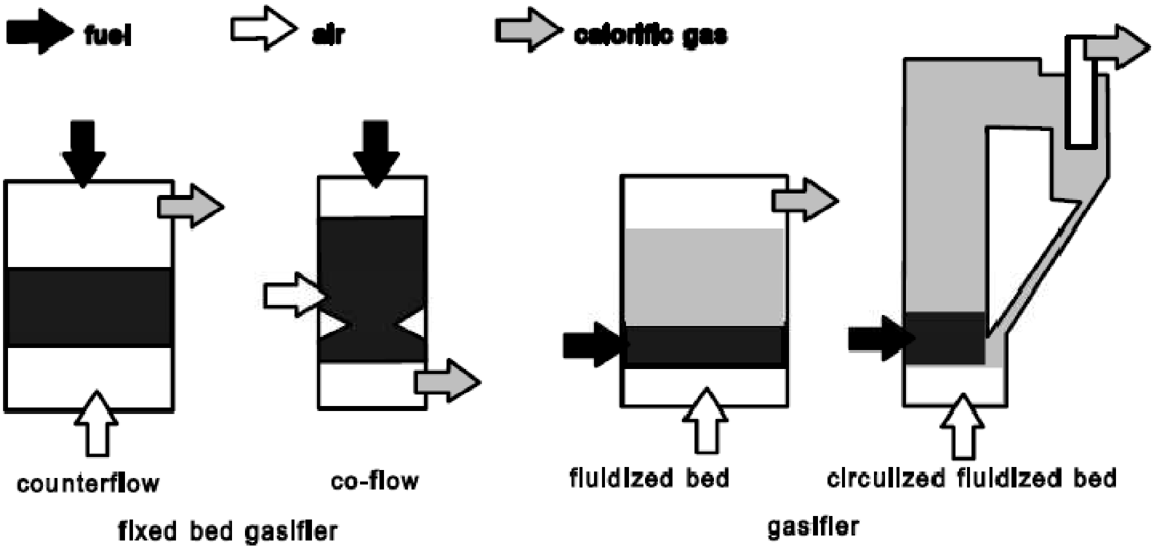

Fig. 1.1: Functional principle of gasifier.

All of the schematically shown gasifier produce a calorific gas with more or less high concentrations of tar, particles and other impurities which needs further gas cleaning and conditioning for fuel synthesis. On the left side is shown the counter flow gasifier.

Due to the counter-flow an excellent heat exchange between the hot product gas and the supplied fuel is realized, unfortunately this produces a lot of tar. The co-flow is also a fixed bed gasifier with a hot glowing zone at the bottom where the produced gas has to pass working as tar cracker. The operation of fixed bed gasifier demands a high fuel quality, particularly a homogenous piece size. More flexible concerning operation, fuel, scale and the use of a gasification agent are fluidized bed type gasifiers. Inert bed material is used (e.g. silica sand) to realize homogenous conditions and rapid heat transfer in the fluidized bed. Fluidized bed technique enables long operation periods and continuous ash removal and bed material renewal. The operation temperature is limited by the ash (and bed material) sintering temperature below 900 °C. Because tar content depends on operation temperature, a medium tar and particle laden gas is produced. A further important principle is the entrained flow gasifier which needs pulverized fuel and is operated above the ash melting point (> 1000 °C). Ash is removed as liquid phase and due to the high temperature tar content is very low. Some technical concepts for fuel generation which are described more detailed later on propose staged processes to use the advantages of different reactor types.

Table 1.5 shows the tar and particle content of the product gases in dependence on the gasifier type. As the tar formation is strongly dependent on temperature and operating conditions, the table gives large intervals for the tar concentrations. In general, high residence time, high temperature and high steam-to-carbon ratio contribute to the reduction of the tar content in the product gas.

Tab.1. 5: Tar and dust content of product gases from different gasifier

Gasification Reactor Type	**Tar Content [g/Nm^3]**	**Dust Content [g/Nm^3]**	**Source**
Co-Current	0.05 -1.0	<10	[6]
Fixed Bed	0.05 – 6.0	1.0 – 3.0	[4]
	0.1 – 2.0		[7]
Counter Current	5.0 – 10.0		[6]
Fixed Bed	10.0 – 100.0	0.01 – 10.0	[4]
Fluidized Bed	1.0 – 30.0	1.0 – 100.0	[4]

1.3.1 Directly Heated gasifier

In directly heated gasifier, the required process heat is supplied by partial combustion of the feedstock. In this case the flue gas is mixed with the product gas. Directly heated gasifier, with oxygen (or oxygen-enriched air) produce a gas with medium heating value and a lower hydrogen concentration as compared to the product gas from indirectly heated gasifier. The inert N2 concentration is negligible when using oxygen. However, the CO2 concentration is relatively increased compared to the gas from indirect heating. The operation temperatures are relatively high (900 to 1500 °C). The main advantage of these gasification processes is the low hydrocarbon concentration (short-chain like methane and long-chain like tars) in the product gas compared to gasifier which operates at lower temperatures. Thus, an additional downstream hydrocarbon conversion (methane reforming/tar conversion) is not necessary. The disadvantage of this technique is the need for an oxygen production unit which increases the capital costs, especially due to the disproportionally high share of the oxygen plant costs for a small decentralised plant. As the downstream synthesis plants operate at pressures of 20 to 100 bar, it is advantageous to operate the gasifier at elevated pressure. The various directly heated gasifiers developed so far, or which are still in development, differ in technical complexity, gas quality, and capital costs. Some interesting approaches with relevance for synthesis gas or hydrogen production are presented below.

RENUGAS Process

The RENUGAS process developed at IGT (Institute of Gas Technology) uses a pressurized bubbling fluidized bed reactor [8]. A demonstration plant for 90 t/day of wood or 63 t/day cane trash as feedstock was constructed by the Pacific International Centre for High Technology Research in Hawaii. The oxygen requirement of the plant is about 0.3 kg/kg wood feed and the lower heating value (LHV) of the resulting dry fuel gas is 11.8 to 13.5 MJ/Nm3. The dry fuel gas yield is 1.0 to 1.2 Nm3/kg wood feed. The gasification operation temperature for wood is 910 °C and the operation pressure is 23 bar. The fuel gas has the following composition: 16 Vol.% CO, 38 Vol.% CO2, 17 Vol.% CH4, and 28 Vol.% H2. A special gas cleanup system was applied, in order to obtain a synthesis-grade fuel gas. A schematic flow sheet of the process is given in figure 1.2.

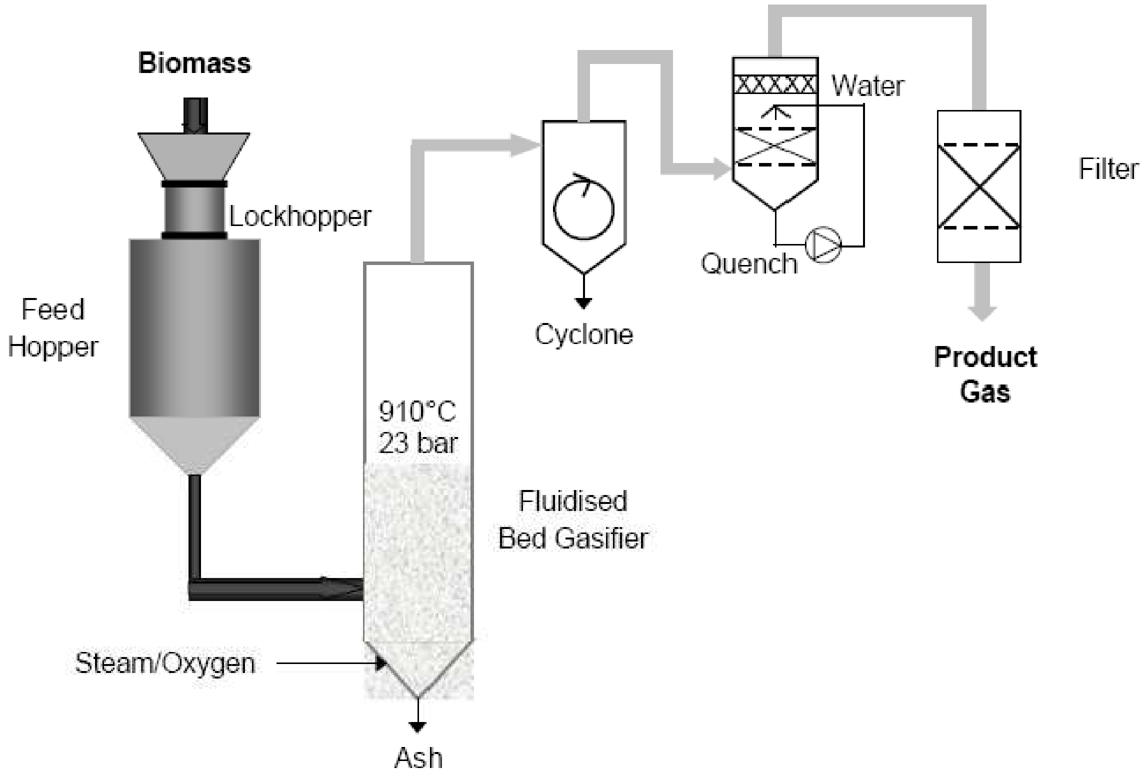

Fig. 1.2: Schematic presentation of the RENUGAS process.

Carbo-V Process

The Carbo-V process is a relatively new development from the Umwelt- und Energietechnik (UET) Company in Freiberg, Germany [9]. It aims to produce a tar-free synthesis gas for synfuel/hydrogen or electricity production. The Carbo-V process is a two-step process. In a first step the biomass is converted into a tar-containing gas and char coal in a pyrolysis unit at ca. 500 °C. The tar-containing gas is fed into a second reactor together with oxygen as a gasification agent, and used for the gasification of grounded charcoal from the first reactor. Here the charcoal is completely gasified at ca. 1500 °C in an entrained flow process. The ash is removed from the system in liquid form due to the high operation temperature. The process-specific advantages of the Carbo-V gasifier are: (I) no special requirements are needed for the feed regarding lumpiness, homogeneity, humidity, etc.; (II) the high operation temperature of the gasifier leads to a largely tar-free gas; (III) after wet cleaning, the product gas meets the high specifications for downstream synthesis or gas engines. A typical product gas analysis is presented in table 6. Figure 3 shows the flow sheet of the Carbo-V process.

Tab.1. 6: Typical product gas composition of Carbo-V process

	Gasification with oxygen	**Gasification with air**
Gas component	***Vol. %***	***Vol. %***
CO	39.2	21.8
CO_2	20.4	11.4
H_2	40.2	22.1
CH_4	0.1	0.0
N_2	0.1	44.7

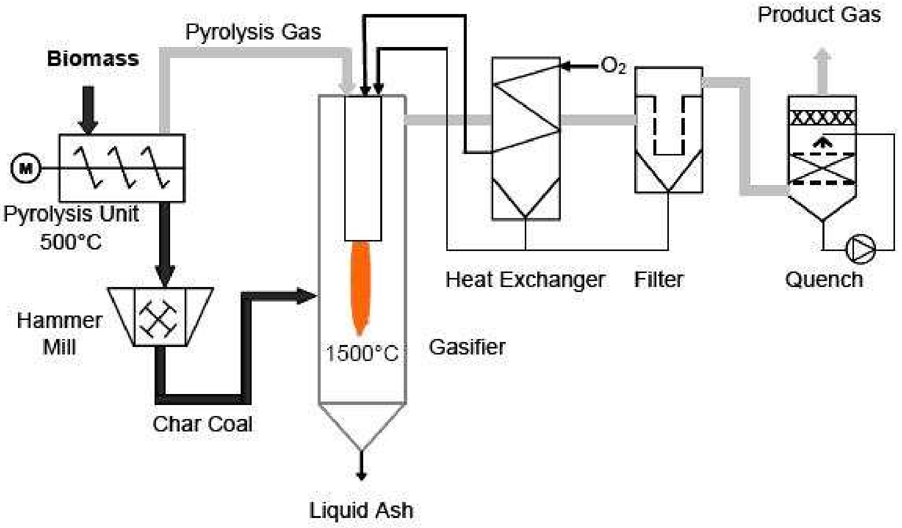

Fig. 1.3: Carbo-V process flow sheet [9].

HTW Process

The High-Temperature Winkler (HTW) process was developed at the Rheinische Braunkohlenwerke AG, Germany, and consists of a pressurized fluidized bed reactor with oxygen/air and steam as the gasification agent. The process operates at pressures up to 10 bar and temperatures in the range of 800 to 1100 °C [10]. The gasifier was extensively tested between 1956 and 1964 with lignite as feedstock. A typical {steam + oxygen}/lignite ratio ({0.41 kgsteam + 0.36 Nm3 O2}/kglignite) gives a carbon conversion of 96 % and a carbon monoxide + hydrogen yield of 1.4 Nm3/kg lignite. A typical dry product gas composition is: H_2 42 Vol.%, CO 39 Vol.%, CO_2 17 Vol.% and CH_4 2 Vol.%. The main characteristics of the process are: (I) high throughput rate, (II) high-purity product gas, suitable for the synthesis of methanol, (III) suitability for a wide variety of feedstock (lignite, wood, biomass, etc.), and (IV) flexibility in the product gas utilization (synthesis gas, reduction gas, hydrogen, gaseous fuel). A demonstration plant with a production capacity of 37,000 Nm3/h of synthesis gas for methanol production (14 t/h) from lignite in Wesseling, Germany, was constructed in 1986. Several other feedstock (wood, peat, etc.) were tested, obtaining a synthesis gas suitable for methanol production. Especially wood can be converted with high efficiency [11].

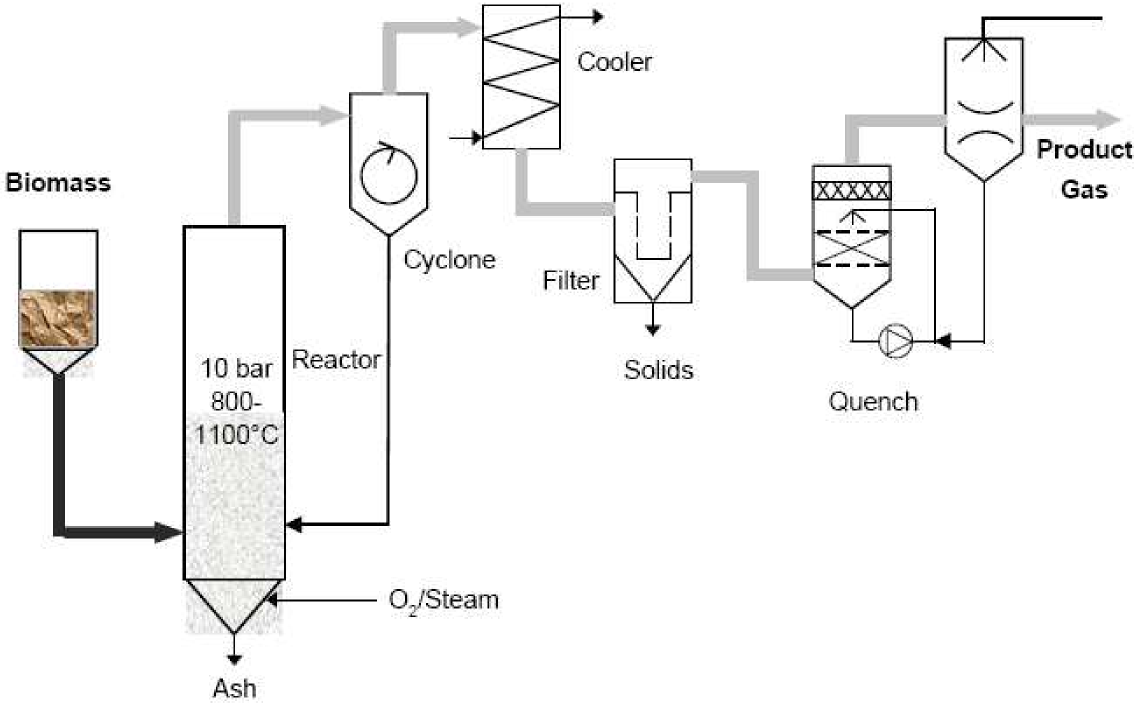

Fig. 1. 4: Flow sheet of the HTW high-pressure biomass/coal fluidised bed gasification [11]

Figure 1.4 shows the flow sheet of the HTW process. The raw product gas is subjected to a complex gas cleanup before methanol synthesis. The gas is separated from the solids in a cyclone and then cooled down. Downstream the gas enters a gas filter and a scrubber. Subsequently, the sulphur components are separated in a second chemical or physical washing step in order to achieve synthesis gas quality.

Texaco Process

The high pressure Texaco process was developed in the eighties. The Texaco process is based on work from the Texaco Development Corp. in the forties [12]. It involves entrained flow gasification with oxygen at high pressures (up to 80 bar) and high temperatures (around 1300 °C). Due to the high gasification temperatures with the Texaco procedure, a carbon conversion close to 100 % and high gas purity can be obtained. Several plants for coal gasification have been constructed in Europe and in the USA for synthesis gas production [12, 13].

Texaco and HTW processes with coal gasification are highly suited for application in combined-cycle power plants [14]. A 100 MWe power plant constructed in 1988 in the USA using the Texaco principle was regarded as the cleanest coal power plant in the world. The environmental and economical advantages of these gasification processes, and their versatility in the use of different fuels, biomass, wood, etc. were fully demonstrated in the eighties and nineties.

Schwarze Pumpe Waste-To-Methanol Process

At Schwarze Pumpe Spreewitz, Germany, three different types of high-temperature gasifiers for co-processing of waste (solid, liquid/paste-like), biomass (e.g. contaminated waste wood), and coal have been operating since 1998. Solid feeds are gasified in a high-pressure fixed-bed gasifier (25 bar, 800-1300 °C) or in a slag bath reactor (1500-1800 °C). Liquid or liquid-like wastes, such as tars, oils, slurry products (oil-water-solids), etc., are processed in an entrained flow reactor (25 bar, 1350-1800 °C). The gasifying agents are water and oxygen. The product gases, after several steps for cleaning, cooling, and conditioning (stoichiometric adjustment), is supplied to a methanol synthesis plant and used for electricity generation. The share of the waste in the feed is up to 75 Wt.% (rest: coal). In 2002, 300,000 t of waste was processed and ca. 100,000 t of methanol was produced [15].

1.3.2 Indirectly heated gasifier

Indirectly heated gasifier are designed to take advantage of the higher reactivity of biomass relative to coal, and to produce a gas with a higher hydrogen content compared to directly heated gasifier. A number of different technologies have been developed to the pilot stage and currently being tested worldwide. The indirect heating leads to a product gas with a medium energy content, which is not diluted with nitrogen (without the use of costly oxygen). In an indirectly heated gasifier, the heat is supplied to the reactor through a heat exchanger or heat-carrying materials like sand (allothermal process). Steam is introduced with the feedstock to the reactor to promote the gasification reaction and to increase the hydrogen yield. The disadvantages of the indirectly heated gasifiers for synthesis gas production are the relatively high methane and tar concentrations in the product gas due to the low operation temperature. Additionally, operation under pressure is difficult with this technology. Some of promising developments in the field of indirectly heated gasifiers for biomass are presented below.

DMT Indirectly Heated Steam Gasifier

In the indirectly heated steam gasifier developed at DMT (Deutsche Montan Technologie, Germany), the process heat needed for the biomass gasification is not supplied using a suitable heat exchanger, but rather through combustion of a part of the product gas. In contrast to other allothermal gasification processes, the flue gas from the combustion process is not separated from the product gas. This process thus leads to lower hydrogen concentrations and an additional oxygen demand when nitrogen must be avoided in the product gas.

The gasification takes place in a stationary fluidized bed reactor at about 4 bar and 850 °C. The hot product gas first enters a cyclone for dust removal, and then passes through a heat exchanger where its heat is released for steam generation. Finally the product gas passes a gas filter, a water quench, and a downstream fixed-bed filter. The gas composition varies depending on whether oxygen or air is used as combustion agent. A typical product gas composition using oxygen as the combustion agent is: H_2 37.5 Vol.%, CO 15.9 Vol.%, CO_2 34.9 Vol.%, CH_4 9.2 Vol.%, C_2H_4 2.2 Vol.%, and N_2 0.3 Vol.% [16].

The use of steam as a heat carrier - compared to a directly heated reactor - generates a product gas with a high hydrogen concentration as well as low dust and tar content. In order to provide the heat in the gasification zone, a part of the product gas is burned with air or oxygen. The heating value of the obtained product gas is improved when using oxygen for steam generation. The lower heating value (LHV) of the product gas is ca. 10.5 MJ/Nm3 if oxygen is used for the combustion process. In a pilot plant with 500 kg/h feed, the gasifier was test-operated at DMT for 27,000 h in the eighties. A flow sheet of the DMT process is shown in figure 1.5 [16].

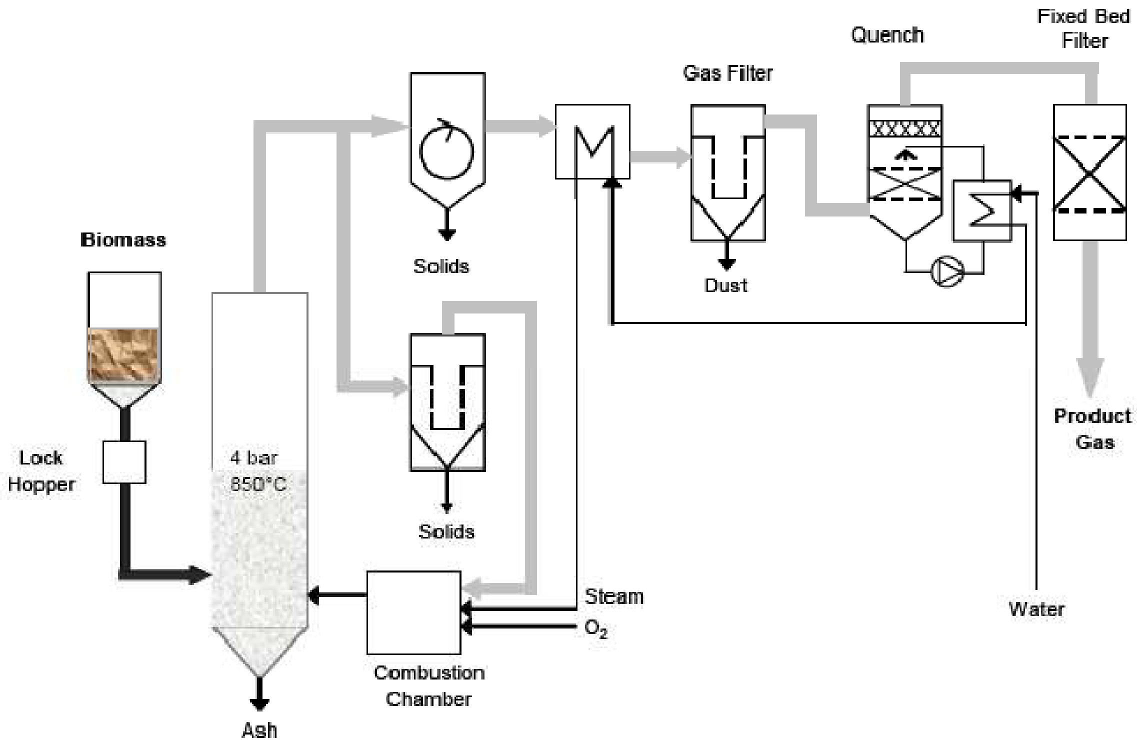

Fig. 1.5: Flow sheet of the DMT process

DM2 Staged Reforming Process

In the first step of the Staged Reforming Process of the DM2 Company, Germany, the biogenous material is decomposed in a pyrolysis reactor at about 500 - 600 °C into a gas (approx. 80 Wt.%) and char (approx. 20 Wt.%) [17]. The heat is supplied by heat-carrying materials, e.g. metal spheres or other inert materials. The char leaves the reactor at the bottom into the firing, the gas and tars move in the opposite direction as the heat-carrying medium, entering the reforming stage and exiting at the top of the reformer, in which the organic compounds (e.g. tars, hydrocarbons) are steam-reformed to H2 and CO. The heat needed for both, pyrolysis and reforming, is supplied by the heat carrier which is heated up to 900 - 1000 °C by the flue gas from the combustion chamber, where the char and residues of the feed material are burnt. The heat carrier first releases its energy at first in the reformer and then in the pyrolysis reactor. A schematic presentation of the process principle is given in figure 6.

A 1 MWth pilot plant was erected in Herten, Germany, in 2001. A feed with 30 % moisture and sizes of up to 50 mm is tolerable /Dimova 2000/. The dry gas composition is expected to be H2 56.7 Vol.%, CO 18.3 Vol.%, CO2 23.5 Vol.% and CH4 1.5 Vol.% [17]. The main advantages of the process are: (I) no oxygen is needed for the gasification, (II) atmospheric process, (III) no special requirements are set for the feed material (variety of feed with a water content < 30 % and size < 50 mm).

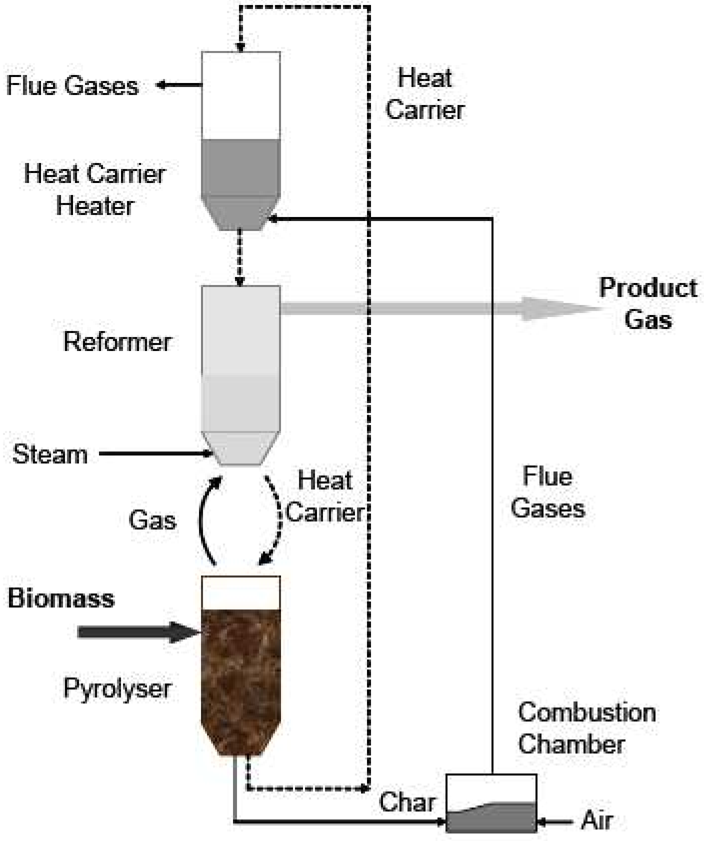

Fig. 1.6: Principle of the DM2 Staged Reforming Process [17].

Indirectly Heated, Twin Fluidized Bed, Steam Gasifier (Battelle/ FERCO)

This process was developed by Battelle in the eighties and tested in a pilot plant. It produces a medium caloric gas without oxygen supply under atmospheric pressure, using twin circulating fluidized-bed gasification [18]. Heat is supplied by circulating a stream of sand between two physically separated fluidized-bed reactors. Biomass enters the first reactor in which it is gasified with steam to produce gas and char (figure 1.7). A cyclone separates the gas from the sand and char, both of which enter a second fluidized-bed reactor, the combustor. The char is burned in the combustor and heats up the sand which is reintroduced into the first reactor where it supplies the heat needed for the gasification. The operating temperature of the gasifier ranges from 650 to 1000 °C. The product gas is cleaned in a scrubber and the tar thus separated is reintroduced into the combustor. The flue gas waste heat is used to dry the biomass feed. Tests have been conducted with wood throughputs of 1.5 to 1.7 t/h.

After successful operation of a pilot plant at Battelle, it was decided to upscale the process to a commercial scale (182 dry tonnes of biomass feed per day). The plant started testing in 1999 in Vermont, USA. A typical product gas composition obtained with the plant is: H_2 18.0 Vol.%, CO 47.0 Vol.%, CO_2 14.3 Vol.%, CH_4 14.9 Vol.%, C_2H_6 1.1 Vol.%, and C_2H_4 4.7 Vol.%. The higher heating value (HHV) of the gas is about 16.8 MJ/Nm^3 [19].

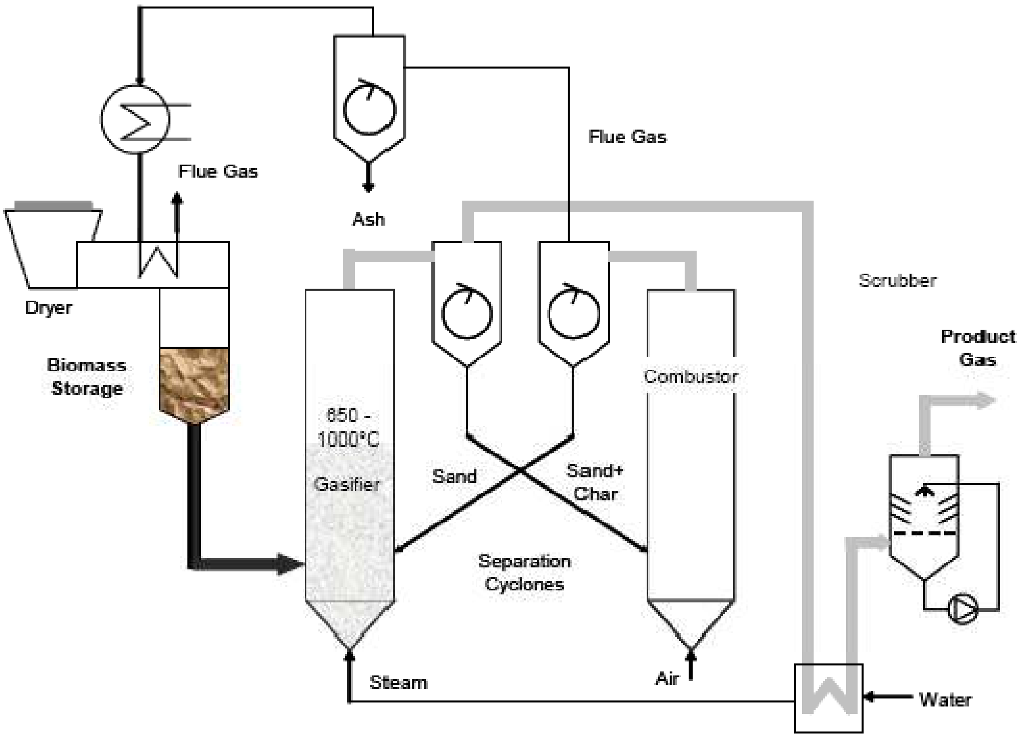

Fig. 1.7: The Battelle/FERCO gasification process [19].

FICFB Gasification

The FICFB (Fast Internally Circulating Fluidized Bed) gasification uses the idea of a heat-carrier bed material to supply energy for gasification, somewhat similar to the DM2 process and Battelle/FERCO gasification. A heat carrier (quartz sand, catalytically active olivine) circulates between two reactors, introducing heat from the combustion zone into the gasification zone. There is no gas contact between the two zones. Biomass enters the gasification zone where it is steam gasified. The gasification zone is fluidized with steam and the combustion zone (riser) is fluidized with air. The bed material with char moves from the gasification into the combustion zone, where the charcoal is burned with air. The exothermic reaction in the combustion zone provides the energy for the gasification via the bed material. The product gases are cooled in a heat exchanger and afterwards cleaned from dust and partly from tar with a bag filter. Tar is then separated in a scrubber with bio-diesel as the scrubbing liquid. The advantages of the FICFB process are: (I) allothermal process without oxygen demand, (II) compact reactor design, (III) low investment costs due to the compact construction, (VI) high energy efficiency, and (V) reduced tar and nitrogen content in the product gas.

Based on a 100 kWth pilot plant, a demonstration plant with the FICFB concept was erected in Güssing, Austria, with 8 MWth and an electric output of 2 MWe [20, 21]. The gasification temperature ranges from 790 to 900 °C. A typical product gas analysis at 880 °C shows the following composition: H_2 43 Vol.%, CO 30 Vol.%, CO_2 13 Vol.%, CH_4 9 Vol.%, and N_2 5 Vol.%. [20, 21]. Figure 1.8 illustrates the reactor design for the FICFB process.

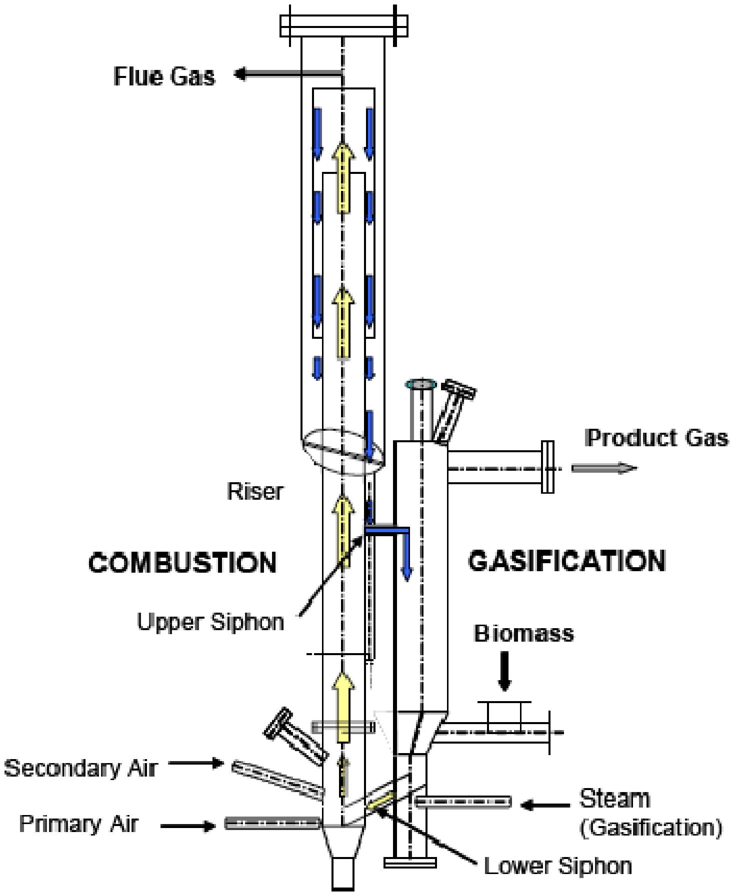

Fig. 1. 8: FICFB gasification reactor [20].

AER Process

With the AER process (Absorption-Enhanced Reforming), biomass steam gasification can continuously produce a raw gas with more than 75 Vol.% hydrogen, suitable for downstream fuel synthesis or electricity production. In this approach, the CO_2 produced during steam gasification is separated from the reaction zone by an absorbent, so that the resulting product gas exhibits a high hydrogen concentration as well as low amounts of carbon oxides and tar [22, 23]. The CO2 absorption shifts the reaction equilibrium towards increased hydrogen concentration. As the reaction of carbon dioxide with the absorber is exothermic, it supplies in situ the heat needed for the reforming/gasification. A flue gas with increased CO_2 concentration is produced when the sorbent is regenerated in a subsequent process step.

The key element of the AER process is the reforming/gasification reaction in the presence of a high-temperature CO_2 absorbent. The absorbent consists of a metallic oxide/carbonate system, e.g. $CaO/CaCO_3$. The AER process combines the reforming/gasification, shift and carbon dioxide removal reactions in one reactor, leading to a hydrogen-rich gas. The principle of the AER process is presented below with CaO as the absorbent:

Biomass steam gasification:

$$CHxOy + (1-y)\ H2O \rightarrow CO + (0{,}5x + 1 - y)\ H2 \qquad \Delta HR > 0 \ (Eq.\ 1)$$

CO-shift reaction:

$$CO + H2O \rightarrow CO2 + H2\ \Delta HR < 0\ (Eq.\ 2)$$

High-temperature CO2 absorption:

$$CaO + CO2 \rightarrow CaCO3\ \Delta HR < 0\ (Eq.\ 3)$$

Overall reaction:

$$CHxOy + (2-y)\ H2O + CaO \rightarrow CaCO3 + (0{,}5x + 2 - y)\ H2\ \Delta HR \approx 0\ (Eq.\ 4)$$

Depending upon the feedstock, the calculated enthalpy difference of the overall reaction can be slightly negative or zero. The process is easily adapted for synthesis gas production with a certain stoichiometry requirement by controlling the absorber amount.

In order to realise continuous operation, two fluidized-bed reactors are coupled. In the first reactor, the biomass gasification with steam takes place with absorbent as the bed material. The second reactor operates in the combustion mode to regenerate the sorbent (figure 1.9). In the technical realization, the reactive bed material circulates between the AER gasification reactor (600 – 700 °C) and the char combustion reactor (800 – 900 °C) for sorbent regeneration.

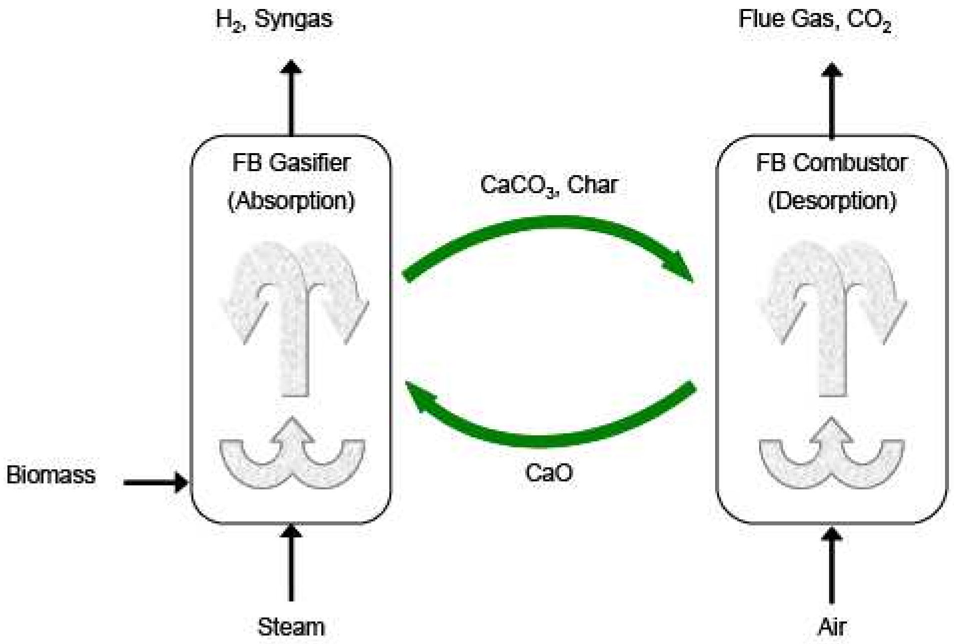

Fig. 1.9: Technical concept of the AER process for continuous synthesis gas/H2 production from carbonaceous fuels with two combined fluidized-bed (FB) reactors: a gasified operating at 600 – 700 °C and a combustor operating at 800 – 900 °C.

The AER process was tested in a 100 kith bench test plant [23]. The advantages of the AER process over conventional biomass steam gasification are: (I) the AER process allows the production of a product gas with a high H2 concentration (> 75 Vol.%) or with a desired stoichiometry factor for downstream synthesis in a single process step, (II) the energy required for gasification/reforming is supplied in situ through the exothermic carbonation reaction of the absorber, (III) reactors for downstream CO shift and CO2 removal are not required, (IV) tar formation is suppressed as a result of CO2 absorption and the tarcracking properties of the sorbent.

1.4 Conclusion

Industry and a number of research institutes are active in the development of biomass gasification technologies. The focus of the R&D activities is the development of the gasifier itself and the cleaning of the product gas. A detailed observation on the current status of biomass Gasification was written by Babu et Al 2005, the leader of IEA Task 33: “Thermal Gasification of Biomass” [24].

The main differences between existing gasifiers for syngas production via biomass gasification are (I) the content of minor components in the product gas (impurities), (II) the content of the major components (H2, CO, etc.) and (III) the necessity of an air separation plant for oxygen production. No existing gasification technology meets all the demands to produce bio-syngas in one process step. Air-driven, directly heated gasifiers are not suitable for synfuel generation due to the high portion of nitrogen in the product gas. Fixed-bed gasifiers are not qualified for syngas generation due to (I) their limited capacity range (< 5 MW) and (II) their disadvantages regarding the automatic control of the process. Indirectly heated gasifiers have the great advantage of high hydrogen content in the product gas, but the disadvantage of high hydrocarbon content (methane and tars). To upgrade this gas to syngas quality, downstream reforming/cracking units are necessary. Entrained flow gasification shows the lowest tar content in the product gas, but it lacks high hydrogen concentrations. They require downstream shift converters, followed by CO2 removal, for adjusting the syngas. Additionally, an air-separation plant is necessary to supply oxygen as gasification agent for entrained flow gasification. Figure 1.10 compares the product gas compositions for different gasification systems which are potentially suitable for synthesis gas production. Gasification processes with high hydrogen content are favourable. However, gas conditioning for adjusting the stoichiometry factor are still necessary with most gasification technologies for a high carbon conversion (with a recycle loop for the non-reacted part of the syngas). Nevertheless, the product gas composition alone is not decisive for selecting a gasification process for synthesis gas production. Besides the concentration of the main gas components and the impurities, energetic efficiency, capital costs, operation and maintenance costs and process complexity have to be considered as well.

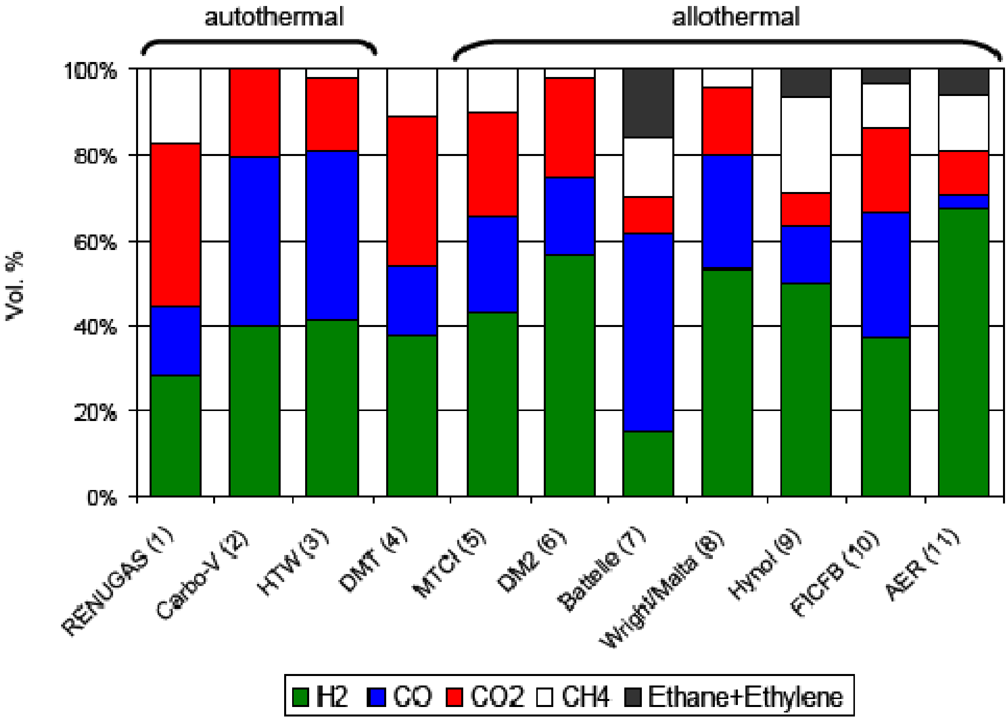

Fig. 1.10: Product gas composition from different gasification technologies (1) Reed et Al 1999[1], (2) www.gastechnology.org 2005 [25], (3) Schrader et Al 1984 [10], (4) Hauserman et Al 1997 [26] , (5) Williams et Al 1995 [27], (6) Dimova et Al 2000 [28], (7) Paisley et Al 2000 [19], (8) Coffman et Al 1981 [29], (9) Norbeck et Al 2000 [30] , (10) Hofbauer 2001 [20], (11) Marquard-Moellenstedt et Al 2004 [23].

Biomass gasification has reached the point of development where first applications, such as co-firing and co-gasification, are becoming commercial. However, none of the processes have been running long enough to provide reliable data on the process performances and costs. The main research activities in the field of biomass to- syngas are (I) the development of gasification technologies with regard to the properties of different biomass feedstock and (II) a gas cleaning and conditioning with regard to biomass-specific impurities like tars and alkali. A significant amount of work must still be done before such plants could be considered for commercial syngas production applications.

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Chapter 2

Thermal Gasification of Biomass

2. Thermal Gasification of Biomass

2.1 Introduction

Gasification of solid fuels, coals and petroleum refinery residual hydrocarbons, is a proven energy conversion technology to produce clean fuels, electricity, and chemicals. At present, around the world in 28 countries, ~ 120 plants are operating more than 380 gasifiers to produce about 46,000 kWth capacity of synthesis gas (equivalent to ~ 650 barrels of oil per day). It has taken over 60 years of worldwide effort to reach this level of fossil fuel gasification production capacity [1, 2]. In contrast, the first modern commercial exploitation of biomass gasification (BMG) was attempted nearly 30 years back, in Scandinavian Countries, at a time when there was uncertainty about the rising cost and accessibility to oil. Although, technical viability of BMG and the related environmental benefits are widely acknowledged, the extent of its commercial utility has mostly been limited to CHP and district heating and a handful of co-firing applications, driven primarily by regional or local environmental or economic considerations. Until recently, the development of advanced processes and broader application of BMG are impeded by competition from low-cost fossil fuels and inadequate market pull. The other contributing factors are the lack of an infrastructure for sustainable supply of quality controlled biomass and the lack of adequate incentive driven policies and partnerships with industry to develop, demonstrate and deploy bioenergy conversion technologies, in particular the high efficiency processes. The last two to three years have witnessed unprecedented volatility in oil and gas prices and raised concerns about security of energy supply. Further, the need to attain several environmental targets is fast approaching, notably related to climate change and the reduction of primary energy usage. Against this backdrop many of the national renewable energy plans are constantly reviewed and revised to implement measures conducive to commercialization of biomass energy technologies. Biomass gasification should play a central role in producing biofuels, substitute natural gas (SNG), value-added chemicals, heat, and power [1, 3, 4].

2.2 Status of BMG Development and Commercialization

The early biomass gasifiers were developed based on the principles of moving bed (or fixed bed) coal gasifiers and deployed essentially for CHP applications. These include the eight, 4 to 5 MWth capacity, automated Bioneer biomass gasifiers that were built in Finland and Sweden during mid-1980s for heating, are still in operation. The most developed and known moving bed biomass gasifiers ***are*** the Babcock Borsig Vølund gasifier developed in Harboore, Denmark and replicated in Japan, the Biomass Engineering Ltd gasifiers in UK**,** XYLOWATT AB systems in Belgium**,** the CTU/Pyroforce gasifiers in Switzerland and Austria [5]**.**

The successful high throughput circulating fluidized bed combustors (CFBC) designs, developed during the 1970's, were later modified to operate effectively as circulating fluidized bed gasifiers (CFBG). The early CFBGs in Scandinavia produced a fuel gas that could readily replace fuel oil in industrial burners. Since, there was little or no gas cleaning involved in these applications, these plants were successfully scaled-up to 100 MWthcapacity, processing about 600 tonnes per day of biomass materials. Since the early 1980s, Ahlstrom (the present Foster Wheeler Energia OY(FWE)) has succeeded in building seven, 3 to 70 MWth CFBGs in Finland, Sweden, Portugal, and Belgium. The recent additions in the last decade to successful Ahlstrom/FWE biomass CFBG plants for co-firing include the 60 MWth plant in Lahti, Finland and the 50 MWth Ruien co-firing gasifiers. The Lahti plant has operated for over 40,000 hours with gasifier availability in excess of 95 %**.** Lurgi has built three CFBG units of which the 100 MWth Rüdersdorf, Germany plant is successfully gasifying waste to produce fuel gas for firing a cement kiln. After some plant modifications, the 83 MWth Essent/Lurgi co-firing plant is now back in operation. In 1988, Götaverken (Now Metso Power) has built one, 25 MWth CFBG in Sweden, which is still in operation. The same year, TPS has designed two, 15 MWth capacity CFBGs for RDF pellets at Greve-in Chianti in Italy which have been shut-down due to non-technical reasons [6, 7]**.**

In the area of CHP and power applications, Sydkraft and Ahlstrom were involved in the development of a second generation pressurized CFBG process for IGCC application, at Värnamo, Sweden. The 18 MWth capacity plant was operated at 18 bar pressure, raw gases were cleaned without condensation employing high temperature filters, and the LCV fuel gas was successfully combusted in a closely integrated Typhoon gas turbine, to generate 6 MWe and 9 MWth of district heat. The Värnamo plant was mothballed in 2000, after more than 8,000 hours of gasifier and 3,600 hours of integrated operation with the gas turbine. Since October 2005, the efforts are in progress to reactivate Varnamo plant as the centerpiece for demonstration for a multinational synthesis gas development project.

The Technical University of Vienna has developed a fast internal circulating fluidized bed (FICFB) biomass gasification process, which incorporates a bubbling bed gasifier and a CFBC unit that has been scaled-up in cooperation with REPOTEC; it is now in continuous operation as the 8 MWth Güssing CHP plant in Austria. Since the process produces a hydrogen-rich synthesis gas, a wide variety of slipstream investigations are being conducted at this plant to evaluate the production of liquid fuels and substitute natural gas (SNG). Based on these studies, 15% of the raw gas stream is completely conditioned and converted to SNG in a closely coupled demonstration plant.

Ahlstrom/FWE has also built a 40 MWth, Corenso bubbling fluidized bed gasifier in Finland. This plant has been operating successfully for about five years, producing energy while recovering metals from the waste feedstock. Carbona/Andritz is now in the process of commissioning a 30 MWth capacity, RENUGAS fluidized bed gasifier for CHP demonstration in Skive, Denmark.

In the area of synthesis gas, there has been a surge of activities recently. Choren has on the basis of a 1 MW pilot built a 45 MW thermal synthesis gas plant fully integrated with a Fischer-Tropsch unit based on Shell technology, commissioning will be initiated 2009. At Forschungszentrum Karlsruhe FZK, Germany a 5 MW plant for the conversion of biomass residues to fuel by pyrolysis and subsequent entrained flow gasification is under construction (bioliq®) with Lurgi. The pyrolysis step is operational, the gasification will be commissioned in 2011. Range Fuel is in the process of building a large scale gasification-based ethanol plant in Georgia, USA. In the forest industry, Stora Enso, UPM and Norske Skog are all engaged in plans for biofuels, the two former conductiong pilot plant scale tests for gas cleaning starting this year.

Other biomass gasification projects worth mentioning are the Lurgi CFBG process in Pöls, Austria, the FERCO SilvaGas Process in Vermont, the TPS Process for the ARBRE demonstration project, and the RENUGAS demonstration in Hawaii. Although, most of these gasifiers have demonstrated technical success, system operation, ranging from handling and feeding low-density feed stocks to heat recovery from raw product gases and gas purification, both in-situ and in series to the gasifier, have presented certain technical problems which are being addressed in several RD&D projects to advance the state-of-the-art of BMG [6, 8, 9].

2.3 Barriers to Technology Commercialization

The main technical barriers to commercialize BMG include, reliable handling and feeding of mixed feed stocks, in particular the low-density herbaceous biomass, reduction of tar formation in gasification reactors, particulate entrainment and their removal, managing carbon, tar, alkali, chlorides and ammonia in fuel gases, ash withdrawal, waste water handling in conventional gas clean-up., This has limited reliable scale-up and successful demonstration of high-efficiency advanced BMG processes. Gasification processes employ in-situ tar decomposition materials and thermal oxidation techniques to minimize tar formation to varying degrees of success. In addition to conventional gas scrubbing with liquids, high-temperature ceramic and sintered metal barrier filters have been developed to successfully remove entrained particulate matter. It has been repeatedly observed that improvements made in the reliability of individual process steps do not necessarily guarantee successful scale-up and integrated operation of the overall process. Therefore, system integration remains an important issue in process scale-up, demonstration, and commercialization. These technical barriers have also, with a few notable exceptions, limited the involvement of engineering contractors in the field of BMG. This lack of proven and well established technologies also results in that learning curve effects up to now has had very limited impact on the design, and CAPEX and OPEX.

At present, limited but significant research is continuing in Europe and USA to address many of the technical hurdles listed above. These include basic research in understanding and modeling the gasification of biomass under entrained flow conditions, producing a tar free syngas at high pressure (Forschungszentrum Karlsruhe, FZK), the formation of tar and its destruction in the BMG reactor as well as on catalytic surfaces. Recent studies conducted at VTT, Finland, TUV, Vienna, the National Renewable Energy Laboratories (NREL) in USA and several other research organizations have evaluated several catalysts and concluded that the best option for tar destruction is to employ calcined dolomite or olivine in the gasifier as the primary tar decomposition agent followed by a secondary or polishing tar destruction step with a Ni or Zr based catalysts. Although Ni has the capability to reform or crack condensable hydrocarbons and even ammonia, at about 800^{o}C, Ni catalysts are also vulnerable to poisoning by sulfur, chlorine, and alkali metals. In addition, handling Ni in these applications and its ultimate disposal present certain safety and environmental problems. Consequently, research is continuing to finding safe, reliable, and environmentally acceptable tar decomposition catalysts and to explore breakthroughs in quantitative gasification of biomass to produce condensable hydrocarbon-free fuel or synthesis gases. Meanwhile, there is merit in investigating the tolerable limits of raw gas contaminants and the types of condensable hydrocarbons in selected gas processing or energy conversion devices (i.e. risk management). However, this requires close collaboration between gasification technology developers and manufactures of energy conversion devices [8, 9].

2.4 Additional Drivers for Advancing BMG

The current strong and unprecedented interest in exploring the techno-economic viability of synthesis gas production and co-production of power, liquid fuels, SNG, hydrogen, and chemicals provide the additional impetus to find new and value-added applications for BMG while also addressing the climate change issue. Co-production concepts and substitution of fossil fuels offer the potential to improve the efficiency and economics of biomass utilization. Increased use of biomass should reduce dependence on imported fossil fuels and stimulate economic growth in rural communities which could take an active role in providing the much needed sustainable supply of biomass feed stock and in the utilization of biomass derived products.

In addition, since renewable portfolio standards (RPS) or carbon dioxide mandates are strengthened in the EU and other areas where they already have been introduced, and now also are expected to be implemented in regions and countries where such policies do not exist, electric utilities may have to provide large quantities of ‘green’ electricity within a short period of time. In this regard, BMG processes should play a significant role to meet part of the RPS. Further, the increasing concern about rising oil prices and the importance of securing supply of transportation fuels have brought into focus the importance of BMG for synthesis gas production and its suitability to produce transportation fuels and fuel additives. When fully developed, advanced BMG processes should have the capability to handle a variety of mixed biomass feed stocks, change the product slate in response to the varying market demands, and offer significant advantages with central bioenergy conversion plants. Furthermore, advanced BMG processes can be designed to co-produce power, fuels, chemicals, and other value-added products, which may offer certain economic benefits.

The increasing global concern for climate change and the search for ‘green’ energy should provide major market drivers to promote renewable energy technologies in many countries. Therefore, emphasis will be given in the proposed work program to review, discuss, and identify mature and near-mature BMG systems that could find immediate application in district heating, cogeneration, co-firing, and dedicated power generation, besides the synthesis gas conversion options mentioned above. The collateral corporate responsibilities should inevitably address new livelihood opportunities for rural communities and to seek their commitment [5, 8, 9].

2.5 References

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Chapter3

Biomass Gasification at ENEA Trisaia Research Centre

3. Biomass Gasification at ENEA Trisaia Research Centre

3.1 Introduction

Enea Research Centre of Trisaia is leader in biomass gasification with its 20 years of experience in this field [1, 2, 3].

Two biomass gasification plants are currently operating at the ENEA Research Centre Trisaia in Rotondella (Italy), based upon different gasification concepts: a dual fluidized bed steam gasifier and a downdraft fixed bed air gasifier. Two more pilot plants, which are now under construction, will be started soon: an interconnected bubbling fluidized bed oxygen/steam gasifier and an updraft fixed bed air/steam gasifier. All of these plants are going to be combined with different producer gas conversion devices, such like, an internal combustion gas engine (already working), a molten carbonate fuel cell, a methanol synthesis reactor [3, 4, 5]. Moreover, Air/Steam-Blown Fixed Bed Updraft Gasifier (150 kWth) with Advanced Gas Cleaning is under construction.

Below, the two gasification plant running in ENEA Research Centre of Trisaia re briefly described.

3.2 Dual Fluidized Bed Gasifier

Dual fluidized bed gasifier is a 500 kWth gasifier that was developed in cooperation with TUV (Technology University of Wien). Figure 3.1 show an image of the plant.

This pilot plant gasifier uses a fast internally circulating fluidized bed (FICFB). Figure 3.2 shows the gasification concept on which the ENEA TRC pilot plant is based. As it can be observed the gasifier is divided into two different units: a gasification or reduction unit, also called simply gasifier, and a combustion unit, also called simply combustor [6, 7].

Figure 3.1: the 500 kWth gasification plant.

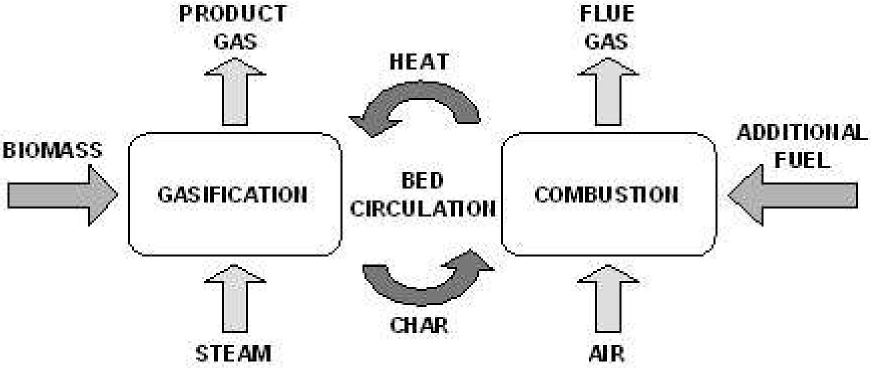

Figure 3.2: FICB gasification concept

In the reduction zone, fluidization occurs by means of steam in order to produce a nearly nitrogen free gas, while in the combustion zone air is used. In this unit, the heat required by the gasification process is generated by the combustion of the residual char from the gasification zone, equal to about 15% of the total carbon content in the biomass feedstock.

The transfer of both char to the combustion zone and heat to the reduction zone is obtained via the circulation of the bed material, which also acts as a barrier between the gaseous mixtures present in the two units. Nevertheless a not negligible infiltration of the flue gas, containing oxygen, carbon dioxide, and nitrogen above all, towards the reduction zone takes place.

Finally an adequate quantity of additional fuel (gasoline), up to approximately 10% of the biomass feedstock, is needed so as to reach the required increase of around 100 °C in the bed material temperature, during its circulation from the gasifier to the combustor [6, 8, 9].

3.2.1 Gas cleaning section

The ENEA TRC pilot plant is provided with a hot gas cleaning up section. As it is shown in Figure 3.3, the raw gas from the gasifier is sent to a first unit, in which the removal of the acid compounds, essentially H_2S and HCl, is performed. Therefore it goes through two additional units for the removal of particulate [5].

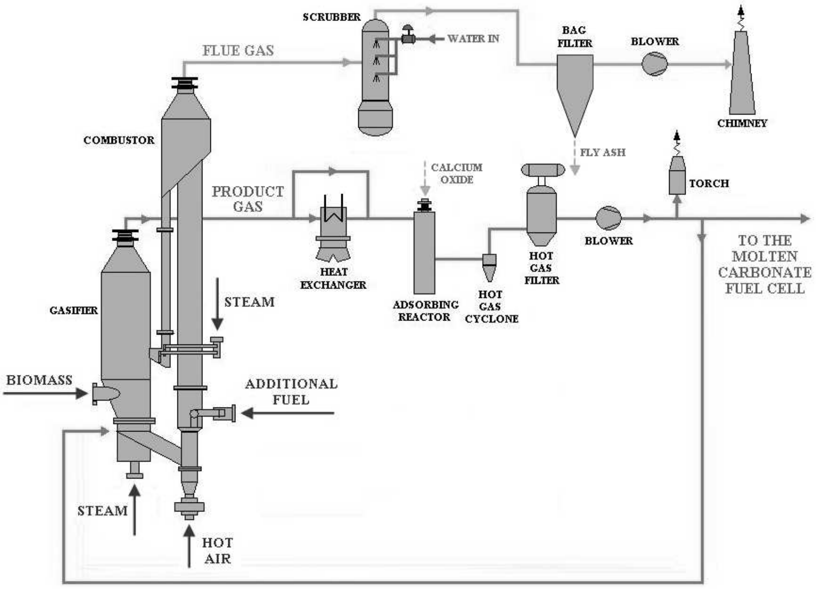

Figure 3.3: ENEA TRC: actually flow sheet

In Table 3.1 the concentration of the main pollutants in the raw gas on dry basis for the gasification of almond shells and the related pilot plant working conditions are reported [6, 7].

*Table 3.1**:** Pollutants concentration in the raw gas on dry basis and related operating conditions*

Pollutant	**Quantity**
H_2S	250 ppmv
HCl	100 ppmv
Particulate	30 g/Nm^3
Tars	10.6 g/Nm^3

The formation of the acid compounds in the producer gas during the gasification process is originated by both the basic environment and the presence of chlorine and sulphur in the biomass feedstock. Nevertheless, the current thermal losses along the producer gas piping line cause a reduction in its temperature to values even lower than the de-chlorinator nominal operating range. This is one of the main factors determining the drop of both the real sulphur and chlorine removal efficiencies with respect to the expected values, like it can be inferred from the experimental data reported in Table 3.2 [6, 7].

*Table 3.2**:** Effective operating conditions and removal efficiencies of the adsorbing reactor*

Parameter	**Value**
Inlet producer gas temperature	508°C
Outlet producer gas temperature	476°C
Outlet gas H_2S concentration	40 ppmv
Outlet gas HCl concentration	30 ppmv
H_2S removal efficiency	84%
HCl removal efficiency	70%

A rise in the temperature of the producer gas entering the adsorbing reactor and, as a result, an improvement in its removal efficiency is certainly viable by implementing a more effective thermal insulation of the piping line. However, it seems to be probable that a more deep acid compounds removal will be necessary, if the gas shall be used to fuel a MCFC, considering its very restricted tolerance to these pollutants.

The presence of particulate in the producer gas is essentially due to the un-reacted char, olivine elutriation, ash, and, if the de-chlorination treatment is operated, the un-reacted CaO and reaction products of the de-chlorinator.

A cyclone immediately at the exit of the adsorbing reactor allows separating the products of the reactions and the excess of CaO from the gas, with a removal efficiency around 95% for particles having a diameter of 2.2 µm or more.

The fine particles removal is then carried out within a successive hot gas filtration unit, working at a temperature around 550 °C. In detail, the particles separation is operated by 39 ceramic filtering candles, each one with a length of 1500 mm and an outer diameter of 60 mm. This system combines the typical high efficiency of small size cyclones with a large cleaning capacity.

Actually, from the data shown in Table 3.3, it can be noticed that under the reported operating conditions the separation efficiency of the hot gas filter is over 99.9% [6, 7].

Table 3.3: Effective operating conditions and separation efficiency of the hot gas filter

Parameter	**Value**
Producer gas flow rate	140 Nm^3/h
Inlet producer gas temperature	360°C
Outlet producer gas temperature	230°C
Pressure drop	12 mbar
Inlet gas particulate concentration	6.4 g/Nm^3
Outlet gas particulate concentration	2.1 mg/Nm^3

Therefore, tars and acid compounds concentration in the producer gas have reduced below the limit for its acceptance as fuel for the MCFC. This is the aim of this study [6, 7, 10, 11, 12].

3.2.2 Plant needed improvements.

In order to combine this gasifier with a 125 kW molten carbonate fuel cell, the existing gas cleaning section has to be optimized, especially in order to reduce tars and acid components concentration in the producer gas.

Moreover, in order to optimize producer gas composition, a higher gasification temperature, above 850 °C, is needed, so an energetic optimization of the whole plant has been performed.

Reducing the use of additional fuel is another goal to reach in order to maximize the energetic performance of the plant.

The idea, that is the starting point of my research, is to use a biodiesel scrubber to remove tar from producer gas. Then, scrubber technology is been tested to remove other pollutants, like acid components and sulfur product.

Then, biodiesel recovered from cleaning section could be used as a fuel in separated MCI activity that are not included in this work.

3.3 Downdraft Gasifiers

The other gasification plant running in ENEA Trisaia Research Centre is a downdraft fixed bed with a potential of 150 kWth. The plant is feed with wood chipped and it works using air like gasifying agents. Figure 3.4 show a picture of the plant.

Figure 3.4: DownDraft fixed bed gasification plant.

This is a demonstration plant used with different feedstocks and air as gasifing agent, the producer gas in principle is used to feed a gas engine.

Also, in this case, the cleaning section in the key step of the process that has to be optimized in order to use the producer gas with power plant like engine or fuel cell [10, 13, 14].

Figure 3.5 shows the flow-sheet of the experimental apparatus. It is divided in three systems: gasification system, producer gas cleaning and cooling system, power generation system.

Figure 3.6 show the sketch of the down-draft fixed bed gasifier, where gasification reaction take place.

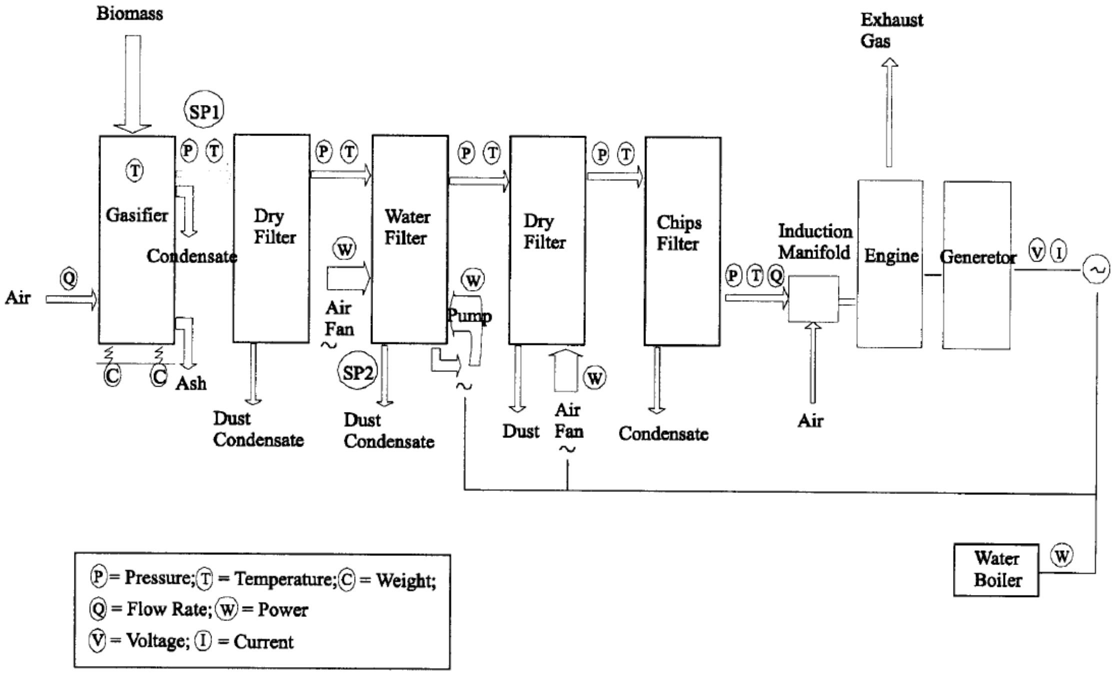

Figure 3.5: DownDraft fixed bed gasification plant: experimental apparatus flow-sheet.

In the gas cleaning and cooling system, there are two cyclone filters to remove charcoal and dust, a water bathing filters to cool gas and remove tars and condensates, a grate filters to remove dust and a sawdust filter to remove dust and water. The power generation system is constituted of a FIAT modified Diesel cycle engine into an Otto cycle engine, a TESSARI electric generator by a 25 kVA 3 phase 380 Volt and an heat exchanger. The heat exchanger is used to adjust power output. Power output are 3 kW, 6 kW, 10.5 kW, 13.5 kW and 15 kW.

The plant core (Figure 3.6) is a double wall cylindrical chamber whose combustion zone is made of stainless steel with a double conic shape. The inner part of this zone contains a plane with nozzles. The double chamber compensates for heat loss and allows a preheating of biomass.

The gasifier normally runs at a temperature of about 850 °C. Air was fed into the gasifier at an average flow rate of 36 N m^3/h.

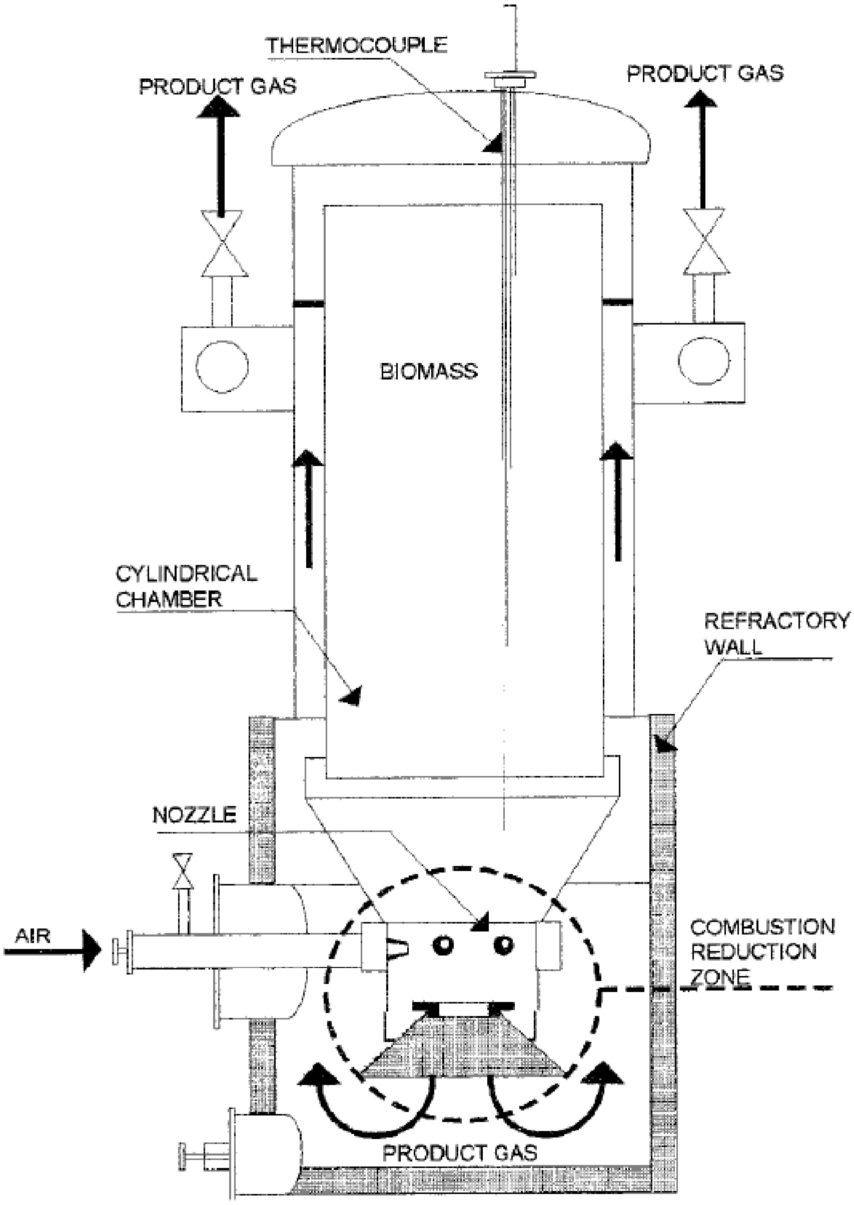

Figure 3.6: Sketch of DownDraft fixed bed gasifier.

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Chapter4

Gasification producer gas cleaning: the state of arts technology.

4. Gasification producer gas cleaning: the state of arts technology.

4.1 Introduction

Gasification of biomass results in a producer gas containing numerous contaminants like dust, tar, (organic) sulphur, nitrogen and chlorine compounds, as well as alkali and heavy metals. Although concentrations could be relatively low depending on the feedstock used and the type of gasifier applied, at least some of these contaminants have to be destructed or removed upstream the final application of the producer gas, whether it is a boiler, gas engine or turbine, fuel cell or synthetic application. Hence, gas cleaning is inevitable in general, whether it is on tar components or non-tar components [1].

Still not many gasifiers are operating commercially on biomass feedstock, in particular when not taking into account those gasification systems (co-)firing the product straight into boilers. The need for gas cleaning, and in particular tar removal technology, for CHP or synthesis purposes is still the Achilles heel of biomass gasification and gas cleaning. Standard technology has proven to be insufficient for tar destruction or removal and has lead to years of (still ongoing) RD&D on thermal and catalytic tar cracking as well as (advanced) scrubbing technologies. For the moment, the latter ones seem to have made the biggest progress, with operating biomass based CHP plants at *e.g.* among others Harboøre and Güssing, and water as well as organic liquid (RME, oil) based technologies being commercially available.

A step by step approach could be considered in which technology is scaled up gradually. There has been a tendency to construct large (demonstration) facilities hoping that these are operated successfully and due to scale are commercially attractive as well. The risks are high though, as solving unexpected issues will require enormous budgets. The risk that such a plant becomes mothballed instead of a commercial success has been proven to be relevant. Examples of this are the 180 ton per day Battelle gasification plant in Burlington, USA, and the 8 MWe ARBRE combined-cycle plant in Eggborough, UK.

Similar to tar removal technology, standard commercially available technology for removal of non-tar components up to now has also proven to be insufficient, in particular for critical applications of the producer gas in fuel cells or synthesis applications. Part of that has to do with upstream tar removal to be either insufficient (*i.e.* to low efficiencies of the tar removal) or not designed for the more stringent producer gas specifications for these applications (*i.e.* trace tar components still present in the gas).

Another part of that is caused by the presence of gas contaminants previously not considered problematic for CHP applications (*e.g.* organic sulfur, dioxins). As can be expected, the biggest progress towards gas cleaning for non-tar components is made by those who are skilful at tar removal.

Over the years there has been a tendency for biomass gasification and gas cleaning to apply conventional technology or mimic coal gasification systems. For the gasification process this philosophy already has been dropped. Also the need for pressurized biomass gasification seems to be abandoned, argued by the complexity of biomass feeding. All commercially running biomass based gasifiers operate at (near) atmospheric pressure, not at the pressure levels of 30 bars and higher, typical for coal and oil based gasifiers.

Concerning gas cleaning, whether it is removal of tars or non-tar components, the operating conditions for commercially available conventional technology (e.g. coal based) will differ significantly from the conditions downstream a biomass gasifier, hence the feasibility of conventional technology will have to be reconsidered or at least tested it in realistic conditions. It might well be that conventional technology is not suitable for biomass based processes.

One of the lessons learned most in RD&D of gas cleaning is that conventional technology is not always applicable without any problems in thermo chemical conversion of biomass. Not only will the producer gas always contain unfamiliar (trace) components, also in many cases operating conditions like temperature and in particular pressure will be different from the conventional operating conditions of the technology just because it is not (yet) possible to operate the thermo chemical conversion process at these conditions. For that reason, it makes sense to test conventional technology first on realistic “biomass based” gases and conditions before installing them on large scale. It could be that due to the different gases and conditions (for the moment) thermo chemical biomass conversion systems need different technologies than bio chemical conversion systems or even thermo chemical coal conversion systems and these have to be developed step by step. A step by step approach becomes even more important for systems with multiple process steps, e.g. biomass gasification based synthesis systems like the production of Substitute Natural Gas (SNG), DME and Fischer-Tropsch (FT) diesel. For the successful development of these complex systems, slipstream testing of the critical catalytic components in gas cleaning and synthesis in an upscaled (demonstration) CHP plant consisting of the upstream gasifier and tar removal could benefit the RD&D of the whole system, as it enables long duration tests with the critical components under realistic gas conditions.

4.2 The distinction between tar and non-tar components

This report is divided into two main sections, one discussing the issues concerning tar contaminants still being considered the Achilles heel of biomass gasification, and the other the issues concerning the remaining non-tar contaminants. For both the tar and the non-tar components, the report includes an overview of the current state of research, development and demonstration in the field of gas cleaning.

A description of commercial facilities, pilot and demonstration initiatives, and research and development is the main part of the report. A distinction is made between technologies focusing on tar components (§4.3) and non-tar components (§4.4).

4.3 Tar components

Tars are still considered to be the major bottleneck or even stumbling blocks in the application of biomass gasification [2]. This holds for fluidized as well as updraft fixed bed based gasification performed at temperatures well below 1000°C, as tar contents in the raw gas can be up to several tens of g/mn^3. A description of tars and the main associated issues are included in the appendices.

The cleaning from these organic species down to values that are acceptable for different downstream processes is of crucial importance for successful implementation of biomass gasification technology. Tar reduction measures can be classified in three main categories, being tar cracking and reforming, mechanical tar removal and physical tar removal. In the following paragraphs, these measures are discussed and compared.

4.3.1 Tar cracking and reforming

Thermal cracking

On thermal tar cracking many studies have been conducted and reported in public literature [3, 4]. These studies are of limited value for gas from biomass gasification plants as they are often conducted with model tar components from pyrolysis of biomass or coal. Thermal tar cracking however, is a proven method to remove tars in large-scale thermal waste treatment plants, for example in the process of ThermoSelect, where the gas is treated at temperatures of 1400-1600 °C for a residence time of seconds.

In these conditions, the synthesis gas from the cracker will only contain low amounts of methane; all other thermodynamically unstable hydrocarbons are cracked.

The application of thermal tar cracking by burning part of the fuel has the disadvantage that the higher (gross) heating value (HHV) of producer gas is decreased significantly, making it more complicated to use this gas in conventional gas turbines or engines. Furthermore, the cold gas efficiency (CGE) of the process drops significantly by cracking all hydrocarbons, including interesting components like CH_4 (useful for producing substitute natural gas) and C_2H_4 (a bulk chemical). This is illustrated in table 4.1, in which an air blown circulating fluidized bed gasifier operated at 850°C is taken as a reference and where the producer gas is partially combusted with air in a thermal cracker [3].

Table 4.1: Effect of thermal tar cracking on the producer gas and the process efficiency

T gasifier (°C)	**T cracker (°C)**	**ER**	**HHV producer gas (MJ/m^3)**	**CGE (%)**
850	-	0.21	7.3	82
850	110	0.28	6.0	76
850	1200	0.31	5.3	72
850	1300	0.34	4.8	69

Roughly, it can be said that every 100°C temperature rise results in a decrease of the calorific value of the producer gas by 0.5 MJ/m_n^3 or a decrease in cold gas efficiency of about 3.5%. Research performed at ECN showed that for thermal cracking of biomass tars to a level of below 100 mg/mn³ the temperature should be raised to a minimum of 1150°C [3], resulting in a CGE loss of approximately 8%.

At the Technical University of Eindhoven (TUe) in recent years research also has been carried out towards non-catalytic partial oxidation with the aim to reduce biomass gasification gas tar contents [5, 6].

Experiments were performed within the temperature range of 900-1150°C and a residence time varying between 1 and 12 seconds. Brandt [7] reports temperatures and residence times needed of 1250°C and 0.5 seconds, respectively. In line with this result is the study of non-catalytic partial oxidation at FZ Karlsruhe [8, 9]. This would lead to the disadvantages of the use of expensive alloys for the tar cracker and, moreover, significant exergy losses in the system. Also, soot is reported to be produced in this tar cleaning method. Recently, the Nexterra Company announced that they had been running such a system in a slipstream of their pilot-plant updraft gasifier in Kamloops and are aiming on installing a gas engine downstream.

The research at the TUe now focuses on the working mechanisms behind partial oxidation in order to acquire the additional knowledge needed to optimize this technology [10]. In tar conversion by partial oxidation, observations are made indicating the significant role of oxygen radicals. The objective of this research is to map the influence of radicals on tar conversion at high temperature immediately after the gasifier unit and to develop a novel technology that combines the benefits of existing technologies. The basic idea behind the tar conversion by flame generated radicals is presented in figure 4.1.

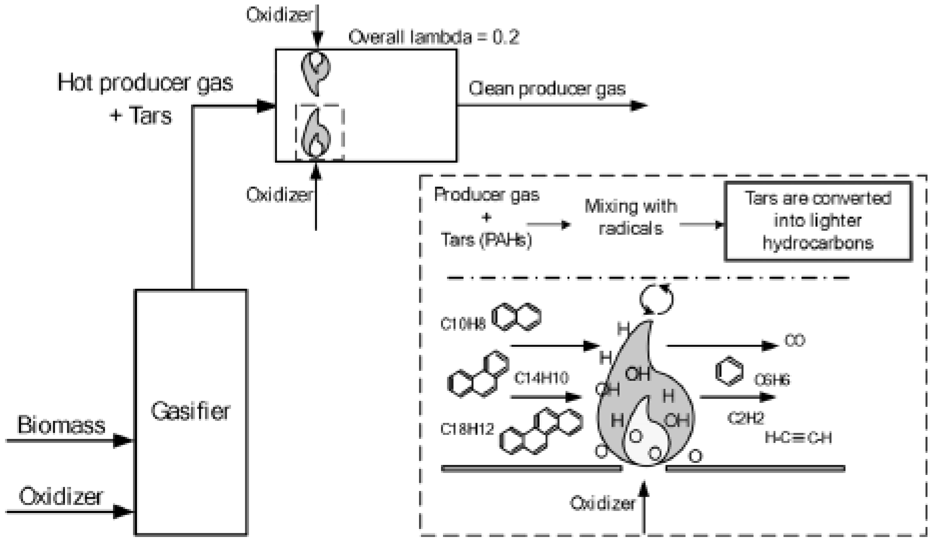


Figure 4.1 Tar conversion by flame generated radicals

Plasma enhanced cracking

Conventional gliding discharges are produced between two horn shaped electrodes placed in a relatively fast gas flow in the direction of the flow. They start at the spot where the distance between the electrodes is shortest, and spread by gliding progressively along the electrodes in the direction of flow until they disappear by themselves after a certain path. Figure 4.2 gives a schematically presentation of the GlidArc process [11], with the gas flowing from the bottom (injection point) to the top. In the gliding discharge, highly energetic electrons are produced, which results in species like ions, secondary electrons, UV radiation, radicals, excited molecules and molecules with attached electrons. This reactive medium, the plasma, is in this project used for the conversion of tar.

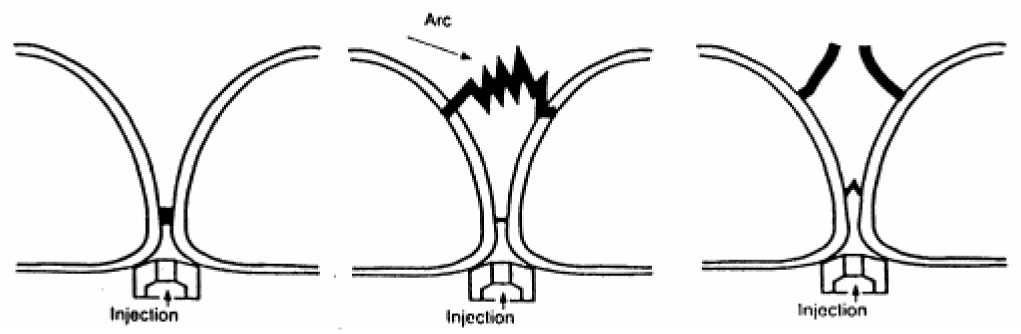


Figure 4.2: Start, life and disappearance of the GlidArc discharges

The GlidArc plasma is combined thermal and cold plasma. About 20% of the energy is dissipated in the thermal part and 80% in the cold part [12]. The thermal part of the plasma is responsible for the plasma activity; in the cold part radicals are responsible for the removal of tars, similar as in the partial oxidation process. The production of radicals in a plasma process is facilitated by electrons in the plasma. The energy level of the electrons must be high enough in order that molecular bonds can be broken and radicals be produced in the plasma. For the GlidArc process the energy level of the electrons in the cold plasma revealed to be too low, as a result of which production of radicals is restricted and in addition the functionality for the removal of tars is too low. The tar conversion in the GlidArc reactor was during tests at ECN at most 40% [13]. Another reason for the low conversion is that the GlidArc plasma does not show any selectivity towards hydrocarbons, not even with increasing temperature. As a result, tar-like compounds as well as other hydrocarbons like methane, ethane, ethylene and benzene are equally converted [13], hence requiring significant amounts of energy for conversion of tars.

In contrast to the poor tar removal results in biomass fuel gas, high conversions can be obtained for the removal of hydrocarbons like toluene and xylene in air [12]. This can be explained by the fact that plasma in air facilitates low-temperature oxidation. Oxygen and in particular nitrogen radicals play an important role in this process, so the air is essential for the efficiency of the plasma assisted hydrocarbon decomposition.

Recent research at the TUe revealed that in absence of nitrogen radicals, conversion is far less, possibly due to the fact that the oxygen radicals (unlike nitrogen radicals) can cause reformation of tars as well. In the commercial plasma processes constructed by e.g. the Plasco Energy Group the generated arc is pushed into a furnace by means of air, hence creating the right conditions. No results on the Plasco plant are published though up till now. In producer gas, the hydrocarbons cannot be “ignited” as the reaction rate with CO_2 or H_2O is much lower than the reaction rate with air. Therefore, the conversions are much lower [13]. An alternative to the GlidArc plasma is a thermal plasma reactor, removing tars at high temperature. An advantage of this plasma reactor in comparison with a thermal tar cracker is the fast and good controllability of the temperature in the reactor without diluting the gas with inert compounds like N_2 and CO_2. Due to the high consumption of electric energy, a sole thermal plasma reactor, however, can not compete energetically with a thermal tar cracker.

At the TUe research is done on fully non-thermal corona plasma for tar removal. The major advantage of using non-thermal plasma is to do chemical conversion of tars at low temperatures and solely rely on the generation of high energy electrons which dissociate molecules and thereby creates the necessary reactive environment. Experimental results have indicated complete conversion of tar by pulsed plasma processing at lower temperature [14]. The investigations also indicate that the gaseous environment, e.g. the presence of nitrogen, has strong influence on tar cracking reactions. As such, it can be expected that tar conversion in producer gas becomes less, in particular for gasifiers producing a gas with initial higher heating value (figure 4.3).

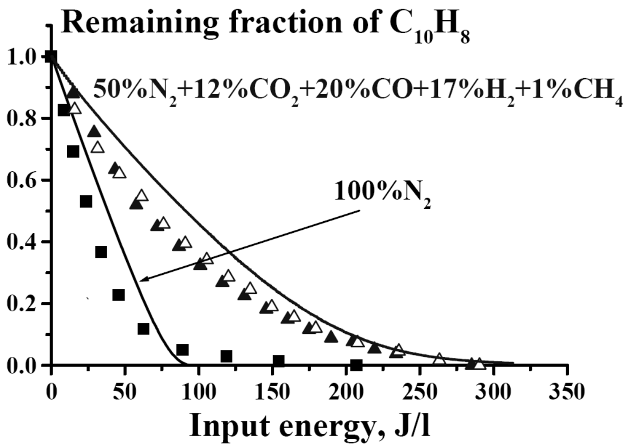


Figure 4.3: Naphthalene conversion as a function of energy input for the corona

The explanation for the conversion of tars being less efficient in realistic producer gases might be found in the tar decomposition scheme e.g. that of naphthalene as presented in figure 4.4 [14]. The H and OH radicals can cause the desired decomposition of the naphthalene; however can also result in the reformation of naphthalene from the intermediate tar radicals. Hence, the more H and OH radicals one might expect present in the producer gas, the less the tar conversion efficiency will be.

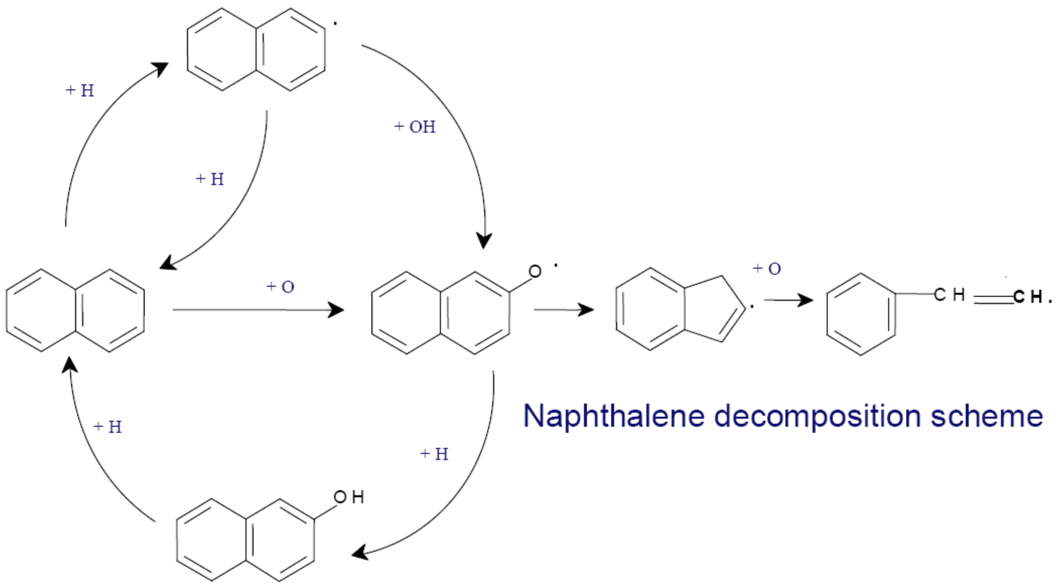


Figure 4.4: Naphthalene radical decomposition scheme

Catalytic cracking

Catalytic tar cleaning is potentially attractive as no additional energy input may be required and hence thermodynamic efficiency losses can be kept to a minimum [15]. Abu El-Rub [16] reviewed different tar cracking catalysts (figure 4.5), with the advantages and disadvantages summarized in table 4.2.

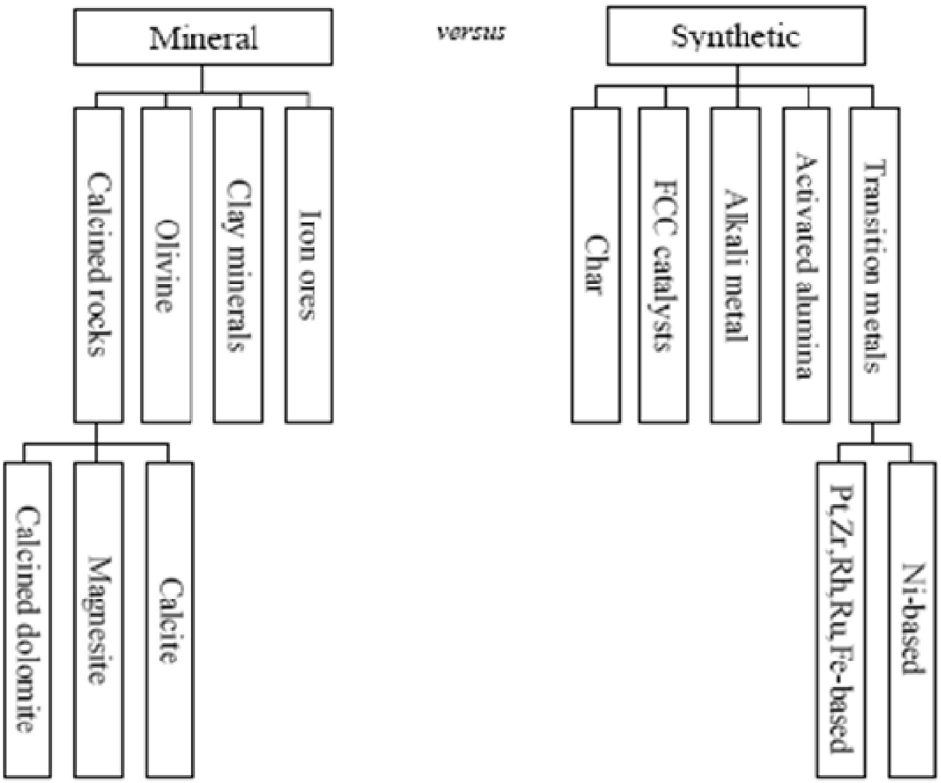


Figure 4.5: Classification and types of catalysts used for tar reduction

In this paragraph, three different systems for catalytic tar cracking are discussed, based on addition of catalytic materials to the bed material of the gasifier or application of catalytic beds, monoliths or filters downstream the gasifier.

Table 4.2: Summary of tar cracking catalysts advantages and disadvantages

Catalyst	**Advantages**	**Disadvantages**
Calcined rocks	Inexpensive and abundant Attain high tar conversion ~95% conversion with dolomite Often used as guard beds for expensive catalysts Most popular for tar reduction	Fragile materials and quickly eroded from fluidized beds
Olivine	Inexpensive High attrition resistance	Lower catalytic activity than dolomite
Clay minerals	Inexpensive and abundant Less disposal problems	Lower catalytic activity than dolomite Most natural clays do not support the high temperatures (>800ºC) needed for tar reduction (lose pore structure)
Iron ores	Inexpensive Abundant	Rapidly deactivated in absence of hydrogen Lower catalytic activity than dolomite
Char	Inexpensive Natural production inside the gasifier High tar conversion comparable to dolomite	Consumption because of gasification reactions Biomass char properties not fixed and depends on biomass type and process conditions
FCC	Relatively cheap but not cheaper than the above More knowledge is known about it from the experience with FCC unit	Quick deactivation by coke Lower catalytic activity than dolomite
Alkali metals	Natural production in the gasifier Reduce ash handling problem when used as a catalyst	Particle agglomeration at high temperatures Lower catalytic activity than dolomite
Activated alumina	High tar conversion comparable to dolomite	Quick deactivation by coke
Transition metals	Able to attain complete tar reduction at ~ 900^{2}C Increase the yield of CO and H2 Ni-based 8 to 10 times more active than dolomite	Rapid deactivation because of sulfur and high tar content in the feed Relatively expensive

In bed materials

- *Natural minerals*

Rock materials like dolomite and limestone are well known as catalytically active bed materials [15], in particular in their porous calcined form. Especially, the dolomites are among the most active and most widely used. They are comparatively active in tar conversion (up to 95%), cheap and are considered to be disposable, which is surely advantageous and this explains their popularity. The catalytic tar reduction potential however strongly depends on morphology factors (pore size, surface area) and content of other metals. Disadvantages are that the material is heterogeneous in nature (differing per region) and in particular that it is soft and thus relatively high attrition rates can be observed [17, 18, 19], leading to losses and increased solids loads to the gas cleaning. Furthermore, calcination is necessary for sufficient reactivity which involves significant energy input. Deactivation of calcined rock material is attributed to carbon deposition and re-carbonation when CO_2 partial pressures are too high in the system [20, 21]. In the 500 kWth air-blown CFB gasifier at Umsicht, Germany, operating at 910-920°C the use of fresh dolomite led to tar concentrations in the gas of about 300 mg/mn^3, however used dolomite resulted in values up to 2.5 g/m_n^3 [22]. This in-time degradation effect is comparable with the data published by Cutec for their steam/O_2 blown 400 kWth CFB gasifier [23]. Here, also, it was indicated that compared to the use of sand, dolomite showed the best reduction of tar. However, still values of 3.5 g/Nm^3 were reported in the raw gas, which is significantly higher than reported by Ising [22] concerning the Umsicht CFB gasifier.

Possibly this is an example of the heterogeneous nature of the dolomite used; also the different oxidizer could play an important role as an explanation for the difference observed. Companies having used, or still using the technology of in-bed use of calcined rock material are TPS, Carbona Inc., Foster Wheeler and Repotec (the latter at the Güssing plant in specific test campaigns).

Another naturally mineral with catalytic activity is olivine sand, which can be represented by the chemical formula $(Mg,Fe)_2SiO_4$. This mineral has also demonstrated tar conversion activity at in-bed use, both in atmospheric and pressurized fixed bed applications for biomass and biomass-plastic mixtures [23-26]. It appeared that giving a heat treatment to this mineral material under oxidizing conditions had a significant positive impact on its activity [27, 28]. Iron oxide, reduced and migrated to the outside of mineral particles is believed to play an important role, although also Ca is considered to be important in this respect [29]. The demonstration plant of Güssing uses olivine as a bed material, clearly showing catalytic activity, although differences are observed in different batches and origins of the material [29]. Research at ECN [30] revealed that the mineral becomes more active after some time of operation under reducing conditions, as was also observed by Rauch et al [29]. It was also observed that Austrian olivine is catalytically more active as a bed material than for example Norwegian olivine. This is shown in Figure

4.6, in which the carbon-in-tar to carbon-in-wood ratio is presented at different gasification temperatures. The difference between

Norwegian olivine and sand as bed material on tar formation is limited, whereas Austrian olivine (as used commercially at the 7000 hours per year running Güssing plant [31]) is active, not only for converting tars, but also for converting methane, acetylene, and ethylene [30].

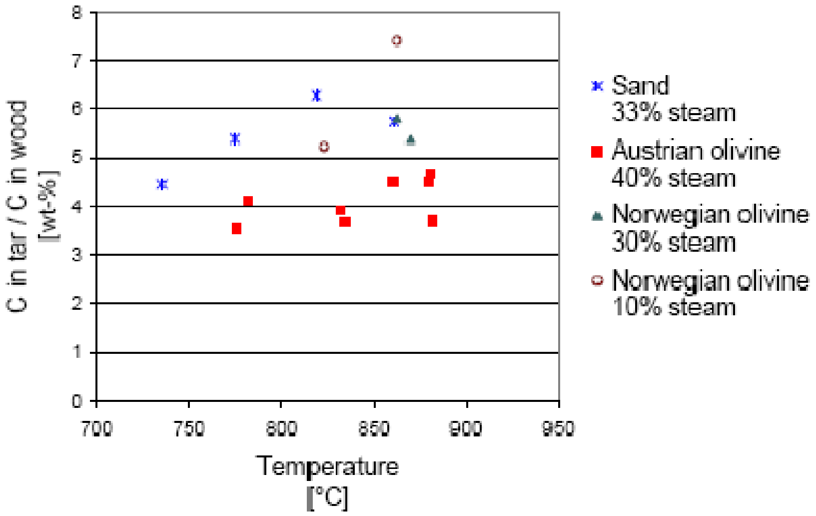


Figure 4.6: Effect of in-bed olivine on tar formation

The claimed advantage of olivine sand is its low price, which is in the same order as of dolomite: some 120 €/ton, in combination with a higher resistance against attrition [15]. Its claimed resistance against attrition as compared to dolomite though is arguable, as the research at ECN showed that the activity of the olivine is strongly dependent on the porosity of the olivine and the migration of iron oxide to the outside of the mineral particles [30]. High cracking activity might well be associated with low resistance against attrition, leading to losses and increased solids loads to the gas cleaning.

Alternative minerals reported and tested to be catalytically active include bauxite, natural alumina, clay minerals and iron ore. One of the latter ones was tested at ECN [30] as well and showed comparable results to Austrian olivine, although its catalytic activity could be related to the associated oxygen transport from the combustor to the gasification zone of the indirect gasifier via the circulating bed material. As in general these alternative minerals show lower activity than dolomite and olivine or are prone to deactivation as a result of coke formation [15], they are not commonly applied as bed materials.

- *Metallic and metal oxide synthetic catalysts*

Conventional nickel steam reforming catalysts, designed for use in fixed bed applications, have been applied as in-bed tar converting catalysts. However they revealed not to be robust enough, as both coke formation and catalyst attrition led to rapid loss of activity [32, 33]. Coke formation is associated with acidity of the catalyst surface and can be made less severe with the help of (earth)alkali oxides [34]. The catalysts have been adjusted to cope with the abovementioned disadvantages, e.g. by using nickel aluminates with lanthanum and cobalt as promoters [35]. Test results of nickel-based in-bed measures for tar reduction are not (yet) available, however up to 80% conversion of toluene as model tar component was achieved under lab conditions. The Co/Ni molar ratio seriously influenced the conversion activity, showing the following order: Ni-Al-La > Ni-Co-Al > Ni-Al [36].

Nickel has also been used to enrich the natural mineral olivine, creating a hybrid between natural material and artificial catalyst, making it more stable than the conventional artificial catalysts. Using up to 40 wt% of this material in an olivine bed led to about 75% decrease of tar content in the gas. The catalyst showed no noticeable deactivation in two tests with a fluidized bed biomass steam gasifier of 30 and 45 h, respectively [37-40].

At the University of Tsukuba, Japan, a ruthenium based catalyst ($Rh/CeO_2/SiO_2$) has been tested as an inbed catalyst [41-45]. The addition of the SiO_2 prevented sintering of the catalyst, which was the biggest issue in tests with the Rh/CeO_2 based predecessor. Although no long-term tests were performed (yet), the indications are positive for this catalyst as practically no coke formation is observed and tar concentration in the final producer gas is reported to be negligible.

Catalytic beds and monoliths

As with in-bed materials, natural minerals and metallic and metal oxide synthetic catalysts can be used for tar conversion in downstream reactors. In this paragraph the progress made in tar conversion in downstream catalytic beds and monoliths is summarized.

- *Natural minerals*

As described, naturally occurring minerals are relatively cheap materials, and are disposable. Their softness and attrition rate are downsides. Also, chlorine present in the biomass fuel may react with CaO to produce $CaCl_2$ and thus reduce the catalytic activity [15]. A substantial amount of research on downstream beds with dolomite and limestone has been carried out worldwide by numerous companies and research institutes. The Swedish Company TPS applies this technology for tar reduction using calcined dolomite (together with oxygen) in a circulating fluidized bed situated downstream of the main air-blown biomass CFB gasifier [46]. Other natural minerals applied for downstream cleaning of tar components are bauxite (Al_2O_3/Fe_2O_3), bentonite ($CaO/Al_2O_3/SiO_2$) and other natural mixed oxides [22]. With inlet concentrations of real tar of the 500 kWth Umsicht CFB gasifier, more than 95% conversion of tars was obtained with the dolomites and the bauxite, and about 75% with the bentonite.

- *Char*

By using char as a catalyst for tar cracking a cheap material is used that is already available in large quantities from the biomass fuel itself. At Twente University as well as Karlsruhe University tests were performed showing that naphthalene conversions at 900°C were practically 100%. At 750°C with typical air-blown gasification gas compositions conversion above 95% was obtained with only little char being consumed [16, 47]. Tests at ECN with the TREC reactor showed though that although char was able to reduce tars (with approximately 75%) it was not very selective for heavy tars. Performance could only be improved by applying more catalytically active bed materials like natural minerals [48].

- *Metallic and metal oxide synthetic catalysts*

Among the artificial catalysts of the transition metal type, applied in downstream beds, nickel based ones are the most popular. Most commercial steam reforming catalysts being supplied by for example BASF, ICI, UCI, Haldor Topsøe and Südchemie all contain this element to a large extent [1]. Corella et al. [49] tested several commercial catalysts for the purpose of biomass gasification gas upgrading. They indicated changes in the main gas constituents occurring with the formation and destruction of methane. When applied at temperatures significantly lower than 900°C, sulfur species in the gasification gas had a poisonous impact on the catalyst activity and a negative effect on the required operating temperature of the catalyst. Also, the commercial reforming catalyst materials are sensitive to other gasification gas trace compounds, like alkali and chlorine species. Moreover, loss of material has been reported [50]. Furthermore, rapid deactivation due to coking has been mentioned by many researchers.

Worldwide a substantial amount of research work has been dedicated to investigation of conventional, commercial nickel based catalysts, and only a small part will be mentioned in the report at hand. In the Netherlands, at BTG commercial nickel based catalysts have been applied in a reverse-flow catalytic tar converter (RF®TC) [51]. Raw producer gas from a biomass gasifier is fed to the reactor at a temperature between 350 and 650°C, hence above the tar dewpoint and heated up at the entrance section to the desired reaction temperature of 900-950°C. The commercial Ni-catalyst is placed in the centre section of the reactor. Tar components, as well as light hydrocarbons including methane, are converted into CO and H_2.

Additionally, nearly all NH_3 is removed. To counterbalance these endothermic reactions air is added to the reactor (about 5% of the producer gas flow). The catalyst used has been tested for over 6000 hrs with wood-derived producer gas. During this period no detectable change in catalyst activity was observed, only when extra sulfur was added. After stopping the additional sulfur supply the original catalyst activity was achieved again. In 2002, BTG implemented the developed RF®TC together with a rotating particle separator downstream a farm-scale poultry litter gasifier system [52]. The whole plant was stopped in 2004 due to problems with the RPS [53].

Research on monolith reactors with Ni-based coating has been performed at different locations in Europe. Monoliths are ceramic blocks of parallel, straight channels on the wall of which a thin layer of catalytically active material is deposited [54, 55]. The honeycomb structure of these monoliths tolerates gas loaded with particulate matter. Figure 4.7 shows a typical monolith element [22, 62]. Toledo et al. [57] concluded that with coated monolith elements tar levels below 200 mg/mn³ can be attained, but the lifetime of the monoliths is very much dependent on the configuration that is chosen to ensure a temperature profile that prevents the occurrence of too high or too low temperatures at the entrance and exit of the monoliths. Also, the feedstock should contain low alkali content, or at least the alkalis should be removed before reaching the monoliths face, as stickiness problems can occur due to the presence of these trace metal species.

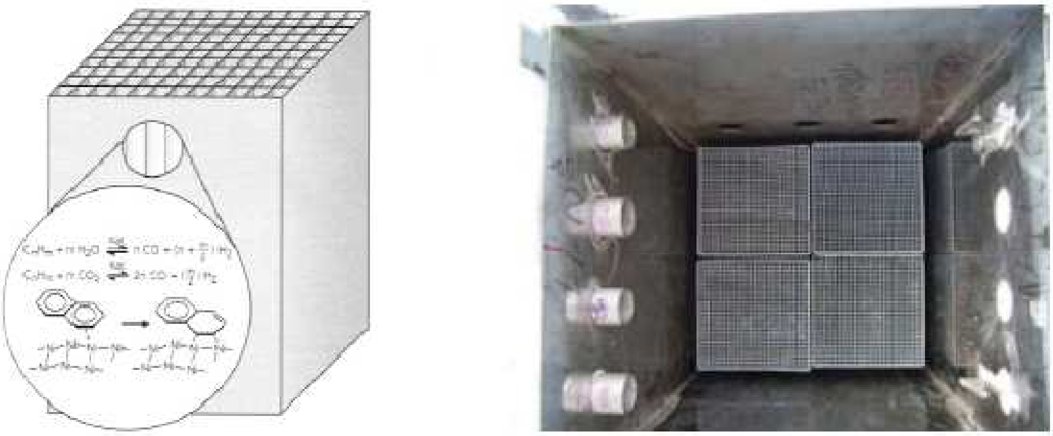


Figure 4.7: Tar reforming monolith and monolith reactor unit

At Umsicht the Ni-based monolith process was tested for 500 hours downstream the 500 kWth CFB gasifier, resulting in lower than 50 mg/mn^3 tar levels, which were aimed at [22]. It showed no significant deactivation, claimed to be also due to periodic cleaning of the monolith unit. The monolith catalyst was scheduled to be tested at the Güssing plant [58], results of these tests have not yet been published. At VTT also a nickel based tar reformer is being developed. In the European FP6 project BIGPower the monolith catalytic tar converter is positioned downstream the 30 MWth Carbona (nowadays Andritz) pressurized gasifier and upstream of a producer gas cooler and a lower temperature filter at the demonstration site in Skive, Denmark [56]. Slip stream testing at the Güssing plant in Austria revealed that almost complete tar and considerable ammonia decomposition could be achieved over this catalyst at temperatures above 850°C. The initial tar content of the gas was however already relatively low, in the order of 1.5 g/mn^3. The published information on methane conversion [59] suggest though that deactivation of the catalyst due to sulfur poisoning was severe (within hours), and that temperatures had to be kept high (above 900°C). At Skive, where similar low initial tar concentrations might be expected due to the application of dolomite as bed material, commissioning of the plant with the VTT tar reformer has started, however the project is delayed and the official opening is postponed to 2009. The delay reflects the inherent uncertainty related to large-scale demonstration of the new technology [60].

As an alternative to the nickel based catalysts, also a lot of R&D has focused on catalysts based on iron, palladium, ruthenium, cobalt, molybdenum, magnesium oxide, zirconia or combinations of those. Reported tar conversion efficiencies and catalysts lifetimes up till now [15,33] however do not suggest that these catalysts are nearer to commercial implementation than the nickel coated monolith reactors.

Catalytic filtration

An alternative to catalytic in-bed materials or downstream catalytic beds is catalytic filtration. This combination of ceramic gas filtration and catalytic tar cracking [61] is being developed by among others Pall (Schumacher) and Madison Filter (in cooperation with Haldor Topsøe) and is a method for particulate removal from hot gases, as by using this method the gas flow can maintain its sensible heat resulting in a higher thermal efficiency compared to the other methods [15]. A filter to remove particles from fluidized bed gasification processes is necessary, as cyclones (even multiple ones in series) are not good enough to eliminate the smallest particulates, whereas for downstream equipment this often is required.

In a two step approach of separated catalytic cracking and filtering, the disadvantage of placing the catalyst unit upstream the filter is the fast deactivation of the catalyst by particle deposition. The disadvantage of placing the catalyst unit downstream the filter is the necessity of having two (expensive) high temperature process units as they should be operated above the tar dewpoint. The catalytic filter combines the two tasks of tar cracking and solids filtration into a single process step. The (ceramic) filter candles are impregnated with catalyst and can be compared to membrane reactors (as shown in figure 4.8) [15, 61, 62, 63].

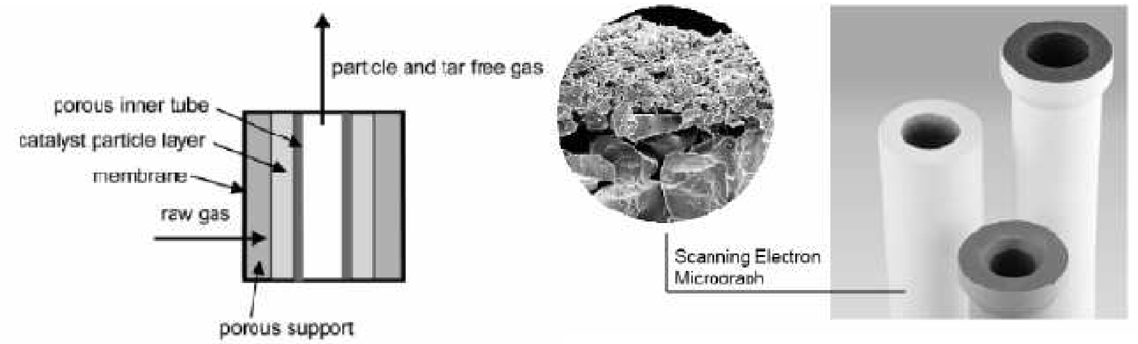


Figure 4.8: Tar cracking catalytic filter and filter elements

The impregnation with catalyst is either done by applying a catalytic coating, adding the catalytic component to the ceramic grain and binder mixture or by using a porous inner tube fixed at the head of the candle to allow integration of a catalyst particle layer [63]. Considerable success under the conditions proposed, for ruthenium at above

900°C and for nickel between 750 and 900°C, has been achieved, but there is a fundamental limitation to the approach in that, at the temperatures required by the catalysts, alkali metal compounds are mostly still volatile. A second, lower-temperature solids removal step will therefore still be required after these components have condensed [62].

4.3.2 Physical tar removal

Physical tar removal is mainly done on the basis of electrostatic precipitators [64], rotating particle separators [65], cyclone separators, filters (either baffle, fabric or ceramic), or scrubbers (either water or organic liquid based) [66-67]. Many of these technologies are applied in combination with each other or with catalytic tar removal technologies as often they are not only removing tars, but also particulates like dust and non-tar components like NH_3. In the following paragraphs, however, mainly their application as physical separator of tars will be discussed.

Electrostatic precipitators

Electrostatic precipitators (ESPs) are widely used to remove fine solids and liquid droplets from gas streams. Although effective with liquid droplets, they prove inefficient when “tar” is in the gaseous phase. This means that, when the target is the “tar” removal, high-temperature operation should be avoided. In such a case gas should be quenched before ESP use (figure 4.9). The basic principle of a wet ESP is gas ionization upon passing between a high voltage electrode and an earthed (grounded) electrode. The ions are produced in a corona discharge and attach themselves to dust particles or droplets of tar and water.

Particles and droplets become charged and are attracted to the grounded electrode due to the electric field. The precipitated dust and droplets flow to the bottom of the ESP where they are collected [13]. Only wet ESP can be used to remove “tar” from biomass gasifier gas, because “tar” condensation on dry ESPs precipitation electrode would progressively inhibit particle removal [68].

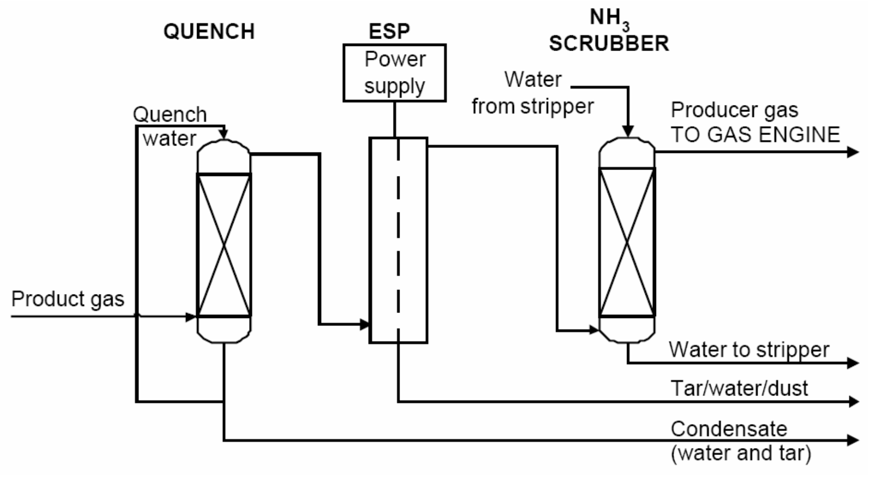


Figure 4.9: ESP based tar clearing

Wet ESP has successfully been applied for electricity generation with gas engines downstream an updraft gasifier in Harboøre, where the gas is quenched with water, and downstream a downdraft gasifier in Wiener Neustadt, where the gas is quenched with RME. At ECN, a wet ESP was installed downstream a circulating fluidized bed gasifier with water quench and also here, the ESP efficiently removed dust and condensable tar droplets from the producer gas [13]. The wet ESP at ECN therefore was also integrated in the oil gas washer OLGA for removing dust and tar aerosols downstream the collector column. The wet ESP is often integrated in the tar scrubbing technologies.

Rotating particle separators

The rotating particle separator (RPS) uses a rotating cylinder, which is centered in a single cyclone. The RPS was successfully implemented for de-dusting of flue gas in combustion systems without associated tar and lead to research on tar removal via RPS as well. For tar removal research two methods were considered, one based on condensation of tars and subsequently removing the droplets of condensed tars from the gas and the other based on injection of a solvent and subsequently capturing saturated solvent [69].

For cleaning of producer gas with the RPS operating in dry mode, useful practical experiences were obtained at the ETH in Switzerland. The RPS was initially tested as a dust filter operated at temperatures above the tar dewpoint downstream a downdraft gasifier. Although the filter operated successfully, it did not capture tars as the operating temperature of the RPS was above the typical tar dewpoint of a downdraft gasifier. During operation of the RPS in dry mode for the removal of organic contaminants [69], separation of heavy tars was observed to be better than for the other components, however very limited with reduction of 30 to 70% reached at temperatures between 130 and 140°C. Research on tar removal with a (wet) RPS at ECN [65] operated at a low temperature, at which water form the producer gas condensed, revealed that the filter element of the RPS blocked by in particular heavy tars within hours after start of the tests (figure 4.10). Cleaning of the filter element by continuous water spray was not sufficient. Although RPS could effectively remove dust, tar aerosols and NH_3, the fouling issue with heavy tars caused the research on RPS to be stopped.

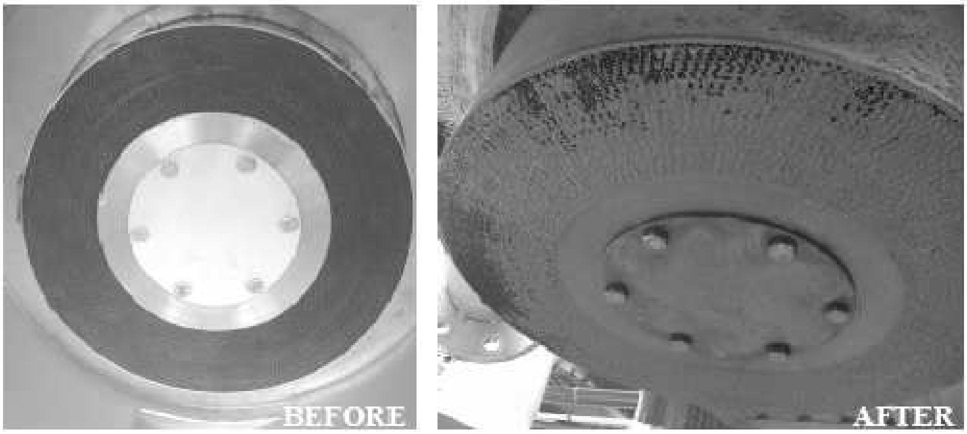


Figure 4.10: Rotating particle separator before and after testing at ECN

BTG went on developing and implemented an RPS together with their own developed RF®TC downstream a farm-scale poultry litter gasifier system [52]. The whole plant was stopped in 2004 due to problems with the RPS [53].

Cyclone separators

Cyclone filters or centrifugal force separators are also mechanical technologies that can potentially be used for tar removal. These technologies operate on the same principles as those for particulate removal, using centrifugal force to separate solids and aerosols from gases. The technologies are best suited for removing larger particles, typically those with diameters of 5 μm or greater. In practice, cyclones and related centrifugal separators are not used for tar removal in biomass gasification systems, although interest has been expressed in the use these types of systems [69, 70]. The combination of particulates and sticky tar in the gas stream, however, creates a deposition of material on cyclone surfaces that is difficult to remove in normal operation. Even if particulates were removed prior to tar condensation, cyclones are ineffective at removing small-diameter tar aerosols that include material below 1 μm size. As a result, cyclones are not a practical means of removing tars from raw biomass gasification products [70].

Filters

Over the years filters of various types have been used in biomass gasification systems for tar removal. The tars are captured by impingement of condensed aerosols on the filter surface. In contrast to solid particulates like dust, tar is more difficult to remove from the filter surface as it exists in a high viscous sticky liquid form. These differences in characteristics make many filters less suitable for tar removal than for particulate removal. Up till now filters, including fabric bag filters and ceramic hot gas filters, are generally inappropriate for tar removal [70], unless coated with a tar cracking catalyst.

Application of packed or granular bed filters has been more successful historically for tar removal and even common practice in small scale gasification systems constructed during the 2nd world war. The packed or granular bed filters consist out of grains, such as sand, (lignite) coal or activated carbon, or sawdust. In some experiences with granular bed filters for the removal of tars as well as particles from biomass fuel gases are presented (table 4.3) [69].

Table 4.3 Experiences with granular bed filters for tar removal from biomass fuel gases

Filter material	Particles removal	Tar removal	Tar definition
Sand	73.0 - 99.8 %	50 - 97 %	Heavy tars
		68 - 98 %	16 EPA PAH
		97 - 99 %	Phenols
Sieved lignite coke	Not determined	50 - 97 %	Heavy tars
		100 %	16 EPA PAH
Saw dust	94.0 - 99.5 %	83 - 85 %	Condensables at 5°C
		50 - 67 %	Condensables at 5°C plus PAH

While packed or granular bed filters provide adequate filtration of tars, they still create operational problems related to cleaning the filter as well as to waste disposal. These filters may be appropriate for small systems operating in remote locations where labour is inexpensive, but they are not being incorporated into designs for larger-scale commercial facilities due to operational and cost considerations, unless as final guard bed [70].

Water scrubber

A water based scrubber tar removal technology has been in operation since 2000 at the Harboøre updraft gasification plant in Denmark, operating on wood chips [71]. The technology has also been licensed to the Japanese company JFE and the German company Relax Umwelttechnik®. The producer gas from the reactor contains about 80 g/mn³ of various tars and acids. The gas temperature downstream the reactor is about 75°C. The producer gas is cooled serially through two district heating shell and tube heat exchangers in which a large amount of tar and water is separated together with most of the particles. Following this the gas is cleaned for remaining water/tar aerosols and dust in a wet ESP. After these processes the contents of tar and dust are both below 25 mg/mn³, and the gas is suitable for fuelling gas engines.

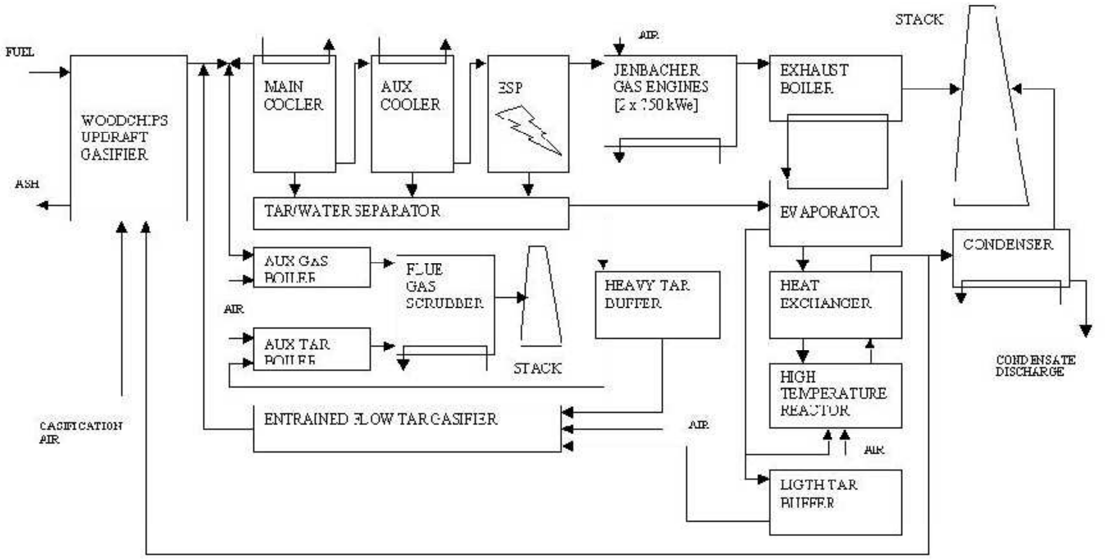


Figure 4.11: Process scheme of the Harboøre process with water based tar scrubber and wet ESP

This water based scrubbing technology results in a huge amount of tar-contaminated water. At the Harboøre plant every 1 kg of wood chips gasified results in approximately 0.6 kg of waste water [71]. This water is separated in a coalescer into heavy (high molecular) tars having a net calorific value of about 27 MJ/kg (approximately 8% on a weight basis) and water contaminated with light (low molecular) tars and acids. The heavy tar is stored in a 150 m³ heated tank and part of this tar is used for district heating peak load firing in the oil/tar hot water boiler. The bulk water fraction can not be discharged because of its phenol, total organic carbon (TOC) and acid content and therefore cleaned in the tar water cleaning system (TARWATC).

The TARWATC uses hot water from the engine exhaust boilers to evaporate the contaminated water and to separate the light tars (having a net calorific value about 14 MJ/kg). The slightly contaminated steam is heated in counter-flow with clean steam from the TARWATC reactor to a high temperature before entering the reactor. The temperature is further increased by burning part of the light tars inside the reactor. The clean steam is condensed in a district heating cooled condenser and fulfils the environmental regulations for discharge into municipal systems [71].

Although the water based scrubbing technology is capable of cleaning the gas sufficiently for some applications [71] and the Harboøre plant operated 8000 hours in 2006 [72], the scrubbing technology shifts the tar problem to (expensive) treatment of wastewater [73].

RME scrubber

As an alternative to water based scrubbers oil wash can be applied as well. This has been done successfully downstream both the indirect gasification process in Güssing [62,74] and the downdraft gasifier in Wiener Neustadt, with the latter one having a wet ESP installed as well to capture tar aerosols. Without an ESP installed, filters would be required for removing these aerosols before the gas can be applied in the gas engines.

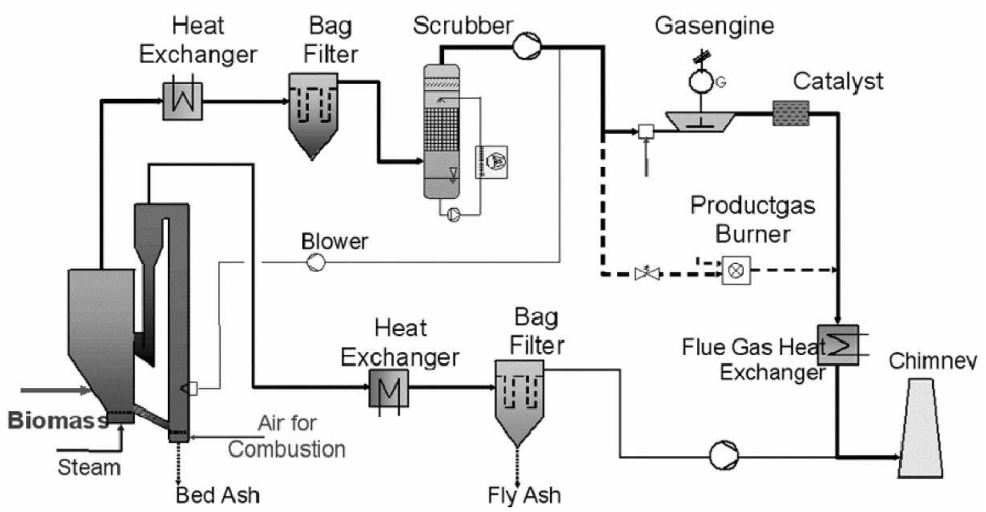


Figure 4.12: Process scheme of the FICFB process with RME based tar scrubber

The tar is almost completely removed by the scrubber using rapeseed oil methyl esther (RME) as a medium. After phase-separation of the condensate, the RME saturated with tar is recycled to the combustor of the indirect gasifier, which means that no liquid waste stream is produced. In order to be able to apply RME as scrubbing liquid, though, the initial tar concentration in the producer gas has to be relatively low, as otherwise the required amount of RME would be too large. At the Güssing plant, the tar concentration of the producer gas therefore is reduced to approximately 2.5 g/mn³ by using olivine as catalytic bed material [74]. Furthermore, the RME contributes significantly to the total ecological impact of the gasification process [75]. Application of the oil based OLGA tar removal technology instead of the RME scrubbing technology reduces this negative effect of scrubbing liquid consumption, as hardly any oil is consumed during operation.

OLGA

The oil gas washing technology OLGA developed by ECN and Dahlman [62,76] is based on a multiple stage scrubber in which the producer gas is cleaned by special scrubbing oil. In the first section of OLGA (the collector, figure 4.13) the gas is gently cooled down by the scrubbing oil. Heavy tars condense and are collected, after which they are separated from the scrubbing oil and can be recycled to the gasifier in order to serve as feedstock of the gasifier. As only tars are recycled to the gasifier, the amount of scrubbing liquid used is not limited like in the RME scrubbing technology and hence higher tar loads in the producer gas are acceptable. In the second stage of OLGA (the absorber/stripper), lighter gaseous tars are absorbed by the scrubbing oil. The tar-laden oil is regenerated in a stripper. In case of an air or steam blown gasifier hot air is used to strip the tars off the scrubbing oil. This air loaded with light tars can be used as the gasifying medium in the gasifier. Hence, the stripper column design is not only based on the tarremoval capacity but also on the amount of air that can be used by the gasifier. All heavy and light tars can be recycled to the gasifier where they are destructed and contribute to the energy efficiency [77]. Tar waste streams are efficiently recycled this way [76].

The OLGA technology has been demonstrated downstream different gasifiers operated on a variety of fuels at ECN and in Moissannes, France. Dahlman is realizing an OLGA tar removal system for a gasification plant which will use 1 tonne per hour of chicken litter and/or forest residues as feedstock. At this moment, the plant is in the engineering phase. It is scheduled to be started in the autumn of 2009. Furthermore, Biomass Gas & Electric, SilvaGas, Dahlman and Solar announced that they are working towards the realization of an advanced biomass gasification plant, scheduled for completion in 2010.

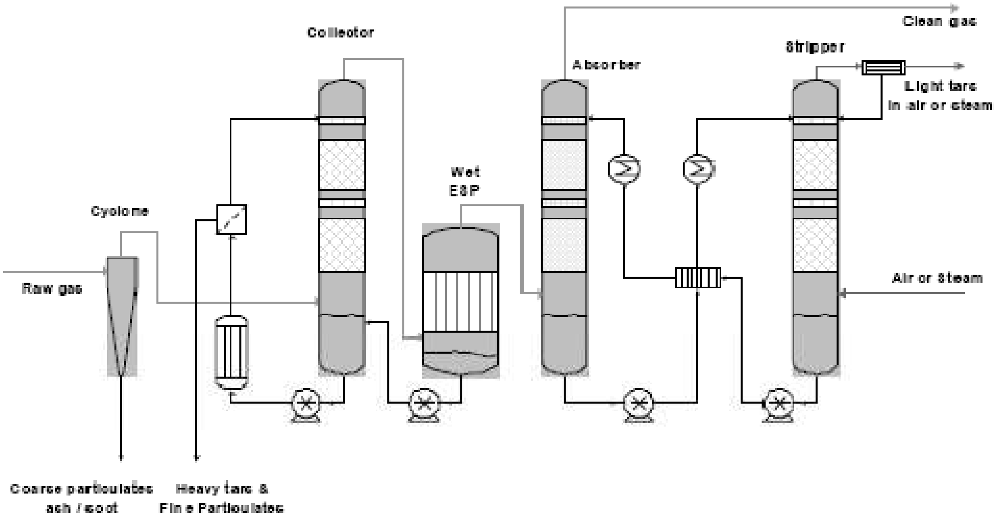
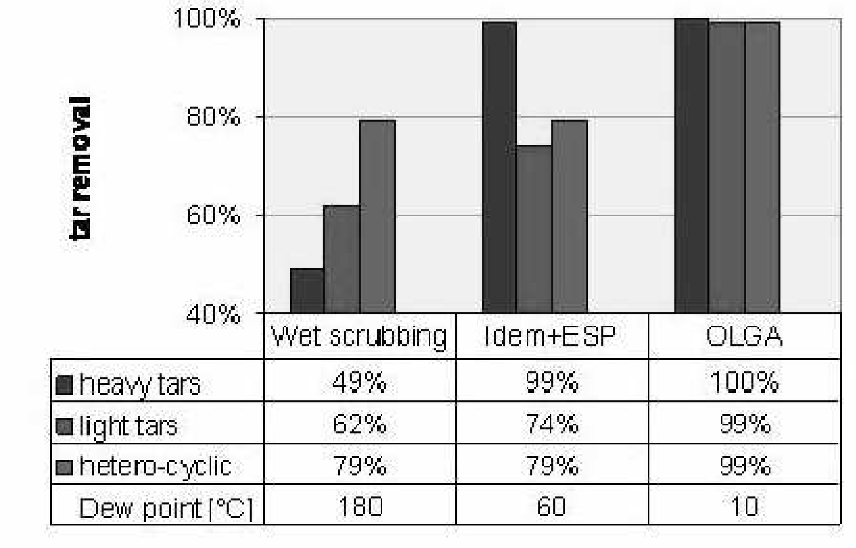


Figure 4.13: Process scheme of the OLGA tar removal technology

ECN operated and tested two aqueous systems and one oil based system, OLGA, downstream their 500 kWth air blown circulating fluidized bed gasifier, producing a producer gas with an initial tar load of 10 to 20 g/mn³ on dry basis. In figure 4.14 the tar removal efficiency of the three tested gas cleaning systems is compared [76].



	Wet scrubbing	Idem+ESP	OLGA
■ heavy tars	49%	99%	100%
■ light tars	62%	74%	99%
■ hetero-cyclic	79%	79%	99%
Dew point [°C]	180	60	10

Figure 4.14: Comparison of scrubbing based tar removal technologies

In the aqueous scrubber the gas was not on specification for a gas engine. With the addition of a wet ESP the heavy tars were almost completely removed and the tar dew point decreased to 60°C. The producer gas could be applied in a gas engine, but the system suffered from wastewater problems. The OLGA removed the tars almost completely. The tar dew point was reduced well below a temperature of 10°C. The water condensate did not contain phenols and the gas could be applied in a gas engine.

4.4 Non-tar components

Whereas tar formation is mainly caused by the operating conditions of the gasifier and less by the composition of the biomass feedstock, for non-tar components the situation is reversed. The elemental composition of the feedstock therefore determines the basic requirements for gas cleaning downstream the gasifier.

Table 4.4 shows an indicative composition of several biomass feedstocks taken from the Phyllis database [78], and shows for example that for non-woody biomass, chlorine, sulfur and ash fractions are much higher than for woody biomass. The use of such fuels will therefore most likely require additional gas cleaning measures to overcome either emission problems, corrosion issues or contamination of downstream processes (i.e. catalyst deactivation, oil degradation, …).

Table 4.4: Composition of several biomass feedstocks

	C (wt%$_{daf}$)	**H** (wt%$_{daf}$)	**O** (wt%$_{daf}$)	**N** (wt%$_{daf}$)	**S** (wt%$_{daf}$)	**Cl** (wt%$_{daf}$)	**Ash** (wt%$_{db}$)	**H_2O** (wt%$_{ar}$)
Untreated wood	48,8	6,0	44,6	0,4	0,03	0,02	1,6	12,8
Treated wood	50,7	6,1	41,7	1,2	0,11	0,08	2,7	17,8
• Demolition	49,4	5,9	43,1	0,9	0,08	0,05	4,3	18,9
• Impregnated	52,5	6,2	40,4	0,6	0,17	0,11	1,5	23,5
• Particle board	50,1	6,2	41,6	2,2	0,08	0,08	2,3	11,1
Grass	49,2	6,0	43,5	0,9	0,16	0,38	3,6	15,4
Straw	50,5	6,1	41,3	1,1	0,15	0,48	10,9	6,1
Manure	51,8	6,4	34,2	4,4	0,85	1,41	32,9	45,7
• Poultry	48,2	5,6	34,8	6,2	0,74	0,73	19,6	30,1
• Cow	53,1	6,8	34,9	2,6	0,95	1,66	43,7	14,9
• Pig	54,1	6,8	33,0	4,3	-	1,84	35,4	92,1
Sludge	50,2	7,2	39,7	2,9	1,00	0,30	25,3	25,3
• Food industry	52,8	8,1	39,9	1,0	0,77	0,01	9,3	7,8
• Paper	49,2	6,0	43,1	1,1	0,45	0,43	33,3	36,8
• Sewage	48,5	7,5	36,2	6,7	1,87	0,53	33,4	31,2
Refuse Derived Fuel	51,8	7,2	39,3	1,1	0,40	0,39	15,0	25,0
Municipal Solid Waste	56,0	5,1	26,6	1,2	0,50	1,13	39,6	34,8

In this chapter, the different gas cleaning technologies for non-tar components are discussed. Also included is a paragraph on unsaturated hydrocarbons still present in the producer gas after tar removal, as these components have a significant influence on downstream synthesis processes, for example on methanation towards Substitute Natural Gas (SNG) [79].

4.4.1 Chlorine

Chlorine compounds are present in most biomass feedstocks, though sometimes chlorine concentrations are extremely low (table 4.4). When present in combination with ammonia, it can form ammonium chloride (NH_4Cl), which at high temperatures is in the vapour phase, but below 250-280°C becomes solid and presents a fouling risk for downstream process steps. When dissolved in (condensed) water it becomes highly corrosive. Similar problems occur in combination with metals present in the feedstock, e.g. potassium and sodium.

Although not part of the gas cleaning, it is mentioned that chlorine can play a significant role in bed agglomeration issues and that its concentration in the producer gas increases with increasing temperatures of gasification [79].

4.4.2 HCl

HCl removal processes can be categorized in two groups: dry and wet processes [79]. In the dry process, the chlorine is removed with an adsorbent, in the wet process with a scrubbing liquid. For dry removal of HCl, two types of adsorbents are commercially available, i.e. sodium carbonate (Na_2CO_3, $NaHCO_3$) and calcium oxide (CaO) [80].

For the cleaning of producer gas, CaO is less suitable as it reacts with CO_2. The CO_2 does not influence the performance of Na-sorbents when applied in the temperature range of 300 to 600°C. The optimum temperature for the reaction was found to be between 400 and 500°C [81], at which HCl concentrations in the producer gas can be reduced to below 1 ppmv [78].

The wet scrubbing process is usually based on either water or a caustic water solution. The amount of water normally present in the producer gas should be able to remove 500 ppmv of HCl from the gas when condensing. If it is not allowed to dispose the condensate onto surface water, additional water treatment (e.g. an ionic exchanger) has to be implemented, which could make the cleaning system rather expensive [78].

The alternative would be to use a caustic scrubber. This will not only remove HCl effectively, but also other components present in the producer gas like CO_2, COS and H_2S [82]. The products formed are all stable salts:

$$\mathbf{HCl + NaOH \rightarrow NaCl + H_2O} \qquad \textit{(eq. 1)}$$
$$\mathbf{CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O} \qquad \textit{(eq. 2)}$$
$$\mathbf{H_2S + NaOH \rightarrow NaHS + H_2O} \qquad \textit{(eq. 3)}$$
$$\mathbf{H_2S + 2NaOH \rightarrow Na_2S + 2H_2O} \qquad \textit{(eq. 4)}$$
$$\mathbf{COS + 2NaOH \rightarrow Na_2S + H_2CO_3} \qquad \textit{(eq. 5)}$$

The reaction with CO_2 should be avoided, as the formed carbonate salt has a low solubility. By having limited residence times, this reaction is avoided.

The reactions between NaOH and HCl as well as H_2S occur relatively fast; hence it is possible to achieve a high selectivity towards HCl and H_2S while limiting the CO_2 removal from the producer gas [82]. For CO_2 removal a more optimal removal technology may be applied.

4.4.3 Dioxins and furans

Dioxins and furans are emitted in all thermal processes, where the combination of an inadequate process temperature (<850°C), the presence of chlorine as well as insufficient concentration of oxygen and residence time (<2s) allows aromatics to form and/or survive [78]. Dioxins, or officially polychlorinated dibenzodioxins (PCDD, figure 4.15), are a group of poly-halogenated compounds which are significant because they act as highly toxic environmental pollutants.

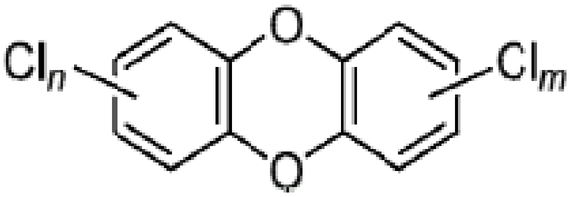


Figure 4.15: General structure of polychlorinated dibenzodioxins (PCDD)

Dioxins can be removed from gases through absorption/adsorption in a polymer material. The ADIOX® technology developed by the Forschungszentrum Karlsruhe and Götaverken Miljö uses polypropylene (PP) doped with carbon particles. The process is based on the high affinity of dioxins to carbon - when in contact, the bond between dioxins and carbon is very strong. By dispersing small particles of carbon in PP a dioxin molecule present in the flue gas is first absorbed into the PP, where it migrates to a carbon particle, on which it is very strongly adsorbed (connected to its surface). The plastic material acts as a selective filter with a preference for molecules like dioxin [83].

An alternative for the removal of dioxins is the oil based scrubbing technology OLGA. Duration tests with OLGA for the fuel cell and gas engine application revealed that dioxins were removed together with tars to a sufficiently low level (below 0.1 ng/m^3) [78]. Considering the general structure of dioxins (figure 4.15) this does not come as a surprise. The OLGA is designed for cleaning the producer gas, however might be applied for cleaning dioxins from gases as well.

A third alternative for the technology based on carbon adsorption is catalytic destruction of dioxin compounds. For flue gases, this is a commercially available technology. The CRI system for example uses a specially developed catalyst to convert dioxins in the presence of oxygen to a mixture of H_2O, CO_2 and HCl.

The specific CRI dioxin destruction catalyst operates at temperatures around 160° C. Dioxin removal straight from the producer gas (with no oxygen present) is not possible with this catalyst.

4.4.4 Sulfur

The sulfur in the biomass is mainly released as H_2S and COS, and only in small amounts as organic sulfur (mercaptanes and thiophenes). The operating temperature of the gasifier mainly determines the exact ratio between the sulfur components [78].

The organic components, in particular mercaptanes, are unstable at high temperatures, however presence of organic sulfur should not be forgotten as it results in issues in downstream processes (emissions, catalyst deactivation) and often is not removed by conventional H_2S and COS removal technologies.

Table 4.5 provides an overview of the pros and cons of different sulfur removal processes.

Table 4.5: Pros and cons of sulphur removal processes

Technology	**Pros**	**Cons**	**Effect on organic S**	**Effect on CO_2**
Dry sorption / Reaction	Limited effect of pressure, wide variety of absorbens available	Waste production, regeneration results in sulphur rich waste gas	Also effective for thiol compounds, unsure for thiophenes	High H_2S selectivity
Physical Absorption	Commonly used, solvent regenerable, removes HCN and Hg	High pressures required, removes HC as well, high OPEX	Removes all organic sulphur compounds	Removes also CO_2
Absorption in alkali solution	Relatively simple, commonly used	Corrosion, high heat consumption for regeneration	Partially effective with amines, with K_2CO_3 only traces	High H_2S selectivity, amines however also remove CO_2
Liquid Oxidation		Large equipment, low quality sulphur	Also effective for thiols, not for COS	High H_2S selectivity
Adsorption	Results in elementary Sulphur	Regeneration results in sulphur rich waste gas	Also effective for some organic sulphur compounds	High H_2S selectivity, can however also remove CO_2
Biological Removal	Mild conditions, limited CAPEX	Functionality unsure for HC containing gas	Unknown	High H_2S selectivity

4.4.5 H_2S

The removal of H_2S is often coupled to CO_2 removal. Kohl [82] gives general guidelines for a preliminary screening for a H_2S and CO_2 removal process, grouping the H_2S removal processes into six types. Table 4.6 gives the list and also suggests the preferred areas of application for each process type. This is particular of interest as conventional H_2S removal technologies might be less interesting for H_2S removal from biomass based producer gases due to the relatively small amount of H_2S present.

Table 4.6: Guideline for H_2S removal processes

	Plant size	Partial Pressure	Sulfur Removal capacity
Absorption in alkali solution	> 25,000 m_n^3/h	< 7 bara	> 10 ton/day
Physical absorption	> 25,000 m_n^3/h	> 7 bara	> 10 ton/day
Liquid oxidation	> 25,000 m_n^3/h	< 7 bara	< 10 ton/day
Dry sorption / reaction	< 25,000 m_n^3/h	< 7 bara	< 10 ton/day
Adsorption	< 25,000 m_n^3/h	< 7 bara	< 10 ton/day
Membrane permeation	< 25,000 m_n^3/h	> 7 bara	< 10 ton/day

Both absorption in an alkaline solution (chemisorption by e. g. aqueous diethanolamine, NaOH solution) and in a physical sorbent (e.g. poly ethylene glycol) are suitable for treating high-volume gas streams containing H_2S and/or CO_2 to below 1 ppmv. However, physical absorption processes are not economically competitive when the partial pressure is low as the capacity of physical solvents is a strong function of partial pressure [78]. The boundary line between physical and chemical solvents is approximately 7 bara [84]. Solid sorption is applicable to low quantities of H_2S. Suitable adsorbents are oxides of Fe (~1 ppmv), Mn (~5), Zn (<0.3), Cu (<1) and Ca (~50), with the final H_2S concentration achievable reported between brackets. Operating temperatures are between 350 and 500°C, except for Ca and Mn (up to 1000°C). Most sorbents cannot be regenerated and must be disposed after being used, although regenerative processes are under development. Adsorption with molecular sieves is a viable option when the amount of sulfur is very low and the gas contains heavier S compounds (such as mercaptane and COS) that must also be removed [78]. The effect on thiophenes, however, is limited.

Membrane permeation involves the separation of individual compounds on the basis of the difference in their rates of permeation through a thin membrane barrier. In general membranes for H_2S removal (< 1ppmv) are applied for small-scale plants with gases containing a high H_2S concentration. The capacity is accomplished by using proportionately increasing number of modules. Therefore, the process does not realize the economy of scale and becomes economically less competitive with absorption processes as the plant size is increased [78].

In general H_2S can be recovered as elemental sulfur, S, by using a biological process or by the reaction with Sox [78]. The standard technology for recovery of concentrated H_2S to elemental sulfur is the Claus process. Normally this process is operated parallel to physical or chemical absorption/desorption process like the Rectisol process or alkanol amine processes. The Rectisol or alkaline amine process removes the H_2S from a diluted gas stream. The gas from the desorption step is concentrated with H_2S and can be applied in the Claus process for the conversion of H_2S to elemental sulfur. In general the Claus process will be too expensive on the small scales associated to biomass applications. Even for large scale biomass gasification facilities the amounts of sulfur are limited, unless typical feedstocks like MSW, RDF, manure or sludge are applied. Alternatively to the Claus process, H2S can be easily and economically converted to elemental sulfur by biological processes, using microorganism to convert S_2- to elemental

S. The H_2S can be removed in an alkaline scrubber from the gas. The chemically absorbed H_2S can consequently be fed to the biological reactor where the H_2S in the solution is converted into elemental sulfur with the bacteria present in the reactor. The THIOPAQ process by Paques [viii] is an example of such a biological process.

4.4.6 COS

Carbonyl sulphide (COS) is an organic sulfur compound, that can not be removed efficiently by physical or chemical removal processes. Thermodynamically, COS will shift towards formation of H_2S though as the gas is cooled down to a low temperature. At a gas temperature of 200 °C, thermodynamically there is no COS present. This implies that it is possible to convert COS to H_2S. Catalysts applied for this conversion include activated alumina, titania on alumina and Mo/Co catalyst. The ZnS product from the absorption of H_2S with ZnO also catalyzes the COS conversion via the hydrogenation reaction. So, when the ZnO bed contains ZnS, COS can be converted into H2S, which is, subsequently, adsorbed by the ZnO. As such, an upstream catalyst for the removal of COS would not be necessary [78].

4.4.7 Other organic sulphur compounds

The principal organic sulfur compounds that are present in the producer gas are carbonyl sulfide (COS), carbon disulfide (CS_2), mercaptans (RSH), thiols (CH_4S, C_2H_5SH), thiophenols (C_6H_6S), and thiophenes (aromatic sulfur, e.g. C_4H_4S). The organic sulfur compounds are much less acidic than hydrogen sulfide (H_2S) and are therefore not effectively removed by conventional alkaline solution based H_2S removal technologies. Physical solvents, however, generally show a very high solubility for organic sulfur compounds [82]. The absorbed organic sulfur compounds end up in the separated acid gas stream.

Although effective for contaminant removal, these physical solvents often also remove considerable amounts of valuable hydrocarbons, among which also (small) amounts of CH_4. As such, they are often not preferred.

For high-efficient processes, e.g. the synthesis of ammonia, substitute natural gas, methanol, and other chemicals, catalytic conversion of the organic sulfur compounds is more interesting [82]. In catalytic conversion, the organic sulfur is hydrodesulfurized upstream the H_2S removal into H_2S via either hydrogenation (e.g. equation 1 to 4) or hydrolysis (e.g. equation 5 and 6):

$$CS_2 + 2H_2 \rightarrow C + H_2S \qquad \textit{(eq. 1)}$$

$$COS + H_2 \rightarrow CO + H_2S \qquad \textit{(eq. 2)}$$

$$RCH_2SH + H_2 \rightarrow RCH_3 + H_2S \qquad \textit{(eq. 3)}$$

$$C_4H_4S + 4H_2 \rightarrow C4H_{10} + H_2S \qquad \textit{(eq. 4)}$$

$$CS_2 + 2H_2O \rightarrow CO_2 + 2H_2S \qquad \textit{(eq. 5)}$$

$$COS + H_2O \rightarrow CO_2 + H_2S \qquad \textit{(eq. 6)}$$

The first hydrogenation reaction (equation 1) demonstrates the risk of carbon formation. The first catalysts used commercially for hydrodesulfurisation at the beginning of 1900 were based on nickel sulfide catalysts, followed in the mid 1900's by copper, iron, zinc, cobalt, or nickel thiomolybdates. All were operated at temperatures between 300 and 450°C. Due to the deposition of carbon the catalysts have to be regenerated on a regular basis [82].

Nowadays, most hydrodesulfurisation (HDS) catalysts are based on cobalt and nickel and molybdenum oxides on an active (possibly titanium enhanced) alumina base (Al-Co-Mo and Al-Ni-Mo). These catalysts are effective at decreased volumes of catalyst charges as well as at sudden change of sulfur content and are operated at temperatures between 250 and 400°C and at elevated pressure (up to 40 bar). Prior to use, the oxidised catalyst has to be sulfided [82], as the active phase in the operating catalyst is the Co-Mo-S or Ni-Mo-S phase. This sulfidation will normally take place by exposing the catalyst as delivered to the normal operating conditions in the plant, i.e. the sulfur for sulfidation is supplied by the feed and at the concentration at which it is available [85]. The CoMo and NiMo catalysts are mainly developed for fossil based technologies and are commercially available from the leading catalyst suppliers such as Haldor Topsøe, Süd Chemie and Johnson Matthey. Application of these catalysts for biomass based processes, as done by ECN [4, 30, 48, 79] and PSI [86, 87, 88] in their SNG development, might cause some issues concerning the sulfur and olefins concentrations in the producer gas and the relatively low operating pressures.

If the sulfur content in the feed is constant and low, the stable sulfur concentration in the catalyst and thus the activity will be low. Although normally not problematic, the catalyst may not convert organic sulfur sufficiently during a short period if the concentration suddenly increases. The catalyst will have to be fully sulfided before the slip of organic sulfur will go down again [85]. If the olefins are hydrogenated as well, this exothermic reaction will cause a significant temperature increase over the HDS reactor. As such, it might be necessary to lower the inlet temperature of the HDS reactor; however this will have a negative effect on the HDS of the organic sulfur compounds [82]. The low operating pressures compared to the normal operating conditions for which the HDS catalysts are designed (10 and 40 bar) also has a significant influence on the HDS catalyst activity. Experiments with a Ni-Mo/SiO_2 catalyst at different temperatures and partial pressures showed a significant effect of both parameters on the catalytic activity, as is illustrated in figure 4.16 [89, 90].

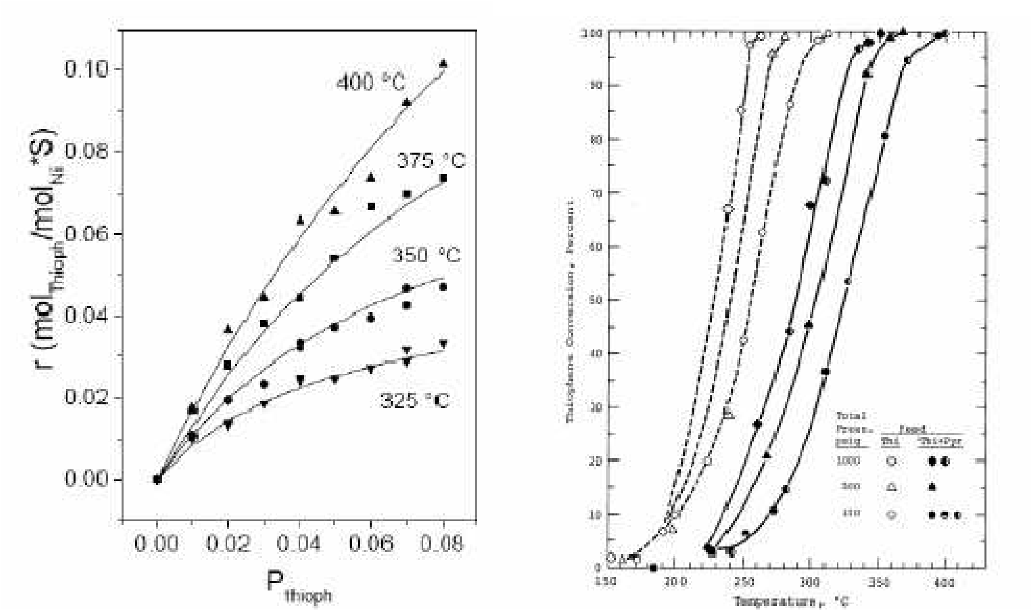


Figure 4.16: Catalytic activity for thiophene HDS versus thiophene (partial) pressure

4.4.8 Nitrogen

Nitrogen present in the producer gas originates either from the feedstock (typically ending up in the form of HCN and NH_3, partially as pyridine, in the producer gas) or from the gasifying agent (in the form of N_2 in case of air-blown gasification, HCN and NH_3 resulting from molecular nitrogen can be neglected) [62]. Compared to coal based gasification, the HCN concentrations in the biomass producer gas are roughly the same (~20 ppmv), the NH_3 concentration, however, can be significantly higher (up to thousands of ppmv compared to up to 40 ppmv for coal) [62, 91].

The presence of NH_3 as well as chlorine in the producer gas might result in the formation of NH4Cl, a chemical that becomes solid below 250-280°C and presents a fouling risk [62]. Ammonia in the presence of H_2S can result in formation of ammonium(poly)sulphide, which solidifies at temperatures below 150°C. HCN is reported to be a potential contributor to the deactivation of for example FT catalysts [91]. When hot producer gas is used to generate electricity in integrated gasification combined cycle (IGCC) power plants, both NH_3 and HCN will partly be converted to nitrogen oxides (NOx) which are difficult to remove and are highly undesirable as atmospheric pollutants. Removal of NH_3 and HCN is therefore often required.

For NH_3 removal either catalytic destruction or wet scrubbing can be applied. Catalytic destruction of NH_3 is possible using catalysts similar to those used for tar cracking or hydrocarbon reforming. Dolomite, Nibased steam reforming catalysts as well as Fe-based catalysts have all been reported to be able to convert NH_3 at temperatures of approximately 900°C [92-94]. Using these catalysts, destruction of >99% of the NH_3 is possible [70]. Although this combined tar and NH_3 removal has the potential to remove both tars and NH_3 from the producer gas while maintaining the heat of the producer gas, commercial tar cracking systems at this temperature are still under development.

Ammonia may also be removed from the producer gas by wet scrubbing. The main problem with wet scrubbing is the presence of tars in the producer gas, which end up in the water as well. At the Harboøre plant the tar and NH_3 contaminated waste water is treated in the tar water cleaning system (TARWATC) [95]. More ideally tars and NH_3 are removed separately in order to avoid contamination of the water with tars. However, this requires the removal of tar before the wet scrubber to such a level that the tar dew point is well below the operating temperature of the water scrubber, i.e. well below approximately 30°C. The oil scrubbing technology OLGA is capable of doing this and therefore allows downstream implementation of a "conventional" water scrubbing system [76]. The NH_3 is soluble in water and can either be neutralized with acids to form ammonia salts, converted biologically into N_2 or stripped from the scrubbing water.

In the latter case, the stripper air containing the NH_3 can be recycled to the gasifier to be converted to N_2 and H_2O. This conversion requires a temperature above 800°C in order to reach over 50% conversion and is nearly complete (>90%) at 850°C [96]. The presence of oxygen or air at the injection point will lead to a much higher rate of NH_3

destruction than observed for pure thermal cracking. Tests at ECN also revealed hardly any NH_3 was converted to NOx.

When applying a biological process to clean the scrubbing water, e.g. via the ANAMMOX® process, bacteria convert NH_3 into N_2 via a combination of nitrification and de-nitrification reactions (figure 4.17). In 2002 the first full-scale plant was started up in the Netherlands and at this moment four installations are operational. The process can be used for the removal of ammonium with a relatively high ammonium concentration (>100 mg/l), however the bacteria's applied are sensitive for hydrocarbon pollution.

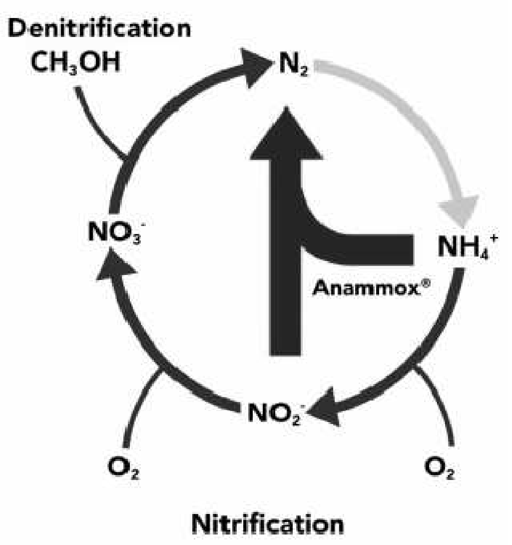


Figure 4.17: Biological ammonia removal

4.4.9 Carbon dioxide

Removal of CO_2 from the producer gas may be necessary for various reasons. In combination with water, it is for example highly corrosive and rapidly destroys pipelines and equipment unless it is partially removed or exotic and expensive construction materials are used. Furthermore, for specific processes like methanol and FT diesel synthesis the inert CO_2 present in the gas will require higher overall operating pressures. Within the framework of the EOS-LT consortium project "Biomass gasification and gas cleaning" though, the removal of CO_2 is mainly done for the purpose of producing (substitute natural) gas with a high enough heating value to comply with the standards of the conventional application of the gas and (to a lesser extent) the purpose of carbon capture and storage (CCS).

For CO_2 removal a wide variety of technologies are commercially available, including conventional absorption processes, such as the BenfieldTM process based on hot potassium carbonate solutions and amine scrubbing processes based on formulated solvents (e.g. MEA, DEA, MDEA). However, also cryogenic as well as adsorption processes (e.g. PSA, TSA) and membranes are commercially available. For a detailed description of all these CO_2 removing technologies reference is made to the Gas purification handbook by Kohl and Nielsen [71].

In the status report at hand, the focus for CO_2 removal is on upgrading the quality of the producer gas. This is comparable with the upgrading of biogas or landfill gas.

4.4.10 Unsaturated hydrocarbons

The existence of unsaturated hydrocarbons in the producer gas varies widely and does not only include tars, but also light unsaturated hydrocarbons like acetylene (C_2H_2), ethylene (C_2H_4) and benzene (C_6H_6). Unlike tars, these components do not create a high fouling risk due to straight condensation. However, they can react with and deactivate synthesis catalysts through carbon deposition or form gummy polymers that subsequently can plug downstream equipment due to condensation. The removal of unsaturated hydrocarbons can be done via physical separation (e.g. amine scrubbing, though with regards to selectivity cryogenics or selective adsorption makes more sense). Selective catalytic hydrogenation is however usually the preferred technique [71].

Platinum or palladium based catalysts typically can be used for the hydrogenation of C_2H_2 and C_2H_4 at relatively low temperatures. The NiMo and CoMo catalysts applied for HDS also demonstrated hydrogenation activity for unsaturated hydrocarbons and are unlike the Pt or Pd catalysts not sensitive for sulfur deactivation. From the hydrocarbon composition before and after the HDS it is clear that the compounds are actually hydrogenated towards CH_4 and C_2H_6, and not cracked into CO and H_2 [79]. Experiments at PSI, however, also reveal that even after HDS not all unsaturated hydrocarbons are removed from the gas [99]. The components still present (i.e. C_3H_6, as well as C_6H_6 and C_7H_8 not completely removed in the tar removal step [79]) cause a significant risk of soot formation on the methanation catalysts applied at ECN and PSI [79, 99]. When using a fluid bed methanation process, this soot formation might not be problematic and the catalyst might continuously be regenerated.

R&D on removal of these components via scrubbing, hydrogenation or reforming is ongoing [79, 99, 100] and is crucial for long-term operation of catalytic synthesis processes downstream tar producing gasifiers. Although conventional (amine or methanol based) scrubbing technology can easily solve this specific problem, severe scrubbing of the producer gas is not considered to be economically attractive due to the efficiency penalty associated with it and the complexity of cleaning the scrubbing medium. Maintaining the hydrocarbons in the producer gas, either as (stable) saturated light hydrocarbons (i.e. CH_4 or even better C_2H_6 and C_3H_8) or if necessary converted to synthesis intermediates (i.e. CO and H_2), will result in significantly higher production efficiencies, and hence ultimately an economically more attractive process.

4.4.11 Particles and alkalis

The need for particulate and alkali removal significantly depends on the use of the producer gas. For gas engines, particulate levels must be reduced to below 50 mg/Nm³, whereas for turbines (< 15 mg/mn³) and catalytic processes (<0.02 mg/mn³) the requirements are even more stringent [70]. These particulates do not only include char and ash present in the initial producer gas of the gasifier, but also alkalis. The mineral matter in biomass contains high levels of alkali salts, particularly e.g. grass, straw and other fast growing biomass, which contain large amounts of potassium. At temperatures of around 800°C, the alkali salts can vaporize and create problems by depositing on cooler surfaces downstream. The alkali will remain in the vapour phase until it condenses due to cooling below about 650°C, typically forming small particulates (<5 μm) or condensing straight on surrounding surfaces like other particulates or the process equipment. In gasification, alkali vapours are removed by cooling the hot producer gas below 600°C to allow for condensation of the material into solid particulates [70]. The solids are then removed using various dry or wet particle removal systems. These particle removal systems not only have to be designed taking into account the chemical behaviour of the condensed alkali salt, but also the effect of tar condensation. As such, particle removal is normally closely linked to and installed together with some kind of tar removal technology. In this paragraph, the main particle removal technologies are discussed briefly, emphasising in particular on the issues that occur when applying these “conventional” technologies in a tar loaded producer gas stream.

Cyclones

In a cyclone, the particles containing producer gas is introduced tangentially into a cylinder. The gas exits the cyclone at the top while the particles, separated from the gas via centrifugal forces, slide along the wall of the cylinder to a dust collection chamber at the bottom of the cyclone (figure 4.18) [101]. Cyclones are particularly effective (>90%) at removing particles larger than a few micrometers with minimum pressure drop [70]. Smaller particles however are not caught.

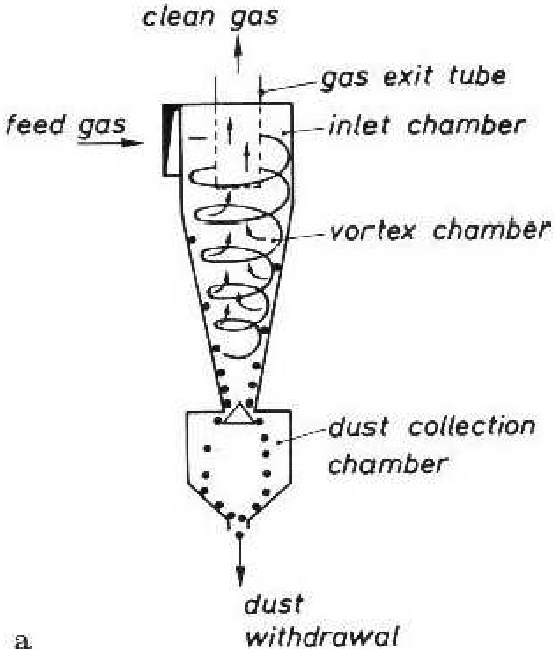


Figure 4.18: The mechanical principle of a cyclone

Cyclones are commonly used, also in biomass gasification systems, and are commercially available from many vendors. Typically they are operated at high temperature to avoid condensation of tars in the cyclone and often they are used as multiple units in series. A circulating fluidized bed gasifier will in general have an initial cyclone operated at the temperature of the gasifier, in which the bulk of unconverted char and ash is separated from the producer gas in order to be circulated to the bottom of the gasifier. Downstream this cyclone, multiple (colder) cyclones can be placed to collect particles with different sizes as well.

The positioning of a cyclone in a gasification system can determine the success of the system. Due to the particle vortex it is possible to operate a cyclone at temperatures (slightly) below the tar dewpoint; the particles can remove some condensed tars from the walls as long as condensation is not too significant. Without the presence of these particles, the cyclone will not be cleaned. For this reason it is also recommended not to position a (final) cyclone upstream gas coolers, as in that case no particles are present capable of removing tars in the difficult producer gas cooling step as well.

Barrier filters

Barrier filters are based on porous materials (e.g. metal or ceramic candles, bag filters, packed bed filters) that allow gases to pass, while blocking the particles (figure 4.19). They effectively remove small-diameter particulates in the range of 0.5 to 100 μm. Removal of smaller particles is also possible though associated with high pressure drops over the filters. The particles can be removed from the filter material by periodically pulsing clean gas through the filter in the reverse direction of normal gas flow [101]. To reduce the overall particulate load, these filters are typically placed downstream cyclones.

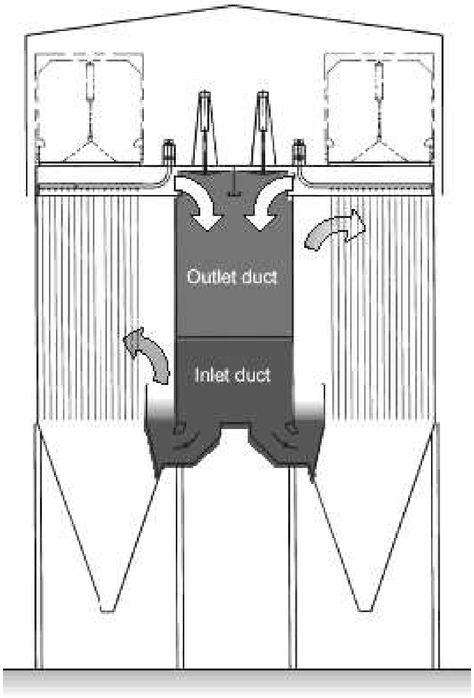


Figure 4.19: The mechanical principle of a barrier filter

Although barrier filters are effective for removing dry particulates, they are less suitable for wet or sticky contaminants such as tars. Tars cling to the filter surface and can undergo subsequent carbonization reactions that lead to fouling and plugging [102]. Hence, in biomass producer gases, these barrier filters are applied either in gases where tars are already significantly removed (e.g. at Güssing) or operated at high temperature, above the dewpoint of tar.

These high temperature gas filters (HGF) were tested at the commercial demonstration facility at Värnamo, Sweden [103] and more recently at the pilot facility at ECN [102]. At both sites, the filters were operated at 350 to 400°C, hence above the tar dewpoint. At Värnamo, the ceramic candle elements broke repeatedly due to the frequent thermal cycling in the demonstration facility that operated intermittently [101]. This has been solved by using metal fibre filters. The tests at ECN were not successful. Fouling of the HGF upstream the OLGA tar removal led to a serious increase of the pressure drop over the HGF (Figure 4.20). The HGF upstream the OLGA system was successfully replaced by an electrostatic precipitator within OLGA.

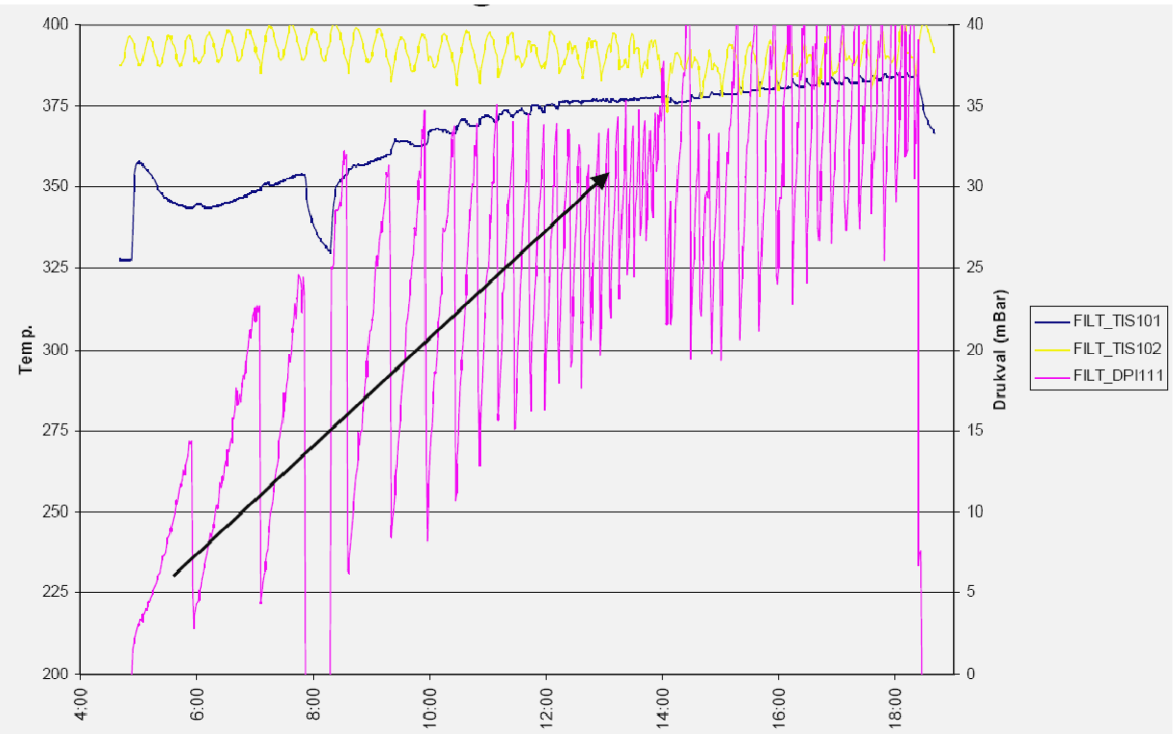


Figure 4.20: Temperature (blue line) and pressure drop (pink line) of the hot gas filter at ECN

HGF research now mainly focuses on the combined ceramic gas filtration and catalytic tar cracking [61] as being developed by Pall (Schumacher) and Madison Filter (in cooperation with Haldor Topsøe). These filters operate at temperatures of around 750 to 900°C, and as a result are relatively large and expensive units. Operation of barrier filters at lower temperatures however often resulted in tar fouling, hence making the filters only applicable downstream some kind of tar removal unit or downstream gasifiers with an initially low tar dewpoint.

Electrostatic filters / scrubbing technology

Electrostatic filters are based on separating charged particles in an electrostatic field. The particles are collected on so called plate curtains (figure 4.21), where the formed particle layer is removed via dry or wet methods [101]. The dry methods are based on mechanical cleaning of the surface area and can operate at high temperatures (up to 500°C), whereas in wet methods the particle layer is removed with a thin film of flowing liquid, usually water. As such the wet ESP has a typical operating temperature below 100°C, or at least below the condensation temperature of the liquid applied. With the ESP being relatively expensive on a small scale, the technology is attractive only for large-scale operation [70].

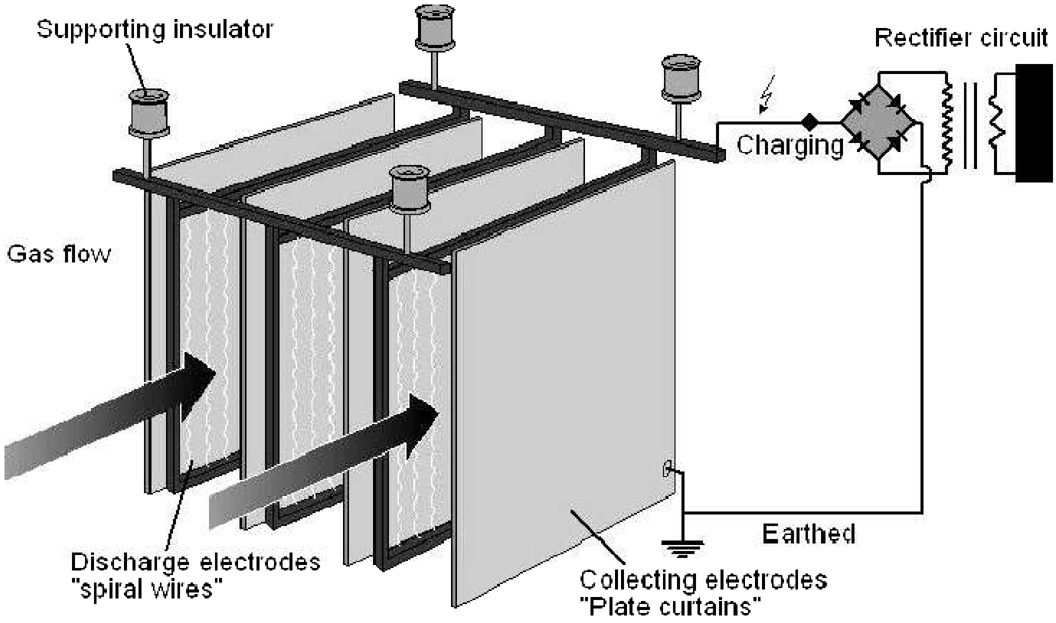


Figure 4.21: The mechanical principle of an electrostatic filter

As good charging of particles would require a minimal particle size of 0.5 μm, an ESP is in general less efficient for small particles. Often though, ESP systems are applied downstream a cooling and scrubbing system, in which small particles present in the gas (e.g. ash, aerosols) grow in particle size due to condensation of a liquid on the particle, being either water, RME or oil. As such, an ESP becomes suitable as well for small particles and hence very high separation efficiencies can be obtained.

The ESP has been applied successfully in several biomass gasification systems and has therefore become a commercially proven and available technology for thermal biomass conversion systems as well. The issues with tar are dealt with by having a scrubber installed upstream the ESP. At Harboøre, the particles (including tar aerosols) grow by condensation of water on the particle and as such are separated in a water based wet ESP. In the RME as well as the oil based OLGA scrubbing technology the principle is the same, however in stead of water, RME or oil is used. As such, the (wet) ESP not only operates as a filter for particles (e.g. ash, dust, alkalis), but also as a tar aerosol filter.

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Chapter5

TAR Removal Analysis.

5. TAR Removing Analysis.

5.1 Introduction

At ENEA Research Center of Trisaia there is a Dual Fluidized Bed 500 kW_{TH} Biomass Gasification Pilot Plant (§3.2). The plant feedstock is almond shells. . The characteristics of the plant are reassumed in the table 5.1 below [1, 2, 3]:

Table 5.1: ENEA Biomass Gasification Pilot Plat characteristics

	Flow rate [kg/hr]	**LHV [MJ/kg]**	**Temperature [°C]**	**Enthalpy [kJ/kg]**
Biomass	100	16	15	
Biomass (dry)	90	18	15	
Steam	70		380	3250
Air	300		450	500
Additional Fuel	10	42	15	

The Pilot Plant has a potential about producer gas floe rate equal to 180 Kg/hr. The produced syngas composition in shown in the following table 5.2 [1, 2]:

Tab. 5.2: Double fluidized bed producer gas composition

Composition Dry gas	**CO_2**	**CO**	**H_2**	**CH_4**	**C_2H_6**	**C_3H_8**	**N_2**	**Tar**
%vol	19.3	25.1	33.1	10.4	0.2	2.3	9.6	10.3 g/Nm^3

The idea is to join the gasification plant to a Molten Carbonate Fuel Cell. Table 5.3 shows the admissible concentration of the principal pollutants [1,2].

Tab. 5.3: admissible concentration of the principal pollutants.

Pollutants	**H_2S**	**HCl**	**NH_3**	**HCN**	**Tar**	**Particle**
Admissible value	<0.1 ppm	<0.1 ppm	< 1%vol	<0.1 ppm	<2000 ppm	<10 ppm (d> 1 µm)

From a comparison between the data reported in tables 5.2 and 5.3 it is clear that an additional cleaning step to remove tars is needed. By an analysis of the main gas cleaning methods (Chapter 4), the choice of absorbing tower, running with biodiesel like absorbing liquid, to reduce the level of tars in the producer gas it seems to be the best. Biodiesel is used in order to remove tars [3, 4, 5]. By using a modeling, an investigation and optimization of this innovative cleaning solution has been carried out.

5.2 Simulation method

Basing upon the ChemCAD commercial code the absorption reaction has been simulated. The equilibrium and kinetic rate controlled approaches are both assumed to model the reactions. To simulate the absorption tower a standard impingement-plate scrubbers is used. In fact, the scrubbing tower certainly represents the standard scrubber, with its high collection efficiency, and it is known everywhere for its unbeatable intrinsic performance levels and reliability in holding the set limit values over the long-term. Syngas fed was simulated by an ideal mixture of the gas component. On the other hand, by a comparison between produced bio-diesel characteristics and the chemical and physics characteristics of the diesel available in the ChemCAD database 1,1 Bicyclohexyl was chosen to simulate bio-diesel. Tars behavior was simulated by its most present component [13, 14]. Figure 5.1 show the composition of tars in producer gas.

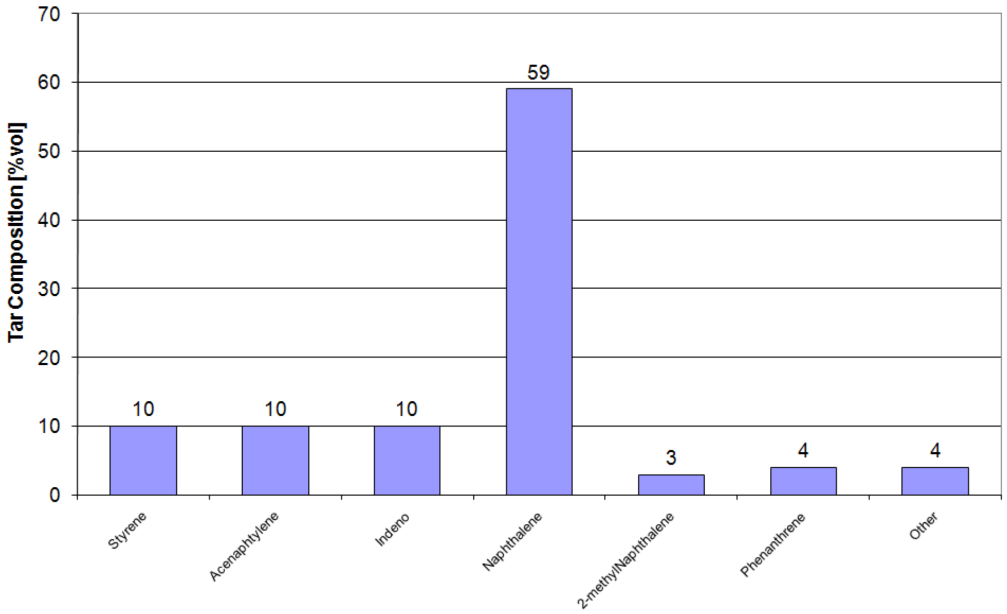

Figure 5.1: Tars composition

5.3 Simulation results

Three different simulations were carried out. The first one has been performed using pure biodiesel like absorbing fluid.

The second simulation considering a mixture of 50% water and 50% biodiesel and the last one with only water like absorbing fluid in order to compare the results and to evaluate the absolutely tars removal efficiency of biodiesel.

Simulation results are shown in figure 6.

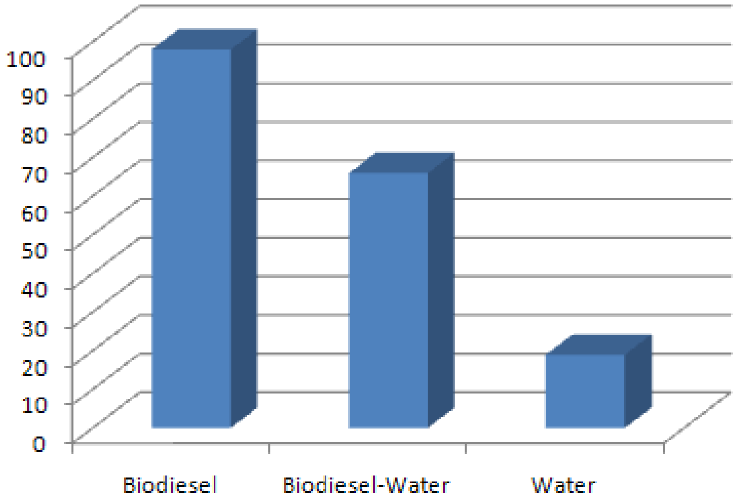

Figure 5.2: Tars removal efficiency

From the first simulation we obtain as output a gas flow with an amount of tar equal to 0.0016 g/Nm^3 only is calculated. Thus a reduction in tar concentration in the syngas fed equal to 99.8% is estimated.

The other two simulations give us worst results. As matter of fact, the second simulation using biodiesel-water mixture like absorbing fluid report a tar removal efficiency equal to 66%. While, sing only pure the efficiency is only equal to 19%. This is an expected result in fact using water only condensable tars are removed.

By this simulation we've also estimated the fed of biodiesel needed to remove tars that is equal to 40 Kg/h for 1 m3/h of producer gas feed.

5.4 DownDraft Gasifier.

The same analysis has been carried out for the DownDraft gasifier operating in Enea-Trisaia research centre. Table 5.4 show the composition of producer gas for this plant [15]:

Tab. 5.4: DownDraft gasifier producer gas composition

Composition Dry gas	**CO_2**	**CO**	**H_2**	**CH_4**	**O_2**	**N_2**	**Tar**
%vol	13.7	17.3	14.3	1.0	1.7	52.0	37.5 g/Nm^3

Figure 5.7 show the composition of tars in producer gas [14].

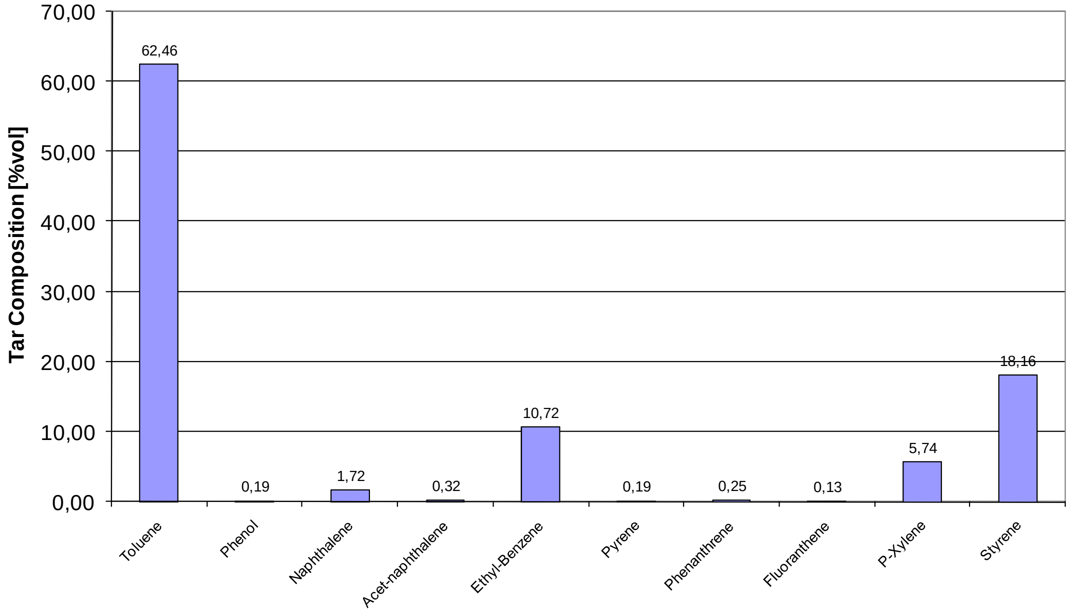

Figure 5.7: DownDraft Gasifier Tars composition

Figure 5.8 show the result obtained by using ChemCad simulation.

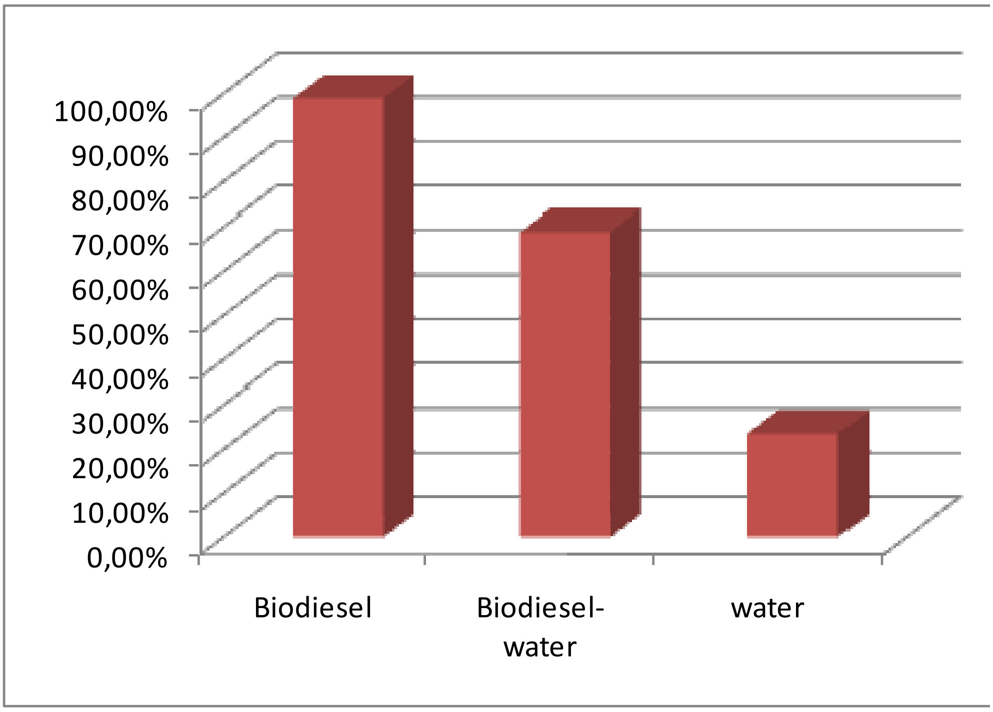

Figure 5.8: DownDraft gasifier, Tars removal efficiency.

5.5 UpDraft gasifier

The same analysis has been carried out for a tipical UpDraft gasifier producer gas. Table 5.5 shows the composition of producer gas considered.

Tab. 5.5: DownDraft gasifier producer gas composition

Composition Dry gas	**CO_2**	**CO**	**H_2**	**CH_4**	**HCl**	**H_2S**	**Tar**
%vol	6.2	21.44	20.25	3.65	0.13	0.08	47.5 g/Nm^3

Figure 5.9 show the composition of tars in producer gas.

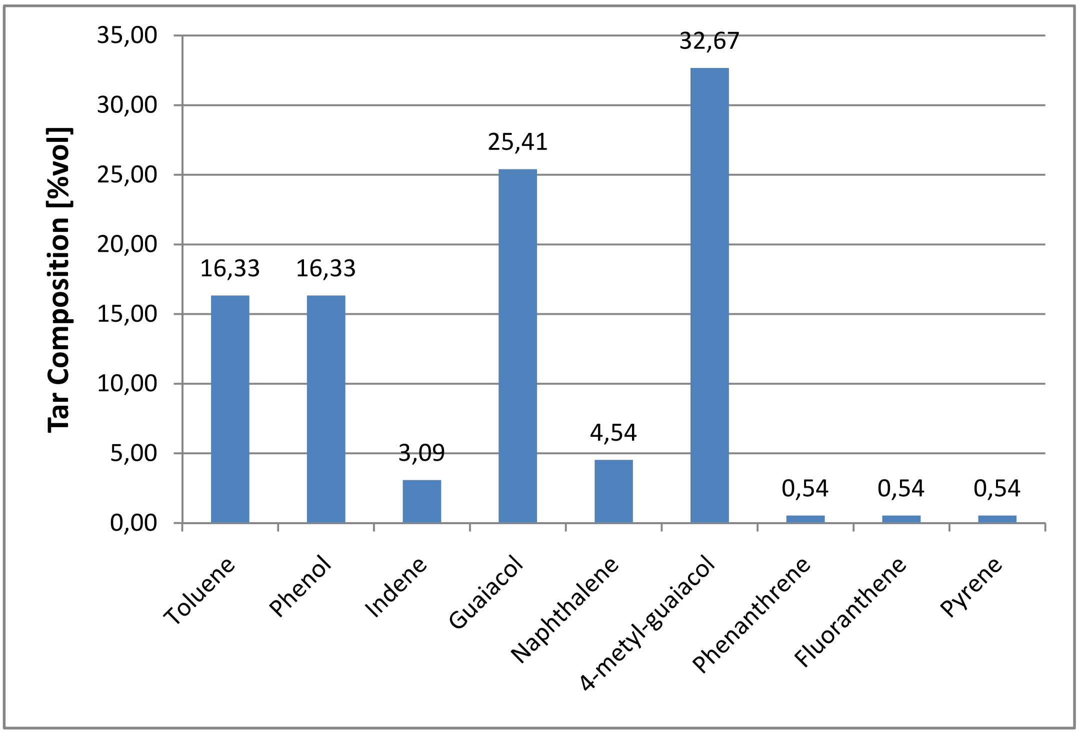

Figure 5.9: UpDraft Gasifier Tars composition.

Figure 5.10 show the result obtained by using ChemCad simulation.

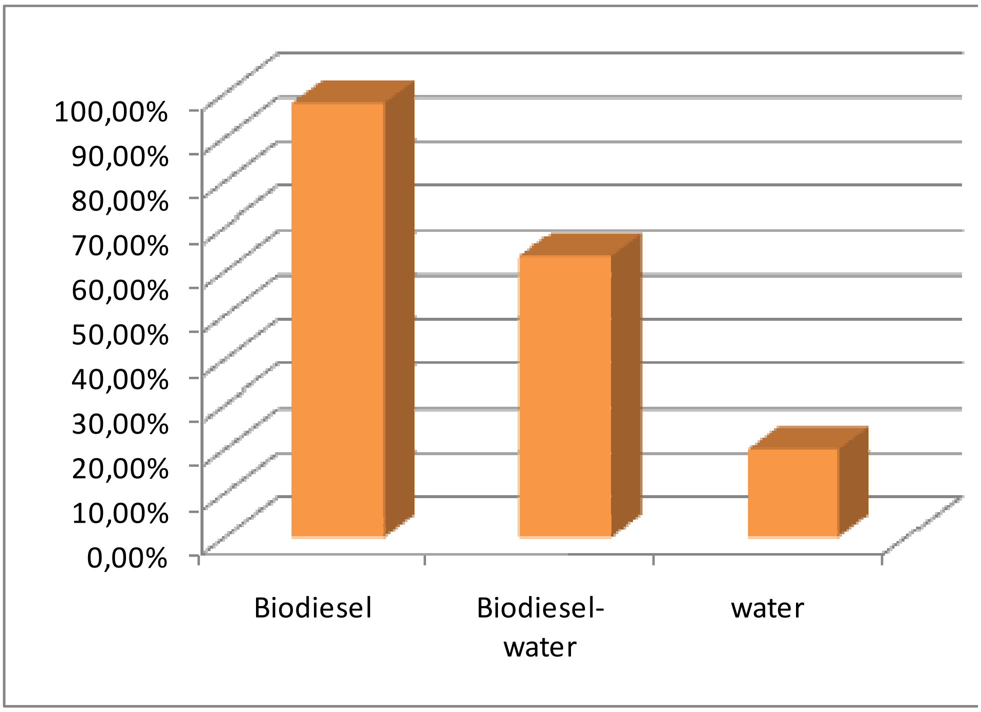

Figure 5.10: UpDraft gasifier, Tars removal efficiency.

5.6 Conclusion

The simulation carried out give us great result in term of tar reduction. These results are more important if compared with a traditional water scrubber data. Biodiesel scrubber is able to remove tars from producer gas with efficiency equal to 98%.

The simulations carried out confirm the great flexibility of ammine mixture scrubber that is able to remove tars for the three gasification technologies analyzed

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Chapter6

No TAR Removal Analysis.

6. No TAR Removal Analysis

6.1 Introduction.

The development of high efficiency systems for biomass conversion into electricity is a strategic issue to achieve an advanced use of these renewable resources. A combination of gasification and fuel cells may be valuable solution for small to medium scale applications.

One of the major issues in biomass gasification is to deal with high efficiency cleaning section. In this framework, integrated gasification combined cycle systems appear to be the key answer for large scale applications, while combination of gasification and fuel cells may be valuable solution for small to medium scale applications [1, 2].

Gas cleaning is one of the main problems to deal with in biomass gasification, especially in case of an advanced use of the producer gas, such like in a combined cycles or a fuel cell [3].

The current focus of biomass conversion research and development is to produce fuel derived from cellulosic biomass, especially waste biomass or feedstock grown on marginal lands that generate little carbon today. Gasification of biomass feedstock to generate syngas for further downstream fuel synthesis is a viable and promising approach. Biomass feedstocks contain low percentages of protein-derived sulphur which is converted primarily to H_2S during gasification. The H_2S concentrations, on a dry basis, in biomass-derived syngas range from about 20–50 ppmv for hardwood to 500–600 ppmv for corn stover. The sulfur content of the syngas needs to be removed because it deactivates catalysts used downstream and is corrosive.

Low temperature removal of H_2S offers the potential of better thermal efficiency in the overall biomass gasification to fuels process, reduced waste stream generation, and lower biofuel production cost in fact the use of a scrubbing process leads to a very flexible process. Several types of sorbents have been developed over the last two decades to remove H_2S from dry coal-derived syngas at low- to midtemperature ranges [1]. However, further research is necessary because biomass syngas contains much higher steam and hydrocarbon content than coal syngas. The work presented here used materials developed for produced gas desulfurization as a starting point to begin sorbent development for biomass syngas desulfurization [4, 5].

.Similarly an excessive amount of acid compounds, such like sulphur and chlorine, in the producer gas, may be intolerable by conversion devices, such like turbines or fuel cells [3, 6, 7].

So, the idea to test an absorbing tower to remove sulphur compounds and acid pollutants has been performed.

The same approach shown in the previous chapter has been carried out.

6.2 Desulphuration

By using data of syngas produced, a design and a modeling of an innovative upgrading of gas cleaning section have been carried out.

This upgrading consists in an adsorbing tower so as to reduce the level of sulphuric compounds in the producer gas. In order to reach this target we choose to use a scrubbing tower running with an alkaline solution. The idea is to compare the performance of a two different alkaline solution: the first one is a mixture of with water and ammonia, while the second one is a mixture of water with methyl-diethanol-ammine, (MDEA). The idea is to compare the performance of a commercial product with the performance of a product just tested to remove sulphuric compounds from produced gas.

6.2.1 Simulation model

Basing upon the ChemCAD commercial code the absorption reaction has been simulated. The equilibrium and kinetic rate controlled approaches are both assumed to model the reactions. To simulate the absorption tower a standard impingement-plate scrubbers is used. In fact, the scrubbing tower certainly represents the standard scrubber, with its high collection efficiency, and it is known everywhere for its unbeatable intrinsic performance levels and reliability in holding the set limit values over the long-term. Syngas fed was simulated by an ideal mixture of the gas component. To simulate the absorption fluid an ideal mixture of water and ammonia, or water and MDEA, has been chosen [8, 9].

6.2.2 Results and discussion

Two different simulations were carried out considering a mixture of water and ammonia. The first one using a solution 70% water – 30% ammonia. The second simulation considering a mixture of 50% water and 50% ammonia.

Simulation results are shown in figure 6.1 and 6.2.

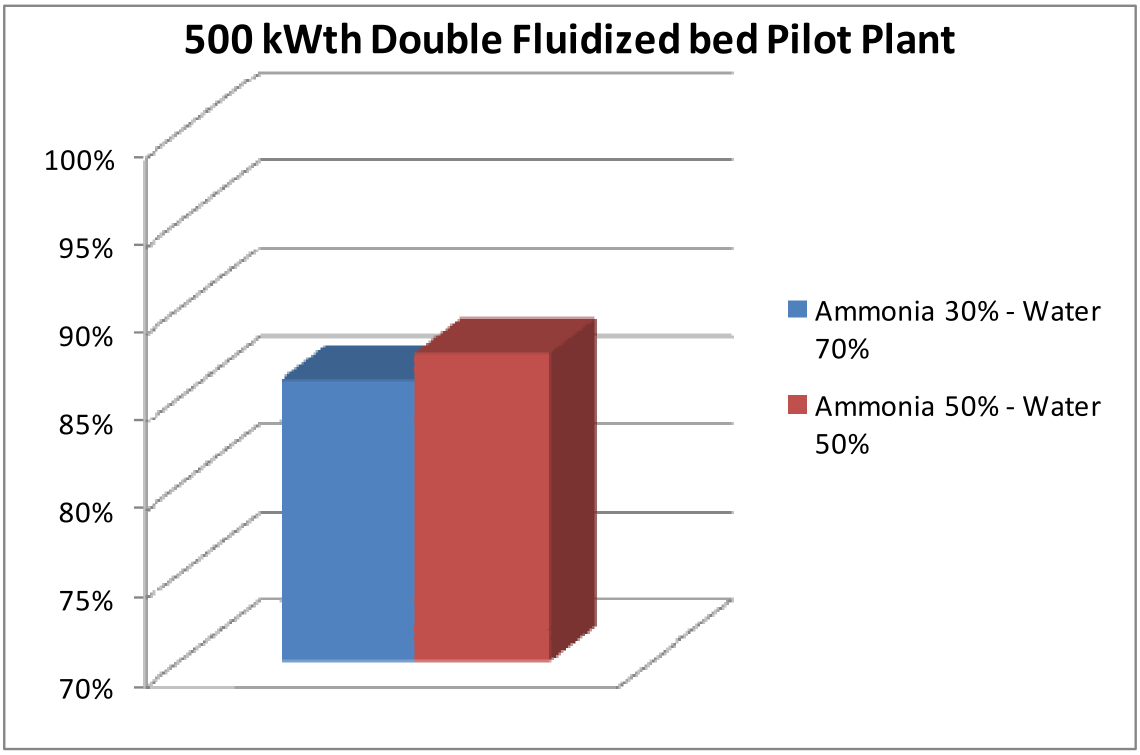

Figure 6.1: the 500 kWth gasification plant: sulfuric compounds removal efficiency.

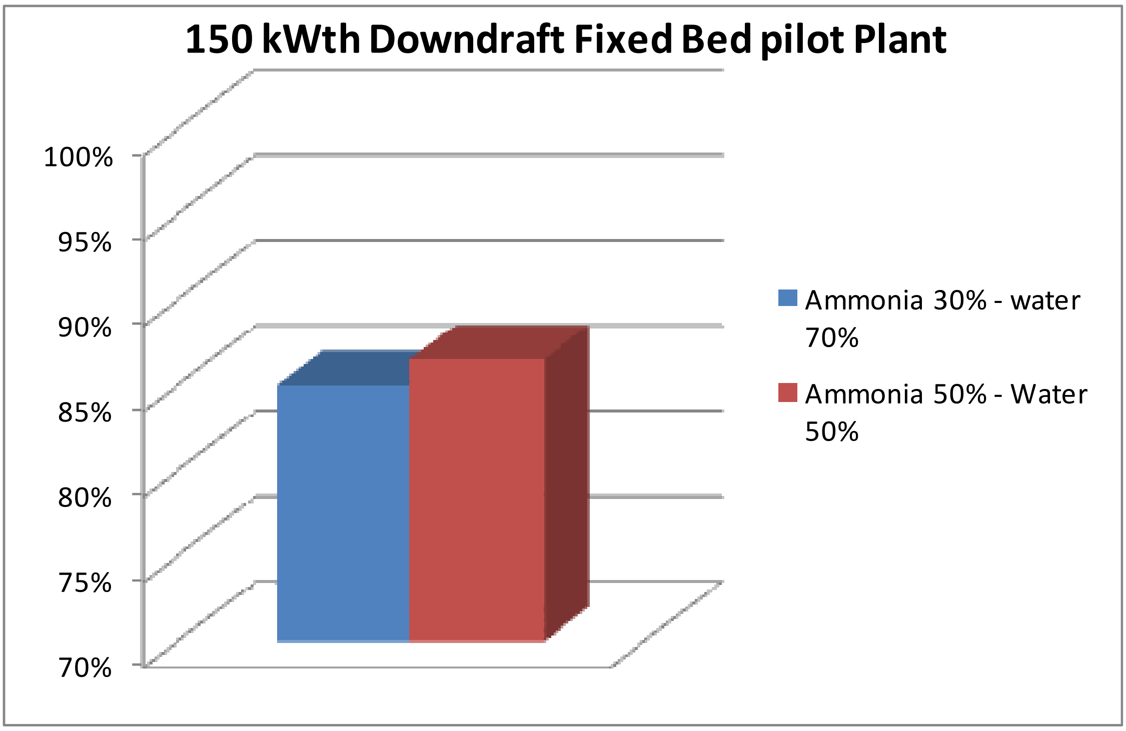

Figure 6.2: the 150 kWth gasification plant: sulphuric compounds removal efficiency.

How is shown in Figure 5 and 6, all results obtained in terms of sulphuric compounds removal efficiency are very close one to each others. In the two case, the mixture 50% ammonia – 50 % water show us a better removal efficiency, but the results are so close that it could be better to use a mixture 30% ammonia – 70% water in order to avoid the problems that a strong alkaline solutions involve.

The result obtained are very close for the plants considered, this confirm the great flexibility of scrubbing tower that it's suitable for different technologies and so for different produced gas.

Another series of two simulations has been carried out in the case of a mixture of water and MDEA. The first one considering solution 70% water – 30% MDEA and a second one using a mixture of 50% water and 50% MDEA.

The results of this simulation are shown in figures 6.3 and 6.4.

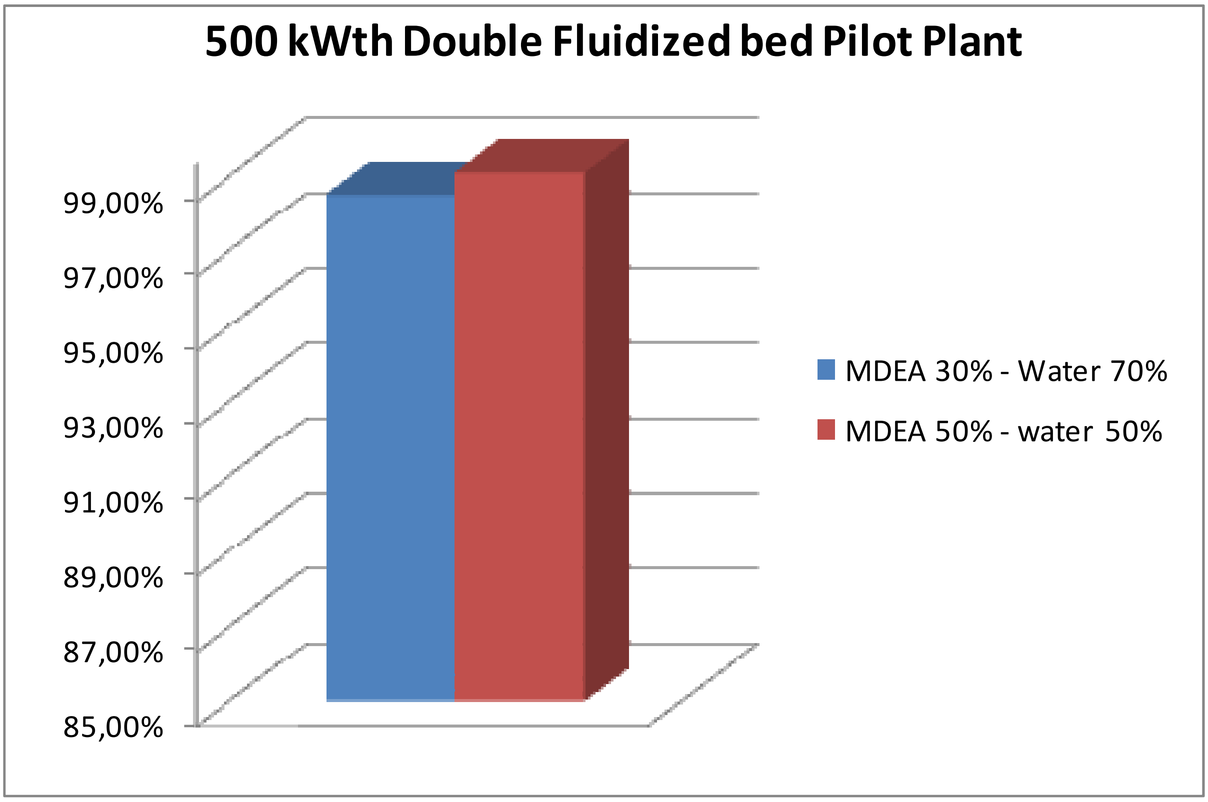

Figure 6.3: the 500 kWth gasification plant: sulphuric compounds removal efficiency.

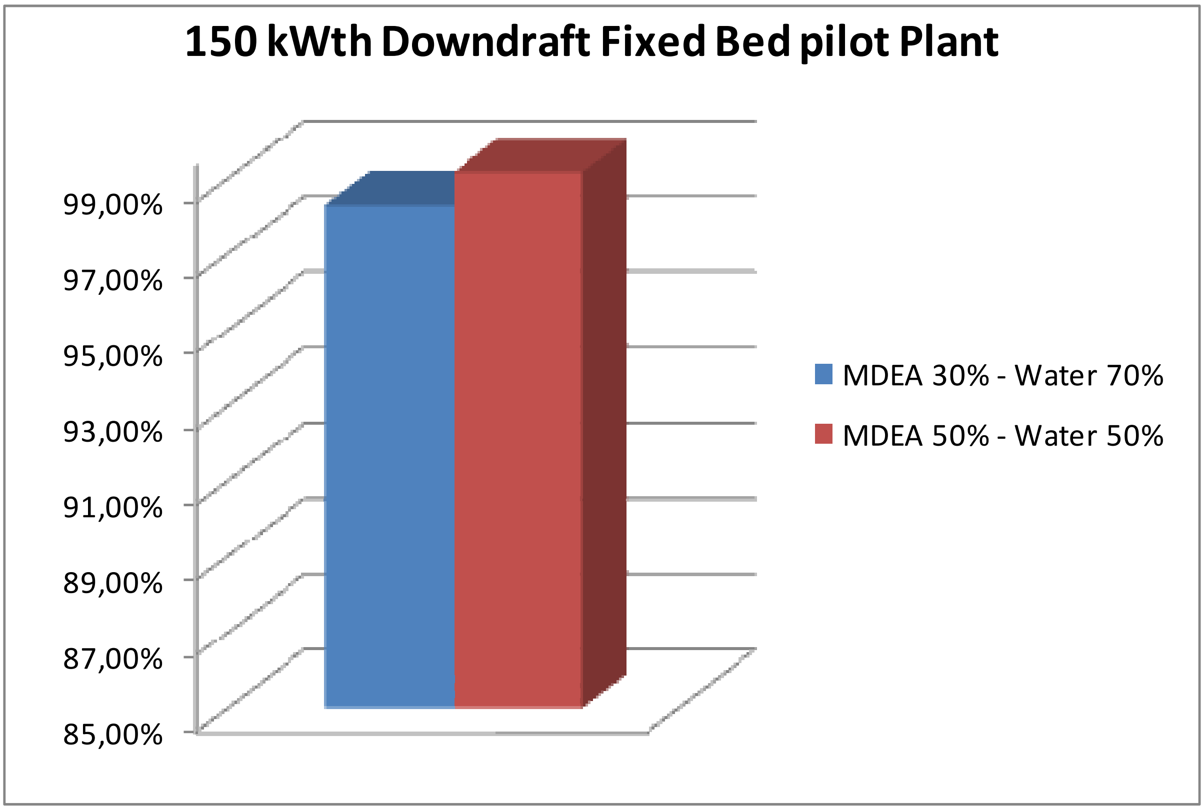

Figure 6.4: the 150 kWth gasification plant: sulphuric compounds removal efficiency.

The MDEA – water mixture show a stronger efficiency to remove sulfuric pollutants from the produced gas, showing a removal efficiency upper than 99 %.

All the series of simulation follow the same trend. We can note a really good sulfuric components removing. MDEA-water mixture show a best removing efficiency respect to ammonia-water mixture in every case analyzed.

Also in this case, using a 30% MDEA – 70% Water mixture seems to be the best solution in order to remove sulfur pollutants without using strong alkaline solutions.

The flexibility of scrubber solution is confirmed also in this second series of simulations.

A sensitivity analysis has been carried out to test the influence of pressure on scrubber efficiency. The results of these simulations are shown in figure 9 for 30%MDEA – 70% water mixture using the 500 kith double fluidized bed pilot plant produced gas.

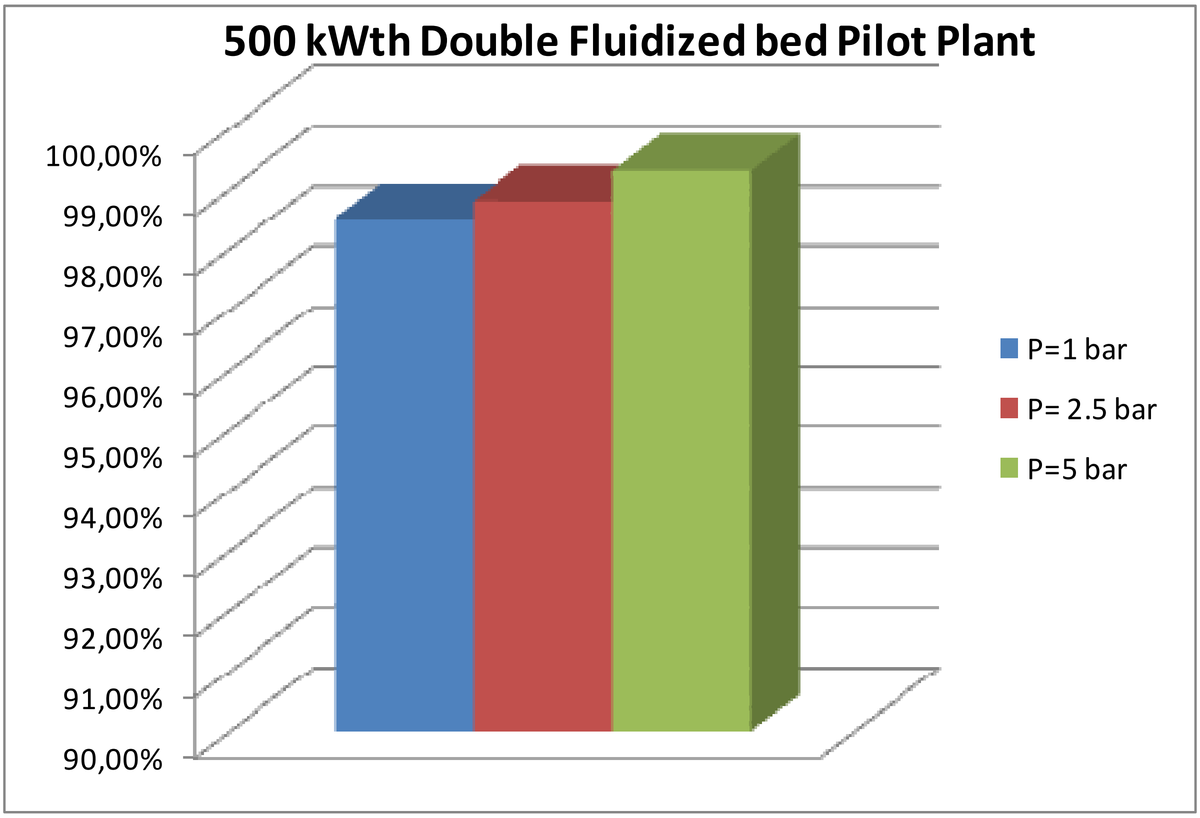

Figure 6.5: Sulphuric compounds removal efficiency for different operative pressure.

How it is expected, higher pressure test presents an higher removal efficiency, but also in this case, the great closeness of the results lead us to prefer to work using 1 bar like scrubber running pressure.

Literature data has been used to validate the model results and to compare the results obtained with the proposed technology to those relevant to a hot sulphur removal technology.

Orsini et Al confirm the great flexibility of low temperature technology and the great efficiency of MDEA scrubber to remove sulphuric pollutants [10, 11].

Siriwardane et Al analyzed Zinc Oxide-Based Regenerable Sorbents for Desulfurization of syngas arriving to results very close to the results of our simulations [12, 13].

Brooks et Al studies the possibility of syngas desulfurization over metal zeolites in a high temperature process. This technology shows a trend of removal efficiency close to our simulation results [14].

6.3 Acid compounds removing

The same approach has been followed to analyze acid compound removing. A scrubber tower running with an alkaline solution with soda or ammonia is dedicated to the removal of acid compounds [15, 16, 17, 18].

6.3.1 Simulation model

Basing upon the ChemCAD commercial code the absorption reaction has been simulated. The equilibrium and kinetic rate controlled approaches are both assumed to model the reactions. To simulate the absorption tower a standard impingement-plate scrubbers is used. Syngas fed was simulated by an ideal mixture of the gas component. To simulate the absorption fluid in the second tower, an ideal mixture of water and ammonia has been chosen [7, 9].

6.3.2 Results and discussion

Also in this case, we have carried two series everyone consisting three different simulations.

The first series is about acid components removing by using an ammonia-water mixture. In this series of simulation the first one was carried out considering a mixture of 50% ammonia and 50% water. The second simulation considering mixture 25% ammonia and 75% water and the last one considering like absorbing fluid pure water. The second series of simulation tests was performed by using a soda-water mixture to remove acid components from producer gas.

Also in this case we considered three different possibilities for the absorbing fluid: a mixture of 50% soda and 50% water, a mixture with 25% soda and 75% water and pure water.

The results of these tests have shown in figures 6.6 and 6.7.

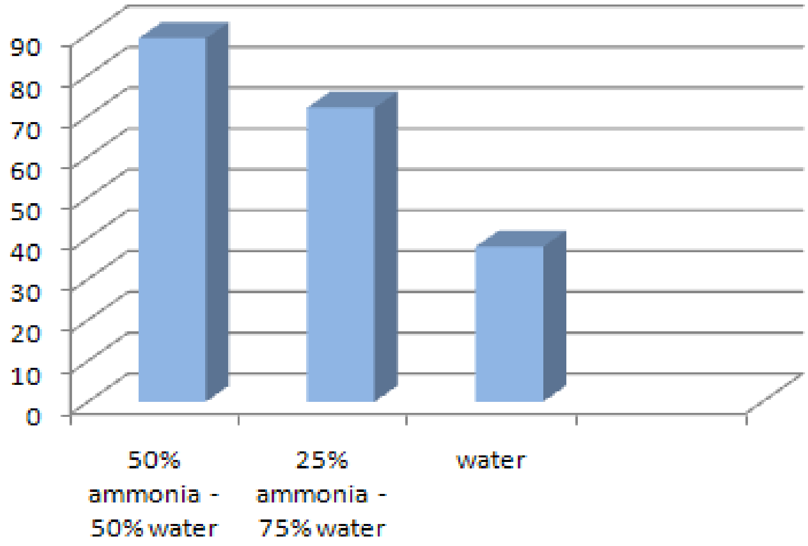

Figure 6.6: Acid component removal efficiency by using ammonia –water mixture

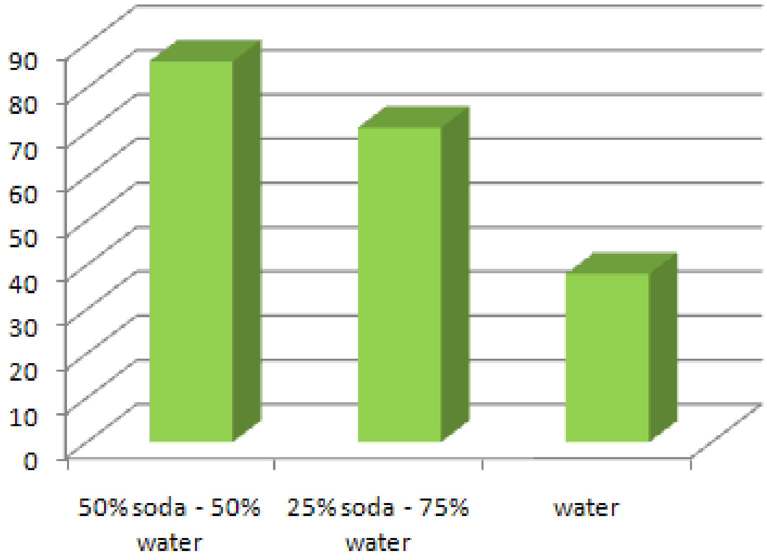

Figure 6.7: Acid component removal efficiency by using a soda –water mixture

In this case to verify simulation results, literature data about acid compounds removing experimental test has been used [7, 8, 9].

Figures 6.8 and 6.9 show the results of these comparisons.

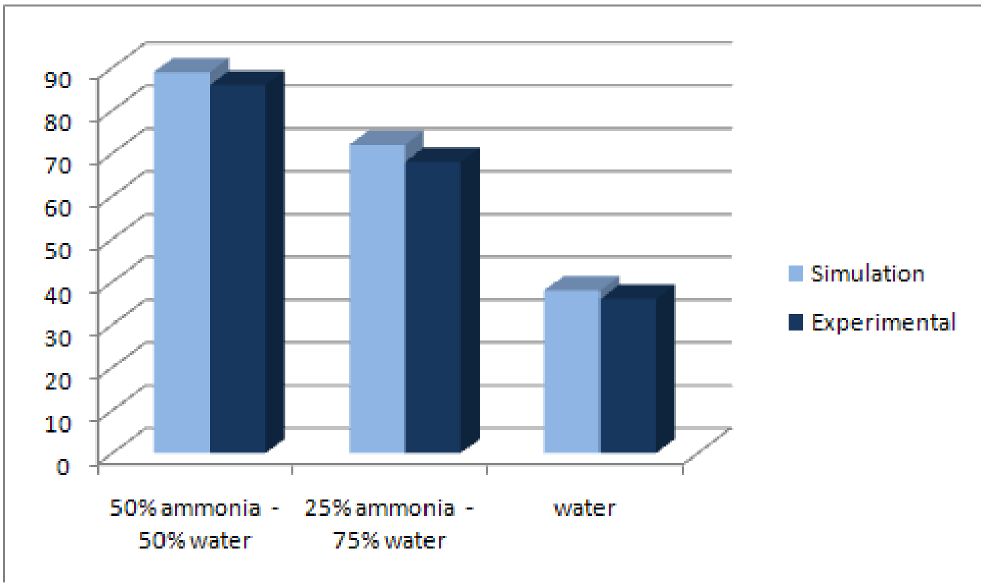

Figure 6.8: Acid component removal by using ammonia-water mixture: Simulation and experimental results comparison.

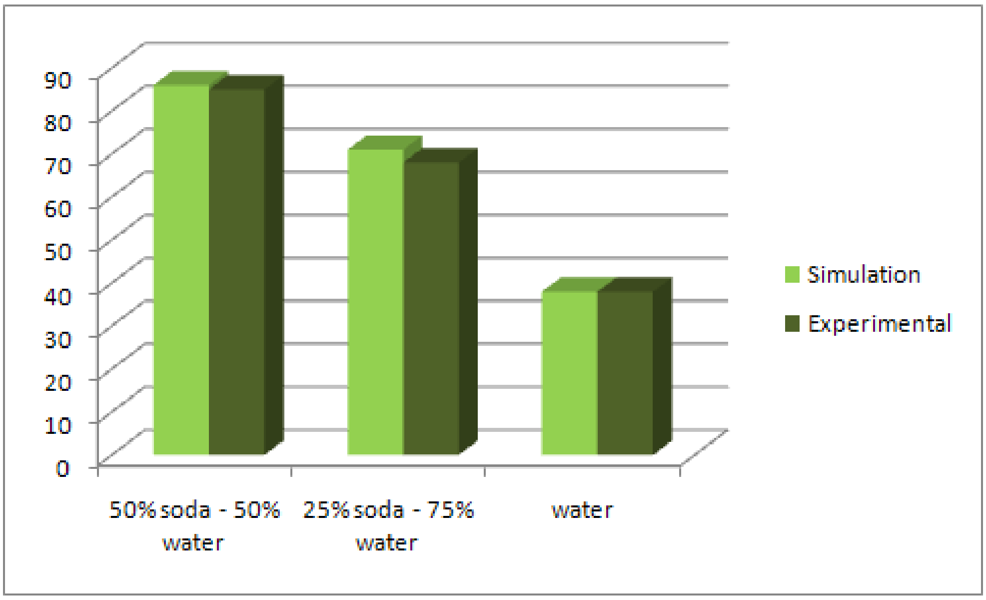

Figure 11: Acid component removal by using soda-water mixture: Simulation and experimental results comparison.

The two series of simulation and experimental data follow the same trend with a really good accordance. We can note a really good acid components removing. Ammonia-water mixture show a best removing efficiency respect to soda-water mixture in every case analyzed. Ammonia 50% - water 50% seems to be the best solution. In this case the amount of ammonia-water mixture necessary to remove acid components is equal to 30 kg/h for every Nm^3 of producer gas

6.4 Conclusion

The technology proposed is able to remove sulphuric pollutants and acid compounds from syngas produced.

For the desuphuration step, the simulations carried out confirm the great flexibility of ammine mixture scrubber that is able to remove sulphur compounds for the two gasification technologies analyzed.

The best solution is to use a mixture of 30% MDEA – 70% water that show a high removal efficiency without using a strong alkaline solution.

High pressure process guarantees a higher efficiency. Low temperature process shows removal efficiency comparable to high temperature process with an easy process technology.

For the acid compounds removing step, the two solutions tested, ammonia-water mixture, and soda-water mixture, are both able to remove acid components from syngas.

In this direction ammonia50%-water 50% mixture seems to be the best solution.

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Chapter 7

Analysis of the integration of a molten carbonate fuel cell in a biomass steam gasification pilot plant

7. Analysis of the integration of a Molten Carbonate Fuel Cell in a biomass steam gasification pilot plant.

7.1 Introduction

Fuel cell technology is generally considered as a promising solution for decentralized electricity generation with high efficiency and very low environmental impact, especially if feed fuel gas is produced via renewable energy sources, such like biomass.

In this framework, the assessment of the viability of the utilization of the producer gas from biomass gasification as the feed stream for a fuel cell is a key element. Moreover, the combination of two technologies, such like fuel cell and advanced gasification, which are both still under development, certainly constitutes an innovative concept. Actually no integrated gasification fuel cell (IGFC) system is in operation worldwide. As it can be observed from the literature survey, most of the available studies in this field deal with general aspects of the involved technologies and perspectives of their combination [1, 2, 3].

An analysis of the performance of the upcoming integration of a fuel cell into the gasification pilot plant operating at the ENEA Trisaia Research Centre has been carried out. Differently from previous studies, the analysis is based upon experimental data also and strictly referred to a real gasification pilot plant. The investigation is especially focused on:

- the identification of the auxiliary devices required for combining the fuel cell with the gasifier;
- the assessment of the producer gas quality in order to be accepted as the anodic feed by the fuel cell;
- the evaluation of the fuel cell performance when fuelled by the producer gas instead of pure hydrogen;
- the estimation of the energy and environmental overall balance of the IGFC system.

Being the technical feasibility the current barrier of the system under investigation, economic aspects will be only mentioned.

Concerning the approach towards the previous objectives, the characterization of the producer gas is based on the experimental results of the tests carried out on the ENEA Trisaia gasification pilot plant, while the data available in the literature are used in order to define the fuel cell gas quality requirements [4]. Furthermore the results from the simulation of the real fuel cell to be combined with the gasifier [5] are assumed for the estimation of fuel cell energy efficiency and CO2 emission under different feed conditions. Finally a gasifier model, which was formerly developed [6], is used in order to evaluate the effects of the gasification process variables on the fuel cell efficiency, thus obtaining useful indications about the possible optimization of the IGFC system.

7.2 Molten carbonate fuel cell

The fuel cell to be integrated into the existing DFB steam gasification pilot plant is a molten carbonate fuel cell (MCFC).

Under the maximum load conditions of 1100 A, this MCFC can generate 125 kW. The stack operating temperature is around 650 °C, in order to avoid the carbonate salt mixture solidification, and the operating pressure is 3.5 bar, in order to create the appropriate fluidodynamic conditions for the system.

The MCFC technology offers the advantage of converting into electricity also carbon monoxide, which is an important fraction of the producer gas of around 25% vol. on dry basis [7], via a preliminary water-gas shift reaction at the anode. Thanks to the high operating temperature of the stack, this reaction reaches rapidly equilibrium, thus a greater amount of H_2 is made available for the subsequent anodic reaction with respect to the quantity initially entering the fuel cell.

On the other hand methane, ethane and propane, which are also components of the producer gas, even if in a lower percentage in comparison with CO, are not converted into electricity by the MCFC, but they can be exploited to generate the heat required to keep the stack at the operating temperature.

$CO + H_2O \rightarrow CO_2 + H_2$ **_(water-gas shift reaction)_**

$H_2 + CO_3^{=} \rightarrow H_2O + CO_2 + 2e-$ **_(anode reaction)_**

$\frac{1}{2}O_2 + CO_2 + 2e- \rightarrow CO_3^{=}$ **_(cathode reaction)_**

$H_2 + \frac{1}{2}O_2 + CO_2 \rightarrow H_2O + CO_2$ **_(global reaction)_**

Furthermore, by considering the reaction at cathode also and, as a result, the global fuel cell reaction, it can be observed that CO_2 is concurrently captured at the cathode and discharged at the anode. This demonstrates the success in CO_2 emission reduction related to the use of the MCFC with respect to conventional systems for electricity production.

The MCFC configuration is reported in Figure 7.1 [5]. Both anodic and cathodic streams are fed at 300 °C only; then an internal heat exchange allows the temperature to rise up to the needed operating value. The thermal energy is supplied by a catalytic burner (CB), where the fuel in excess together with methane, ethane and propane is used. A blower is included in the vessel also in order to perform the recirculation of a large amount of the gas leaving the cathode, thus reducing the energy consumption and costs related to the compression of fresh air up to 3.5 bar and the assisting gases (N_2, CO_2) requirements.

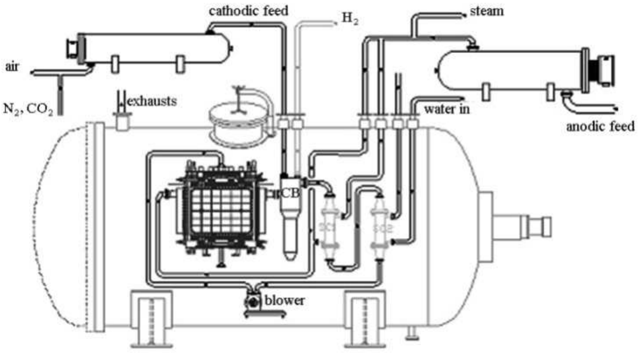

Figure 7.1: MCFC horizontal configuration.

Finally, it is to be noticed that exhaust gases leaving the vessel are still at high temperature (around 600 °C); therefore they can be exploited in order to both fulfil the fresh air compressor power demand and generate additional electricity via a gas micro-turbine.

7.3 Auxiliaries

The operation of the described MCFC with the fuel gas produced by the DFB steam gasifier requires various support devices. Among them, it is to be mentioned the fuel gas compressor, which is used to boost the clean producer gas pressure up to the MCFC operating value, thus presumably consuming a not negligible share of the generated power.

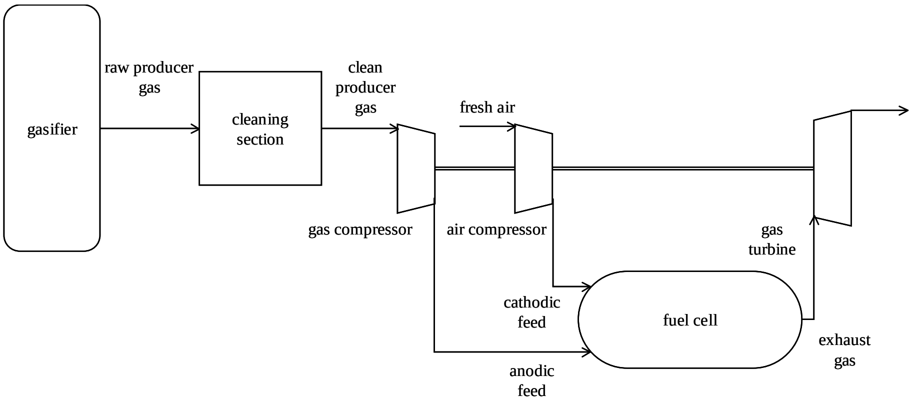

Figure 7.2: General process scheme of the IGFC system

In Figure 7.2 the general process scheme of the IGFC system, as it is hypothesized for an enhanced commercial application, is shown. The additional power produced by the gas turbine (GT), as described in section 7.2, is used to run both fuel gas and fresh air compressors, while heat requirements of the systems are fulfilled by its overall thermal optimisation. These practicable improvements are outside of the scopes of the experimental IGFC system under construction at the ENEA Trisaia Research Centre.

Furthermore, during MCFC heating up, cooling down and, at a lower degree, power generating, a significant quantity of assisting gases, namely H_2, N_2, CO_2, is needed.

7.4 Methodology

7.4.1 Definition of MCFC efficiency

The fuel cell thermodynamic efficiency is provided by the ratio in the global cell reaction of the Gibbs function change (ΔG), which measures the electrical work, to the enthalpy change (ΔH), which measures the heating value of the fuel. Basing on the values of ΔH and ΔG for the hydrogen/oxygen reaction, the efficiency of the ideal fuel cell can be estimated in around 83% [8].

However, when the fuel cell supplies electricity, the cell voltage diminishes in comparison with the open circuit voltage, because of the losses caused by electrochemical reactions. As it is shown in Figure 7.3, these losses may be attributed to three different phenomena: activation polarization (reaction rate loss), ohmic polarization (resistance loss), and concentration polarization (gas transport loss) [2].

Moreover, the average fuel utilization factor, which is calculated as the ratio of the fuel effectively converted into electricity to the total inlet fuel, must be included in order to assess the actual energy performance of a fuel cell. This factor can not be equal to 1, since some fuel must be certainly consumed to produce the thermal energy required to keep the stack at the operating temperature. Furthermore being the fuel residence time at the anode limited, electrochemical reactions can not reach their equilibrium.

As a result, the typical actual MCFCs efficiency ranges from 0.45 to 0.55 [8], being markedly lower with respect to its ideal value. This figure may be increased of 10-15% if MCFC is combined with a GT, as described in section 7.2.

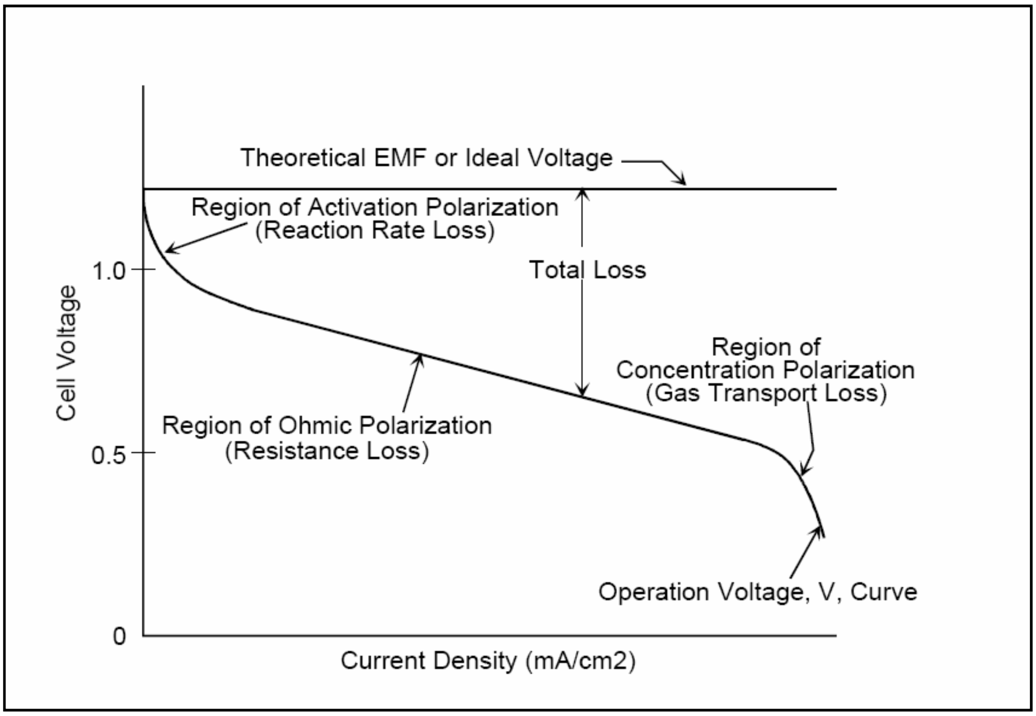

Figure 7.3: Ideal and Actual Fuel Cell Voltage/Current Characteristic [2]

Being rich in carbon monoxide and including methane also, the use as fuel of the producer gas from gasification processes presumably leads to a further reduction in the fuel utilization factor and, consequently, in the MCFC efficiency, with respect to the case of pure hydrogen. On the other hand energy losses associated to the H_2 production process must be added, in order to estimate the overall efficiency of the conversion of H_2 into electricity operated by MCFCs.

The focus of this study is exactly to evaluate the effects on MCFC efficiency of the use as anodic feed of the gas produced by the steam gasification pilot plant operating at the Trisaia Research Centre.

From the available experimental data a plausible gas composition was extrapolated [5, 7]. Then a model of the real MCFC was used to simulate mass and energy balances under different load conditions [5].

Table 7.1: MCFC mass balances under different load conditions using producer gas from steam gasification as anodic feed [5]

	Stand-by	550A	1000A
Air flow rate [Nm³/h] 621	699	854	
Fuel flow rate [Nm³/h] 47	74	113	
Exhausts flow rate [Nm³/h]	693	812	1019
Exhausts temperature [°C]	572	600	610
Discharged CO_2 [kg/h] 52	82	119	

In Table 7.1 the MCFC mass balances together with additional significant results of the performed simulations (exhaust gas temperature, CO2 concentration in the exhaust gas) are reported, with reference to stand-by and on load conditions, with a load equal to 50% and 91% of its nominal value, respectively.

It is to be noticed that the maximum load is limited, due to the high CO concentration in the fuel gas, which leads to a significant additional generation of thermal energy, because of the exothermicity of the water-gas shift reaction. Clearly the produced heat increases with the anodic feed flow rate and, as a result, a lower feed temperature and a higher cathodic feed flow rate are required in order to keep the stack temperature within the allowed operational range. According to the simulation results, 1000 A appears to be a precautionary value for the load, corresponding to the generation of a still tolerable amount of thermal energy.

The data reported in Table 7.1 are subsequently used to estimate the overall energy balance of the MCFC system, according to the process scheme reported in Figure 7.2.

For this calculation efficiencies of 0.85 and 0.80 were assumed for gas turbine and both air and gas compressor, respectively. The resulting figures under different load conditions are reported in Table 7.2.

Table 7.2: MCFC system energy balances under different load conditions using producer gas from steam gasification as anodic feed

	Stand-by	550A	1000A
Fresh air compressor [kW]	40.5	45.5	55.7
Fuel gas compressor [kW]	3.3	5.1	7.9
Exhausts fired turbine [kW]	57.2	68.7	86.7

In order to compare the use of the producer gas from steam gasification with other possible fuels for the MCFC in terms of energy performance, two additional anodic feeds were considered:

a) gas from a conventional air gasification process, such as a downdraft fixed bed gasifier;

b) mixture of H2 (80% vol.) and CO2 (20% vol.) from natural gas steam reforming.

The related MCFC mass balances carried out from the simulations are reported in Table 7.3 and Table 7.4 [5], respectively.

Table 7.3: MCFC mass balances under different load conditions using producer gas from air gasification as anodic feed [5]

	Stand-by	550A	750A
Air flow rate [Nm³/h]	699	768	873
Fuel flow rate [Nm³/h]	224	317	382
Exhausts flow rate [Nm³/h]	985	1152	1309
Exhausts temperature [°C]	569	637	643
Discharged CO_2 [kg/h]108	181	250	

Table 7.4: MCFC mass balances under different load conditions using H_2 and CO_2 mixture from natural gas steam reforming as anodic feed [5]

	Stand-by	550A	1100A
Air flow rate [Nm³/h]	272	311	624
Fuel flow rate [Nm³/h]	67	74	130
Exhausts flow rate [Nm³/h]	335	377	738
Exhausts temperature [°C]	574	599	644
Discharged CO_2 [kg/h] 33	29	51	

As it can be observed from Table 7.3, the maximum load is limited to only 68% of its nominal value when a producer gas from air gasification is used as anodic feed. Actually, being rich in nitrogen, this fuel gas implicates higher anodic feed flow rates with respect to the other considered feed streams. On the other hand, according to the manufacturer experience, anodic feed flow rate should not exceed 400 Nm^3/h, in order to avoid an excessive overpressure between the feeding system and the vessel. Basing on the simulation results, this maximum value corresponds to a load of around 750 A.

Finally, by using a similar approach with respect to the previous case, the overall energy balance of the MCFC system was calculated for both gas from air gasification and gas from natural gas steam reforming as anodic feed. The results are reported in the following Table 7.5 and Table 7.6, respectively.

Table 7.5: MCFC system energy balances under different load conditions using producer gas from air gasification as anodic feed

	Stand-by	550A	1000A
Fresh air compressor [kW]	45.6	50.1	57.0
Fuel gas compressor [kW]	15.6	22.1	26.6
Exhausts fired turbine [kW]	79.9	100.5	114.4

Table 7.6: MCFC system energy balances under different load conditions using H_2 and CO_2 mixture from natural gas steam reforming as anodic feed

	Stand-by	550A	1000A
Fresh air compressor [kW]	17.7	20.2	40.5
Exhausts fired turbine [kW]	26.6	30.6	63.4

Obviously, no gas compression is needed when H2 and CO2 mixture from natural gas steam reforming is used as anodic feed. On the other hand, the actual overall efficiency of the MCFC system should be appropriately reduced in this case, by including the energy losses related to the steam reforming process [9].

7.4.2 Definition of the MCFC environmental performance

As described in section 7.2, MCFC acts as a carbon sequestration device also. Therefore, the quantity of CO_2 in the exhaust gas discharged in the atmosphere per produced kWh is assumed in order to evaluate the MCFC environmental performance. The absolute value relevant to this parameter according to the simulation results is already given in Table I. From the data reported in Table 7.2, it is then possible to calculate its value per produced kWh.

7.5 Results and discussion

7.5.1 Assessment of producer gas quality

The presence of impurities in both anode and cathode feeds can be detrimental on the duration and performance of the MCFC stack.

The maximum admissible level of the main pollutants coming from biomass gasification on the basis of preliminary literature data are reported in Table 7.7 [4].

Table 7.7: Maximum admissible level of the main pollutants from biomass gasification [4]

Pollutant	Maximum value
H_2S	0.1 ppm
HCl	0.1 ppm
Tar	2000 ppm
Particulate	10 ppm

Basing on the removal efficiency of the current hot gas cleaning section installed on the ENEA Trisaia gasification pilot plant, particulate concentration in the clean producer gas meets the MCFC requirements listed in Table 7.7, while additional devices for abating sulphur and chlorine are needed [7]. Concerning tar removal, no system is presently installed on the pilot plant. However according to literature data relevant to the same gasification technology, the maximum level of tar indicated in Table 7.7 is certainly achievable [10].

7.5.2 Assessment of MCFC energy efficiency

Basing on the data reported in Tables from I to VI, both stand-alone and combined with GT MCFC efficiency as a function of the load were calculated, according to the three different anodic feeds introduced in section 7.4.1. The results are plotted in Figure 7.4.

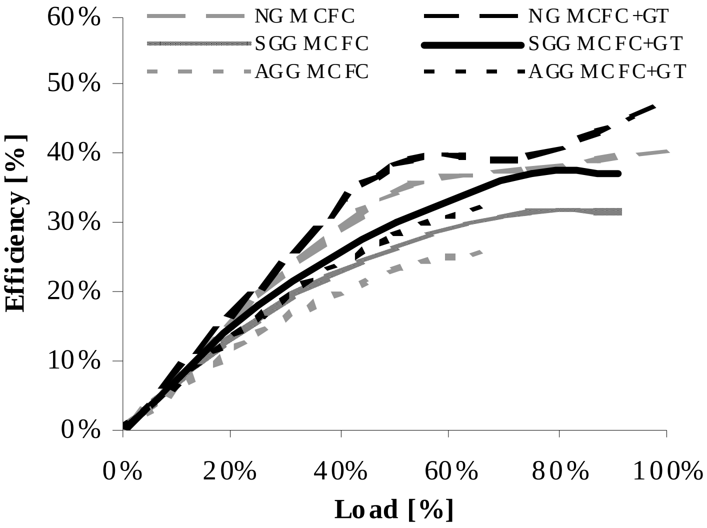

Figure 7.4: MCFC efficiency according to different feed conditions and system configurations

It can be observed that MCFC and GT combined system efficiency achieves its highest value of nearly 50% when H_2 and CO_2 mixture from natural gas steam reforming is used as anodic feed, but efficiency of the steam reforming process should be included [9]. For this anodic feed, GT contribution to the total electricity generation becomes significant at high loads, as a result of the remarkable increase in the exhaust gas flow rate.

If the anodic feed is the producer gas coming from the steam gasification pilot plant operating at the ENEA Trisaia Research Centre, the stand-alone MCFC efficiency (some 32%) is comparable to the efficiency of a conventional gas engine. On the other hand, if the gas turbine is included, combined system efficiency grows up to nearly 40%.

A further diminution in the MCFC energy performance is observed if the producer gas coming from a downdraft fixed bed air gasifier is used. In this case the contribution of the GT to the total electricity generation of the combined system is predominant, due to the very high exhaust gas flow rates. The lower MCFC utilization and the higher system and auxiliaries size per installed kW are two additional drawbacks associated to the use of the diluted producer gas coming from an air gasifier as anodic feed.

7.5.3 Assessment of MCFC environmental performance

Concerning the calculation of the environmental performance of the MCFC fuelled by the gas coming from the steam gasifier, the results reported in Tables 7.1 and 7.2 show that the CO_2 emission per produced kWh is around 0.9. Therefore a marked reduction is achieved with respect to conventional systems for electricity generation from biomass. According to the available experimental data [7], the quantity of CO_2 discharged from the Trisaia Research Centre steam gasification pilot plant combined with a conventional gas engine would be approximately 1.8 kg per produced kWh, when almond shells are used as feedstock.

The environmental benefits correlated to the use of the IGFC system for electricity production are therefore evident, if the general assumption that biomass is carbon-neutral is considered to be valid. It is to be noticed that the best available technology for electricity production from fossil fuels, that is the natural gas combined cycle (NGCC), is characterized by an all-inclusive CO_2 emission of around 0.5 kg per produced kWh [11]. This figure clearly increases dramatically when fossil fuel fired systems for decentralized generation is assessed.

7.5.4 Assessment of the effects of process variables

Basing on the simulated data from a model appositely developed for the Trisaia Research Centre steam gasification pilot plant [6], a sensitivity analysis of the MCFC efficiency with respect to the main process variables was carried out. Fundamentally, the effects on the gas composition and, as a result, on the MCFC efficiency of the changes in the gasification temperature, steam to biomass ratio and residence time of biomass into the reactor, were calculated.

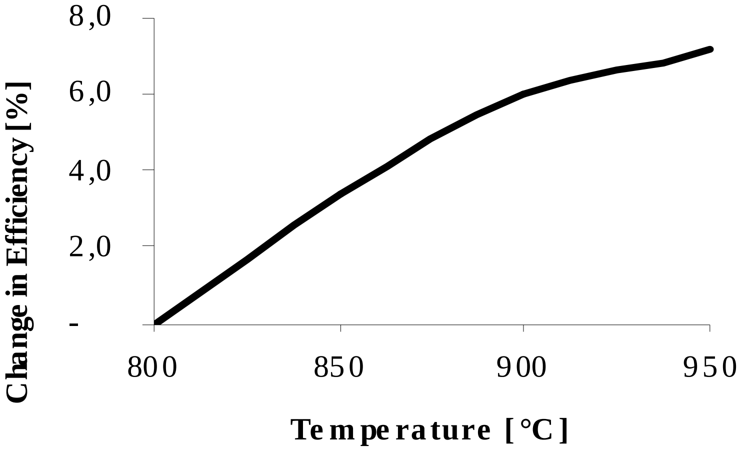

Figure 7.5: Variation in the MCFC efficiency as a function of the gasification temperature

The curve in Figure 7.5 shows that a higher operating temperature of the gasification process has a positive effect on the variation in the MCFC efficiency, due to the increase in the H_2 percentage in the producer gas to the detriment of the CH_4 percentage.

A similar result, even if at a lesser level, was found for the residence time, while the increase in the MCFC efficiency related to the operation with higher steam to biomass ratios is absolutely prejudiced by the diminution in the chemical efficiency of the gasification process.

7.6 Simulation of Molten Carbonate Fuel Cell

In order to estimate both energy and environmental effectiveness of the conversion process under different feed conditions, a simplified MCFC model has been properly developed via the ChemCAD commercial code [12] by assuming the following hypotheses:

- steady-state working conditions;
- simplified stack design;
- ideal gas;
- heat losses from the vessel equal to 30 kW.

Concerning the MCFC operating conditions, the configuration illustrated in Figure 7.1 is adopted in the model. Under the maximum load conditions equal to 1100 A, this MCFC can generate 125 kW. Considering that the anodic feeding stream is assumed to be a fuel gas having a composition similar to the producer gas from the steam gasification pilot plant, a gas flow of approximately 110 Nm^3/h on dry basis is required at full load. Under the same condition, an air flow of 850 Nm^3/h at least is needed at cathode. The stack operating temperature is fixed around 650 °C in order to avoid the carbonate salt mixture solidification, whereas the operating pressure is of 3.5 bar in order to create the appropriate fluidodynamic conditions for the system.

7.6.1 Simulation results and discussion

The simulations have been performed for the following five different anodic feeding streams for the MCFC:

- **Biogas.**

This fuel gas is obtained by adding an appropriate amount of steam to the producer gas from the biomass DFB steam gasification pilot plant. In effect the gas coming from the gasifier is first cooled down in order to achieve the condensation of its vapour content, thus optimizing its cleaning and compression up to 4 bar. After that the feeding stream needs to be properly humidified in order to guarantee that no coal is formed inside the electrochemical module.

- **Simulated Biogas.**

Simulated biogas is a feeding gas with a composition similar to the real producer gas. This fuel gas is obtained by mixing the auxiliary gases, H2, CO2, N2, CO, which are required for MCFC operation and specifically for MCFC heat up and cool down. Then steam is added similarly to the previous case. The scope of the use of gas is to test the MCFC in stand alone configuration also, but using a realistic fuel gas from biomass gasification. In this feeding stream methane is replaced by nitrogen. This solution does not affect the behaviour of the MCFC but it can significantly influence its heat balance.

- **Diluted Simulated Biogas.**

This feeding stream is obtained with the same approach as in the previous case, but the gas is more diluted with nitrogen in order to simulate the typical composition of a producer gas from biomass air gasification. It is to be noticed that a downdraft fixed bed air gasification pilot plant is in operation also at the ENEA Trisaia Research Centre.

- **Natural Gas.**

It is composed by hydrogen and carbon dioxide with the typical proportion of a gas produced via the steam reforming of natural gas, which is currently used for the characterization of the stack during its preliminary testing. The interest in the use of this gas is to provide a comparison of the stack field performances with the results of post-conditioning tests.

- **Landfill Gas.**

This fuel gas is hypothesized to be obtained via the steam reforming of the gas typically produced by anaerobic digestion of biomass in order to investigate the potential of the combination of MCFC with this process also. Obviously since the composition of biogas from anaerobic digestion varies in a rather wide range according to biomass and process characteristics, the results related to the use of this type of gas are to be considered as merely indicative.

The compositions on dry basis of the five considered feeding streams are reported in Table 7.8.

Table 7.8 – Feeding streams composition

	BIOGAS	***SIM. BIOGAS***	***DIL. BIOGAS***	***NATURAL GAS***	***LANDFILL GAS***
H_2 [% vol.]	42.3	42.3	20.4	80.0	64.4
CH_4 [% vol.]	8.6	0	0	0	0
CO [% vol.]	31.3	31.3	7.4	0	10.3
CO_2 [% vol.]	13.7	13.7	17.2	20.0	24.7
N_2 [% vol.]	4.2	12.8	54.9	0	0.6

For each stream, the total inlet fuel (dry) and the amount and composition of exhaust gas have been evaluated, starting from stand-by conditions up to 100% of load conditions, with a load step of 25%.

The maximum load has been limited for biogas, and obviously simulated biogas, as well. This is due to the high CO concentration in both gases, which leads to a significant additional generation of thermal energy, because of the exothermicity of the water-gas shift reaction. Clearly the produced heat increases with the anodic flow rate and, as a result, a lower feed temperature and a higher cathodic flow rate are required in order to keep the stack temperature under the maximum operational value. Therefore, according to the performed simulations, the maximum load has been limited to the precautionary value of 1000 A, corresponding to the generation of a still tolerable amount of thermal energy.

The calculation of the fuel flow rate required for each feeding stream at full load condition allows to directly evaluating the efficiency of the corresponding conversion process. Basing upon the results of the simulation carried out, an efficiency of some 0.35 can be extrapolated for biogas, simulated biogas and diluted simulated biogas, while a value greater than 0.40 is found for both natural and landfill gas.

On the other hand for these gases the efficiency of the methane steam reforming process should be included for a complete performance comparison of a real application [9]. However it can be concluded that, according to these preliminary evaluations, the combination of MCFC with biomass gasification causes no significant increase in efficiency in comparison with typical gasification systems for power generation on small to medium scale [13].

Concerning the quantification of the environmental benefits, simulations performed shows that natural gas is the best feeding stream in terms of CO_2 emissions. Under this feed condition, the quantity of CO_2 discharged in the atmosphere per produced kWh by the 125 kW MCFC system is comparable to the value relevant to the most effective fossil fuel fired power generation system for large scale applications, such like Natural Gas Combined Cycle (NGCC) [14]. Moreover, it is to be noticed that the exhaust gas may be exploited for an additional power generation by combining a gas turbine with the MCFC. This is the ordinary MCFC configuration, which allows producing approximately 25 kW in excess of the energy consumed by the compression of the cathodic feeding stream, thus reducing the CO_2 emissions of the combined system to little more than 0.3 kg per kWh of produced power.

An analogous conclusion can be deduced when MCFC is combined with different types of gasification processes. From simulation results, it can be observed that the amount of CO_2 per kWh discharged in the atmosphere after the fuel conversion into power is around 1 kg per kWh for biogas and diluted simulated biogas. Under both feed conditions the realistic hypothesis that the additional power generated by the gas turbine is fully used to compress both the fresh air at the cathode and the fuel gas at the anode has been assumed. However, in both cases a marked reduction is achieved with respect to conventional power generation systems from biomass. For example according to the available experimental data [7], the quantity of CO_2 discharged from the DFB steam gasification pilot plant operating at the Trisaia Research Centre has been roughly estimated in 1.8 kg per produced kWh, if almond shells are used as feedstock.

On the other hand, as it is well-known, biomass is considered carbon-neutral, since the quantity of CO_2 discharged in the atmosphere following biomass conversion process into energy is in principle equal to the quantity of CO_2 removed from the atmosphere during biomass growth. Therefore MCFC fuelled by gas from biomass gasification or anaerobic digestion appear as the best solution in terms of reduction of CO_2 emissions, since it increases the produced kWh on equal quantity of discharged CO_2 thus leading to a positive carbon balance in the atmosphere.

7.7 Conclusions

An integrated steam gasification molten carbonate fuel cell system for a commercial application needs several auxiliaries, such like fresh air and fuel gas compressors, exhaust gas turbine, assisting gases storage and conditioning systems, etc.. These devices may have a strong impact on IGFC system investment cost for small-scale installations. Therefore these systems do not appear to be competitive with respect to conventional gasification plants for decentralised electricity generation at the current level of technological development.

The producer gas coming from the ENEA Trisaia Research Centre dual fluidised bed steam gasification pilot plant appears to have an adequate quality in order to be used as fuel for a MCFC. Being limited durability one of the main drawbacks of the MCFC technology, long-term tests are however necessary in order to assess the stack deterioration under this feed conditions.

The combination of MCFC with biomass steam gasification does not imply any significant increase in the conversion efficiency with respect to conventional systems, such like gas engines. This is a general problem of the MCFC, being its efficiency relatively low also if natural gas is used as fuel and the energy losses correlated to the steam reforming process are included. On the other hand, if a combined MCFC and gas turbine plant configuration is adopted the conversion efficiency from producer gas into electricity grows up to nearly 40%, corresponding to a significant achievement for decentralised electricity generation from biomass. The MCFC overall performance declines markedly if the producer gas from an air gasification process is used as fuel instead.

The IGFC system offers valuable environmental benefits with respect to conventional gasification for decentralised electricity generation, since it reduces CO_2 emission per produced kWh of exactly 50%. Basing on the general assumption that biomass is carbon-neutral, it can be stated that the combination of biomass gasification and MCFC leads to a “positive” balance of the CO_2 in the atmosphere.

IGFC system efficiency can be enhanced via the optimisation of the gasification process operating parameters. Specifically an increase in the gasification temperature has a marked positive effect. A similar result, though at a lower degree, comes from the increase in the biomass residence time into the reactor, while no significant improvements can be achieved by acting on the steam to biomass ratio.

Being both DFB steam gasification and MCFC technologies at the research and development stage, substantial improvements in the energy efficiency and costs of future IGFC systems are expected in the short to medium term.

According to the performed simulation, the the H_2 amount in the producer gas in order to approach the composition and, as a result, the performance of natural or landfill gas. combination of MCFC with biomass steam gasification does not imply any significant increase in the overall efficiency with respect to conventional conversion devices such like gas engines. The energy effectiveness of a DFB steam gasifier and MCFC combined system can be enhanced via its overall optimization [6], especially aimed at increasing the H_2 amount in the producer gas in order to approach the composition and, as a result, the performance of natural or landfill gas.

7.8 References

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Chapter 8

Biodiesel production: current state of arts.

8. Biodiesel production: current state of arts.

8.1 Introduction

Biodiesel is a clean-burning fuel currently being produced from grease, vegetable oils, or animal fats. Its chemical structure is that of fatty acid alkyl esters. Biodiesel is produced by transesterification of oils with short-chain alcohols or by the esterification of fatty acids. The transesterification reaction consists of transforming triglycerides into fatty acid alkyl ester, in the presence of an alcohol, such as methanol or ethanol, and a catalyst, such as an alkali or acid, with glycerol as a byproduct [1].

Chemical reaction at supercritical conditions without the use of a catalyst has also been proposed [2]. In the United States, oil is the fuel of transportation. Coal, nuclear, hydropower, and natural gas are primarily used for electric power generation. The United States with 5% of the world's population, consumes 25% of the world's petroleum, 43% of the gasoline, and 25% of the natural gas. According to Oil and Gas Journal (O&GJ) estimates, worldwide reserves at the beginning of 2004 were 1.27 trillion barrels of oil and 6,100 trillion cubic feet of natural gas. These are proven recoverable reserves. At today's consumption level of about 85 million barrels per day of oil and 260 billion cubic feet per day of natural gas, the reserves represent 40 years of oil and 64 years of natural gas.

Thus, because of diminishing petroleum reserves and the deleterious environmental consequences of exhaust gases from petroleum diesel, biodiesel has attracted attention during the past few years as a renewable and environmentally friendly fuel. Since biodiesel is made entirely from vegetable oil or animal fats, it is renewable and biodegradable. Biodiesel also contains very little sulfur, polycyclic aromatic hydrocarbons, and metals. Petroleum-derived diesel fuels can contain up to 20% polycyclic aromatic hydrocarbons. For an equivalent number of carbon atoms, polycyclic aromatic hydrocarbons are up to three orders of magnitude more soluble in water than straight chain aliphatics. The fact that biodiesel does not contain polycyclic aromatic hydrocarbons makes it a safe alternative for storage and transportation.

Like petroleum diesel, biodiesel operates in compression- ignition engines. Biodiesel is most often blended with petroleum diesel in ratios of 2% (B2), 5% (B5), or 20% (B20). It can also be used as pure biodiesel (B100).

Biodiesel fuels can be used in regular diesel vehicles without making any changes to the engines, although older vehicles may require replacement of fuel lines and other rubber components. (Biodiesel has similar materials compatibility to ultralow sulfur diesel (ULSD); so vehicles built to run on that should be compatible with pure biodiesel). It can also be stored and transported using diesel tanks and equipment. Since biodiesel is oxygenated, it is a better lubricant than diesel fuel, increasing the life of engines, and is combusted more completely. Indeed, many countries are introducing biodiesel blends to enhance the lubricity of low-sulfur diesel fuels [3]. The higher flash point of biodiesel makes it a safer fuel to use, handle, and store. With its relatively low emission profile, it is an ideal fuel for use in sensitive environments, such as heavily polluted cities.

There are several technical challenges that need to be addressed to make biodiesel profitable. First, the high cost of virgin vegetable oil as the source of triglycerides plays a large role in process profitability. To reduce production costs and make it competitive with petroleum diesel, low cost feedstocks, such as nonedible oils, waste frying oils, and animal fats, could be used as raw materials. However, the relatively higher amounts of free fatty acids and water in this feedstock results in the production of soap in the presence of alkali catalyst. Thus, additional steps to remove any water and either the free fatty acids or soap from the reaction mixture are required. In fact, commercial processors often employ an acid-catalyzed esterification reactor to process excess free fatty acids prior to base-catalyzed transesterification.

Considerable research has been done on biodiesel made from virgin vegetable oils (e.g., soybean oil, sunflower oil, rapeseed oil) using alkali catalysts. The majority of biodiesel today is produced by alkali-catalyzed (e.g., NaOH, KOH) transesterification with methanol, which results in a relatively short reaction time [4]. However, the vegetable oil and alcohol must be substantially anhydrous and have low free fatty acid content, because the presence of water or free fatty acid or both promotes soap formation. The soap formed lowers the yield of esters and renders the downstream separation of the products difficult [4], requiring additional processing.

As matter of fact, triglycerides source plays a key role in biodiesel synthesis. So this state of arts has been focused on examination of different biodiesel sources (edible and nonedible), virgin oil versus waste oil, algae-based biodiesel that is gaining increasing importance, the role of different catalysts including enzyme catalysts, and the current state-of-the-art in biodiesel production.

8.2 Edible sources virgin oil

Biodiesel production from soybean oil is very popular. Researchers have focused on different catalyst systems, different solvents, and different acyl acceptors. Soybean oil has five fatty acids: approximately equal amounts of palmitic acid, oleic acid, and linolenic acid (about 13% each), linoleic acid (approximately 55%), and stearic acid (approximately 4%). The average US production of soybean oil from 1993 to 1995 was 6.8 billion kg, and in 2002, soybeans were harvested from more than 30 million ha across the United States, which accounts for 40% of the total world soybean output [5]. This production capacity accounts for more than 50% of the total available biobased oil for industrial applications. A useful industrial application of soybean oil is in biodiesel blends. According to Kinney and Clemente [5], soybean oil-derived biodiesel possess enhanced biodegradation, increased flashpoint, reduced toxicity, lower emissions, and increased lubricity.

However, oxidative instability and cold flow in northern climates limit the usefulness of a soybean oil-derived biodiesel as a fuel. The tools of biotechnology could be utilized to modify the fatty acid profile of soybean for performance enhancement, which may increase the attractiveness of biodiesel derived from this commodity crop [5]. There is still some disagreement in the literature over the oxidative stability of biodiesel, and in particular how well the ‘‘iodine value’’ characterizes its stability.

The iodine value is a measure of the level of ‘‘unsaturation’’ of the fatty acids in the oil, with more saturated fatty acids being less susceptible to oxidation. However, other factors also significantly affect the stability, such as the level of natural antioxidants (such as vitamin E) in the fuel [6].

Soybean oil has a high iodine value compared to many other biodiesel feedstocks (indicating a relatively low level of saturation compared to other oils, such as rapeseed and canola), but Mushrush et al. [7] conducted storage stability tests and found soybean biodiesel (in concentrations up to 20%) to be stable in the ‘‘stable’’ fuel and to reduce the instability in the ‘‘unstable’’ fuel significantly. In addition to fuel storage stability, fuel solubility, and oxidative stability, seawater stability should also be taken into consideration in water environments [8]. According to Mushrush et al. [8], US Navy shipboard fuel tanks compensate for diminishing fuel by the addition of seawater to the fuel tank. The authors found that this can lead to ‘‘fuel instability problems such as filter stoppage and other serious engine damage.’’ Presence of trace fatty acids in the oil and seawater led to the formation of a soapy emulsion at the interphase. When using recycled oil, care should be taken to remove all acidic components or the biodiesel will not be stable [9].

Freedman et al. [4] have investigated the effect of the molar ratio of the alcohol to oil, type of catalyst (base vs acid), temperature and degree of refinement of the oil on the yield of biodiesel. They reported a 98% yield of biodiesel in 1 h using alkali catalysts such as sodium hydroxide or sodium methoxide with alcohols such as methanol, ethanol, and iso-butanol [10]. For the alkali catalyzed reaction, the effect of alcohol to oil ratio was found to be the most important variable affecting the yield, while temperature had a significant effect on the initial reaction rate. Their study also shows that acid catalysts would be more effective when the degree of refinement of oil was low, and for oils that had a high free fatty acid content.

8.2.1 Enzyme catalysts

Biocatalysts are gaining more attention nowadays and have the potential to outperform chemical catalysts for biodiesel production in the future. New biochemical routes to biodiesel production, based on the use of enzymes, have become very interesting [11-17]. Most of the articles published have used a variety of substrates such as rice bran oil, canola, sunflower oil, soybean oil, olive oil, and castor oil. Several lipases from microbial strains, including Pseudomonas fluorescens [18,19], Pseudomonas cepacia [20], Rhizomucor miehei [19], Rhizopus oryzae [21], Candida rugosa [22], Thermomyces lanuginosus [23], and Candida antarctica [14], have been reported to have transesterification activity.

Lipase has been shown to be effective in the transesterification of sunflower oil in a solvent-free medium [24]. One problem that arose was the inhibition of the enzyme due to glycerol formation. A number of different acyl acceptors have shown to be effective with lipase as the catalyst. Methanol and ethanol are the most commonly used alcohols. Longer chain alcohols have also been shown to be effective, but they provide lower yields than methanol.

Recent studies using methyl acetate as the acyl acceptor and soybean oil show that the use of this acyl acceptor does not lead to inhibition of the enzyme [25]. Also, since no glycerol is produced in the process, this method is very convenient for recycling the catalyst, and byproduct triacetylglycerol shows no negative effect on the fuel property [26].

The results of biodiesel production by transesterification of olive oil using lipase as a catalyst were recently reported [16]. The final conversion and yield of biodiesel were unaffected by initial enzyme concentrations above 500 U/ml olive oil. The optimum reaction temperature was 60 °C. The effect of different solvents and three different acyl acceptors on the transesterification of triolein (as a model compound) has been recently investigated [27]. The yield of biodiesel (methyl or ethyl ester) was monitored as a function of time. The yield of the product was also determined in a solvent-free system for two different modes of stirring. The results indicated that the highest yield was obtained in a solvent-free system with mechanical stirring. Methyl acetate was also effective as a solvent and acyl acceptor.

8.2.2 Other catalyst systems

In an attempt to reduce the problems with separation and soap formation, some nonenzymatic heterogeneous catalysts have been investigated. ZrO_2, ZnO, SO_4 2-/SnO_2, SO_4 2-/ZrO_2, KNO_3/KL zeolite, and KNO_3/ZrO_2 are some solid catalysts that were studied in the transesterification of palm and coconut oil [28]. The reaction was carried out at 200 °C, 50 bar, 3 wt% catalysts, and a 6:1 molar ratio of methanol to oil. All the solid catalysts exhibited some activity for both palm and coconut oil. The sulfonated metal catalysts gave the highest fatty acid methyl ester yields overall. ZrO_2 gave an 86.3% yield for coconut oil and 90.3% yield for palm oil. The study shows that SO_4 2-/ZrO_2 is deactivated quickly but can easily be regenerated. Other sulfonated solid catalyst can be used to catalyze the transesterification reaction. Recently, one of the more interesting sulfonated solid catalysts was derived from amorphous carbon [29]. Carbon rings present in compounds such as starches and sugars provide a large number of sites available for sulfonation. Studies were performed using glucose and sucrose as carbon sources. The carbon source was pyrolyzed at low temperatures resulting in carbon rings. The sheets were then sulfonated by sulfuric acid. The result is an inexpensive solid catalyst that has properties similar to Nafion. The authors show that it is an effective catalyst for the esterification of oleic and stearic acid. They claim an activity greater than half that of sulfuric acid and greater than regular solid catalysts at 80 °C.

If true, this catalyst offers an inexpensive alternative to immobilized enzyme catalysts. However, studies carried out in our laboratory both with virgin oil and waste oil showed substantially lower yields compared to enzyme catalysts. In these studies, the catalyst was made by a similar technique, which involved pyrolizing the sugar first and then sulfonating it. Sucrose was placed in test tubes in a tube furnace and was heated to 375 °C for a period of 15 h. The result was a black powder, which was ground using a mortar and pestle. The black powder was combined with 150 mL of 96 wt% sulfuric acid and was heated to 150 °C for 15 h. The solution was then vacuum-filtered using glass wool filters. The solid was washed with distilled/ deionized water until the pH of the wash water was near neutral. Experiments were run with triolein, olive oil, and used olive oil as the source. The reactions were carried out at 85 °C with 0.05 g of the sugar catalyst. An 8:1 molar ratio of methanol to triolein was used. The yields in all cases were very small compared to Novozym 435. A high temperature was used, because runs at 40 °C showed an even smaller yield.

Other catalyst systems have also been investigated. Xie and Huang [30] have reported the synthesis of biodiesel from soybean oil using KF/ZnO catalyst. The catalyst with 15% KF loading and that calcined at 873 K showed the optimum activity. The results showed that the activity of the catalysts correlated well with their basicity. Wang and Yang [31] investigated the transesterification of soybean oil with nano-MgO in supercritical and subcritical methanol. The authors report an increase in the transesterification rate when nano-MgO was added from 0.5 to 3 wt%.

8.2.3 Other recent advances

Recently, Fabbri et al. [32] reacted soybean oil with di-Me carbonate (DMC), which avoided the coproduction of glycerol. The main difference between the biodiesel like material, which the authors call DMC-BioD, and biodiesel produced from vegetable oil and methanol (MeOH-biodiesel) was the presence of fatty acid glycerol carbonate monoesters (FAGCs) in addition to FAMEs. The authors report that the presence of FAGCs influenced both fuel and flow properties, while the distribution of main pyrogenic compounds, including polycyclic aromatic hydrocarbons (PAHs), was not affected.

Dube´ et al. [33] have developed a membrane reactor to produce biodiesel from canola oil and methanol via both acid- and base-catalysis. Several tests, using food-grade canola oil, were performed in the semibatch two-phase membrane reactor at various temperatures, catalyst concentrations, and initial feed loadings. The novel two-phase membrane reactor was particularly useful in removing unreacted canola oil from the fatty acid methyl ester product yielding a high purity biodiesel. In a recent article [34], canola oil was transesterified using methanol and caustic in a reactor with membranes of varying pore sizes.

It was shown that all the membranes could retain the canola oil in the reactor, which indicated that the oil droplets present in the reactor were larger than all the pore sizes tested.

Other vegetable oils that have been used in biodiesel production include corn, sunflower, cottonseed, peanuts, canola, and rapeseed. However, expanding the use and production of a particular feedstock must be evaluated in terms of the environmental and economic impacts.

According to a recent United Nations report, the global rush to switch from oil to energy derived from plants will drive deforestation, push small farmers off the land, and lead to serious food shortages and increased poverty unless carefully managed. The United Nations report points to crops like palm oil, maize, sugar cane, and soya and urges governments to beware of their human and environmental impacts, some of which could have irreversible and damaging consequences. Thus, it makes sense to examine biodiesel production from waste oil and other nonedible sources. This will be done in the following sections.

8.3 Waste oil

Several studies have been done on the production of biodiesel from waste oils or animal fats [35] describing the feasibility of making quality biodiesel from this feedstock while identifying the problems with the free fatty acids present in the raw materials. The presence of free fatty acids and water in this feedstock results in the production of soap in the presence of alkali catalyst. Thus, additional steps to remove any water and either the free fatty acids or soap from the reaction mixture are required. Despite the lower reaction rate associated with sulfuric acid-catalyzed transesterification processes, this approach has several advantages over the base-catalyzed method [36]: it employs a one-step process as opposed to a two-step process; it can handle feedstock with a high free fatty acid content; downstream separation of the biodiesel is straightforward; and a high quality glycerol byproduct is produced.

The acid-catalyzed process suffers from a number of drawbacks. In addition to the low reaction rate, a drawback of the acid-catalyzed process is the requirement for the reactor to withstand an acidic environment. Yet another drawback to the acid-catalyzed process is that high alcohol to-oil ratios are necessary to promote the conversion of oil to fatty acid alkyl ester [10]. In their study on acid-catalyzed transesterification of soybean oil, Canakci and Van Gerpen [36] found that water strongly inhibits the ester-formation reaction. They recommended that the concentration of water in the reaction mixture should be less than 0.5%. Therefore, water formed by the esterification of free fatty acid would limit the presence of free fatty acid in oil to 5%. However, this is highly dependent on the amount of alcohol present.

The use of insoluble solid catalysts (such as immobilized enzymes) facilitates its removal from the glycerol and fatty acid alkyl ester products and leads to a reduction in waste material requiring disposal. The biggest advantage of enzyme catalysts is the absence of soap formation. Aside from enzymes, several researchers have attempted to use acid or alkali solid catalysts (e.g., zinc and calcium oxides, calcium and barium acetates, hydrotalcite, NaX faujasites, titanosilicate structure-10, calcium carbonate rock, tungstated zirconia-alumina) [37]. Almost all the catalysts require temperatures in excess of 200 °C to achieve conversions greater than 90% within the time scale of the experiment. Recently, mesoporous silica multifunctionalized with both organosulfonic acid and hydrophobic organic groups such as allyl and phenyl was shown to be effective in esterifying free fatty acids while excluding water, a byproduct that inhibits the reaction, from the proximity of the active sites [38]. Such a catalyst seems promising because of its relatively high surface area, flexible pore size, and its potential for controlling catalytic functionalities at the molecular level.

One of the authors, Vasudevan and his student Xiangping Shen, have recently investigated biodiesel production by transesterification of waste olive oil with methanol and Novozym_435. Experiments were carried out to investigate the influence of the molar ratio of methanol to triolein, mode of methanol addition, reaction temperature, and mixing speed on biodiesel yield.

For waste olive oil, the experiments results indicated that a molar ratio of 9:1 for methanol to triolein resulted in the highest biodiesel yield. This ratio is higher than the stoichiometric ratio of 3:1 probably due to the presence of other fatty acids in the feed and due to the fact that waste oil was used. At ratios higher than 9:1, the yield became lower due to enzyme deactivation by methanol.

Stepwise addition of methanol resulted in higher yields of biodiesel probably due to less inhibition of the enzyme by methanol. Higher yields of biodiesel were also obtained at a reaction temperature of 60 °C, which resulted in higher reaction rates and lower inhibition of the enzyme active sites by methanol. Mixing speed in the range 100–400 rpm had relatively little effect on the yield. The effect of different acyl acceptors or solvents or both on biodiesel yield was also evaluated. The highest yields were obtained when tert-butanol and methanol were both present as solvent/acyl acceptor perhaps due to the synergy that resulted as a result of better dispersion of the oil in the mixture.

The efficacy of Novozym_435 was also determined by reusing the enzyme after washing it with a solvent. The results showed that enzyme was very stable and still retained a high activity after several runs.

Wang et al. [39] investigated lipase-catalyzed alcoholysis of soybean oil deodorizer distillate (SODD) for biodiesel production. In this system, free fatty acids and glycerides were converted to biodiesel simultaneously.

Butanol was adopted as the reaction medium in which the negative effects caused by excessive methanol and byproduct glycerol were eliminated. There was no obvious loss in lipase activity even after 120 cycles. Studies by Vasudevan and Shen have not demonstrated such high enzyme stability.

The addition of a cosolvent to generate a homogeneous reaction mixture has been discussed [40]. While this enhances reaction rate significantly, the cosolvent must eventually be separated from the biodiesel and this requires additional processing. Another issue that has an adverse effect on biodiesel production is the removal of residual triglycerides and glycerol from the biodiesel product. The employment of multiple water wash steps creates an environmental challenge due to the need to treat the wastewater. The presence of unreactable materials in waste oil leads to poor flow properties of the biodiesel in cold weather. The use of homogeneous base catalysts coupled with the presence of free fatty acids and the chemical nature of the reaction components serve to yield a low quality glycerol byproduct.

If the goal is to reduce or eliminate the formation of soap and/or to process more waste oil and produce high quality biodiesel and glycerol, then enzyme catalysis is very attractive. Unfortunately, the process is not economically viable. In 2005, Novozymes (Bagsværd, Denmark) in conjunction with National Renewable Energy Labs (NREL) announced a 30-fold enzyme cost reduction in the conversion of pretreated corn stover to ethanol. The cost of the enzyme was approximately $0.10/gal of ethanol. A similar reduction in the cost of lipase would make enzymatic transesterification/esterification process economically very viable. In fact, current research in our laboratory and other laboratories is focused on ways to minimize inactivation of the enzyme by methanol. This can be achieved by utilizing different acyl acceptors and solvents (such as tert-butanol or higher alcohols), which in turn will increase the number of times the enzyme can be regenerated and reused. Thus, if better solvents are developed that minimize enzyme deactivation and/or if better enzymes are made through directed evolution resulting in an increase in the number of regenerations, then the cost of the enzyme can be proportionally higher. Elimination of solvents and the use of a single acyl acceptor-solvent will also lead to a reduction in costs.

There is also renewed focus on finding alternate uses for the byproduct glycerol or to convert glycerol to more useful products (including methanol or ethanol) via fermentation. Focus should also be on technologies to improve the conventional process for biodiesel production by perhaps utilizing membrane reactors to handle waste oil.

8.4 Nonedible sources

Nonedible oils, like Jatropha, Pongamia, Argemone, Castor, Sal, etc., can be used for the production of biodiesel. Jatropha curcas has tremendous potential for biodiesel production. A tropical plant that grows in low to high rainfall areas (rainfall as little as 25 cm per year) can be used to reclaim marginal soil.

Shah et al. [41] have investigated three different lipases (Chromobacterium viscosum, Candida rugosa, and Porcine pancreas) for transesterification of Jatropha oil in a solvent- free system to produce biodiesel; only lipase from Chromobacterium viscosum was found to give appreciable yield. Immobilization of lipase (Chromobacterium viscosum) on Celite-545 enhanced the biodiesel yield to 71% with a process time of 8 h at 40 °C.

Tiwari et al. [42] optimized the three important reaction variables in biodiesel production—methanol quantity, acid concentration, and reaction time for reduction of free fatty acid (FFA) content of Jatropha curcas oil. The optimum combination for reducing the FFA of Jatropha curcas oil from 14% to less than 1% was found to be 1.43% v/v H_2SO_4 acid catalyst, 0.28 v/v methanol-to-oil ratio, and 88-min reaction time at a reaction temperature of 60 °C.

This process gave an average yield of biodiesel of more than 99%. The fuel properties of Jatropha biodiesel were found to be comparable to that of diesel.

Karmee and Chadha [43] have investigated biodiesel production from the nonedible oil of Pongamia pinnata by transesterification of the crude oil with methanol and KOH as catalyst. A maximum conversion of 92% (oil to ester) was achieved using a 1:10 molar ratio of oil to methanol at 60 °C. When tetrahydrofuran was used as cosolvent, the conversion increased to 95%. Important fuel properties of methyl esters of Pongamia oil biodiesel compared well with ASTM standards.

8.4.1 Algae-based biodiesel

There is growing interest in algae-based biodiesel especially as more states in the United States mandate blending biodiesel with petroleum diesel. In the following paragraphs, we examine the pros and cons of algae-based biodiesel. It is important to keep in mind that any biofuel is ultimately a means of collecting solar energy and storing it in an energy dense chemical. To make such a system as efficient as possible, it is beneficial to understand the entire process from beginning to end.

Photosynthesis begins with a photon being captured by a 2p electron in a ring of conjugate double bonds within a pigment molecule (with the 2p electron being part of a conjugate pi bond), causing a p–p* excitation (where the energy level of this excitation determines the wavelength of light that can be ‘‘harvested,’’ with the pigments in photosynthetic organisms allowing the capture of photons with wavelengths from 400 to 700 nm). Recently published research [44] appears to finally explain the near 100% efficiency with which this captured energy is transmitted to the reaction center of a chloroplast. Their observation of coherent electronic oscillations between donor and acceptor pigment molecules (classically viewed as exchanging energy through virtual photon emission and absorption) demonstrates the wavelike behavior of the excitation energy transfer through the chromophore, accounting for almost loss-less energy transmission.

At the reaction center, the excitation energy is used to split CO_2 and H_2O molecules, ultimately producing carbohydrates (through the many steps of the Calvin cycle), with an overall process that can be summarized as $6CO_2$ þ $12H_2O$ þ photons ! $C_6H_{12}O_6$ þ $6O_2$ þ $6H_2$

A crude analysis of the quantum efficiency of photosynthesis can be done without getting into the details of the Calvin cycle; rather simply by looking at the photon energy required to carry out the overall reaction and the energy of the products. The Z-scheme, wellestablished in photosynthesis research, indicates that eight photons must be absorbed to split one CO_2 and two H_2O molecules, yielding one base carbohydrate (CH_2O), one O_2 molecule, and one H_2O (which, interestingly, is not made of the same atoms as either of the two input H_2O molecules).

With the average energy of ‘‘photosynthetically available radiation (PAR)’’ photons being roughly 217 kJ, and a single carbohydrate (CH2O) having an energy content taken to be one-sixth that of glucose [(CH2O)6], or 467 kJ/ mole, we can make a rough maximum efficiency of 26.9% for converting captured solar energy into stored chemical energy. With PAR accounting for 43% of incident sunlight on earth’s surface, the quantum limit (based on eight photons captured per CH2O produced) on photosynthetic efficiency works out to roughly 11.6%.

In reality, most plants fall well below this theoretical limit, with global averages estimated typically between 1 and 2%. The reasons for such a difference generally revolve around rate limitations due to factors other than light (H2O and nutrient availability, for example), photosaturation (some plants, or portions of plants receive more sunlight than they can process while others receive less than they could process), and Rubisco (the protein that serves ultimately as a catalyst for photosynthesis) also accepting atmospheric O2 (rather than CO2), resulting in photorespiration, releasing some of the already captured carbon.

In the United States, the average daily incident solar energy (across the entire spectrum) reaching the earth’s surface ranges from 12,000 to 22,000 kJ/m2 (varying primarily with latitude). If the maximum photosynthetic efficiency is 11.6%, then the maximum conversion to chemical energy is around 1,400–2,550 kJ/m2/day, or 3.8 9 1012 J/acre-year in the sunniest parts of the country.

Assuming the heating value of biodiesel to be 0.137 GJ/ gal, the maximum possible biodiesel production in the sunniest part of the United States works out to be approximately 28,000 gal/acre-year, assuming 100% conversion of algae biomass to biodiesel, which is infeasible.

It is important to keep in mind that this is strictly a theoretical ‘‘upper limit’’ based on the quantum limits to photosynthetic efficiency, and does not account for factors that decrease efficiency and conversion, or the efficiency with which algae convert carbohydrates into triglycerides (which is not well quantified at this point, and is dependent on many environmental factors). Based on this simple analysis though, it is clear that claims of algal biodiesel roduction yields in excess of 40,000 gal/acre-year or higher should be viewed with considerable skepticism.

While such yields may be possible with artificial lighting, this approach would be ill-advised, as at best only about 1% of the energy used to power the lights would ultimately be turned into a liquid fuel (clearly, one needs to look at the overall efficiency).

This upper limit also allows us to assess how truly inefficient many crops are when viewed strictly as biofuel producers. With soybeans yielding on average 60 gal of oil (and hence biodiesel) per acre-year, the actual fuel production is staggeringly small in comparison to the amount of solar energy available. This should further make it clear that using typical biofuels for the purpose of electricity generation (as opposed to the transportation sector) is an inefficient means of harnessing solar energy. Considering that photovoltaic panels currently on the market achieve net efficiencies (for solar energy to electrical energy) of the order of 15–20%, with multilayer photovoltaics and solar thermal-electric systems achieving efficiencies twice that in trial runs, biomass to electricity production falls far behind (considering typical plant photosynthetic efficiencies of 1–2%), with conversion of that biomass energy to electrical energy dropping the net efficiency to well under 1%.

Viewed in this light, it becomes clear that biofuels must offer some other benefits in addition to fuel production, to be energetically (or economically) appealing, in terms of how efficiently we can harness an energy source (solar energy) and turn it into a higher value form. Corn and soy, which dominate US agriculture, have long been grown for producing animal feed. The emerging ethanol and biodiesel industries, which have primarily relied on these crops, are ultimately a coproduct from crops grown as a food source for humans and animals. But, the relatively low net photosynthetic efficiency of the crops, and low total fuel yields, means that neither is a desirable approach if our goal is producing more fuel than that could be produced from those crops as a coproduct of animal feed production.

As the search for other feedstocks continues, it would be desirable to look for crops that can give a high net conversion of solar energy to energy in the form of fuel, while providing additional side benefits (coproducts, for example), since the net efficiency for harnessing solar energy through photosynthesis into liquid fuels is rather low.

Aquatic species such as microalgae have become appealing because of the potential for significantly higher average photosynthetic efficiency than with typical land crops, due to their aquatic environment providing them with better access to water, CO_2, and nutrients (depending on the system they are grown in). Additionally, while land crops may require substantial energy inputs for irrigation, planting, fertilization, and harvesting, these can be greatly minimized with an aquatic crop, with a well-designed system. Unfortunately, there are significant challenges to making this an economically viable energy crop.

While any form of biomass can be processed into a liquid fuel through various thermochemical processes (such as pyrolysis or gasification and Fischer-Tropsch synthesis), the energy and economic requirements of such processes are substantially greater than is required for transesterifying plant oils into biodiesel. Therefore, it is desirable to have a higher oil content to minimize processing costs (energetic and economic).

The storage of energy as oil rather than as carbohydrates slows the reproduction rate of any algae; so, higher oil strains generally grow slower than low oil strains. The result is that an open system (such as open raceway ponds) is readily taken over by lower oil strains, despite efforts to maintain a culture of higher oil algae. Attempts to grow higher oil extremophiles, which can survive in extreme conditions (such as high salinity or alkalinity) that most other strains cannot tolerate, have yielded poor results, in terms of the net productivity of the system. While an extremophile may be able to survive in an extreme condition, that does not mean it can thrive in such conditions.

Many research groups have therefore turned to using enclosed photobioreactors of various designs as a means of preventing culture collapse or takeover by low oil strains, as well as decreasing the vulnerability to temperature fluctuations. The significant downside is the much higher capital cost of current photobioreactor designs. While such high costs are not prohibitive when growing algae for producing high value products (specialty food supplements, colorants, pharmaceutical products, etc.), it is a significant challenge when attempting to produce a low value product such as fuel. Therefore, substantial focus must be placed on designing much lower cost photobioreactors and tying algae oil production to other products (animal feed or fertilizer from the protein) and services (growing the algae on waste stream effluent to remove eutrophying nutrients, or growing nitrogen fixing algae on power plant emissions to remove NOx emissions).

An additional challenge, when trying to maximize oil production with algae, is the unfortunate fact that higher oil concentrations are achieved only when the algae are stressed—in particular due to nutrient restrictions. Those nutrient restrictions also limit growth (thus limiting net photosynthetic efficiency, where maximizing that is a prime reason for using algae as a fuel feedstock). How to balance the desire for high growth and high oil production to maximize the total amount of oil produced is no small task. One of the goals of DOE’s well-known Aquatic Species Program was to maximize oil production through nutrient restriction; however, their study showed that while the oil concentration went up, there was a proportionally greater drop in reproduction rate, resulting in a lower overall oil yield.

One approach to balancing these issues has been successfully tested on a small commercial scale (2 ha) by Huntley and Redalje [45], using a combination of photobioreactors and open ponds. The general approach involves using large photobioreactors for a ‘‘growth stage,’’ in which an algal strain capable of high oil content (when nutrient restricted) is grown in an environment that promotes cell division (plentiful nutrients, etc.)—but which is enclosed to keep out other strains. After the growth stage, the algae enter an open raceway pond with nutrient limitations and other stressors, aimed at promoting biosynthesis of oil. The nutrient limitations discourage other strains from moving in and taking over (since they also require nutrients for cell division).

The economic picture Huntley and Redalje [45] presented is perhaps rosy due to the inclusion of substantial revenue from selling a high-value carotenoid coproduct, astaxanthin. Producing coproducts is perfectly fine and desirable; unfortunately, the potential market for a carotenoid is far smaller than the potential market for biodiesel—so, it could only help out with the economics of fuel production until that market is saturated. Since carotenoid synthesis increases with oil synthesis, the same conditions can be employed though to maximize total yield of each (resulting in an average oil yield of 25% of dry weight, using Haematococcus pluvialis).

The average biomass energy production reported by Huntley and Redalje [45] of 763 GJ/ha/year at their site in Hawaii works out to a net photosynthetic efficiency of just over 1%, based on an assumed average daily solar radiation of 19,300 kJ/m2 (or 70,445 GJ/ha/year, calculated by NREL based on the National Solar Radiation Database).

Unfortunately, this is not substantially different from what is routinely achieved with typical land crops. However, the average oil yield reported was 422 GJ/ha/year, roughly 0.6% of incident solar energy, equating to over 1,200 gal of biodiesel per acre-year—far better than conventional oil bearing crops. While their trials can be counted a success by many measures, it is worth pointing out how low the yield is in terms of comparison to the potential yield based on the quantum limits of photosynthetic efficiency, as well as compared to other means for harnessing solar energy. It should be no surprise though that their yield achieved came well short of the potential yield, since nutrient depletion in the open pound phase greatly limits cell division and hence biomass production (ultimately limiting photosynthetic efficiency for converting sunlight to chemical energy). An open pond system probably could be useful in cultivating high oil algaes either through the approach taken by Huntley and Redalje [45], in which nutrient restriction in the pond prevents any form of algae from growing well (thus preventing takeover) and forcing oil concentration in the algae cultivated in a nutrient-rich photobioreactor stage, or through the use of an oil-rich ‘‘extremophile’’ algae that can survive in an extreme environment (such as very high salinity) that other strains cannot tolerate. One form of this approach would be engineering algae to be resistant to an inhibitor that would be dumped into an open pond to keep other strains out, but this is likely to be controversial.

It may also be possible to increase algal biosynthesis of oil by identifying the enzyme that regulates lipid production and attempting to increase its activity through genetic engineering. Acetyl-CoA carboxylase (ACCase) catalyzes the carboxylation of acetyl-CoA to maloynl-CoA, believed to be the rate-limiting step in fatty acid synthesis in plants and animals [46]. While efforts focused on genetic manipulation to increase the activity of ACCase have been going on for at least 15 years, and certainly much has been learned in that time, the research has not yet reached the stage of actually being able to substantially increase the net oil yield from algae (and thus increase the commercial viability). Most of the research has focused on developing a detailed knowledge of the enzymatic pathways for lipid biosynthesis, before beginning to pursue genetic modification.

NREL has identified a gene that plays a large role in controlling ACCase activity, and has studied naturally occurring genetic mutations in algae strains that affect oil synthesis [47].

Another area where genetic engineering of microalgae could prove useful would be reducing the size of pigment antenna. Algae tend to have long pigment antennas for absorbing incident sunlight, to allow individual cells to thrive in low-light conditions. This also results in individual algae ‘‘harvesting’’ more energy (photons) in individual photosystems than the metabolic processes can handle, with excess energy being radiated as heat or fluorescence.

In high light conditions, without good agitation to rotate the algae nearest the surface, up to 80% of incident sunlight can be wasted through this photosaturation [48]. Maximizing efficiency in high sunlight would require either physical agitation or other means to rotate algae to the solar exposure region, or shortening (through selective breeding or genetic manipulation) of the pigment antennae to reduce the amount of light harvested by each algae.

Overall, while there is significant interest in algal biodiesel; it is important to keep in mind that this is still years away from being ready for actual commercial implementation. If we want to grow high oil algaes, two approaches appear possible—the use of an ‘‘extremophile’’ that can tolerate extreme conditions, and therefore be grown in an open pond under those conditions (which other strains cannot tolerate), or the use of photobioreactors for keeping invasive strains out, and optimizing the growth environment. The biggest challenge with the latter approach is the capital cost of current photobioreactors.

Unfortunately, the focus does not appear to be in developing lower cost photobioreactors to bring down the capital cost for building a ‘‘photobioreactor farm,’’ which ultimately will present a barrier to commercialization.

Many current designs use vertical tube systems, which require expensive metal support structures. Economic viability will likely require much simpler, less expensive systems that can be placed on the ground—such as simple troughs covered with plastic film.

8.5 Biodiesel: Advantages/Disadvantages

From a national & global perspective biodiesel use has a number of advantages:

- Fossil fuels. Although one can argue about the extent of the world’s reserves of coal, oil and natural gas it is indisputable that ultimately the supply of these fuels is limited.

- Greenhouse gas emissions. The burning of fossil fuels since the start of the industrial revolution over 150 years ago has increased the level of carbon dioxide and other “greenhouse gases” in the atmosphere. One researcher deftly expressed this by stating that “Within a few centuries, we are returning to the atmosphere and the oceans the concentrated organic carbon stored in sedimentary rocks over hundreds of millions of years”. What harm this is doing to our planet is, as you all know, the subject of serious debate. Biodiesel is said to be approximately neutral in this regard since the vegetable matter will have absorbed carbon dioxide while it was alive.

- Reducing Air Pollution. Use of biodiesel reduces many air pollutants especially in urban areas.
- Geopolitical. For petroleum oil importing nations it reduces their dependence on unstable countries & regions for their energy supplies. Biodiesel does have some disadvantages, for example in terms of power and economy particularly in colder climates, but this is not to the extent that would detract from its use.

8.5.1 Food and/or Energy

Now almost everything we eat can be converted into a fuel of some sort. Whenever the food value of a crop drops below its fuel value, the market will convert it into fuel. This dynamic has the potential to drive up world food prices and destabilize governments in low-income countries.

Until quite recently we thought of ourselves as being in the food sector. With the unprecedented interest in biodiesel we now find ourselves being considered to be in the energy sector as well.

Mineral oil prices are now affecting vegetable oil prices (Figure 8.1). In the short term this has the potential to distort prices for vegetable oils and fats since the normal supply and demand factors will continue to apply regardless of mineral oil prices.

A number of large biodiesel factories have been and are being constructed in Europe, Asia and the Americas to cater for the anticipated demand; so many in fact that in Malaysia the authorities have stopped issuing licenses for anymore to be built.

If all these factories operate at anywhere near full capacity it will divert a very substantial portion of vegetable oils away from their traditional use in food and into energy. The effect can only be to push up the price of edible oils, everything else being equal. However, if this is overdone governments, particularly in developing countries, are likely to use taxation to redress the balance. In importing countries such as Europe, public opinion will not support the subsidizing of palm oil, particularly if this threatens the rain forests or the economics of local crops and tax policies will be shaped accordingly.

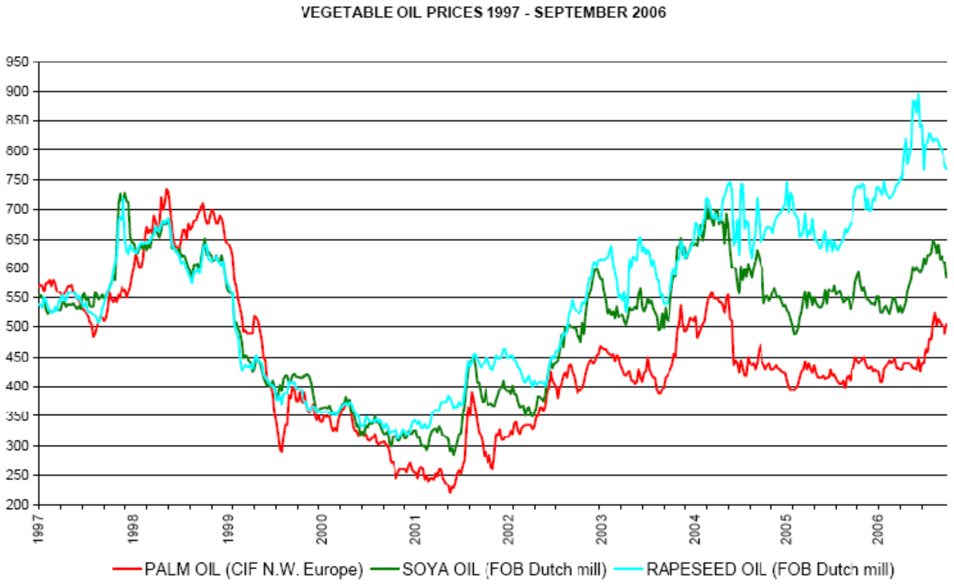

Figure 8.1: vegetable oil prices 1997-2006

8.5.2 Alternative Fuels

They say necessity is the mother of invention & this has certainly been true for fuels. For example, Germany, which is petroleum-poor but coal-rich, invented a process (Fischer-Tropsch) in the 1920s which produced liquid fuel from coal. It was used by Germany & Japan during WWII to produce alternative fuels. Germany's synthetic fuel production reached 6.5 million tonnes in 1944.

Although biofuels are a reality, some experts are predicting that within a decade, current biofuel production methods could be replaced by what are known as "second generation" fuels. These "second generation" fuels will be produced by the use of lignocelluloses, which is, basically, the use of biomass or everything that grows. This includes the non-edible parts of existing crops, & from plants that can be grown on soils & climates unsuited for food crops.

There are other alternatives like electric hybrids, hydrogen and fuel cells, algae, human and animal waste etc., but in present, practical terms, biodiesel and other biofuels offer the most promising alternative for the immediate future.

8.6 Conclusions

Biodiesel is a clean-burning fuel that is renewable and biodegradable. A recent United Nations report urges governments to beware of the human and environmental impacts of switching to energy derived from plants.

There should a healthy debate about turning food crops or animal feed into fuel and the consequences of the switch to biofuels needs to be carefully thought out. The focus of biodiesel production needs to be on sources like waste oil and grease, animal fats, and nonedible sources. It is important to ascertain a priori what quantities of these materials may be annually collectible, and what proportion of transportation-fuel needs these sources could supply. Current research has focused on these areas as well as on algae-based biofuels. Many technical challenges remain and these include development of better and cheaper catalysts, improvements in current technology for producing high quality biodiesel, use of solvents that are no fossil-based, conversion of the byproducts such as glycerol to useful products such as methanol and ethanol, and development of low cost photobioreactors

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Chapter 9

Analysis of process variables in biodiesel synthesis.

9. Analysis of process variables in biodiesel synthesis.

9.1 Introduction

In recent years, biodiesel has gained a primary importance position in global biofuel scenario. The production has increased dramatically due to rising prices of fossil fuels, development of policies and incentives, and increasing concern for environmental sustainability [1, 2].

During 2008, the biodiesel industry has suffered a major stopping place in Europe and in America and South-East Asia. The main reason is attributed to the relationship between the price of diesel and agricultural products. In the past two years, the prices of wheat, oil plants, and products for animal feed and agricultural products in general have had an enormous increase so that the market price of biodiesel is ultimately tied to the price of fossil fuels. In order to post the production of biodiesel from food crops, it was decided to develop good technology to optimize the production of this biofuel from waste materials such as fried oils or animal fats.

This choice allowed us to pursue a triple aim. First the choice of using waste materials as triglycerides source provides a lower cost of biodiesel produced. The emancipation from traditional energy sources allows us to pursue the objectives set by the Kyoto Protocol with regard to biofuels targets that would be utopian to think to reach only by using traditional crops [3].

In this last option, it allows to find a solution to the disposal of this waste material that otherwise it would be a cost for society.

Hence the idea of developing a fluidized bed reactor, which could synthesize biodiesel by using heterogeneous catalysts. This would maximize the amount of catalyst to be used and make it easier and its economic recovery and reuse.

Moreover, the choice of this innovative reactor configuration has enabled us to develop an untested continuous process certainly more suited to an industrial scale-up and then a further effect of reducing production costs related to a scale effect.

In the experimental work some acidic zeolites have been tested in order to combine the advantages of heterogeneous catalysis with the advantages of the acid one. Heterogeneous catalysis guarantees us an easy recovery and reuse of the catalyst used while the acid property of catalysts used permit to get transesterification reaction without saponification by-product. This is a way to reduce costs for separation and purification of biodiesel product [4, 5].

9.2 Analysis of variables and optimization of the production process

The used oil is a raw material with a higher content of impurities and a much higher fraction of free fatty acids than palm or rapeseed oils, usually used for the production of biodiesel [6, 7].

That increased levels of free fatty acids may induce, as explained above (§8.1), a marked presence of secondary reactions and therefore to the high production of soap by-products during the transesterification reaction. This implies a greater expenditure in pre- and post-treatment, a rise of the section of separation and loss in yield of final product desired.

Therefore the use of an innovative catalysis that results in secondary reactions and production of soaps give you an edge in terms of ease of installation and especially in economic terms due to the low cost of funds handled [8, 9].

9.2.1 The catalysis

From studies of literature, the acid catalysis has largely been tested and works well, but with lower reaction rate than the more common basic catalysis. The clear benefits of acid catalysis are the absence of secondary reactions of saponification reaction thereby reducing separation and purification of the final product.

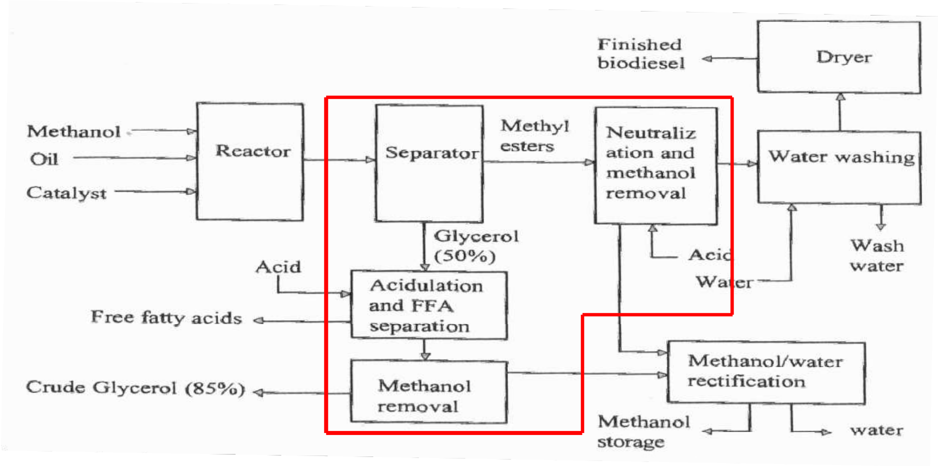

Fig. 9.1: Flow-sheet of a traditional plant for biodiesel production by use basic catalysis.

On the flow-sheet, shown in Fig. 9.1, which represents a typical process of biodiesel producing using conventional basic catalysis, were shown, circled in red, the part of the plant that might be relieved using the acid heterogeneous catalysis [10, 11].

Indeed, as mentioned, the use of an acid catalysis would avoid the presence of secondary reactions such as soap formation without necessity of their separation. The absence of these by-products would then lead to an easing of the entire separation and purification section of the product and oils pre-treatment section with a significant cost savings.

The first heterogeneous catalysts tested has been acidic zeolites (Beta, Silicalite-1, FAU-X) already prepared [11, 12].

The use of this kind of catalysts had the advantage to combine the benefits of acid catalysis (no saponification reactions so an increased yields in biodiesel and significant easing of separation and purification section) with the advantages of heterogeneous catalysis (easy recovery and reuse of the catalyst).

This choice of using heterogeneous catalysis has allowed us to study also different and more efficient reactor configurations [11, 12, 13].

9.2.2 The reactor

The greatest part of research on biodiesel has always focused on the use of batch reactors in which reagents were mixed together with the catalyst, traditionally homogeneous, and at the end the reaction time products were then collected.

The choice of using heterogeneous catalysts has instead provided the developing of continuous reactor configuration different from traditional batch reactors.

Continuous processes in fact offer significant advantages over batch process. Firstly, they are more suitable for subsequent industrial scale-up and therefore they bring with them the economic advantages connected with scale-up like production cost reduction. Moreover, this choice about the reactor gives us the chance to change and optimize in continuous the reaction time making a continuous spillage of the product. This is also a way to move the reaction toward the products formation.

The idea underlying all subsequent experiments was to design and optimize a continuous reactor where the catalyst was packed inside so ensuring a close contact reagents/catalyst.

Being acid catalysis slower than the traditional basic catalysis, one of the key variables in this type of configuration is the choice of reaction temperature, which would clearly be high. So it becomes crucial in the design of the reactor to optimize the technology to provide the necessary heat to the reacting system.

The idea behind the design of the new reactor for biodiesel synthesis is to work in a continuous process using heterogeneous catalysts.

But, considerations of maximizing the reaction kinetics and so the necessity to work with high temperatures and with a large catalyst amount led us to develop different ideas to find the reactor configuration that would ensure the highest performance in terms of biodiesel yield and energy efficiency [10].

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Chapter 10

Synthesis of biodiesel from waste source: A comparative analysis between continuous and discontinuous process

10. Synthesis of biodiesel from waste source: a comparative analysis between continuous and discontinuous process.

10.1 Introduction

Biodiesel production represents one of the most attractive alternatives to the traditional diesel fuel derived from a petroleum refinery, especially by considering the recent steep increase in the petroleum cost and the predicted shortage of fossil fuel.

The American Society for Testing and Materials (ASTM) defines biodiesel fuel as monoalkyl esters of long chain fatty acids derived from a renewable lipid feedstock, such as vegetable oil or animal fat.

The most widely used and effective catalysts in transesterification step are sodium and potassium hydroxide. Acid catalysts have been tested as effective in this reaction, too.

Despite alkaline catalysis is characterized by a higher reaction rate in comparison to an acid-catalyzed reaction, some severe drawbacks must be accounted in this case: the presence of moisture and free acidity that strongly influence the process performance and economics.

In fact, both water and free fatty acids (FFAs) react rapidly with the catalyst, consuming it and giving way to long-chain soaps.

Moreover because of their specific properties do not allow an efficient separation of the pure glycerol in the final step of the process. As matter of fact, when the source oil contains a lot of FFAs (> 1%), an acid pre-treatment have to be applied.

The necessity to improve the economic competitiveness of this process with respect to petroleum-derived diesel fuel and the increasing global market demand of biodiesel results in a growing interest toward the utilization of waste raw materials of both vegetal and animal origin.

The main problem involved in the utilization of these low-cost raw materials is represented by the high content of free acidity (free fatty acids, FFAs) that must be reduced below the threshold limit value of 0.5-1.0% by weight to ensure the feasibility of the subsequent transesterification step.

A great economical disadvantage for the improving of separation and purification cost due to the great amount of by-products.

In order to exceed these problems, the activity of some catalysts has been studied.

Acid transesterification allows obtaining a biodiesel production without formation of by-products.

The idea to use some acid catalysts zeolites (MFI, FAU-X) to join the advantages of the heterogeneous catalysis with those obtained by the acid-transesterifcation has been taken in account.

Moreover, using heterogeneous catalysis give us the possibility to investigate different reactor configuration, Plug-flow reactor, more suitable for continuous industrial operation respect to the traditionally studied batch configuration.

Opposite to the relatively high availability in the literature of batch experimental data, no any information has been reported concerning the possibility to perform the esterification reaction of long chain fatty acids with methanol in plug flow reactor using zeolites as catalyst.

10.2 Aims of the work

The aim of this work has been to compare the performances of olive oil and cooked oil source in acid and heterogeneous transesterification carried out in a batch reactor and in a Plug-Flow Reactor.

The results of these two processes have been compared in term of product yield and reaction rate.

A comparison with the traditional base homogeneous catalysis process has been done, too.

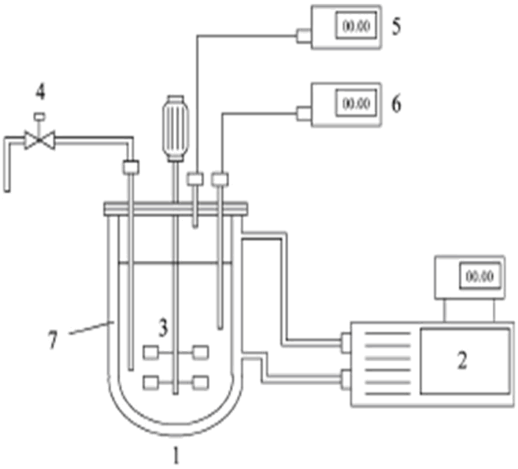
The optimization of the reaction parameters (temperature, reactants ratio and catalysts amount) has been carried out.

10.3 Experimental session

The experimental runs have been performed in a classic batch reactor and in a PFR planned ad hoc for these tests.

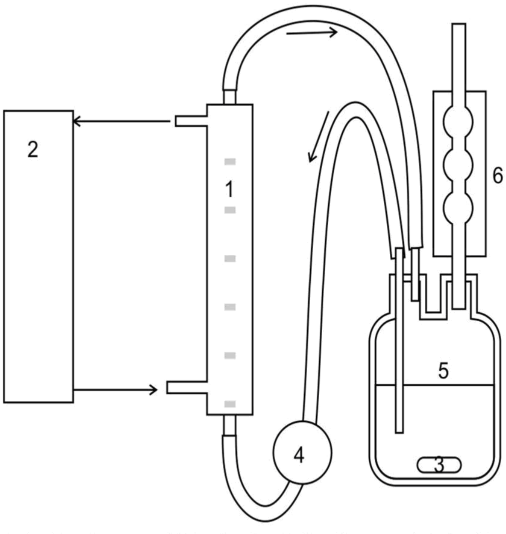
This reactor is generated by a continuous series of micro CSTR. Every micro-CST reactor is made by vessel in which heterogeneous catalysts are fluidized.

Figure 1 shows the flow-sheet of CST reactor.



Scheme of the reactor: 1, reactor; 2, circulation thermostat; 3, stirrer; 4, sampling valve; 5, indicator for pressure transducer; 6, indicator for liquid-phase thermocouple; 7, reactor jacket.

Figure 10.1: Scheme of experimental apparatus using batch reactor.



1, catalyst bed reactor PFR; 2, circulation thermostat; 3, stirrer; 4, pump; 5, two neck flask; 6, condenser.

Figure 10.2: Scheme of experimental apparatus using plug flow reactor.

This kind of reactor gives us the possibility to work with a large amount of catalysts without any problem of mixing and it gives us the chance to change and optimize in continuous the reaction time making a continuous spillage of the product.

This is also a way to move the reaction toward the products formation.

The acid zeolites have been synthesized with standard procedures. The used obtained materials have been characterized by usual techniques.

The methyl esters content was determined by GC-analysis using an internal standardization method.

The transesterification reaction performed into the two different reactors was carried out at reaction temperatures ranging between 60÷140 °C. Molecular ratio of methanol/oil fed was included between 4/1 and 20/1.

Table 10.1 shown the different parameters investigated.

Table 10.1: Parameters investigated

Parameters	Investigation range
Oil/Methanol ratio	1/4 -1/20
Temperature	60 – 140 °C
Catalyst amount	10 – 30 %wt
Reaction time	24 -48 h
Reactor configuration	Batch - PFR

10.4 Results and discussion

Initially, olive oil transesterification reactions have been carried out in order to evaluate the effective feasibility of acid zeolite transesterication.

A series of test at different temperature, have been performed using MFI, FAU-X and BEA catalysis.

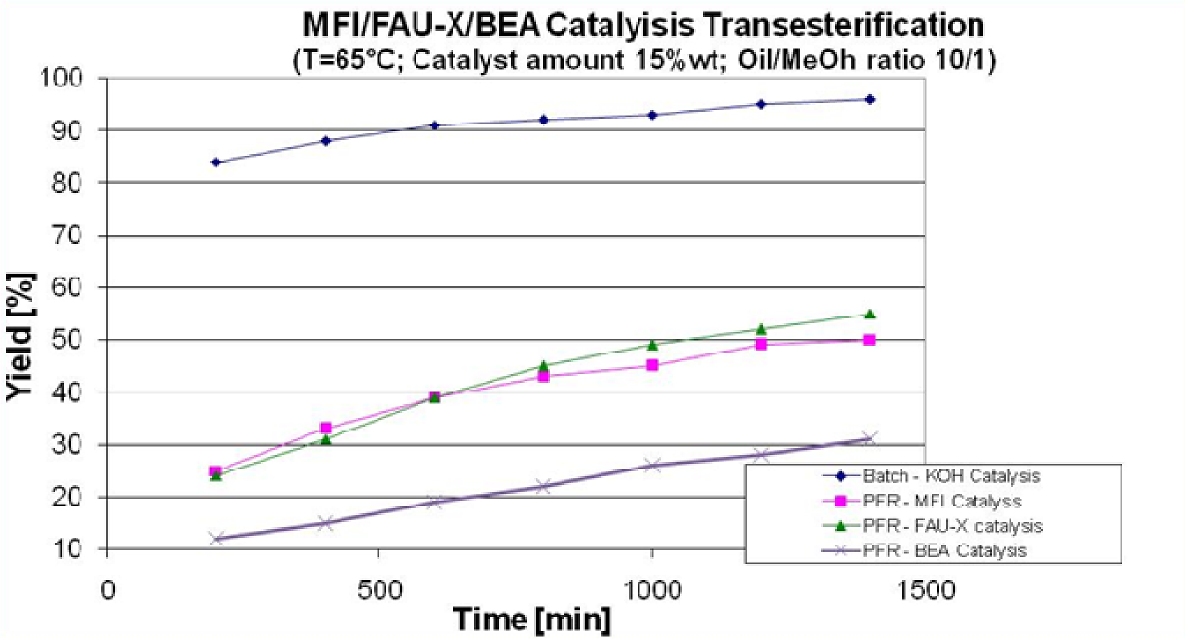


Figure 10.3: Comparison among the experimental conversion in MFI,FAU-X and BEA Catalysis Transesterification (Plug-flow reactor; T=65°C; Catalyst amount 15%wt; Oil/MeOh ratio 10/1) and KOH Catalysis Transesterification (batch reactor; T=65°C; Catalyst amount 15%wt; Oil/MeOh ratio 10/1)

Figure 10.3 and shows us like the three zeolites tested are effective to catalyze transesterification reaction both, and it give us a comparison between traditional KOH catalysis and acid zeolites catalysis about reaction rate.

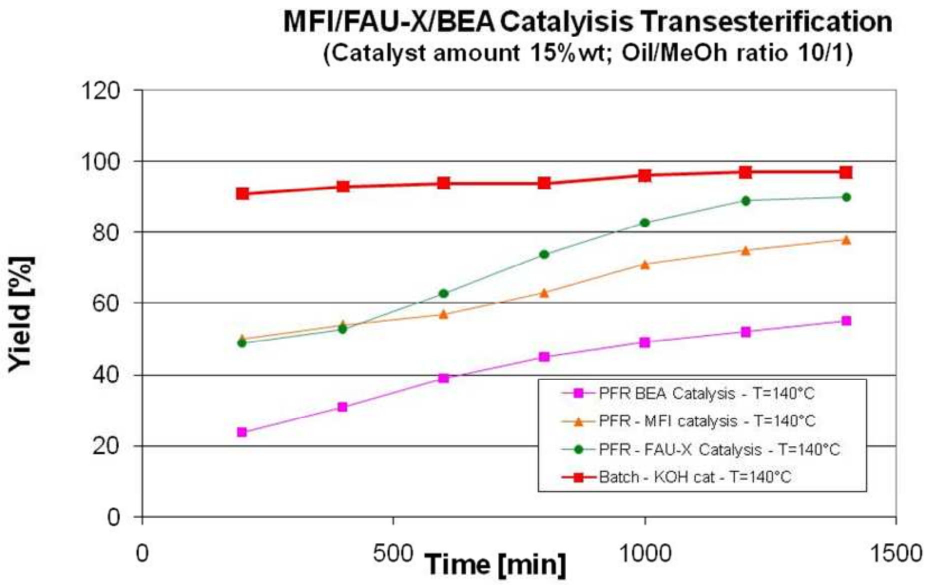


Figure 10.4: Comparison among the experimental conversion in MFI,FAU-X and BEA Catalysis Transesterification (Plug-flow reactor; T=140°C; Catalyst amount 15%wt; Oil/MeOh ratio 10/1) and KOH Catalysis Transesterification (batch reactor; T=140°C; Catalyst amount 15%wt; Oil/MeOh ratio 10/1)

Acid catalyst transesterification shows a reaction rate lower than KOH catalysis transesterification, but it’s also able to achieve a good conversion, close to traditional catalysis process, after 24 h, at temperature of 140°C.

Only BEA catalysis appears to be no effective in transesterification reaction. It could be due to tridimensional porous structure of BEA zeolite.

The great influence of temperature on acid transesterification is shown in figure 10.5.

A series of tests at different temperature have been carried out for the three acid zeolite selected.

Tested zeolites need an elevate temperature value (> 80 °C) to show a reaction rate compared with base catalysts (KOH).

The best catalysts activity is given from FAU-X that also shows a greater sensibility at temperature value exchange.

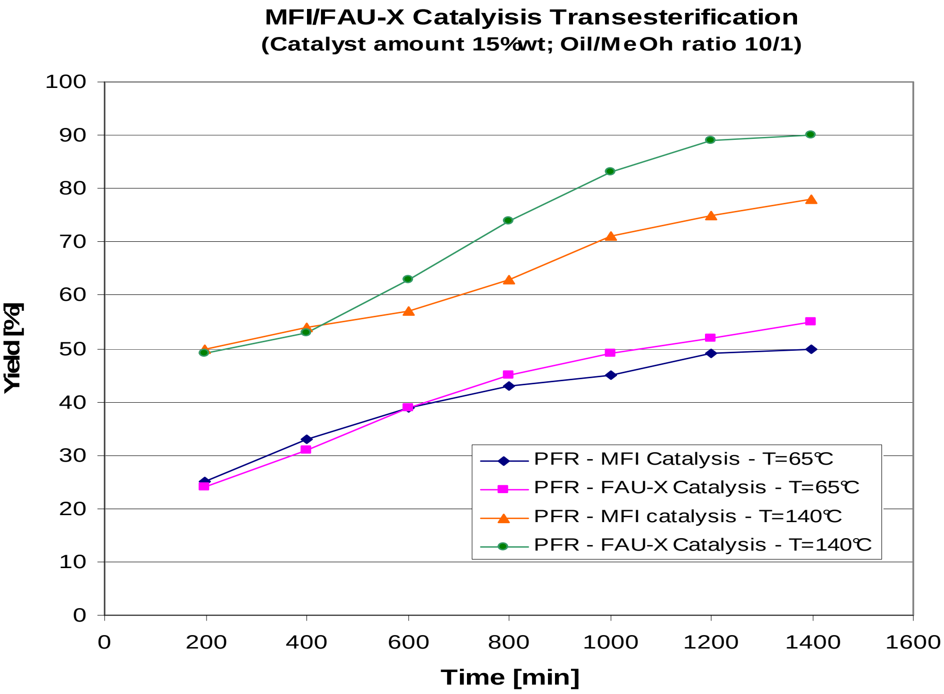


Figure 10.5: Comparison between the experimental conversion in MFI and FAU-X Catalysis olive oil Transesterification at different temperature (Catalyst amount 15%wt; Oil/MeOh ratio 10/1)

Figure 10.6 and 10.7 show the trend of biodiesel yield Vs time for olive oil and cooked oil transesterification reaction at low (T=65°C) and high (T=140°C) temperature.

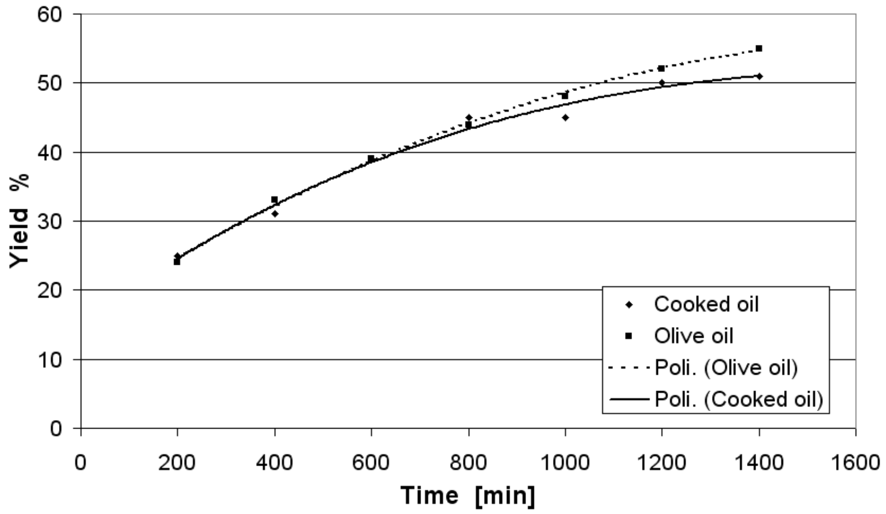


Figure 10.6: Comparison between the experimental conversion in olive oil and cooked oil transesterication (MFI Catalysis; plug-flow reactor; T= 65°C; Catalyst amount 15%wt; Oil/MeOh ratio 10/1)

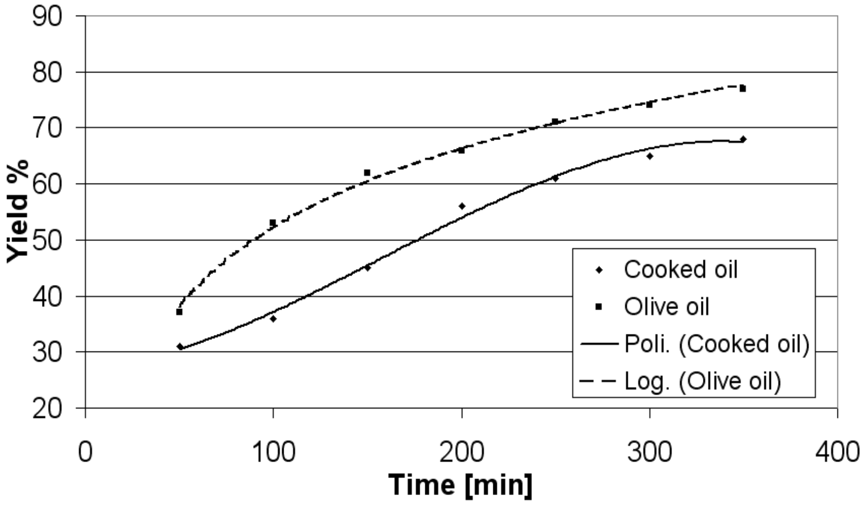


Figure 10.7: Comparison between the experimental conversion in olive oil and cooked oil transestericaton (MFI Catalysis; plug-flow reactor; T= 120°C; Catalyst amount 15%wt; Oil/MeOh ratio 10/1)

From Figure 10.6 we can see how the two processes show a similar trend for low temperature reaction.

Figure 10.7, instead, shows that olive oil source reaction has, at the first time, a higher reaction rate respect to cooked oil source reaction, but the two reactions both achieve to a good product yields.

By a comparison between Figure 10.5 and Figure 10.6 we have the confirmation (also for cooked oil transesterifications) that production yield and reaction rate are strongly influenced by reaction temperature and that we need high temperature to reach a conversion close to traditional basic catalysis transesterification.

The important advantages of this kind of catalysis are the absence of soap-products formation also in cooked oil process and so its applicability to the high FFA substrates. In fact, acid catalyzed transesterification reaction also allows to reduce the acidity of the oil used as triglycerides sources. This parameter for biodiesel fuel is closed to 0.5 mg KOH/g by the EN 14214 normative. Further, the stream of glycerol can be recovered free by catalyst derived impurities.

The different reaction parameters (catalyst amount and oil/Methanol ratio) optimization is performed caring out the transesterification reaction at fixed value of temperature

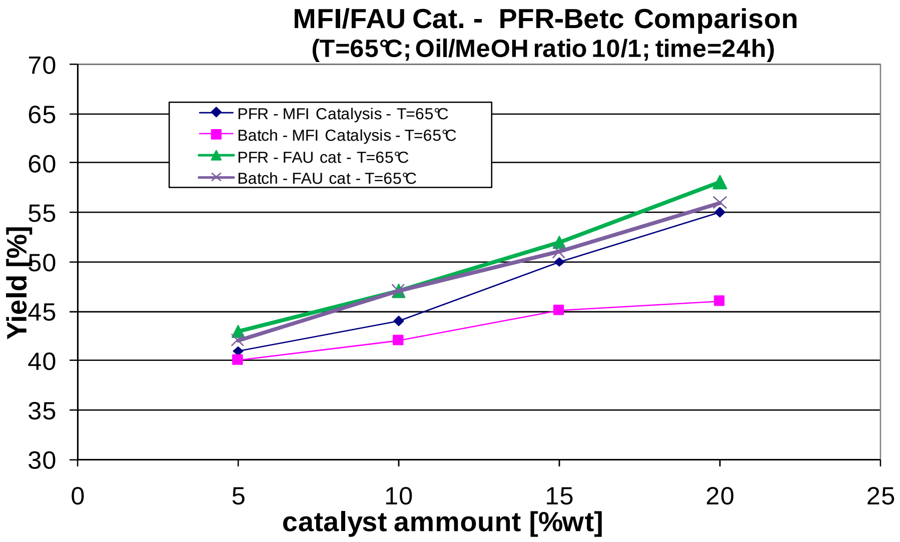


Figure 10.8: Comparison between the experimental conversion, changing catalyst amount, in batch reactor and plug-flow reactor cooked oil transestérication (MFI Catalysis; T= 65°C; Oil/MeOh ratio 10/1; t=24 h)

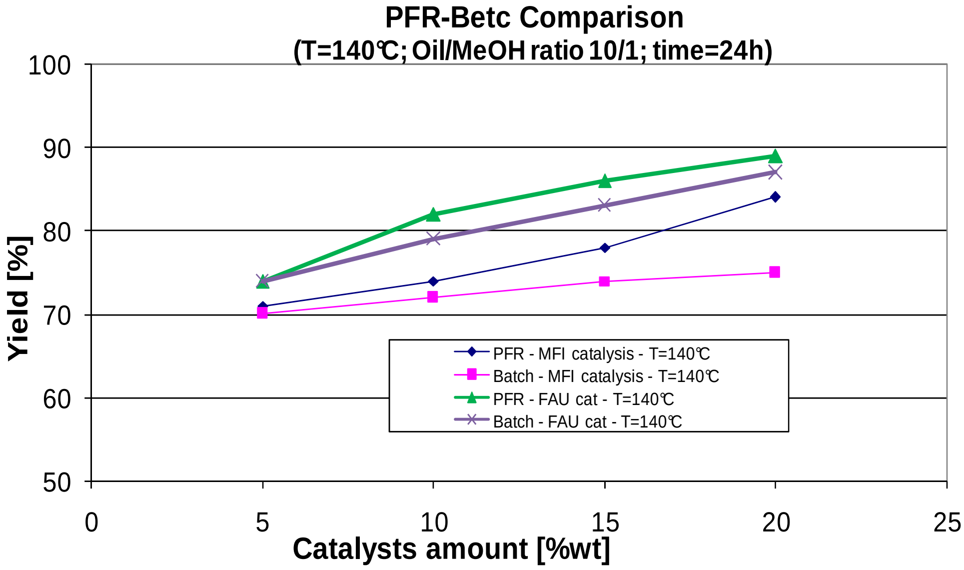


Figure 10.9: Comparison between the experimental conversion, changing catalyst amount, in batch reactor and plug-flow reactor cooked oil transestérication (MFI Catalysis; T= 140°C; Oil/MeOh ratio 10/1; t=24 h)

Figure 10.8 and 10.9 show us the influence of catalyst amount on biodiesel production. Excess of catalyst leads the transesterification reaction to the product formation and to a conversion. Reactions carried out in PFR show a greater sensitivity to this parameter, in fact, this new configuration is able to use all catalyst added.

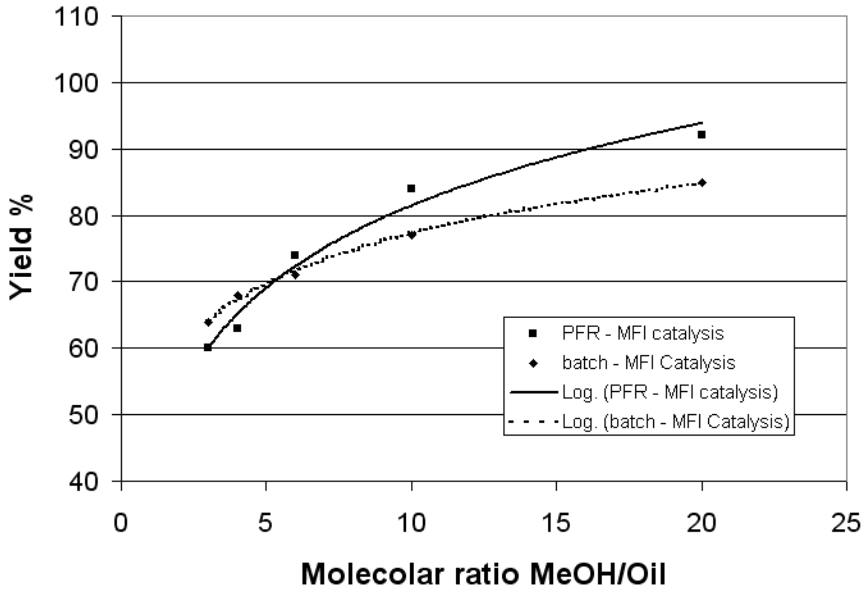


Figure 10.10: Comparison between the experimental conversion, changing oil/methanol ratio, in batch reactor and plug-flow reactor cooked oil transestericationn (MFI Catalysis; reactor; T= 140°C; Catalyst amount 15%wt; 1; t=48 h)

In Figures 10.10 is reported the conversion in methyl esters for different oil/Methanol ratio.

In this case, excess of methanol leads transesterification reaction to the product formation too, which depends on methanol excess used. Reactions carried out in PFR show a greater sensibility to this parameter.

10.5 Conclusion

All tested catalysts are able to catalyze the transesterification reaction both of olive oil and cooked oil fatty acids.

The plug-flow reactor is able to carry out olive oil and cooked oil transesterification. Every micro CSTR is a perfect fluidized bed that guarantees the perfect mixing of the catalysts with the reactants mixture. In this way, the perfect plug-flow, the complete use of the catalyst fed (also for elevated amount) is insured.

All acid catalysts tested needs an elevate temperature value (> 80 °C) and methanol amount to show a reaction rate compared with base catalysts (KOH).

The fastest step of reaction is the triglycerides break-up to glycerol and free fatty acids formation. The second step, the esterification one, is the slowest that require high time and temperature.

In the two processes and for every kind of catalysts tested, we obtain a different amount of methyl- esters.

An important advantage of this kind of catalysis is the absence of soap-products formation with a large amount of glycerol.

In fact, this kind of catalysis guarantees the absence of soap-products formation and it’s applicability to the high FFA substrates.

Tests carried out had shown the great influence of reaction variables on the reaction rate and product yield in olive oil and cooked oil to biodiesel acid catalyzed transesterification. Moreover, working at high temperature is a need to achieve a final conversion comparable to the traditional basic catalyzed transesterification.

PFR has shown a greater sensibility than batch traditional process to reaction parameter variations.

PFR has also shown us a greater flexibility to run with great catalyst amount and with an excess of methanol.

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Conclusions

A cleaning section upgradind has been carried out and the technologies proposed is able to remove tars, sulphuric pollutants and acid compounds from syngas produced.

So the producer gas coming from the ENEA Trisaia Research Centre dual fluidised bed steam gasification pilot plant appears to have an adequate quality in order to be used as fuel for a MCFC.

Moreover, the simulations carried out confirm the great flexibility of absorbtion tower that is able to remove the pollutants for the three gasification technologies analyzed

The performed simulation, the combination of MCFC with biomass steam gasification does not imply any significant increase in the overall efficiency with respect to conventional conversion devices such like gas engines.

The use of MCFC for power generation offers valuable environmental benefits with respect to conventional technologies, such like steam turbine or combined cycle power plants.

In biodiesel synthesys, all tested catalysts are able to catalyze the transesterification reaction both of olive oil and cooked oil fatty acids.

All acid catalysts tested needs an elevate temperature value (> 80 °C) and methanol amount to show a reaction rate compared with base catalysts (KOH).

Tests carried out had shown the great influence of reaction variables on the reaction rate and product yield in olive oil and cooked oil to biodiesel acid catalyzed transesterification. Moreover, working at high temperature is a need to achieve a final conversion comparable to the traditional basic catalyzed transesterification.

Continuous system has shown a greater sensibility than batch traditional process to reaction parameter variations.

Morevore, continuous configuration has also shown us a greater flexibility to run with great catalyst amount and with an excess of methanol.

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