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Henrik Romar

BIOMASS GASIFICATION AND CATALYTIC CONVERSION OF SYNTHESIS GAS

CHARACTERISATION OF COBALT CATALYSTS FOR FISCHER-TROPSCH SYNTHESIS

UNIVERSITY OF OULU GRADUATE SCHOOL;
UNIVERSITY OF OULU,
FACULTY OF SCIENCE, RESEARCH UNIT OF SUSTAINABLE CHEMISTRY;
KOKKOLA UNIVERSITY CONSORTIUM CHYDENIUS;
NORWEGIAN UNIVERSITY OF SCIENCE AND TECHNOLOGY

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BIOMASS GASIFICATION AND CATALYTIC CONVERSION OF SYNTHESIS GAS

Characterisation of cobalt catalysts for Fischer-Tropsch synthesis

Academic dissertation to be presented with the assent of the Doctoral Training Committee of Technology and Natural Sciences of the University of Oulu for public defence in the Campus auditorium, Kokkola University Consortium Chydenius (Talonpojankatu 2, Kokkola), on 12 May 2015, at 12 noon

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Supervised by
Doctor Pekka Tynjälä
Professor Ulla Lassi

Reviewed by
Professor Tapani Pakkanen
Doctor Matti Reinikainen

Opponent
Professor Claudia Bianchi

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University of Oulu, P.O. Box 8000, FI-90014 University of Oulu, Finland

Abstract

Biomass gasification as a thermochemical treatment method is typically used for heat and power production. Instead of burning the producer gas, it can be converted to added-value products, i.e to fuels and chemicals. One such conversion is the catalytic Fischer-Tropsch synthesis (FTS) which converts synthesis gas to a chain of aliphatic hydrocarbons (FT diesel) as studied in this thesis. This requires, however, proper cleaning steps of producer gas, such as the removal of tar compounds and other impurities. These cleaning steps are not considered in this thesis.

The first goal of the thesis was to determine the tar content in the producer gas from a small scale biomass gasifier. This subject is discussed in Paper I. The second and main goal of the thesis was the preparation and characterization of cobalt (or iron) catalysts for catalytic conversion of a gas mixture close to the synthesis as discussed in Papers II-V. The overall aim of the second part was to study the effects of promoters on the reducibility of cobalt and the effects of different calcination conditions on the degree of reduction and size of the metallic cobalt particles. In this later part different catalytic supports were used.

According to the results of the thesis, naphthalene and toluene were the main tar compounds in the producer gas representing almost 80 % of the GC detected tar compounds. Only traces of polycyclic aromatic compounds were detected and no phenolic compounds were found in the gas.

Further, a number of supported heterogeneous catalysts for FTS using cobalt (Co) or in some cases iron (Fe) as the active metal were prepared and characterized. These catalysts were supported on alumina (Al_2O_3), titanium dioxide (TiO_2) or silicon carbide (SiC). Catalysts were promoted with Ru, Re or Rh in the concentrations of 0, 0.2, 0.5, and 1.0 mass-%. Several characterization methods (such as H_2-TPR, catalytic activity measurements, N_2 physisorption, CO chemisorption, X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD)) were used to find answers to the behaviour of these catalysts under selected conditions and in the model reaction of FTS.

Based on the results, there are significant differences in the characteristics of the catalysts, the differences are dependent of the supports used, promoters added and calcination conditions used. The properties of the support, especially the pore size distribution will effect the distribution of products formed in the Fischer-Tropsch synthesis. Addition of promoters and variatons in calcination conditions will effect the dispersion and the particle size of the active metal.

Keywords: biomass, catalyst, characterization, cobalt, Fischer-Tropsch, gasification, tar

Romar, Henrik, Biomassan kaasutus ja synteesikaasun katalyyttisessä konvertoinnissa käytettävien Co-katalyyttien karakterisointi.
Oulun yliopiston tutkijakoulu; Oulun yliopisto, Luonnontieteellinen tiedekunta, Kestävän kemian ja luonnonvarojen tutkimusyksikkö; Kokkolan yliopistokeskus Chydenius; Norwegian University of Science and Technology
Acta Univ. Oul. A 649, 2015
Oulun yliopisto, PL 8000, 90014 Oulun yliopisto

Tiivistelmä

Biomassan kaasutus on termokemiallinen prosessi, jota käytetään pääosin sähkön- ja lämmöntuotannossa. Polton sijaan kaasutuksessa muodostuva synteesikaasu voidaan puhdistaa ja hyödyntää edelleen katalyyttisesti polttoaineiden ja kemikaalien valmistuksessa. Eräs mahdollisuus synteesikaasun hyödyntämiseen on Fischer-Tropsch synteesi (FTS), jossa koboltti- tai rautakatayyteillä voidaan tuottaa alifaattisia hiilivetyketjuja (FT-dieseliä), mitä on tutkittu tässä työssä. FT-synteesi vaatii kuitenkin puhtaan tuotekaasun ja sen vuoksi tervayhdisteet ja muut epäpuhtaudet on poistettava kaasusta. Kaasun puhdistusta ei ole kuitenkaan tutkittu tässä työssä.

Työn ensimmäisenä tavoitteena oli määrittää biomassan kaasutuksessa käytettävän pienikokoisen myötävirtakaasuttimen kaasun koostumus ja tervayhdisteet ja niiden pitoisuudet (julkaisu I). Toisena, ja tämän työn päätavoitteena oli Fischer-Tropsch -synteesissä käytettävien kobolttI- ja rautakatalyyttien valmistus ja karakterisointi sekä käyttö synteesikaasun katalyyttisessä konvertoinnissa (julkaisut II-V). Erityisesti tutkittiin promoottorimetallien ja kalsinointiolosuhteiden vaikutusta koboltin pelkistymiseen ja kobolttimetallipartikkelien kokoon. Lisäksi tutkittiin ja vertailtiin erilaisia tukiaineita.

Työn tulosten perusteella naftaleiini ja tolueeni olivat pääasialliset tervayhdisteet myötävirtakaasuttimen tuotekaasussa ja niiden osuus oli yli 80 % kaasukromatografisesti havaittavista tervayhdisteistä. Lisäksi havaittiin pieniä määriä polysyklisiä aromaattisia yhdisteitä, kun taas fenolisia yhdisteitä ei havaittu tuotekaasussa.

Työssä valmistettiin ja karakterisoitiin lukuisa määrä erilaisia FT-katalyyttejä, joissa aktiivisena metallina oli koboltti tai rauta. Katalyyteissä tukiaineena oli alumiinioksidi (Al_2O_3), titaanidioksidi (TiO_2) tai piikarbidi (SiC) ja promoottorimetallina joko Ru, Re tai Rh (pitoisuudet 0, 0.2 tai 1.0 massa-%). Katalyyttien karakterisointiin käytettiin useita menetelmiä, kuten H_2-TPR, N_2-adsorptio, CO-kemisorptio, XPS, XRD ja lisäksi määritettiin katalyyttien aktiivisuus ja selektiivisyys valituissa olosuhteissa FT-synteesin mallireaktioissa.

Tulosten perusteella katalyyttien välillä havaittiin selkeitä eroja riippuen käytetystä tukiaineesta, promoottorista ja kalsinointiolosuhteista. Tukiaineen ominaisuudet, erityisesti huokoskokojakauma vaikuttavat FT-synteesin tuotejakaumaan. Promoottorien lisäys katalyyttiin sekä kalsinointiolosuhteet vaikuttavat lisäksi dispersioon ja aktiivisen metallien partikkelikokoon.

Asiasanat: biomassa, Fischer-Tropsch, kaasutus, karakterisointi, katalyytti, koboltti, terva

“Nobody Knows the Troubles I've Seen”

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Kokkola, 30th March, 2015 Henrik Romar

Symbols and abbreviations

Alumina	Al_2O_3
BET	Brunauer, Emmett, Teller isotherm
BJH	Barrett-Joyner-Halenda
C_{5+}	Hydrocarbons with a chain length of 5 carbons or more
Co	Cobalt
FT(S)	Fischer-Tropsch (synthesis)
GC	Gas chromatography
GC-FID	Gas chromatography with flame-ionization detector
GC-MS	Gas chromatography with mass spectrometric detector
IPA	2-propanol, isopropanol
PAH	Polycyclic aromatic hydrocarbons
TPR	Temperature programmed reduction
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Original publications

This thesis is based on the following scientific publications and manuscripts, which are referred throughout the text as Roman numerals from I to V:

I Romar H, Tynjälä P, Lassi U (2013) Biomass gasification in an air-blown down-draft gasifier: Determination of tar compounds from producer gas. Bioresources 8(3): 3620-3629.

II Romar H, Lahti R, Tynjälä P, Lassi U (2011) Co and Fe catalysed Fischer-Tropsch synthesis in biofuel production. Topics in Catalysis. 54: 1302-1308.

III Romar H, Rivoire E, Tynjälä P, Lassi U (2015) Effects of calcination conditions on the dispersion of cobalt over Re, Ru and Rh promoted Co/γ-Al_2O_3 catalysts. Manuscript.

IV Romar H, Lillebø AH, Tynjälä P, Hu T, Holmen A, Blekkan EA, Lassi U (2015) H_2-TPR, XPS and TEM Study of the Reduction of Ru and Re promoted Co/γ-Al_2O_3, Co/TiO_2 and Co/SiC catalysts. Manuscript.

V Romar H, Lillebø AH, Tynjälä P, Hu T, Holmen A, Blekkan EA, Lassi U (2015) Characterisation and catalytic Fischer-Tropsch activity of Co-Ru and Co-Re catalysts supported on γ-Al_2O_3, TiO_2 and SiC. Manuscript.

The present author was the primary author of publications I–V and has been responsible for performing the majority of experimental work within these papers. XRD, TEM and XPS characterizations were done in close collaboration with Dr. Tao Hu.

Contents

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1 Introduction

1.1 Background

Decreasing sources of fossil fuels combined with an increasing demand for energy has led to higher energy prices and a global search for renewable energy sources. Currently, the only renewable source of carbon is biomass and different types of biomass have been used for the production of bio-based fuels. Early biofuels (1st generation biofuels) were produced from sources such as wheat or sugar cane which resulted in the production of biofuels competing with food production, leading to increased food prices worldwide (Fiorese *et al.* 2014, Mitchell. 2008, Sims *et al.* 2008). First generation biofuels were normally prepared by processes such as fermentation of sugars, transesterification of fatty acids and microbial digestion of biomass as described in Table 1.

Table 1. First generation biofuels, corresponding biomass feedstocks and production processes, modified from (Zhang. 2010).

Biofuel	Biomass feedstock	Production processes
Bioethanol	Sugar beet, grains	Hydrolysis/fermentation
Vegetable oil	Pure plant oil	Cold pressing/extraction
Biodiesel	Oil Crops (rape seed)	Cold pressing/extraction/ Transesterification
Biodiesel	Waste/cooking/frying oil animal fat	Transesterification
Biogas	Wet biomass	Digestion
BIO-ETBE	Bioethanol	Chemical synthesis

As the understanding of bio-technology and the need for energy continued to increase, the direction of energy production moved towards biofuels produced from biomass fractions regarded as waste (2nd generation biofuels). This led to new possibilities for the production of energy, chemicals and transportation fuels whilst reducing biomass waste. Some processes used for the production of 2nd generation biofuels are described in Table 2. It was agreed by the European Parliament that the share of biofuels in all transport fuels (petrol and diesel) should be increased, first up to 5.75% by 2010, and later to 10% by 2020 (European Parliament 2009/28/EC).

Table 2. Second generation biofuels, processes related to their preparation, modified from (Sims *et al.* 2008, Zhang. 2010).

Biofuel group	Specific biofuel	Production process
Bioethanol	Cellulosic ethanol	Advanced enzymatic hydrolysis and fermentation
Synthetic biofuels	Biomass-to-liquids (BTL) Fischer-Tropsch (FT) diesel synthetic diesel Biomethanol Heavier alcohols (butanol and mixed alcohols) Dimethyl ether (DME)	Gasification and catalytic processes
Methane	Bio-synthetic natural gas (SNG)	Gasification and catalytic processes
Bio-hydrogen	Hydrogen	Gasification and synthesis or biological processes.

There are two main routes available for the conversion of 2nd generation biomass into chemicals and transportation fuels, i.e. the enzymatic and thermochemical pathways. For the enzymatic pathway, sugars present in the biomass are released by enzymatic or by a combination of enzymatic and acid treatments. The sugars released can be further converted into bioethanol by fermentation. The enzymatic pathway is used to a great extent for the conversion of starch based biomass.

By thermochemical treatment of lignocellulosic biomass under restricted supply of oxygen (biomass gasification) the biomass can be transformed into producer gas (Berndes *et al.* 2003, Bludowsky & Agar. 2009, Sims *et al.* 2008). Producer gas consists of hydrogen and carbon monoxide as the main chemical compounds with a number of other compounds also possible depending on the gasification conditions.

After proper cleaning and the removal of unwanted compounds, the producer gas is converted into synthesis gas, a platform chemical that can be further converted to a number of chemicals by catalytic processes. Some of the compounds initially present in the producer gas can have a negative effect on the catalysts used in the upgrading steps. Therefore, the concentrations of these compounds have to be known in order to set up the proper cleaning procedures (McKendry. 2002b, McKendry. 2002c, Milne & Evans. 1998, Sims *et al.* 2008).

One possibility for catalytic conversion of synthesis gas is the Fischer-Tropsch synthesis (FTS), a process that produces a mixture of hydrocarbons, mostly aliphatic ranging from methane (C_1) up to long-chained waxes (C_{60+}). The Fischer-Tropsch process was patented as early as the 1920’s (Fischer & Tropsch. 1923, Fischer & Tropsch. 1925), but is still subject to intense research today. The Fischer-

Tropsch reaction is known to be a reaction that is sensitive to several reaction parameters such as reaction pressure, temperature and ratio of H_2 to CO in the reaction gas used.

Much research has been done regarding the Fischer-Tropsch reaction, but there are still a number of open research questions such as the composition of the active phase, the mechanism of promoters and deactivation processes (Dry. 1996, Tsakoumis *et al.* 2014). The basic mechanisms of the FTS has been subject to intense research during the last few decades and they are to some extent understood. The effects of the addition of promoter metals on the activity and selectivity of catalysts has also been studied but the mechanisms for these effects are still unclear. One main problem is that the methods used to study catalysts such as X-Ray Photoelectron Spectroscopy (XPS) operates under a low or ultralow vacuum while the FTS operates at high temperatures and pressures (Morales & Weckhuysen. 2006). In order to obtain new information on the mechanisms of promoters new analytical methods have to be developed in order to study the catalysts under real operation conditions (Morales & Weckhuysen. 2006).

The catalytic process for the conversion of syngas, and especially the Fischer-Tropsch synthesis are processes that have been investigated to a large extent during the last 5 - 10 years. A search on the ScienceDirect database for “fischer-tropsch” and “fischer-tropsch catalysts” resulted in 1259 and 1039 hits respectively for the years 1995-2014 (see Fig. 1).

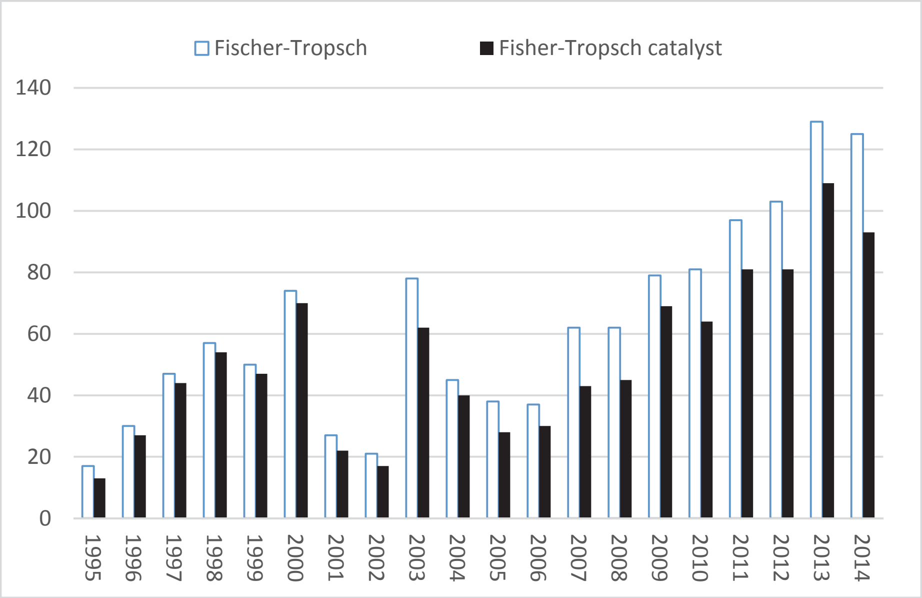

Fig 1. Number of publications found with two different search phrases at www.ScienceDirect.com for the years 1995-2014.

Most of the studies reported in scientific journals concerning biomass gasification and especially tar determinations are performed with large scale gasifiers (>1 MW). These gasifiers are usually fluidized bed gasifiers. When it comes to small-scale gasifiers, a lot of scientific research of down draft gasifiers (<500 kW) has been performed but the results from these investigations are mostly presented as industrial reports and in-house publications, most of them are hard to find. These small-scale gasifiers are, however, of great interest when local, distributed heat and energy systems (CHP plants) are considered for heat and power production. A better understanding of the gasification process and the composition of the gas obtained is therefore needed.

1.2 Aims of this thesis

The research and results presented in this thesis were performed and obtained within the projects HighBio and HighBio2 (Lassi & Wikman. 2011, Lassi *et al.* 2013). The aims of these projects were to investigate the small-scale gasification of biomass, mainly logging residues, characterization of the producer gas with a special focus on the tar content, utilization of carbon residue and calculation of mass and energy balances over the gasification process.

The thesis consist of two parts; in the first shorter part the determination of tars in producer gas is studied. In the main part of the thesis a number of catalysts prepared by different methods and promoted by a number of metals are characterized.

One of the main objectives of this thesis was to study tar compounds present in the producer gas from a small-scale (down-draft) gasifier, and to develop and characterize supported cobalt catalysts to convert synthesis gas to aliphatic hydrocarbons.

The first part of this thesis is focused on sampling and characterisation of tar compounds from wood chips gasification processes. It is essential that these properties are known when evaluating the needs for cleaning steps for producer gas. Based on this, the first research questions were: What levels of tars are produced in a small scale down-draft gasifiers in order to predict the needs for cleaning steps? This research question is discussed in Paper I.

The second objective in this thesis as presented in papers II-V focused on the preparation and characterization of Fischer-Tropsch catalysts. For these papers, the main research questions were how the catalyst preparation conditions affect the dispersion of the active metal, and what are the effects of catalyst supports used on the properties of the catalysts. The effect of different promoter metals on the catalyst properties were also investigated.

The novelty of my thesis can be found in the broad approach of the subject matter covering the characterization of producer gas, especially tars formed during the gasification of biomass and the determination of these compounds combined with studies on the preparation conditions for and characterisation of catalyst for FTS supported on different supports. Finally the effects of adding different promoter metals in combination with different preparation conditions are studied.

2 Biomass gasification and cleaning of producer gas

Biomass is defined as biological, carbon containing, material derived from living, or recently living organisms. Another definition of biomass is “Recent organic matter originally derived from plants as a result of the photosynthetic conversion process, or from animals, and which is destined to be utilized as a store of chemical energy to provide heat, electricity and transport fuels” (Dry. 1999, Dry. 2002, McKendry. 2002a, McKendry. 2002b, Ohara 2003, Sims. 2002). In the context of biomass for energy this is often used to mean plant based material, but biomass can also apply to both animal and vegetable derived material such as waste from food production and, to some extent, municipal waste (Maity. 2015a, Maity. 2015b). From a sustainability point of view biomass can be considered as the only renewable source of carbon available.

Biomass and especially lignocellulosic biomass can be transformed into new products or heat by thermal treatment. Thermal treatment can be divided according to the supply of oxygen into different processes (see Fig. 3): 1) Combustion; direct burning of biomass using excess oxygen, 2) Gasification; restricted supply of oxygen and 3) Pyrolysis; thermal treatment with no oxygen present (McKendry. 2002a, McKendry. 2002b, Pollex *et al.* 2012).

Gasification of biomass is a thermal treatment process under restricted oxygen supply; normally about 30% of the stoichiometric amount of oxygen required to complete oxidation of the biomass is used (McKendry. 2002c). Gasification of biomass is a complex process including a number of steps; these reactions will be considered later on in this chapter.

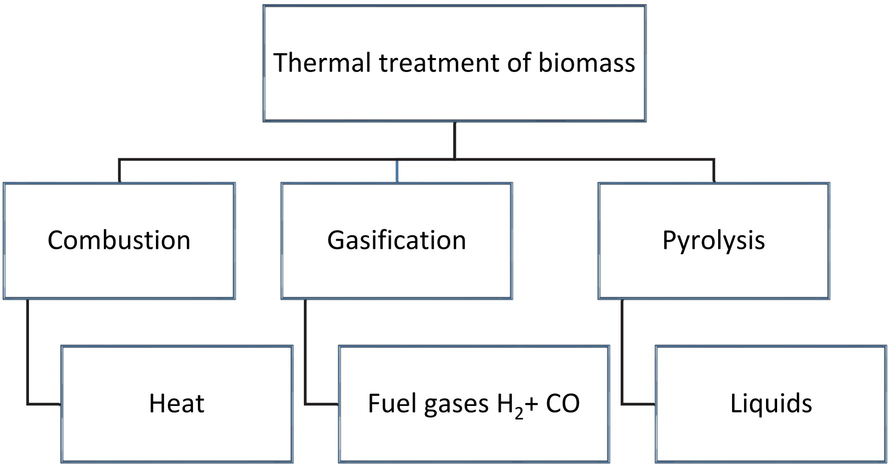

Fig 2. Different routes for the conversion of biomass according to the supply of oxygen.

2.1 Reactions during gasification

A number of reactions take place during the gasification of solid biomass. The main steps during this process are (Knoef 2005):

1. thermal decomposition of the biomass to gas, vapours and char (pyrolytic step)
2. thermal cracking of vapours to gas and char
3. gasification of char by steam or carbon dioxide
4. partial oxidation of combustible gas, vapours and char

These steps are schematically presented in Fig. 3.

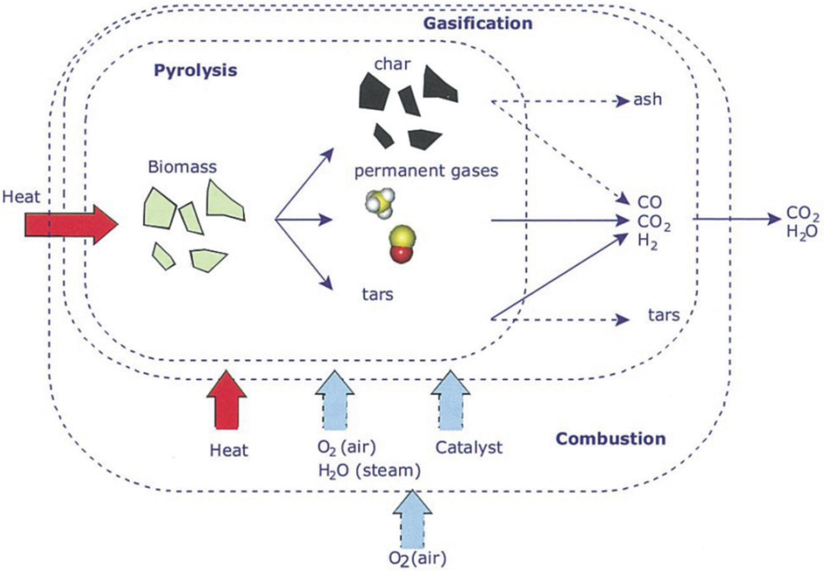

Fig. 3 The gasification process (Reprinted with permission from Knoef 2005).

During the gasification process a number of chemical reactions take place. A summary of the reactions can be described as (Sims. 2002):

$$[CH_2O] + O_2 + \text{heat} \Rightarrow C + CO_2 + CO + H_2O + \text{hydrocarbons} + \text{heat} \quad (1)$$

Table 3. Main reactions during biomass gasification (modified from Sims 2002).

Reaction type	Reaction	ΔH
Combustion reactions in the oxidation zone:	$C + O2 \Rightarrow CO_2$	+393.8 kJ/mol
	$C + \frac{1}{2} O_2 \Rightarrow CO$	+ 123.1 kJ/mol
Reduction reaction	$C + H_2O \Rightarrow CO + H_2$	-118.5 kJ/mol
Boudouard reaction	$C + CO_2 \Rightarrow 2CO$	-159.9 kJ/mol
Water gas shift reaction	$CO_2 + H_2 \Rightarrow CO + H_2O$	-40.9 kJ/mol
Methanisation reaction	$C + 2H_2 \Rightarrow CH_4$	87.5 kJ/mol

The producer gas from the gasification process contains carbon monoxide (CO) and hydrogen (H_2) as the main compounds as well as water (steam), methane (CH_4), carbon dioxide (CO_2) and nitrogen (N_2). Nitrogen content of the gas can be up to 50 volume % if the gasifier is air-blown. Composition of the gas is dependent on factors such as the temperature used for gasification, biomass used, gasification conditions and type of gasifier. Besides the main compounds, the gas also contains a number of other compounds and even solid particles. These compounds are regarded as impurities that are to at least some extent harmful for processes downstream of gasification.

2.2 Impurities found in the producer gas

The main compounds in the producer gas obtained by small-scale gasification of biomass are carbon monoxide, hydrogen and nitrogen but carbon dioxide, methane and water are also found in the producer gas (Asadullah. 2014, Ruiz *et al.* 2013). Beside these main compounds there are a number of impurities in the gas. These impurities originate from the biomass and are released or formed during thermochemical treatment. Impurities found and the concentration of each compound is mainly dependent on the biomass and the type of gasifier used (Borg *et al.* 2011). Most of the impurities can affect the use of the producer gas and many of them can damage the equipment downstream from the gasifier gasification causing a blockage of tubings or inactivation of catalysts used for conversion of the synthesis gas (Devi *et al.* 2003, Ruiz *et al.* 2013, Shen & Yoshikawa. 2013a). Depending on the final use of the gas different levels of gas purification are needed. The quality of gas needed for some applications is presented in Table 4.

The use of biomass as the source for synthesis gas makes the process much more demanding compared to the use of natural gas or coal. Biomass is composed of cellulose, hemicellulose and lignin that can undergo a chain of reactions during thermal treatment.

Table 4. Gas quality requirement for various uses of producer gas, modified from (Asadullah. 2014).

Conversion method	IC-engine	Gas turbine	FT synthesis
Tar, mg/Nm^3	<100	<5	<1*
Particulate matter, mg/Nm^3	<50	<0.1	0
Alkali max, ppb	-	20-1000	<10
S components (H_2S, SO_2, CS_2), ppm	-	<1	<1
N-components (NH_3+ HCN) ppb	-	-	<20
HCl, ppm	-	<0.5	<0.1
Alkali metals, ppb		<50	<10

*unit ppmV

2.2.1 Particles and soot

A large number of particles are formed during the gasification of biomass. These particles consist of ash from the gasified feedstock fuel, unconverted carbon and soot. Particles can be removed from the gas by a cyclone or different filtering processes. Normally heated filters in order to avoid condensation of organic compounds or electrostatic filters are used.

2.2.2 Sulfur containing compounds

Sulphur containing compounds in the producer gas originate from sulphurous compounds in the feedstock. The main components found in producer gas are compounds such as carbon disulphide (CS_2), oxygen containing sulphur compounds (COS) and hydrogen sulphide (H_2S). These compounds are known to interact with catalysts used for further conversion of the gas in an irreversible way and drastically decrease the lifetime of the catalyst.

2.2.3 Halides

Halides like chloride (Cl), bromide (Br) and fluoride (F) originate from the biomass used and evaporate during the gasification process and are observed in the producer gas. Most of these compounds are corrosive and will damage the tubing of the gasifier. They also interact with catalysts used for further conversion of the gas in a negative way decreasing the lifetime and activity of the catalyst used.

2.2.4 Tar compounds

Tars are a heterogeneous group of organic compounds formed during the thermal treatment of biomass. The tars originate from the building blocks of lignocellulosic biomass; cellulose, hemicelluloses and lignin (Göransson *et al.* 2011, Milne & Evans. 1998, Monteiro Nunes *et al.* 2007) and are formed by the decomposition of these building blocks during thermal treatment. By definition tars are organic compounds with a molecular mass greater than that of benzene (MWbenzene = 78) and are mostly cyclic or heterocyclic, consisting of one or more aromatic rings (Milne & Evans. 1998). A summary of the different tar groups and their properties is shown in Table 5.

During the gasification process tars undergoes a maturation process that is dependent of the gasification temperature used as presented in Table 6 (Milne & Evans. 1998). The amounts of tars formed and the type of compounds present in the tar fraction is dependent on a number of factors. The most important factors are gasification temperature and type of gasifier used. Tar compounds present in the producer gas may foul a gasifier by clogging the tubing of the reactor. Tars are also known to severely damage or totally inhibit catalysts used in processes downstream from the gasifier. This concerns tars especially from Class 5 because of the nature of these types of tars, (Font Palma. 2013, Shen & Yoshikawa. 2013).

Table 5. Classification of tar compounds (modified from Milne & Evans 1998).

Tar class	Class name Property	Representative compounds
1	GC-undetectable. Very heavy tars, cannot be detected by GC	Determined by subtracting the GC-detectable tar fraction from the total gravimetric tar
2	Heterocyclic aromatics. Tars containing hetero atoms; highly water soluble compounds	Pyridine, phenol, cresols, quinoline, isoquinoline, dibenzophenol
3	Light aromatic (1 ring). Usually light hydrocarbons with a single aromatic ring; do not pose a problem regarding condensability and solubility	Toluene, ethylbenzene, xylenes, styrene
4	Light PAH compounds (2–3 rings) compounds with 2 and 3 aromatic rings; condense at low temperature even at very low concentration	Indene, naphthalene, methylnaphthalene, biphenyl, acenaphthalene, fluorene, phenanthrene, anthracene
5	Heavy PAH compounds (4–7 rings) Larger than 3-ring, these components condense at high-temperatures at low concentrations	Fluoranthene, pyrene, chrysene, perylene, coronene

Table 6. Maturation of tars (modified from Milne & Evans 1998).

Mixed oxygenates	⇨	Phenolic Ethers	⇨	Alkyl phenolics	⇨	Heterocyclic Ethers	⇨	PAH	⇨	Larger PAH
400 °C		500 °C		600 °C		700 °C		800 °C		900 °C

2.3 Methods for gas cleaning

The raw gas (producer gas) contains a number of other compounds alongside the main components. Most of these compounds are regarded as impurities and have to be removed prior to any catalytic step. The cleaning steps needed in order to produce a gas clean enough to be used for catalytic conversion reactions can be regarded as the most demanding and also the most expensive step in the route from biomass to reaction products (Anis & Zainal. 2011). One example of the setup of a gasifier, gas cleaning units and a Fischer-Tropsch reactor is presented in Figure 4. The unit presented in Figure 4 consists of a gasifier, followed by a number of cleaning steps including, for example, tar crackers and particle filters, heat-exchange units, condensers and compressors before the catalytic Fischer-Tropsch reactor. This unit highlights the complexity of the processes needed to clean the gas produced by gasification of biomass as described by (Anis & Zainal. 2011). This setup contains a number of cleaning steps including tar cracker, unit for removal of HCl, HCN and H_2S and finally removal of NH_3 and sulfur compounds.

2.4 Catalytic conversion of synthesis gas

Synthesis gas (syngas) can be derived from a number of sources such as coal, natural gas and biomass. Procedures used for these conversions differ in complexity depending on the raw material used. The gas resulting from the gasification process, syngas, consists of two main components; carbon monoxide (CO) and hydrogen (H_2), the ratio between H_2 and CO varies from 0.8:1 to 2.2:1 depending on the source of the syngas. If the syngas is derived from biomass the ratio of CO to H_2 is rather low, usually in the ratio of 1:1 or even lower.

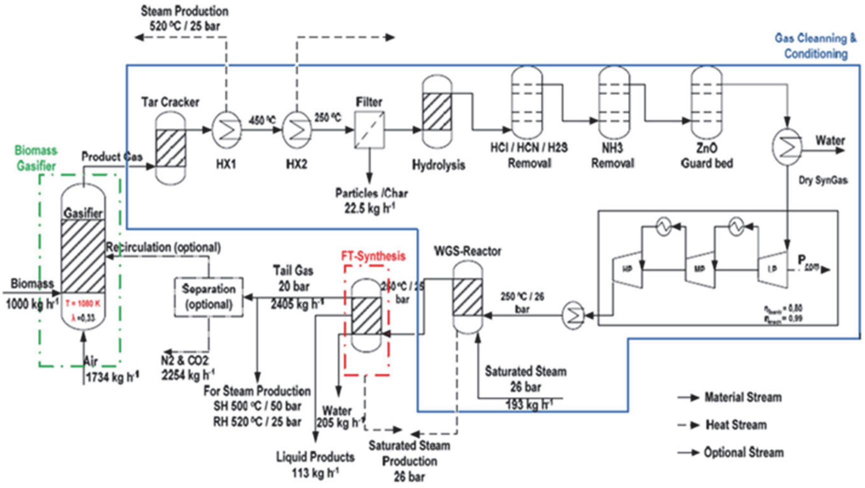

Fig. 4 Setup for a unit with gasification, gas cleaning and FTS. Reprinted with permission from (Spyrakis *et al.* 2009).

Since syngas can be regarded as a platform chemical; it can be converted into a number of chemicals, most of the synthesis routes to these chemicals are catalytic ones. There are two main routes in the catalytic conversion of syngas as described in Fig. 5. One route starting from the syngas itself and the other including a first synthesis step into methanol in which a number of chemicals can be produced by catalytic processes. In this study the direct route from syngas to Fischer-Tropsch is considered.

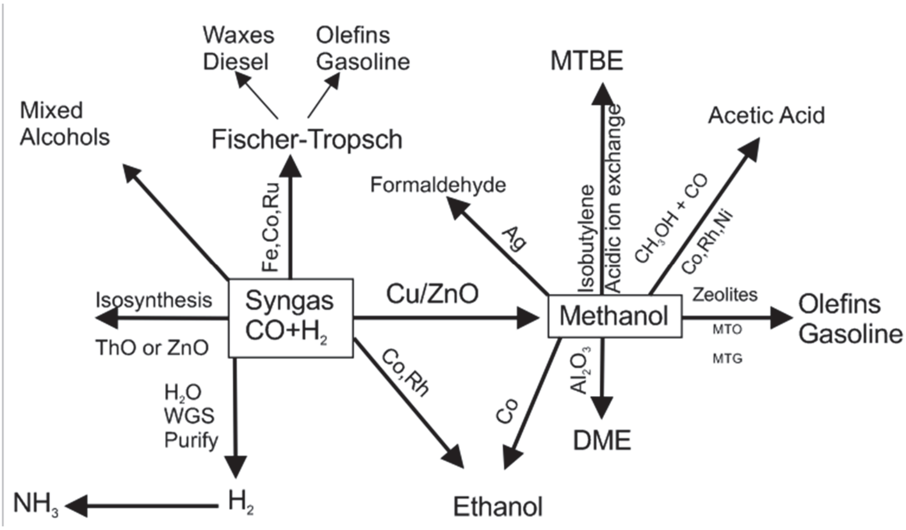

Fig. 5 Some catalytic conversion routes starting from purified syngas. (Modified from Spath & Dayton 2003).

2.5 Fischer-Tropsch synthesis

The Fischer-Tropsch synthesis (FTS) was developed by two German chemists Franz Fischer and Hans Tropsch who patented the reaction in 1920 (Fischer & Tropsch. 1923, Fischer & Tropsch. 1925). In FTS, carbon monoxide and hydrogen reacts under elevated pressure and temperature on a catalyst forming a series of hydrocarbons, most of them linear aliphatic hydrocarbons but also oxygenates, branched hydrocarbons and olefins are produced. The original reaction was catalysed by iron catalysts but over time new, more efficient catalysts with better stability and performance have been developed.

In a historical review of FTS by Bartholomew (Bartholomew. 2003) the development of the FTS process is divided into five periods: (1) discovery (1902-1928), (2) commercial development of cobalt and iron catalysts (1929-1949), (3) the Iron Age (1950-1974), (4) rediscovery of cobalt (1975-1990), and (5) GTL and the return to cobalt (1991-present). During recent years much of the research has been focused on the study of active sites on cobalt and promoting effects of precious metals (Bartholomew. 2003).

As described earlier in this paper (Fig. 5), there are a number of catalytic routes available from syngas. All of these reactions are catalysed by heterogeneous catalysts. In FTS, CO and H_2 react to form $–CH_2-$ groups and water as the main reaction as described in reaction 2.

$$CO + 2H_2 \rightarrow -CH_2- + H_2O \qquad \text{(reaction 2)}$$

A heterogeneous FTS catalyst is composed of a support and at least one active metal. Additionally there can be one or more promoter metals added, usually in low concentrations, less than 0.5 mass%. There are two main types of catalysts used for the Fischer-Tropsch conversion of syngas into traffic fuels; iron catalysts and cobalt based catalysts. Besides iron and cobalt there are metals like ruthenium and rhenium which possess the same activity as Fischer-Tropsch catalysts. However, because of the high prices of these metals they are not commercially used in a FT catalyst for other purposes than for promoter metals. FTS is known to be a process that is very structurally sensitive regarding the catalysts used (Fischer *et al.* 2013, Girardon *et al.* 2007, Khodakov *et al.* 2007). A number of parameters like metal used, size of the metal particles, supports used and pore size distribution of the supports will have an effect on the activity of the catalyst used. With the promoted cobalt catalyst the process occurs at 210-230 °C at pressures ranging between 20 and 50 Bar.

2.6 Catalysts for F-T synthesis

2.6.1 Supports

Catalytically active metals are normally deposited on a support. The role of these supports is to provide an environment where the active components can be stabilized as small particles. Porous materials with large surface areas are used as supports for heterogeneous FTS catalysts. Mostly used support materials are aluminum oxide, titanium dioxide and silicon dioxide but many others have been used (Borg *et al.* 2007, de la Osa *et al.* 2012, Dry. 1996, Serp *et al.* 2003, Shimura *et al.* 2013, Tristantini *et al.* 2007. Properties expected for the supports are, for example, large surface areas, pore distributions suitable for the size of the Fischer-Tropsch products, chemical and mechanical stability and stability against the water formed in the reaction. When it comes to industrial applications factors such as thermal and mechanical strength and attrition resistivity, these are important properties too (Pham *et al.* 2003). In this work three different supports have been applied; i.e. alumina, titanium dioxide and silicon carbide.

2.6.2 Active metals

As previously mentioned in the paper by Bartholomew (Bartholomew. 2003) the development of FT-catalysts can be divided into iron-age and cobalt-age meaning that the majority of metals used in FTS catalysts are iron (Fe) and cobalt (Co) even if other metals have been proven to have activity in FTS. The reason for this can be found in the amount of energy required for splitting the CO molecules into carbon and oxygen according to reaction 3:

$$CO + 2^* \rightarrow C^* + O^* \qquad \text{(reaction 3)}$$

In the reaction above * denotes the active surface sites on the catalyst.

A plot of catalytic activity against the dissociative CO adsorption energy produces a volcano plot as presented in Fig. 6 (Bligaard *et al.* 2004, Frey. 2008). For elements on the left slope of the volcano plot, e.g. Fe and Re, the removal (desorption) of C and O from the surface to form products is the rate determining step. Adsorption is strong for these elements whereas for elements on the right slope, such as Ni, the dissociation of CO is the rate determining step because of weak adsorption (Bligaard *et al.* 2004). Catalysts with Co or Ru have the highest activity but due to the high price of Ru this metal is most often used as promoter metal only.

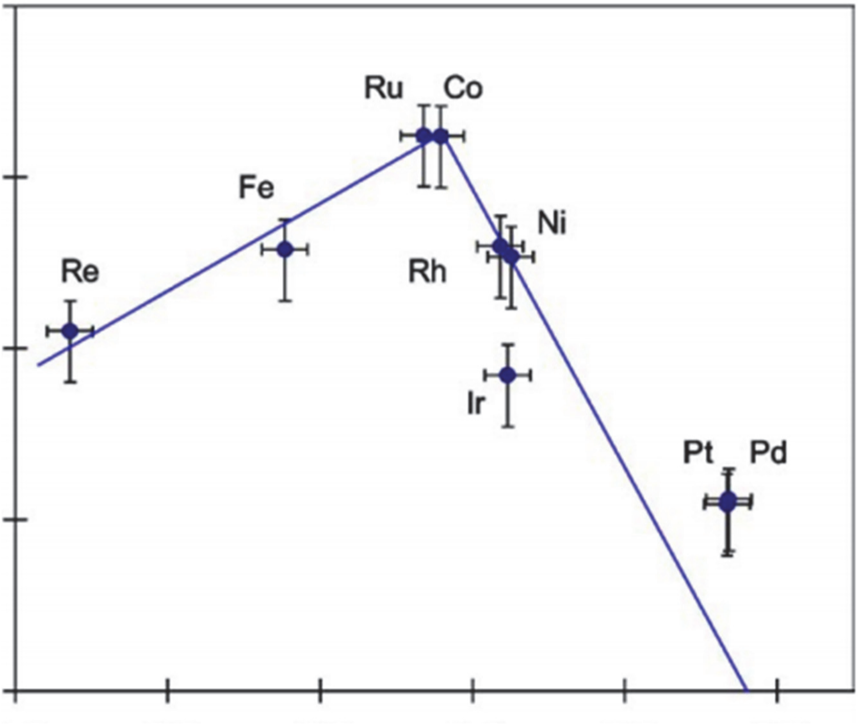

Fig. 6 Volcano plot for the activity of various transition metals used in FTS against the CO dissociative adsorption energy [eV] (reprinted from Bligaard *et al.*, 2004, with permission from Elsevier).

Fe-based catalysts are used at temperatures higher than those used with Co based catalysts. Reaction temperatures of around 350 °C are used with Fe based catalysts for High Temperature FTS (HTFTS) compared to 200-230°C for Low Temperature FTS (LTFTS) with the use of Fe or Co based catalysts. A comparison of HTFTS and LTFTS is presented in Table 7. Fe catalysts produces hydrocarbons and olefins while the cobalt catalyst produces waxes. The oxygen present in the reaction leaves as CO2 with Fe catalysts and as H_2O with Co catalysts.

Table 7. Comparison of High and Low temperature reactions for FTS (Dry 2002, Wender 1996)

Variable	HTFTS	LTFTS
Active metal	Fe	Fe or Co
Reaction temperature, °C	300-350	200-220
Reaction pressure, Bar	20-50	20-50
Reaction product	gasoline	paraffins
	linear low molecular-mass olefins	linear hydrocarbons
	oxygenates	
Oxygen from CO	released as CO_2	released as H_2O

2.6.3 Promoters

Cobalt is known to interact wery strongly with the supports making it rather har to reduce. The main function of addition of promoter metals to cobalt catalysts will make the metal easier to reduce compared to unpromoted catalysts (Morales & Weckhuysen. 2006).

Promoter metals are metals that affect the performance of catalysts. The addition of these metals to the catalyst can make the catalyst more active, more selective and easier to reduce. Promoter metals are added to the catalysts in small quantities, their concentrations are usually less than 0.5 mass-%. The addition of promoter metals can affect the active metal in a number of ways: 1) as a structural promoter, 2) as an electronic promoter to electronically modify the active metal site and 3) as a textural promoter, such as catalyst support and support modifier, which is used typically to increase the dispersion of the clusters, improve attrition resistance and enhance sulphur tolerance.

As promoters are substances, they are most often noble or transition metals but also alkali or earth alkali metals can be used. Promoter metals are added in order to enhance the properties of the catalyst but can also have an effect on the activity and selectivity of catalysts. Some of the metals used as promoters can also enhance the electron flow over the catalyst. Most of the effects due to the addition of promoter metals concerns the activity and stability of the catalysts, whereas only the promoters that affect the electron flow have a positive effect on the selectivity of the catalysts.

Table 8. A summary of the metals used as promoter and the effects of the promoters on the catalysts, modified from (Morales & Weckhuysen. 2006).

Promotion type	Promotion mode	Influence on catalyst			Element reported in literature to play a role in this promotion effect
		Activity	Selectivity	Stability	
Structural	Support stabilization	+		+	Mg, Si. Zr, Nb, Rh, La, Ta, Re, Pt
	Cobalt glueing	+		+	B, Mg, Zr
	Cobalt dispersion increase	+		+	Ti, Cr, Mn, Zr, Mo, Ru, Rh, Pd, Ce, Re, Ir, Pt, Th
Electronic	Decorating cobalt surface	+	+	+	B, Mg, K, Ti; V, Cr, Mn, Zr, Mo, La, Ce, Gd, Th, Ni, Cu, Ru, Pd, Ir, Pt, Re
	Cobalt alloying	+	+	+	Ni, Cu, Ru, Pd, Ir, Pt, Re
Synergistic	Water gas shift		+		B, Mn, Cu, Ce
	Coke burning			+	Ni, Cr, Gd
	H_2S adsorption			+	B, Mn, Zn. Zr, Mo

2.7 Dispersion of the cobalt metal

A heterogeneous catalytic reaction is a surface reaction where the gaseous or liquid reactants react on the surface of a solid supported catalyst or catalytic metal. An increase in the surface of the active metals will increase the catalytic activity, i.e. the reaction rates of the chemical reactions.

The active metal is usually present at solid crystals on the support. The catalytic reaction takes part on the surface atoms of this crystal while the bulk atoms are unreactive. The proportion of surface Co0 atoms to the total number of atoms of the active metal is called dispersion (Cook *et al.* 2012, de la Osa *et al.* 2012b, Okal *et al.* 2007, Yu *et al.* 2013). The portion of surface atoms increases with decreasing particle size while the addition of small amounts of promoter metals has been proven to increase the dispersion of cobalt in Fischer-Tropsch catalysts (Morales & Weckhuysen. 2006).

The activity and also the selectivity of catalysts for FTS is related to the size of the Co crystals within certain particle sizes. Using catalysts with Co particles 10 to 200 nm in size the FTS activity is independent on the size of the Co particles (Borg *et al.* 2008, Rytter *et al.* 2007, Shetty & van Santen. 2011, Storsæter *et al.* 2005). Furthermore, the selectivity against C_{5+} is rather independent of the particle size in the region 10-200 nm even if a slightly increased selectivity against CH_4 has been observed for the largest particles of 200 nm (Storsæter *et al.* 2005).

When it comes to smaller Co-particles from 1 to 10 nm there seems to be a linear relationship between the activity of the catalysts and the particle size (Borg *et al.* 2008). On the other hand, opposite effects have been reported by other researchers (den Breejen *et al.* 2009). The differences in data might be a result of the fact that when it comes to small particles less than 10 nm in size, it is difficult to separate the effects of metallic particles and the effects from the supports used (Frey. 2008). One possible solution to this is that the effects of the supports can be eliminated using model systems with carbon nanotubes as support (Bezemer *et al.* 2006, den Breejen *et al.* 2009).

This size effect can be explained with the fact that the most active parts of the crystal are those with high coordination numbers such as corners, steps or dislocations at the crystal surface which are not present if the crystals are too small. The effect of steps and corners on the dissociation of CO on Rh surfaces have been previously investigated by (Mavrikakis *et al.* 2002).

3 Experimental

3.1 Tar sampling and chromatographic analysis of tars

A number of techniques for the collection of tars from producer gas have been used, including among others; gravimetric, fluorometric and chromatographic methods (Baumhakl & Karellas. 2011). In most of these methods tars are absorbed into some solvent before being analysed.

In order to unify tar measurements and to make the results easier to compare, a common method for collection was developed. This method is known as the "Tar protocol" or as the "European Tar protocol" (CEN/TS 15439. 2006, Good *et al.* 2005, Simell *et al.* 1997). According to the Tar protocol, the producer gas from the gasifier is passed with a known gas flow through six impinger bottles (see Fig. 7). Five of these bottles (bottles 1-5) contain 2-propanol (isopropanol, IPA) as an absorbing solution while bottle 6 is an empty bottle used for condensation only. Three of the bottles (bottles 1, 2 and 4) are kept at -20 °C and the remaining three are kept at +30°C (bottles 3, 5 and 6).

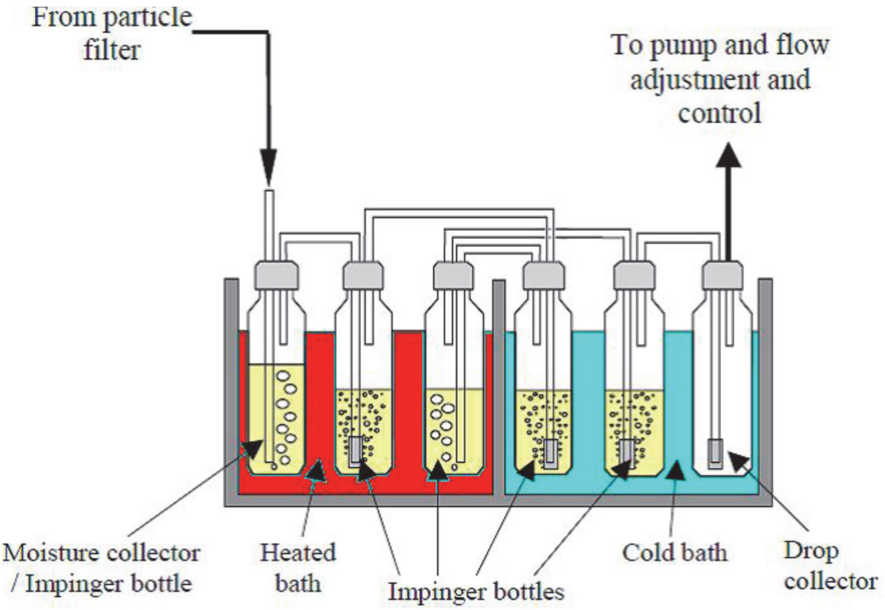

Fig. 7 Set-up of the unit used for tar collection, modified from (Good *et al.* 2005).

In this study the Tar protocol is applied for collection and determination of tar compounds in the producer gas from biomass (wood chips) gasification. Tar sampling was performed on two different small-scale downdraft gasifiers A and B. Each gasifier had a capacity of 150 kW and was operated at 1100-1200 °C. Producer gas from gasifier A was cleaned by passing the gas through a filter bed of woodchips and samples were taken after the cleaning unit. In gasifier B, the gas was cleaned by passing it through a water scrubber wet filter while gas samples were taken from both the raw gas and after the cleaning unit.

After gas collection the contents of all bottles were combined, bottles were washed with IPA and the resulting solution was made-up to a known volume. For quantitative determinations a known amount of internal standard (o-terphenyl) was added before finally adding IPA to create a known volume.

Individual tar compounds were separated on a gas-chromatograph equipped with a mass spectrometry detector (GC-MS). Before chemical analysis, samples were stored light protected at +5 °C. Aliquots of the combined solution were transferred to autosampler bottles and analyzed with GC-MS using the parameters presented in Table 9. Compounds were identified from their fragmentation patterns against a NIST traceable library.

Table 9. Setup of and parameters for the GC-MS system used for tar analysis.

Instrument	Agilent 7890
Detector	Agilent MSD 5975C
Column	HP-5MS 30 m * 250 μm * 0,25 μm
	(5%-Phenyl)-methylpolysiloxane
Injector	Split 1:50, 1 μl injected
	300 °C
Oven program	40 °C 3 min hold
	5 °C/min to 300°C, 10 minutes hold
Carrier gas	He 1 ml/min.

Quantitation was made using the peak areas for individual peaks to the area of the known internal standard. The appearance of each individual tar compound (given as % area) was calculated by dividing individual peak areas with the total peak area. Tar sampling and analysis procedure is described in detail in Paper I.

3.2 Catalysts used in the study

Catalysts used in this study were supported onto three different supports. The main support was alumina (Al_2O_3) Puralox SCCa (Sasol, Germany). This support was used in all studies except Paper II where bimodal alumina in a pelleted form was used. Bimodal Al_2O_3 pellets were provided by AlphaAesar. In Papers III, IV and V, supports used were silicon carbide (SiC, SicCatalysts) and titanium dioxide (TiO_2, Degussa P25) beside alumina. Common properties for all the supports are a large surface area and a pore distribution suitable for Fischer-Tropsch synthesis.

All catalysts used in this study were prepared by a one-step incipient wetness impregnation or by pore impregnation (Haber *et al.* 1995). Individual metal precursor salts were dissolved in distilled water in volumes equal to the pore volumes of the support. Prior to impregnation the supports were dried at 80 °C for 1-2 hours. The dissolved precursor and dried supports were combined and mixed continuously for 16 hours.

Table 10. Properties of catalyst supports used in this thesis (information given by the suppliers).

Support		Surface area m^2/g	Pore volume cm^3/g	Average pore diameter nm	Used in paper
Al2O3	Sasol Puralox SSCa	195	0.52	10.6	II-IV
Al2O3	Alpha Aesar1/8" pellets, bimodal	255	1.14	7 500	II
SiC	Sicat β-SiC UHP3 LO	25	0.15	24.0	IV,V
TiO2	Degussa Aerosile P-25	54	0.18	13.5	IV,V

Following impregnations the catalysts were dried, first at 60 °C at a sub atmospheric pressure followed by drying at 105 °C for 2-3 hours. Dried catalysts were crushed in a mortar and sieved. Fractions between 50 and 100 μm were collected and calcined for 16 hours at 420 °C with an initial temperature ramp of 100 °C/hour in order to decompose the precursor. The sieving procedure was not performed on the pelleted catalysts used in Paper II. Finally, catalysts were reduced in a flow of hydrogen (100 % H_2) at 350 °C for 16 hours. The reductions were performed in the reactor tube prior to activity and selectivity tests. A summary of the catalyst preparation is presented in Fig. 8.

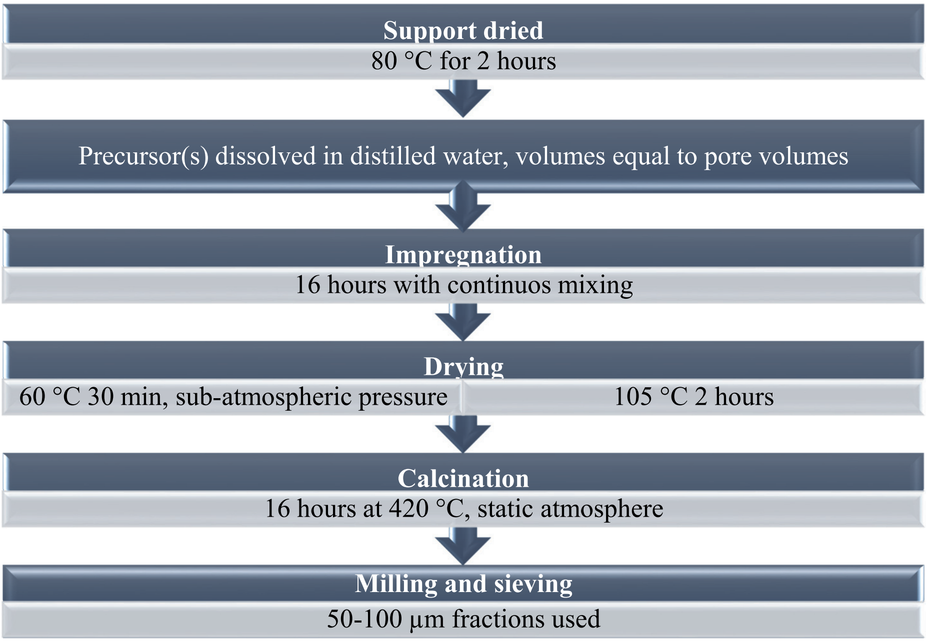

Fig. 8 Flow diagram for the preparation of catalysts used in Papers III-V.

3.3 Methods used for catalyst characterisation

The catalysts used in this thesis have been characterized by a number of experimental techniques including microscopy and spectroscopy methods as well as activity and selectivity measurements (Papers II-IV).

3.3.1 Metal content

Metals were added to the catalysts during impregnations. In order to confirm the metal content in the catalyst, small portions of the catalysts were dissolved in a mixture of HCl-HNO_3 and the resulting solutions were diluted and analysed for metal contents by Inductively Coupled Plasma (ICP-OES).

3.3.2 Surface areas and pore distributions

Surface areas of calcined supports and catalysts were measured according to the BET-method (Brunauer *et al.* 1938) using nitrogen as the adsorbate (Papers II-V). A portion of each sample was weighed into a measuring glass whilst prior to analysis, samples were evacuated and heated in order to remove any adsorbed components and moisture. Measurements were then performed under isothermal conditions by immersing the sample holder into liquid nitrogen. Samples were evacuated and pulses of nitrogen were added. BET surface areas were then calculated from the obtained adsorption isotherms. Pore distributions of the supports and catalysts were calculated from the adsorption isotherms using the BJH method.

3.3.3 Dispersion of active metal and size of metal

Metal dispersion and metal particle sizes were measured on calcined samples by chemisorption of carbon monoxide (CO) assuming a stoichiometric ratio of 1:1 between cobalt particles and adsorbent. A portion of each sample (about 100 mg) was weight into a U-shaped quarts tube in which the sample was supported on both sides by quartz wool. Instrumental parameters used for the chemisorption measurements are given in Table 11. Small pulses of CO were added to the catalysts and adsorbed onto the Co surface. The quantity of gas adsorbed was plotted as a function of the pressures used. As a result of this, metal dispersions and sizes of the Co metal particles were calculated using adsorption data (isotherms) from the pressure rise (direct measurement) and from the difference between pressure rise and pressure drop (difference measurement). Metal dispersions and sizes of the Co metal particles were calculated from the obtained data assuming a stoichiometry of 1:2 between CO and cobalt.

Table 11. Steps included in the CO chemisorption analysis for Co catalysts.

Task Number	Task Name	Gas	Temp (°C)	Rate (°C/min)	Time (min)
1	Evacuation	He	110	10.0	30
2	Flow	H_2	100	10.0	10
3	Flow	H_2	350	10.0	120
4	Evacuation		350	10.0	120
5	Evacuation		40	10.0	120
6	Leak Test		40	10.0	
7	Evacuation		40	10.0	20
8	Analysis	CO	40	10.0	

3.3.4 Chemical and electronic state of the metals and supports

X-ray photoelectron spectroscopy (XPS) analysis (in Paper IV) was performed using a Thermo Fischer Scientific ESCALAB 250Xi XPS System at the Center of Microscopy and Nanotechnology, University of Oulu (Finland). The catalyst samples were placed on Indium film and passed with an energy of 20 eV: spot size of 900µm (accuracy of the reported binding energy was ±0.2 eV). Al, O, Co, Re or Ru, C, In and N were measured for all samples. Measurement data was analysed by a Casa XPS Version 2.3.16 PR 1.6 while C1s (284.6 eV) was used as a standard reference for the calibration of all the samples.

3.3.5 Reducibility of cobalt particles

H_2-TPR measurements (in Paper IV) were performed on a Quantachrome 3000 using 7% H_2 in Ar as the reducing gas. Prior to analysis the samples were dried at 105 °C for 2 hours. Measurements were performed by weighing 100 mg of each catalyst into a U-shaped quartz tube equipped with a temperature sensor. The temperature inside the reactor was increased from 50 °C to 800 °C with a rise of 10 °C /min. The signal from the TC-detector and the reactor temperature were plotted against the reaction time. Temperature programmed reduction (TPR) was performed on a series of promoted catalysts supported on Al_2O_3, SiC and TiO_2. Ruthenium or rhenium were used as the promoting metals in concentrations of 0, 0.2 or 1.0 mass%. Prior to analysis catalysts were dried at 105°C for 2 hours.

3.3.6 Determination of the degree of reduction

The degree of reduction for the Ru and Rh promoted catalysts were measured by reoxidation of reduced catalysts. Small portions, about 25 mg, of each catalyst were weighed into a quartz tube. The samples were dried at 100°C for 1 hour and then reduced for 1 hour at 350°C in a flow of 10% H_2 in Ar according to reactions (1) and The degree of reduction for the Ru and Rh promoted catalysts were measured by reoxidation of reduced catalysts. Small portions, about 25 mg, of each catalyst were weighed into a quartz tube. The samples were dried at 100°C for 1 hour and then reduced for 1 hour at 350°C in a flow of 10% H_2 in Ar according to reactions (1) and (2). Co surface was rinsed with He flow until the signal from the TCD detector returned to the baseline. Small pulses (1 ml each) of oxygen (5% in He) were added until the area of the signals from the TCD-detector with a constant area were obtained. Between the pulses the signal was allowed to return to baseline before applying the next pulse.

The degree of reduction was calculated from the moles of oxygen consumed assuming that all Co^0 was oxidized to Co_3O_4 according to reaction (3) compared to the amount of oxygen theoretically needed for a complete re-oxidation of Co^0. Any oxidation of the promoter metals or other reductions/ oxidations of other Co-species were not considered in the calculations.

$$Co_3O_4 + H_2 \rightarrow 3CoO + H_2O$$
$$CoO + H_2 \rightarrow Co^0 + H_2O$$
$$3Co^0 + 2O_2 \rightarrow Co_3O_4$$

3.3.7 Determination of catalytic activity and selectivity

A fixed bed reactor was constructed for activity and selectivity tests (Papers II, IV-V). In short; gas was fed to the reactor over mass flow controllers, pressure was measured prior to the reactor tube and was regulated by a needle valve post reactor. The reactor itself was a stainless steel tube 10 mm ID kept in a tubular oven with three heating zones controlled by a controller unit. Products formed during the reactor were collected in two traps; one heated to 85 °C for heavy waxes and water, the other trap was kept at room temperature for lighter compounds. Gaseous compounds exiting from the traps were measured for permanent gases (CO, H_2, CO_2, N_2 and CH_4 and light hydrocarbons (C_1-C_7) on a gas chromatograph connected online after the reactor. Temperatures of the catalytic bed were measured with a movable thermoelement placed inside a pocket in the middle of the catalytic bed.

Reaction gases were fed from gas cylinders; in the early experiments as separate gases and later on from a special gas mixture containing CO, H_2 and N_2; CO and H_2 were present in the feed gas at a ratio of 1:2, N_2 (internal standard) had a concentration of 3.1 volume %. Conversion levels were calculated during the experiments from the ratio of peak areas of CO and N_2.

For activity and selectivity tests 1 g of each catalyst, sieved to a particle size of 50-100 µm; was mixed with 16 grams of silicon carbide (SiC). The mixture was placed in a fixed bed reactor and supported by glass wool.

Catalysts were reduced prior to tests in the reactor tube in a flow of hydrogen for 16 hour at a temperature of 340 °C. After reduction temperature of the catalyst bed was lowered to 190 °C and the reactor was pressurized with nitrogen to give a pressure reading of 20 Bar. At a pressure of 20 bar the gas was switched to synthetic syngas. The reactor temperature was slowly increased; first to 200 °C with a temperature rise of 5 °C/min), the final reaction temperature (220 in paper II or 210 °C in paper IV and V) was reach by manual increments of the temperature in 0.1 °C steps.

In the early experiments presented in paper II the catalytic reactor was operated at a maximum pressure of 10 bar, usually a pressure 9 bar was used. Later on the reactor was rebuilt and operated at 20 bars (papers IV-V). The different conditions are compared in Table 12.

The reactor was kept at 210 °C for 24 hours with a gas flow of 250 ml gas/min, after which the stabilisation period conversion level was set to 50% by decreasing the gas flow. The reaction continued for another 24 hours at a conversion level of 50%. Activity and selectivity were calculated from the gas chromatographic data obtained from the on-line gas chromatograph.

Table 12. Reaction pressures and gas feeds used.

Reaction pressure bar	Gas feed initial cm^3/min	Gas feed reaction cm^3/min	Used in paper
9-10	50 H_2 25 CO	50 H_2 25 CO	II
20	250 ml Syngas	50% conversion	IV-V

4 Results and discussion

Tar analysis

4.1 Determination of tars in producer gas

In order to predict the need for producer gas cleaning for catalytic conversion into traffic fuels and chemicals the gas has to be accurately characterized and defined. In this study tar compounds in producer gas from two small scale downdraft gasifiers are collected, identified and quantified.

The tar determination procedure used is presented in detail in Paper I, in summary gas samples were withdrawn in duplicates from two different down-draft gasifiers operating at temperatures of 1100-1250°C.

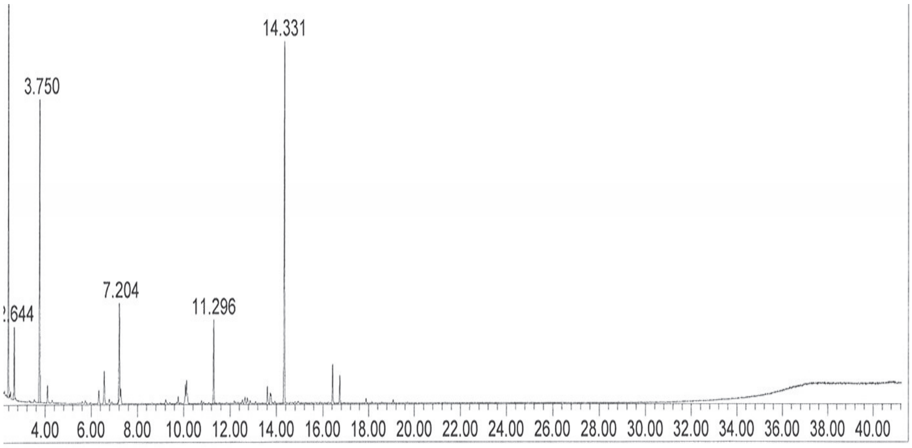

Fig. 9 A typical chromatogram obtained from GC-MS analysis of sampled tars (from gasifier A). The main peaks are RT 2.38 min, benzene, RT 2.64 min, unknown; 3.75 min toluene, 7.20 min styrene, 11.29 min indene, 14.33 min naphthalene.

From the results obtained, there are only few major tar compounds present in the producer gas after the water scrubbing unit “water scrubber” which is used as a purification unit in gasifier B. Toluene and naphthalene are the most abundant tar compounds detected in the gas samples. These two compounds represent together about 70% of total mass of the measured tars in the samples. This is consistent with the results presented by (Gautam *et al.* 2011) who concluded that toluene (28%) and naphthalene (18%) were the main components from the down-draft gasifier.

No phenolic compounds nor any polyaromatic compounds were detected under the collection and analysis procedures used; this finding can be compared to the findings of (Gautam *et al.* 2011) who reported phenolic compounds at levels ranging between 7 and 70 mg/dm^3. Of the GC-detected and identified compounds 89% were aromatic 1-ring compounds and 11% were aromatic 2-ring compounds.

The concentration of GC-detectable, identified tar compounds was 211 mg/m^3, the concentration of GC-detected but unidentified tar compounds was 27 mg/m^3. The results obtained can be compared with the results by (Jordan & Akay. 2012) who reported a tar concentration of 378 mg/m^3 for a small scale (50kW) airblown gasifier.

For one of the gasifiers, the effect of gas cleaning using a wet-scrubber was tested. This cleaning procedure had some effect on the organic compounds benzene and toluene, the other main compounds that appear to accumulate in the cleaner as presented in Fig. 10.

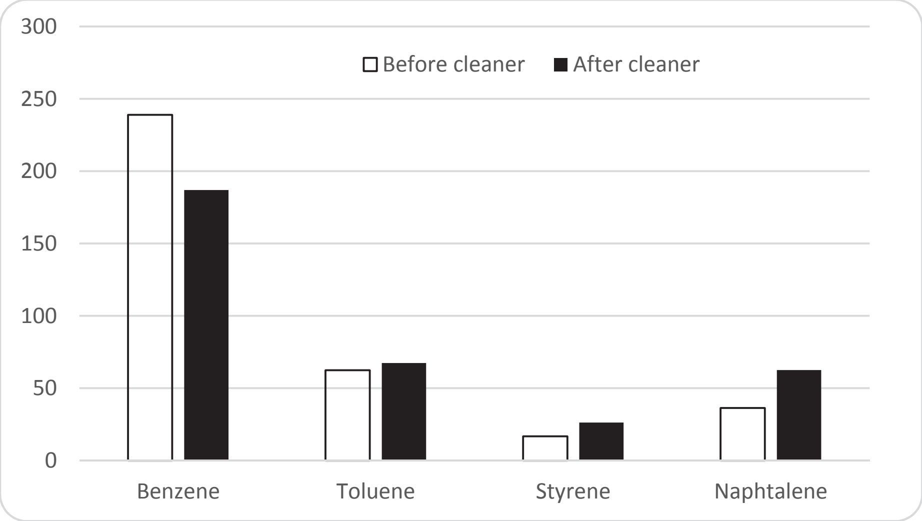

Fig. 10 Concentrations (mg/m^3) of some major tar components before and after the gas-cleaner stage used in gasifier B.

Tars are very difficult to sample and analyse resulting in many research groups developing their own analysis methods, which makes it difficult to compare results.

To avoid this discrepancy, we have adopted the Tar Protocol for the sampling and analysis of tars in this study.

The tar levels obtained in this study are in line with the results of (Gautam *et al.* 2011, Xu *et al.* 2010) or 376 mg/m^3 whose samples were obtained from a gasifier of about the same size as the ones used in this study. Normally much higher tar levels have been reported (Tuomi *et al.* 2015) but in most of these cases larger gasifiers have been used. It is not surprising that there is no or little change in the tar levels before and after the water cleaner for gasifier B. Because of the aromatic nature of tars water is not regarded as the best solvent for tar-removal. The water cleaner can however be used for removal of polar substances like phenols present in the producer gas as described by (Kurkela *et al.* 2000).

In this study no phenolic tar compounds were detected. According to the maturations scheme presented in Table 2 phenolic tar compounds are formed in temperatures ranging from 500 to 600 °C. The high gasification temperatures used in this study might be the reason for this observation.

The measured tar levels are still much higher than the maximum levels suggested for catalytic purposes. In order to use the gas for catalytic conversion the tar level has to be strongly reduced by either physical removal of the tars or by catalytic cracking of the compounds.

Catalytic cracking may be a better option since it will result in an increased level of hydrogen and carbon monoxide in the synthesis gas (Shen & Yoshikawa. 2013b, Xu *et al.* 2010). This route provides the subject for future investigations.

Catalysts and catalyst characterization

A summary of the catalysts prepared, characterized and used in papers II-IV is presented in Table 13

Table 13. Catalysts prepared and used in this thesis.

Metal	Concentration %	Precursor	Promoter	Precursor	Concentrations %	Support*	Used in paper
Co	20	$Co(NO_3)_3$* $6H_2O$	Ru	$Ru(NO)(NO_3)_3$	0,5	Al_2O_3	III
Co	20	$Co(NO_3)_3$* $6H_2O$	Re	$HReO_4$	0,5	Al_2O_3	III
Co	20	$Co(NO_3)_3$* $6H_2O$	Rh	$Rh(NO_3)3$	0,5	Al_2O_3	III
Co	20, 15	$Co(NO_3)_3$* $6H_2O$	Ru	$Ru(NO)(NO_3)_3$	0, 0.2, 1.0	Al_2O_3, TiO_2, SiC	II, IV, V
Co	20, 15		Re	$HReO_4$	0, 0.2, 1.0	Al_2O_3, TiO_2, SiC	IV, V
Co	20	$Co(CH_3COOH)_2$	Ru	$RuCl_3$	1	$Al_2O_{3(p)}$	II
Fe	20	$Fe(NO_3)_3$	Ru	$RuCl_3$	0, 0.1	$Al_2O_{3(p)}$	II
Co	20	$Co(NO_3)_3$* $6H_2O$	Ru	$Ru(NO)(NO_3)_3$	2	$Al_2O_{3(p)}$	II
Co	20	$Co(CH_3COOH)_2$	Ru	$Ru(NO)(NO_3)_3$	0.2	Al_2O_3	II
Co/Fe	10/10	$Co(NO_3)_3$* $6H_2O$ $Fe(NO_3)_3$				Al_2O_3	
Co	20	$Co(CH_3COOH)_2$	Ru	$Ru(NO)(NO_3)_3$	1	Al_2O_3	II
Co	20	$Co(CH_3COOH)_2$	Ru	$RuCl_3$	1	Al_2O_3, $Al_2O_{3(p)}$	II
Co	20	$Co(NO_3)_3$* $6H_2O$	Ru	$RuCl_3$	1	Al_2O_3	II
Co	20	$Co(NO_3)_3$* $6H_2O$	Ru	$Ru(NO)(NO_3)_3$	1	Al_2O_3-SiO_2	II

4.2 Effect of support

In this research several Co and Fe catalysts were prepared and tested in the hydrogenation of CO. Catalytic activities were also tested using a gas mixture that simulates gas from biomass gasification. Different supports were tested, i.e. one pelleted γ-Al_2O_3, bimodal with both large and small pores, 7 nm and 500 nm, (support A, provided by Alfa Aesar), one small-particle γ-Al_2O_3 with small pores, 4-10 nm, (support B, Puralox SSCa provided by Sasol) and one small-particle Al_2O_3-SiO_2 (60% Al_2O_3-40% SiO_2, Sisal 40 provided by Sasol) with small pores (4-10 nm).

Catalysts used in this study were Ru promoted Co catalysts, Ru promoted Fe catalysts and mixed Co/Fe-catalysts. In these experiments the reactor was pressurized to 9 bar. The catalysts tested and operating conditions used are presented in Paper II.

In figure 2a of Paper II the effect of the bimodal support can be seen, showing an unusual, non-linear distribution of the produced waxes as measured by the GC-MS. The catalyst used in this experiment war a Ru-promoted Fe-catalyst (10 mass-% Fe, 0.1 mass-% Ru). The reason for this distribution can most likely be explained by the biomodal pore structure of the support containing pores of 7 nm and 500 nm as described by (Borg *et al.* 2009). Most likely different products are formed in the small 7 nm and the larger 500 nm pores. Alternatively different sizes of the active metal are formed in the pores.

Some time-dependent changes in the behavior of the catalyst could be observed as presented in Figure 3 in Paper II. There is a lower production of longer carbon chains (C_{10}-C_{18}) and an increased production of short carbon chains (C_7-C_8) after 48 hours on-stream compared to the results obtained at 24 hours on-stream. The results were obtained with an unpromoted catalyst containing 20 mass-% Co supported on Puralox SSCa. The reason for this change can be some time-dependent change of the catalyst surface. This phenomena was not studied for the other catalyst where the products were collected after completing the reaction only.

Calcination and reduction temperatures used in Paper II were most likely too high, there is an obvious risk that under the preparation conditions used the catalysts produced were not the most active ones. The yield in form of liquid waxes from these first experiments were collected but the gaseous compounds could not be measured.

XRD results for the Re promoted cobalt catalysts supported on Al_2O_3 are presented in Paper V. Pure Al_2O_3 calcined at 420 °C for 16 hours was used as a reference material and had a surface area of 195 m^2/g. The Al_2O_3 support material was proved to be γ-Al_2O_3 with a face-centered cubic phase Fd-3m according to standard JCPDS card no. 00-50-0741. The 2θ peaks at 32°, 38°, 39° and 46° correspond to the (220), (311), (222) and (400) reflections of γ-Al_2O_3, respectively. Furthermore, the peaks of alumina were broad which denoted a nano-sized material whilst the calculated crystallize size from the XRD pattern was 8.1 nm for pure Al_2O_3.

The sample A20 with Co impregnation only has two high 2θ peaks at 36.8° and 42.7°, which correspond to CoO (111) and CoO (200) according to face-centered cubic CoO (Fm3m) (JCPDS card no. 00-71-1178). There is also a shoulder between CoO (200) and Al_2O_3 (400), which may be caused by the (111) reflection of cubic cobalt (2θ of 44.3°) being merged with Al_2O_3 (400) (2θ of 45.7°) and CoO (200) (2θ of 42.8°). Therefore, we can assume metal Co may also exist according to the Co pattern (JCPDS 04-014-0167).

For other catalysts samples containing the Re promoter, the Co (111) peak can be identified more easily. For A20Re1 and A15Re1 catalysts which have a higher Re content of 1 wt%, the peaks are overlapped and merged together while a larger shoulder can be identified between the CoO (111) and Al_2O_3 (400) peaks. However, Re reflections were difficult to identify because of the low concentration (≤1 wt%) and the strongest 2θ peak at 42.9° of Re (101) (JCPDS card no. 01-071-6589) mixing with CoO (200) at 42.4°.

For Ru promoted cobalt catalysts samples with Al_2O_3 supports, the XRD patterns were quite similar to the Re promoted samples (Figure 3b, Paper V). Both Co and CoO were presented in the samples because Co (111) and CoO (111) can be identified from the patterns. However, the peaks of Ru were difficult to identify since the concentration of Ru is relatively low (≤1 wt%) and the strongest peak of Ru (101) at 44.0° is mixing with Co (111) (2θ of 44.3°) according to JCPDS card no. 00-006-0663 of hexagonal Ruthenium.

XRD spectra for TiO_2 supported catalyst samples are shown in Figure 4, Paper V. The pure TiO_2 support material contains two phases which is a mixture of 85 wt % anatase with a body-centered tetragonal phase (JCPDS card no. 01-070-6826) and 15 wt% of rutile with its tetragonal phase (JCPDS card no. 01-089-4920). Calculated crystallize size from the XRD pattern was 16 nm for pure TiO_2. The reflections of the strongest peak (111) of cubic cobalt (JCPDS card no. 04-014-0167) can be clearly observed at 44.3° for the four TiO_2 supported catalyst samples. Re (101) with 2θ of 42.9° or Ru (101) at 44.0° were not identified due to their low concentrations.

XRD spectra for SiC supported catalysts are shown in Figure 5, Paper V. For pure SiC, the XRD patterns matches very well with hexagonal silicon carbide of JCPDS card no. 00-049-1428. It is clear to see the five peaks at 2θ of 34.1, 35.65, 38.1, 41.4 and 60.0 which corresponds to (101), (102), (103), (104) and (108) of the hexagonal silicate phases. Calculated crystallize size from Equation (1) was 26 nm for pure SiC. For all the SiC supported cobalt catalysts samples, it is obviously that an observed peak at 2θ of 44.3° corresponds to Co (111), the highest peak of cubic cobalt, according to JCPDS card no. 04-014-0167. One small peak at 47.4° can also be detected and its intensity varied for different samples, which may correspond to the highest peak of hexagonal Co (101) according to JCPDS card no. 01-071-4239.

4.3 Effect of promoter metals on the dispersion and reducibility of cobalt

A number of cobalt catalysts for Fischer-Tropsch synthesis were considered in the study, prepared by impregnation of cobalt precursors in two different concentrations on to alumina oxide. Rhenium or ruthenium was added to some of the catalysts as promoter metals in different concentrations ranging from 0 to 0.2 mass-%. The catalysts were characterized by a number of methods such as BET, chemisorption, SEM, TEM and XRD in order to investigate the interactions between support and the active metal and also the effect that occurs from the addition of promoting metals. Some of the most promising catalysts according to characterizations were tested for activity and selectivity in the Fischer-Tropsch reaction. The effects that occur from the addition of these promoter metals on the dispersion of the cobalt metal and the reducibility of the cobalt (Co_3O_4) are investigated in Papers IV and V

4.3.1 Dispersion and size of Co particles

The addition of Ru and Re as promoters to supported Co catalysts had an obvious effect on the particle size of the Co particles and on the dispersions of Co. From the results obtained an increase in the dispersion of the metallic cobalt particles could be observed and as an effect of increased dispersion, the particles were smaller in the promoted catalyst. This dispersion effect can be observed for all supports used in this study even if it was more pronounced for the catalysts supported by alumina.

A summary of the effects of promoter addition on the dispersion of Co particles and on the size of the same particles can be seen in Table 1, Paper V.

4.3.2 Reducibility

The resulting effect from the addition of two different promoters (Re and Ru) on the reduction of cobalt oxide (Co_3O_4) into metallic Co^0 was studied in Paper IV which also included detailed data on the measurements. The reduction of Co_3O_4 into Co^0 proceeds in two separate steps, each step is represented by a distinct peak in the TPR spectra. Remaining nitrate (reduced to NH_4) could be seen as an early peak in some of the TPR spectra. The interaction between the support and the metal oxides had a strong influence on the reducibility of the cobalt oxide, this interaction can be seen from the fact that the reduction process, especially when Co was supported on Al_2O_3, was not complete even at 800°C for some of the tested catalysts.

The addition of Re as the promoter metal shifted the first peak representing the reduction step Co_3O_4 to CoO to lower temperatures as presented in Fig. 2 in Paper IV whereas, the addition of Ru as the promoter metal shifted both peaks. The second peak represents the reduction step of CoO into Co^0 to lower temperatures, again presented in Fig. 2 in paper IV. A summary of these temperature shifts are presented in Table 14 and in Table 2 of Paper IV.

Table 14. Temperature shifts for the reduction of Co in Ru and Re promoted Co catalysts (only catalysts with 20 mass-% Co shown).

Catalyst	Co3O4→CoO	CoO→Co0
A20	450	540
A20Re0.2	410	690
A20Ru0.2	325	650
S20	425	500
S20Re0.2	425	500
S20Ru0.2	300	450
T20	450	575
T20Re0.2	390	460
T20Ru0.2	310	500

4.4 Effect of promoter addition and the calcination conditions on the degree of reduction

A number of catalysts from the previous serie of catalysts promoted with Ru or Rh were calcined at different conditions as presented in Table 13. According to the results no direct correlation between particle size and the degree of reduction even if the highest degree of reduction (82%) is achieved with one of the smallest particles. This high degree of reduction (82%) was measured on a Rh promoted catalyst calcined in an air flow at 400 °C, having a Co particle size of 12 nm.

Table 15. Results from the measurement of the degree of reduction performed as back-oxidation of reduced catalysts.

Catalyst	Promoter	Gas atmospehre	Calcination temperature	Particle size	Degree of reduction
Co-Rh	Rh	ambient	350	13	33 %
Co-Ru	Ru	air	450	12	48 %
Co-Rh	Rh	air	400	12	82 %
Co-Ru	Ru	air	400	13	37 %
Co-Rh	Rh	N_2	350	13	65 %
Co-Rh	Rh	ambient	450	15	39 %
Co-Ru	Ru	ambient	400	15	55 %
Co-Ru	Ru	N_2	350	n.d.	51 %
Co-Ru	Ru	ambient	350	15	62 %
Co-Rh	Rh	air	450	n.d	43 %
Co-Rh	Rh	air	350	n.d	55 %
Co-Ru	Ru	air	350	n.d	49 %
Co-Ru	Ru	N_2	450	14	42 %

4.5 Effect of calcination conditions and the addition of promoters on the dispersion of cobalt

The effects of catalyst calcination conditions, such as temperature and gas phase composition on the dispersion of cobalt particles over Co/γ-Al_2O_3 catalysts were studied. A number of catalysts were prepared by incipient wetness impregnation of cobalt onto γ- Al_2O_3 and promoted with ruthenium, rhenium and rhodium respectively. Metal dispersions of active metals were studied by chemisorption of carbon monoxide. According to the results, calcination conditions had an effect on the catalytic properties, as expected. The highest dispersion for the Co/γ-Al_2O_3 catalyst was achieved by calcination at 400 °C in a N_2 flow. Co metal dispersion also seems to be increased after the calcination steps if a flowing gas was used instead of static calcination conditions.

In this study the effects of calcination conditions were also investigated on a series of Co catalysts supported on Al_2O_3, in which their resulting effects were measured as changes in the size of the Co particles and as the dispersion of the metallic Co. The calcination conditions are described in detail in Paper III.

Although Co metal dispersions were low, values between 4.4 and 8.0 % were measured for all calcined catalysts which is consistent with earlier results reported for FT catalysts prepared using cobalt nitrate as the precursor and water as the solvent (Borg *et al.* 2008, Iglesia. 1997). Based on the results, calcination of the catalyst in a flow of nitrogen gas significantly decreased the size of the Co particles compared with calcination in air in the static system.

Highest dispersion (8.4%) were obtained at a calcination temperature of 400 °C in an atmosphere of flowing nitrogen for Rh promoted catalysis. Almost similar results (8.0%) were obtained Re and Ru promoted catalysts under the same conditions. These dispersion correspond to particle sizes of 11.4 and 12 nm respectively and a surface area of 13.4, and 11 m2/g.

Catalysts calcined under static conditions in an atmosphere of air had the lowest dispersions independent of the promoter used. Using flowing gas during the calcination step will make a clear increase in the dispersion of the active metal (cobalt). The addition of promoter metals like Ru, Re or Rh also enhances the dispersion of the active metal. Of these promoter metals Re and Ru are known to be structural and at least in the case of Ru also electronic promoters. A summary of the results can be found in Tables 2-4 in paper III.

4.6 Summary of the results

The active metals in the Fischer-Tropsch catalysts prepared in this study are in bounded to the oxide supports Al_2O_3, SiC and TiO_2 used. The supports are present as oxides as measured by the XRD measurements. The active metal is present both as Co and CoO in the catalysts even if some reoxidation might happen after the reduction step prior to the measurement. The effect of different supports can be seen in the particle sizes of the cobalt particles. An addition of promoter metal reduces the size of the cobalt particle to a size in the region were catalytic activity is independent of particle size. Catalyst calcination under a flow of gas reduces the size of the cobalt particles. The activity and selectivity of the tested catalysts can be compared to the results of commercial FT-catalysts.

5 Summary and conclusions

Throughout the course of this experimental work and the writing of this thesis, main research questions were, and still are:

1. What are the tar compounds from the small-scale biomass (wood chips) gasifier and at which concentration level they appear?
2. How the catalyst preparation and calcination conditions affect the dispersion of active metal?
3. How the promoter metals and different supports affect catalyst properties?

As presented in this thesis, the thermal treatment of biomass (gasification) followed by a proper gas cleaning and a catalytic conversion of the resulting synthesis gas into chemicals or traffic fuels is a series of complex processes and chemical reactions.

The formation of polluting compounds and especially tars has often been regarded as the Achilles heel in the use of biomass for catalytic production of traffic fuels and chemicals. Tars can be removed by a number of methods but these methods will increase the costs of gas cleaning equipment making the whole process much more expensive. Therefore, new types of catalysts must be developed that are less sensitive to pollutants and that can perform tar cracking and convert tars into hydrogen and carbon monoxide with the aid of a selective FTS activity. This in turn could make the whole FTS process more feasible.

For the sampling of tar compounds and chromatographic conditions used in this research according to the Tar -protocol, no or only trace levels of heavier tar compounds could be detected in the gas from biomass gasifier. According to the maturation scheme (described earlier in Table 5), a high gasification temperature (>900 °C)produces producer gas containing more polycyclic aromatics whereas producer gas produced at lower temperatures contain more phenolic compounds. In this research, these polyaromatic compounds were not detected under the collection and analysis procedures used. Due to the nature of the polycyclic aromatics (as described in Table 6), these compounds will easily condensate on surfaces even at low concentrations and high temperatures, and so they will not appear in the chromatograms.

Tar levels obtained in this study are consistent with earlier studies concerning small scale gasifiers (Gautam *et al.* 2011), even if no phenolic components nor heavier tars could be identified. The tar cleaning procedures used in this study, water scrubber and wood chips are not efficient enough to remove tars in the gas to a level low enough to be used for catalytic processes.

In this thesis, an approach to development and characterization of FT catalysts is presented. Most of the Fischer-Tropsch syntheses are performed using sources like natural gas or coal for the production of synthesis gas. Catalysts used in these processes, mostly cobalt or iron based have directly been transferred and used for the conversion of syngas derived from biomass. However, producer gas from biomass contains much more compounds that can damage or totally inhibit the catalytic activity and these processes include massive gas cleaning procedures. Therefore, commonly applied FT catalysts seems not to be suitable for FT synthesis from biomass derived gas, and new knowledge of the effect of promoter metals and supports is required. There might be even a need for completely different new, more active and selective tailored catalysts for the conversion of FTS from biomass derived syngas, as substantiated in this thesis. These new catalysts must be much more tolerant against gaseous pollutants like sulphur containing compounds and halides.

Fischer-Tropsch synthesis produces a mixture of compounds from methane to long aliphatic waxes. Usually long chained waxes must be cracked into suitable shorter carbon chains to be used as transportation fuels. The use of catalysts that can perform both FTS and cracking of long chained waxes in a single step would make the final cracking step unnecessary. This type of catalysts have been recently presented, consisting of a core of active metal surrounded by components with cracking performance, like zeolites in H-form. The right combination of active metal and a size selective or cracking component will break the traditional ASF distribution and make it possible to produce selected ranges of compounds.

The conclusions that can be drawn from the results of the work can be presented as following theses:

1. Tar compounds from small-scale biomass gasifier contain mainly naphthalene and toluene. Total tar concentrations are at quite a low level, but purification steps of gas are still needed for catalytic FT synthesis.
2. Tailored catalysts are needed to improve catalytic performance, i.e. catalytic activity and selectivity of FT synthesis of biomass derived syngas.
3. Catalyst preparation, especially calcination conditions, has clear effect on the dispersion of metal particles. Further, different supports and promoter metals studied also affect the catalyst properties, in particular in metal dispersion and pore size distribution.

4. In addition to scientific contribution, the results of this work can be further used in the development of small-scale gasification for simultaneous heat and power production (CHP) and uilization of carbon residue from gasification process e.g. as catalytic support. This further increases the cost-efficiency of small-scale gasification plants.

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