Catalytic partial oxidation of methane over nickel and ruthenium based catalysts for GTL applications

Jorge A. Velasco
Catalytic partial oxidation of methane over nickel and ruthenium based catalysts for GTL applications
JORGE A. VELASCO

TRITA-CHE Report 2015:63
ISSN 1654-1081
ISBN 978-91-7595-753-1

Akademisk avhandling som med tillstånd av Kungliga Tekniska högskolan i Stockholm framlägges till offentlig granskning för avläggande av teknologie doktorsexamen, fredagen den 27 november 2015 klockan 10:00 i sal K1, Teknikringen 56, Kungliga Tekniska högskolan, Stockholm.

© Jorge A. Velasco, November 2015

Tryck: Universitetsservice US-AB
To Magaly, Javier and Papá E
Abstract

The Gas to Liquids (GTL) process is an important alternative for monetizing natural gas through the production of long-chain liquid hydrocarbons, e.g. diesel fuel. The GTL process involves three main steps: synthesis gas production to obtain H₂ and CO, Fischer-Tropsch synthesis to obtain a synthetic crude oil, and upgrading/refining to obtain final products. Since the synthesis gas production is the most expensive step, there is great interest in optimizing and exploring new routes for syngas production.

This thesis focuses on the conversion of methane, the main component of natural gas, into synthesis gas by catalytic partial oxidation (CPO). Several aspects of the CPO reaction in the context of the GTL technology are discussed. The work contributes to an increased knowledge concerning utilizing a CPO reactor as pre-reformer in the synthesis gas production process as well as the influence of catalyst properties and composition on the catalytic behavior when using nickel and ruthenium-based catalysts in the CPO reaction.

The thesis is a summary of five publications. The first two publications (Papers I and II) review the current status of both the GTL technology and the catalytic partial oxidation of methane. Paper III analyzes a process configuration comprising of a CPO pre-reformer followed by an autothermal reforming (ATR) reactor using a thermodynamic equilibrium approach. It was found that a proper manipulation of the process conditions is needed to obtain a suitable synthesis gas for GTL applications simultaneously of minimizing the risk of carbon formation in the CPO reactor; the operation of the CPO reactor demanded low O₂/CH₄ and H₂O/CH₄ feed molar ratios. Accordingly, in paper IV, the partial oxidation of methane at low O₂/CH₄ and H₂O/CH₄ ratios is investigated over nickel and ruthenium catalysts supported on MgO/MgAl₂O₄ and compared with a commercial nickel-based catalyst. The extent or impact of the combustion and reforming reactions along the catalytic bed are substantially influenced by catalyst properties and composition. Deactivation by carbon formation is also discussed; ruthenium-containing catalysts might positively overcome carbon formation.
To gain greater insight concerning the influence of the catalyst composition and properties on carbon formation, a set of nickel and bimetallic nickel-ruthenium catalysts, supported on $\alpha$-Al$_2$O$_3$, $\gamma$-Al$_2$O$_3$ and MgO/MgAl$_2$O$_4$, is tested in the CH$_4$ decomposition reaction in Paper V. For these catalysts, the resistance towards carbon formation is mainly correlated with the nickel particle size.

**Keywords:** catalytic partial oxidation, carbon formation, GTL, nickel, ruthenium, synthesis gas, thermodynamic equilibrium.
Sammanfattning

Ett viktigt alternativ för att ta till vara naturgas är processen ”gas till vätskor” (GTL) för framställning av högmolekylära flytande kolväten såsom dieselbränsle. GTL-processen involverar tre steg: framställning av syntesgas (väte och kolmonoxid), Fisher-Tropsch-syntes för att producera syntetisk råolja och till slut en krackningsprocess för att få fram de önskade produkterna. Syntesgasframställningen är det dyraste processteget. Därför är det av stort intresse att optimera hela processen genom att hitta nya sätt att producera syngas.

Forskningsarbetet i denna avhandling fokuserar på omvandling av metan, som är huvudkomponenten i naturgas, till syngas, via katalytisk partiell oxidation. Detta arbete ger en ökad förståelse för användningen av katalytisk partiell oxidation för produktion av syntesgas. Dessutom har, för Ni- och Ru-katalysatorer, påverkan av katalysatorsegenskaperna och sammansättningen studerats för den katalytiska aktiviteten.

ytterligare förståelse av påverkan av katalysatorns egenskaper och sammansättning på kolbildningen har följande katalysatorer testats för sönderdelningsreaktionen av metan: Ni och bimetalliska Ni-Ru-katalysatorer, på olika bärarmaterial såsom α-alumina, γ-alumina och MgO/MgAl$_2$O$_4$. För dessa katalysatorer har man kunnat visa att motståndet mot kolbildning huvudsakligen kan korreleras med Ni-partikelstorleken.
Publications referred to in this thesis

The work presented in this doctoral thesis is based on the following publications. The papers are appended at the end of the thesis and referred to in the text using Roman numerals (I – V).

I. **J.A. Velasco**, L. Lopez, M. Velasquez, M. Boutonnet, S. Cabrera, S. Järås
   *Gas to liquids: A technology for natural gas industrialization in Bolivia*

II. **R. Lanza, J.A. Velasco**, Sven G. Järås
    *Recent developments in catalytic partial oxidation of methane with and without addition of steam*

III. **J.A. Velasco**, L. Lopez, S. Cabrera, M. Boutonnet, S. Järås
    *Synthesis gas production for GTL applications: thermodynamic equilibrium approach and potential for carbon formation in a catalytic partial oxidation pre-reformer*

IV. **J.A. Velasco**, C. Fernandez, L. Lopez, S. Cabrera, M. Boutonnet, S. Järås
    *Catalytic partial oxidation of methane over nickel and ruthenium based catalysts under low O\textsubscript{2}/CH\textsubscript{4} ratios and with addition of steam*

V. **J.A. Velasco**, V. Montes, H. Kusar, S. Cabrera, M. Boutonnet, S. Järås
    *Methane partial oxidation and methane decomposition over Ni and Ni-Ru supported catalysts for synthesis gas production*
    Submitted to Applied Catalysis A: General.
Contributions to the publications

I. I am the main author of this paper.

II. The review is a joint effort between all the authors. My main responsibility was the part concerning catalytic partial oxidation of methane in presence of steam.

III. I am the main author of this paper. L. Lopez helped in the analysis of data.

IV. I am the main author of this paper. C. Fernandez performed some experimental work and helped in the analysis of data.

V. I am the main author of this paper. V. Montes performed the TEM and helped with the interpretation of data.
Other publications and conference contributions

Peer-reviewed publications:

L. Lopez, J.A. Velasco, S. Cabrera, M. Boutonnet, S. Järås
Effect of syngas conversion and catalyst reduction temperature in the synthesis of ethanol: concentration of water vapor in mesoporous Rh/MCM-41 catalyst

L. Lopez, J.A. Velasco, V. Montes, A. Marinas, S. Cabrera, M. Boutonnet, S. Järås
Synthesis of ethanol from syngas over Rh/MCM-41 catalyst; effect of water on the product selectivity
Catalysts, 5 (2015) 1737-1755

Conference contributions:

J. A. Velasco, M. Boutonnet, S. Cabrera, S. Järås.
Catalytic partial oxidation of methane to synthesis gas

L. Lopez, J. Velasco, S. Cabrera, M. Boutonnet, S. Järås
Rh, Li on Si/Zr Mesoporous oxides for the conversion of syngas to oxygenates
Poster presentation, 16th International Zeolite Conference, Sorrento, Italy, 2010.

L. Lopez, R. Andersson, J. Velasco, S. Cabrera, M. Boutonnet, S. Järås
Rhodium-based catalysts promoted by lithium on Si/Zr mesoporous oxides applied in syngas to ethanol conversion
Poster presentation, 14th Nordic Symposium on Catalysis, Helsingør, Denmark, 2010.

J. A. Velasco, L. Lopez, S. Cabrera, M. Boutonnet, S. Järås
Synthesis gas production over Ni/Ru–based catalysts by partial oxidation of methane in presence of steam
Poster presentation, 22nd North American Catalysis Society Meeting, Detroit, USA, 2011.
J. A. Velasco, L. Lopez, S. Cabrera, M. Boutonnet, S. Järås
Partial oxidation of methane in presence of steam over Ni-Ru/Al₂O₃ and Ni-Ru/CeO₂-Al₂O₃ for synthesis gas production
Poster presentation, EUROPACAT X Congress, Glasgow, Scotland, 2011.

J.A. Velasco, L. Lopez, S. Cabrera, M. Boutonnet, S. Järås
Catalytic partial oxidation of methane at low O₂/C and H₂O/C ratios over Nickel and Ruthenium catalysts
Poster presentation, Syngas Convention, Cape Town, South Africa, March–April, 2012.

J. A. Velasco, M. Boutonnet, S. Järås
Monetizing natural gas: synthesis gas production for Gas to Liquids applications

J.A. Velasco, S Cabrera
Development of the energy and petrochemical industry towards the benefit of the country
Oral Presentation, Internacional meeting "Potenciamiento de la Capacidad Investigativa de la UMSA, en función del Desarrollo Regional y Nacional”, La Paz, Bolivia, June, 2014.
Contents

1. Introduction .................................................................................................................. 1
   1.1. Setting the scene ................................................................................................. 1
   1.2. Scope of the work .............................................................................................. 2

2. A brief description of GTL ............................................................................................ 3
   2.1. Introduction ........................................................................................................ 3
       2.2.1. Natural gas monetization ........................................................................... 6
       2.2. Indirect liquefaction ....................................................................................... 7
   2.3. The Gas-to-Liquids technology ......................................................................... 8
       2.3.1. GTL technology development ................................................................... 8
       2.3.2. The main steps in the GTL process ............................................................ 9
   2.4. Synthesis gas generation from natural gas ....................................................... 10
       2.4.1. Raw materials: Natural gas ....................................................................... 10
       2.4.2. Synthesis gas generation unit: SGU .......................................................... 11
           2.4.2.1. Purification ......................................................................................... 11
           2.4.2.2. Pre-reforming ..................................................................................... 12
           2.4.2.3. Reforming .......................................................................................... 13
               Steam reforming (SR) .................................................................................. 14
               Partial oxidation (POX) .............................................................................. 15
               Autothermal Reforming (ATR) .................................................................. 15
               Alternative routes ....................................................................................... 16
   2.5. Fischer-Tropsch synthesis ................................................................................ 17
       2.5.1. Fischer-Tropsch gas loop .......................................................................... 18
   2.6. Product work-up .................................................................................................. 19
   2.7. Commercial GTL plants ..................................................................................... 20

3. Catalytic partial oxidation of methane ...................................................................... 23
   3.1. Introduction ......................................................................................................... 23
   3.2. Thermodynamics ............................................................................................... 24
3.3. Catalysts ................................................................................................................. 25
  3.3.1. Nickel-based catalysts .................................................................................... 26
    3.3.1.1. Nickel catalysts promoted by noble metals ........................................ 27
  3.3.2. Noble metal-based catalysts ............................................................................ 27
3.4. Carbon formation on nickel catalysts ................................................................. 28
  3.4.1. Whisker carbon ............................................................................................... 29
  3.4.2. Gum carbon ................................................................................................... 30
  3.4.3. Pyrolytic carbon ............................................................................................ 31
3.5. Some obstacles to the commercialization of the CPO technology .............. 31
  3.5.1. High catalyst temperatures ........................................................................... 32
  3.5.2. The low inlet temperature of the CPO reactor ........................................... 32

4. Opportunities of a CPO-reactor in the GTL context: a CPO pre-reformer ................................................................. 35
  4.1. Introduction ........................................................................................................... 35
    4.1.1. Some considerations for the thermodynamic analysis .......................... 36
  4.2. Effect of the operational variables in the CPO + ATR configuration ...... 37
  4.3. Potential of carbon formation .......................................................................... 38
    4.3.1. Carbon limits: the equilibrated gas principle ............................................ 38
    4.3.2. Analysis of carbon formation in the CPO reactor .................................... 39

5. Catalytic evaluation of nickel and ruthenium–based catalysts. . 45
  5.1. Preparation of the catalysts .................................................................................. 45
  5.2. Catalyst characterization ...................................................................................... 46
    5.2.1. N₂ adsorption .............................................................................................. 46
    5.2.2. H₂ chemisorption ....................................................................................... 48
    5.2.3. X-ray diffraction ......................................................................................... 49
    5.2.4. Temperature-programmed analysis: TPR and TPO .............................. 49
    5.2.5. Transmission electron microscopy (TEM) .............................................. 53
  5.3. Catalytic tests: equipment and experimental procedures ............................ 55
    5.3.1. CPO activity tests in the presence of steam .......................................... 55
1. Introduction

1.1. Setting the scene

Mankind literally needs energy to survive. Energy is considered by some “the single most important scientific and technological challenge facing humanity in the twenty first century” [1]. The global demand for energy continues to grow, especially transportation fuels, as the world population increases in number and economies develop. This growing demand is also being intensified by the pursuit of cleaner sources of energy to reduce the impact on the environment.

The demand for natural gas is likely to increase more markedly than other fossil fuels due to its availability, versatility, accessibility, and smaller environmental footprint [2]. Currently, natural gas plays a strategic role in the global markets of power generation, space heating, transportation fuels, and petrochemicals. However, an important fraction of the global natural gas reserves remains stranded in remote onshore and offshore locations. Furthermore, in order to facilitate oil production, an important amount of natural gas is sometimes flared or vented representing an environmental concern. Therefore, finding efficient and clean processes to exploit the natural gas reserves still represents a critical step in solving both economic and environment-related issues.

An interesting alternative for producing liquid fuels from remote and non-expensive natural gas is the so-called Gas to Liquids (GTL) process. GTL is a commercial technology that involves the production of long-chain liquid hydrocarbons from natural gas; the obtained liquid hydrocarbons can be transported more easily to the markets than natural gas. At the same time, the GTL fuels, particularly diesel fuel, are considered high quality and environmentally friendly fuels since they are practically free of sulfur and nitrogen compounds.

The GTL process involves several complex chemical reactions and process integration; however, it inevitably consists of three main technologies: synthesis gas (syngas) generation, Fischer-Tropsch synthesis, and product
upgrading/refining. Even though these three technologies are well established, individually optimized, and commercially proven, a cost effective combination of them is still challenging; this represents a driving force for the development of new technologies.

At industrial scale, the synthesis gas production is the most capital-intensive step. This has created an increased interest in developing new and alternative technologies as well as in optimizing and adapting the conventional technologies for synthesis gas production. One of these alternative and promising technologies is the catalytic partial oxidation (CPO) of methane.

1.2. Scope of the work

The objective of the work presented in this thesis was to study the influence of operating conditions as well as catalyst properties and composition on the catalytic behavior, and deactivation by carbon, during the catalytic partial oxidation (CPO) of methane in the context of the GTL technology. Several aspects of chemical engineering and chemistry, ranging from large-scale process considerations to material science and catalysis, are discussed both theoretically and experimentally, in particular: (I) The effect of operating conditions on the performance of a process configuration consisting of a CPO pre-reformer followed by an autothermal reforming (ATR) reactor as well as on the risk for carbon formation in the CPO reactor; (II) The effect of the composition and properties of nickel, ruthenium and nickel-ruthenium based catalysts on the catalytic performance during the CPO of methane; and (III) The effect of the composition and properties of nickel and nickel-ruthenium based catalysts on carbon formation during the methane decomposition reaction.

The work included in this thesis was mainly conducted at the Department of Chemical Engineering and Technology at KTH Royal Institute of Technology, Stockholm, Sweden. Experimental work was also performed at the Natural Gas Institute at the Higher University of San Andres, La Paz, Bolivia.
2. A brief description of GTL

2.1. Introduction

In the nineteenth and early twentieth century, coal was the fuel of choice; however, after World War II, it was gradually substituted by oil and its derivatives. During the last three decades, natural gas has slowly but gradually increased its share of the energy mix (Figure 2.1). Total energy demand is forecast to increase by about 60% in 2040 [3]. Currently, fossil fuels account for about 85% of the world’s primary energy; it seems that this scene is not likely to change drastically in the upcoming two or three decades [4].

Fossil fuels are abundant. World proven reserves of conventional oil, natural gas, and coal as well as their Reserves-to-Production (R/P) ratio, are shown in Table 2.1. Since the “reserves” depend on technology, infrastructure and commercial restrictions, it is conceivable that fossil fuel reserves over time could increase, even though globally we continue to produce and consume more and more of them, as a result of investment in new and optimized technologies and infrastructure, changes in market conditions, and further exploration success [4].

Figure 2.1. World energy consumption by fuel type. Adapted from [5].
Table 2.1. World’s oil, coal and natural gas proven reserves [4, 5].

<table>
<thead>
<tr>
<th></th>
<th>Proven reserves* (2013)</th>
<th></th>
<th>R/P**</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Common units</td>
<td>Tonnes oil</td>
<td>[years]</td>
</tr>
<tr>
<td>Oil</td>
<td>1688 x 10^9 barrels</td>
<td>230 x 10^9</td>
<td>53</td>
</tr>
<tr>
<td>Coal</td>
<td>891 x 10^9 tons</td>
<td>594 x 10^9</td>
<td>113</td>
</tr>
<tr>
<td>Natural gas</td>
<td>6558 x 10^12 cubic feet</td>
<td>167 x 10^9</td>
<td>55</td>
</tr>
</tbody>
</table>

* This concept refers only to that portion of the global resources so far discovered that can be produced or recovered with currently available technologies, infrastructure and within the bound of commercial constraints.
** Represents the time that remaining reserves would last if the present levels of production were maintained.

Additionally, current technically (but not necessarily “economically”) recoverable unconventional shale/tight oil and shale gas, assessed in 41 countries, reach 345 x 10^9 barrels (i.e. 345 billion barrels) and 7299 x 10^12 cubic feet (i.e. 7299 TCF or trillion cubic feet), respectively [6]. Accordingly, it seems that global resources of fossil fuels (both discovered and yet-to-be-found) are available in sufficient quantities to dominate the global primary energy supply for many decades to come.

Natural gas, oil and coal can be used for the production of electricity, chemical products, and fuels for watercraft, aircraft, and road vehicles (Figure 2.2). Alternative sources of energy (wind, geothermal, solar, and nuclear) can provide electricity, but not chemicals and transportation fuels; for this reason, many developed countries have intensified the use of biofuels (bioethanol and biodiesel) as an alternative to oil-derived fuels; this adoption is mainly driven by energy security (and thus reducing the dependence on oil) and reduction of CO$_2$ from the transportation sector. However, there are still some issues and debate related to increased biofuels production and use, for example fuel economy, “food, land and water vs fuel” debate, etc. [7]. Biomass can also be converted via thermo-chemical processes (combustion, gasification, and pyrolysis) to produce electricity, fuels and chemicals [8].
There is an increased demand for more energy, especially as transportation fuels, as the world’s population continues to grow and economies develop. Current world liquid fuels consumption is around 90 million barrels per day. By 2040, consumption is estimated to grow by about 40% above the current levels [9]. In current and predicted liquid fuel consumption, almost 85% comes from crude oil and condensates and the remaining 15% from other sources of liquids (natural gas plant liquids, biofuels, liquids from biomass-to-liquids (BTL), Gas-to-Liquids (GTL), Coal-to-Liquids (CTL), kerogen from oil shale, and refinery gain). Furthermore, it is forecast that world oil prices will have a moderately low impact on the total growth of liquid fuels.

**Figure 2.2.** Versatility of fossil fuels and biomass. Adapted from [4].
consumption; however, it will affect the development of the other sources of liquids. Since the production of these other sources is typically more expensive, their economics will benefit from higher oil prices; conversely, a slower growth is expected at low oil prices [9].

2.2.1. Natural gas monetization
Since the rate of new discoveries of natural gas (and also oil) is greater than the rate of consumption, global reserves are increasing. Furthermore, this trend has been accelerated by the rapid expansion in the exploitation of unconventional resources. However, an important percentage of the proven natural gas reserves (as high as 50 %) remains stranded in remote onshore and offshore locations [10]. Monetization of stranded gas (associated and non-associated, see Section 2.4.1) has become a topic of increasing interest to nations and companies with large resources; however, large amounts of capital investment (for processing and transport infrastructure) and long term sales contracts are commonly required to uphold such investments. Furthermore, a considerable amount of associated natural gas is flared or vented in order to facilitate oil production; however, because of environmental concerns, this practice is being strongly discouraged [2, 11].

The main challenge of monetizing natural gas resources is logistical [12]. Generally, gas from reserves that are located close to the markets is often transported by pipeline. Where this is not feasible, natural gas can be liquefied and transported in specially designed tankers (i.e. liquefied natural gas: LNG); however, depending on the natural gas and oil prices, LNG may become uneconomical beyond a certain distance [2, 11]. Another alternative is the so-called Gas-to-Liquids (GTL) processes in which natural gas is chemically converted into long-chain hydrocarbons that are in liquid at or close to atmospheric conditions; these liquids can be shipped in normal tankers or through pipelines. Furthermore, GTL can not only be used for stranded gas monetization, but also represents an interesting option for satisfying local liquid fuel markets (reducing importation) in nations with reserves and production of mainly non-associated natural gas with low liquid fuels (e.g. diesel) production [2, 13].
An important advantage for GTL processes is the ability to further diversify from fuels (middle distillates, naphtha, GLP) to higher value chemical products (detergents, synthetic lubricant intermediates, propylene, α-olefins) [14]. Additionally, fuels from GTL are often considered “clean” because they are practically free of sulfur and nitrogen-containing compounds; they also contain a very low content of aromatics [11].

In the case of the Gas-to-Liquids (GTL) plants, they currently supply a rather small portion of the total world liquid fuels (approx. 0.25 %); however, fuel production via the GTL process is expected to grow in importance (from approx. 0.26 to 0.75 % of the total world liquids by 2040, this represents up to 300 % of today’s total GTL capacity, respectively); this growth will be linked to oil and natural gas prices [9].

### 2.2. Indirect liquefaction

In general terms, the processes used for transforming solid or gaseous carbon-based energy sources, first into synthesis gas and then into products, are known as *indirect liquefaction processes*. The products from these processes are usually fuels or chemicals. Frequently, the Fischer-Tropsch (FT) synthesis, followed by subsequent liquids (syncrude) product refining, is used to convert synthesis gas to a wide spectrum of chemicals and fuels; alternately, methanol formed from syngas can be converted to dimethyl ether (DME) and/or gasoline via methanol to gasoline (MTG) processes [15, 16].

Synthesis gas can be produced from almost any carbon source; however, in the context of indirect liquefaction, the types of feed materials that could be converted into syngas are: coal (coal-to-liquids: CTL), natural gas (gas-to-liquids: GTL), biomass (biomass-to-liquids: BTL), and waste (waste-to-liquids: WTL). Collectively, all of these processes are usually termed XTL conversion processes (Figure 2.3).

In general, the raw feed material limits the technology selection for the syngas generation step, but not for the subsequent downstream steps; thus, the syngas can be conditioned to serve as feed for any synthesis technology.
Nonetheless, obtaining and preparing the feed material may involve very complex operations (e.g. exploration, recovery, transportation, and feed preparation) [16]. An appropriate description of all XTL processes deserves more space and attention than we can provide here, and their study and description are outside the scope of this work. In the following, our attention is focused on the GTL process.

2.3. The Gas-to-Liquids technology

2.3.1. GTL technology development

The successful commercial application of the GTL technology is closely linked to the development of the Fischer-Tropsch (FT) process. The history of the FT process illustrates how closely advances in science and technology are coupled to economic and political circumstances [1].

The Fischer-Tropsch synthesis was pioneered in Germany during the first three decades of the twentieth century and entered into commercialization after ammonia (1913) and methanol (1923) syntheses, in 1930 [17]. By that time, synthesis gas was produced by continuous coal gasification processes. The interest in the process grew rapidly mainly in England, Japan, and the United States. During the Second World War (1939-1945), extensive engineering work and catalyst development continued in Nazi Germany when Germany found itself short of petroleum but with abundant reserves of coal which could be converted into fuel for the war effort. Since there were concerns about short supply of petroleum, the development of new FT reactors designs continued after the War. However, the discovery of large new oil fields in the 1950’s and 1960’s reduced and postponed the interest in Fischer-Tropsch until the Oil Crisis in the 1970’s and the oil embargoes imposed on South Africa during the apartheid era. This encouraged the
expansion of the South African CTL plants by SASOL (South African Oil and Gas Company) in order to become more self-sufficient. Since then, SASOL has actively continued to develop its processes for CTL and GTL, and currently continues to play a major role in the implementation of new plants in other countries (Qatar, Nigeria, etc.). Royal Dutch Shell is also active in the implementation of GTL plants in both Malaysia and Qatar [1, 2]. The renewed interest in Fischer-Tropsch synthesis in the form of GTL for the conversion of natural gas primarily into middle distillates (i.e. diesel) was pushed forward not only as a result of abundant supply of economically priced stranded natural gas, but also by restricted access to crude oil supplies and the global desire for transportation fuels with higher quality in order to improve local air quality in many cities around the world [2].

2.3.2. The main steps in the GTL process

The GTL process involves several complex chemical reactions, multiple processing steps and high levels of heat and process integration. However, as illustrated in Figure 2.4, it inevitably consists of three core technologies (main process units):

a) Synthesis gas generation
b) Fischer-Tropsch synthesis
c) Product work-up (upgrading or/and refining)

Individually, these three technologies are well established, optimized and commercially proven; however, their combined use has not been widely applied (i.e. for GTL applications) and it is still a challenge for technology licensors and engineering companies to obtain the most effective combination [18]. The definitive process units, ancillary units, and utilities, their configuration as well as their operating conditions will strongly depend on the desired final products and technology licensor.

A brief description of the three technologies is given in the following (Section 2.2. to 2.3.2). Special focus is given to the synthesis gas generation since it is the main topic of the thesis.
2.4. Synthesis gas generation from natural gas

As mentioned in Section 2.2, synthesis gas may be generated from a wide range of carbon-containing feedstocks; however, in the context of GTL applications, natural gas (more specifically, low-value natural gas) is the feedstock of interest. The synthesis gas preparation is the most expensive section of a GTL plant and it might account from about 30 to 50 % of the capital expenditures (including the Air Separation Unit: ASU) in large-scale plants [1, 16]. Furthermore, it is also responsible for the largest part of the energy conversion in the plant [20].

2.4.1. Raw materials: Natural gas

Natural gas is obtained from natural reservoirs (non-associated gas) and as a by-product of crude oil production (associated gas). Natural gas always contains some heavier hydrocarbons so-called natural gas liquids (NGL) which, once separated, might be totally or partially co-refined with the syncrude of the GTL plant. This is beneficial for the carbon efficiency of the overall GTL process. Therefore, it makes little sense to use the NGL for synthesis gas production. From an environmental point of view, natural gas should preferably be used as energy carrier (when feasible) rather than using it as raw material for GTL since about 75 % of the natural gas ends up in the FT product. This means that overall, after production and combustion, a
GTL fuel releases about 33 % more CO\textsubscript{2} to the atmosphere than the initial natural gas [11, 16].

2.4.2. Synthesis gas generation unit: SGU

In GTL plants, the synthesis gas generation unit (SGU) commonly consists of:

- Purification
- Pre-reforming
- Reforming

Since the synthesis gas obtained in the reforming sections should be appropriate for the stoichiometry of the Fischer-Tropsch synthesis, the hydrogen-to-carbon monoxide molar ratio (H\textsubscript{2}/CO) should be very close to 2.0 when the FT synthesis uses a cobalt-based catalyst (see Section 2.5).

2.4.2.1. Purification

The objective of the purification step is to remove the species present in natural gas that are poisons for the catalysts employed in the downstream reactors. Even though not all the reforming technologies use catalysts, the purification of the feed ensures that the syngas is free of impurities for the FT synthesis. The most important impurities to be removed from natural gas are H\textsubscript{2}S, other sulfur compounds (COS, mercaptans, sulfides, di-sulfides, thiophenes, etc.), halogens, and arsenic. The removal of other contaminants such as solids, moisture, Hg, and even CO\textsubscript{2} are usually performed upstream the SGU in natural gas processing plants. After purification, there is no general value for the concentration of the impurities; however, very low concentrations (preferably single digit ppb) are desirable to ensure an acceptable lifetime of the downstream catalysts [21]. The typical process concept for natural gas (or similar feedstock) desulfurization consists of two steps:

a) *Hydrogenation* of the sulfur compounds and halogens to H\textsubscript{2}S and hydrogen halides over Co/Mo or Ni/Mo based catalysts at 350–400 °C.
b) Adsorption/Desorption of the H₂S and hydrogen halides over zinc oxide and activated alumina, respectively.

The amount of hydrogen added to the natural gas stream is low since the concentrations of the compounds that need to be hydrogenated are also low. At the typical operating conditions (\(\sim 350 \, ^\circ C\)), the equilibrium reaction constants, for both hydrogenation and adsorption, are very high; therefore, it is possible to reduce contaminants to extremely low concentrations (i.e. some ppb’s) [20, 21].

2.4.2.2. Pre-reforming

At elevated temperatures, long-chain hydrocarbons \((C_{2+})\) present a high tendency toward thermal cracking and consequently the formation of non-saturated compounds and carbon; this might eventually lead to carbon formation on catalysts and/or fouling of heat exchangers and preheaters (carbon formation is described in Section 3.4). These higher hydrocarbons \((C_{2+})\), which are usually present in the feedstock, can be pre-reformed by steam reforming into a mixture of methane, steam, carbon monoxide, carbon dioxide and hydrogen (see Table 2.2).

The pre-reforming is normally carried out adiabatically over a nickel-based catalyst at moderately low inlet temperatures \((350–550 \, ^\circ C)\) [21]. All higher hydrocarbons are quantitatively converted by the endothermic reforming reaction \((R7\) in Table 2.2) which is also accompanied by the water gas shift and methanation reactions \((R6\) and the inverse of \(R3\) in Table 2.2, respectively). Furthermore, the pre-reformer also removes any remaining trace of sulfur in the feed stream. Once the \(C_{2+}\) hydrocarbons are converted in the pre-reforming, it is possible to heat up the pre-reformed stream (i.e. the feed stream of the main reformer reactor) to higher temperatures (around 650 \(^\circ C\)). This is beneficial in terms of plant efficiency (a tubular reformer as the main reformer) and/or reduction of the oxygen consumption (an autothermal reformer as the main reformer) [15, 21].
Table 2.2. Main reactions involved the synthesis gas processes [15, 21].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Process</th>
<th>$-\Delta H_{298}$ [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Partial oxidation</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R1</td>
<td>$\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2$</td>
<td>36</td>
</tr>
<tr>
<td>R2</td>
<td>$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$</td>
<td>802</td>
</tr>
<tr>
<td>R8</td>
<td>$\text{CH}_4 + \text{O}_2 \rightarrow \text{CO} + \text{H}_2\text{O} + \text{H}_2$</td>
<td>278</td>
</tr>
<tr>
<td>R9</td>
<td>$\text{CH}_4 + 1.5\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2\text{O}$</td>
<td>520</td>
</tr>
<tr>
<td><strong>Steam reforming</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R3</td>
<td>$\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2$</td>
<td>–206</td>
</tr>
<tr>
<td>R4</td>
<td>$\text{CH}_4 + 2\text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 4\text{H}_2$</td>
<td>–165</td>
</tr>
<tr>
<td>R5</td>
<td>$\text{CH}_4 + \text{CO}_2 \leftrightarrow 2\text{CO} + 2\text{H}_2$</td>
<td>–247</td>
</tr>
<tr>
<td>R6</td>
<td>$\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$ (WGS)</td>
<td>41</td>
</tr>
<tr>
<td>R7</td>
<td>$\text{C}_m\text{H}_n + n\text{H}_2\text{O} \rightarrow n\text{CO} + (n+m/2)\text{H}_2$</td>
<td>$&lt;0$</td>
</tr>
<tr>
<td><strong>Autothermal reforming</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R9</td>
<td>$\text{CH}_4 + 1.5\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2\text{O}$</td>
<td>520</td>
</tr>
<tr>
<td>R3</td>
<td>$\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2$</td>
<td>–206</td>
</tr>
<tr>
<td>R6</td>
<td>$\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$ (WGS)</td>
<td>41</td>
</tr>
</tbody>
</table>

2.4.2.3. Reforming
In the context of the GTL, the current commercial technologies for synthesis gas manufacture are:

a) Steam reforming (SR)
b) Adiabatic oxidative reforming:
   i. Autothermal reforming (ATR).
   ii. Partial Oxidation (POX).

The composition of the synthesis gas can be manipulated by modifying the process conditions and by means of additional or combined reforming steps. Figure 2.5 illustrates the main types of reactors currently used. In order to obtain a sufficiently high per pass conversion of natural gas, the temperature at the exit of the reactor(s) should be high (around 1000 °C), at these conditions exit compositions are very close to the equilibrium value [15, 22]. Also, the composition should be appropriate for Fischer-Tropsch
synthesis (i.e. H₂/CO=2.0). In the following, the syngas technologies are briefly described.

**Steam reforming (SR)**

Natural gas steam reforming is a highly endothermic process which is carried out in an externally heated multi-tubular reactor over a nickel-based catalyst. Natural gas conversion into synthesis gas is thermodynamically favored by high temperature, low pressure, and high steam to hydrocarbon ratios [22]. Typical conditions are described in Table 2.3. The main advantages of steam reforming in the context of GTL applications are [16]:

a) No oxygen is needed for the reaction (and therefore an air separation unit is not required)
b) H₂O from the reaction can be easily recovered by condensation.
c) It is possible to co-feed CO₂ to obtain a synthesis gas with the desired composition for FT synthesis.
d) The energy for reforming can be supplied by a low quality fuel.

It is claimed that steam reforming could be used as the main reactor for small GTL plants (less than 10000 bpd), provided that water can be supplied at low cost, and/or the natural gas contains high CO₂ levels, and/or the excess of H₂ can be used in other applications [23].

![Diagram of reactors for syngas generation](image-url)

*Figure 2.5. Different types of reactors for syngas generation. Adapted from [16, 21].*
**Partial oxidation (POX)**

In partial oxidation, natural gas and oxygen (generated in an air separation unit) are reacted without a catalyst to produce synthesis gas. The POX reactor is often followed by a section to recover heat (quench or steam generation) as well as a section to remove carbon (soot), ammonia and HCN produced during reaction [23, 24]. Since this technology does not use a catalyst, CO$_2$ cannot be recirculated or fed to the reactor. Typical process conditions are described in Table 2.3.

**Autothermal Reforming (ATR)**

Autothermal reforming is a combined combustion and catalytic process which is carried out in an adiabatic reactor. The reactor consists of a burner, in which proper mixing of the feed is provided, a combustion chamber, and a catalyst bed which equilibrates synthesis gas and destroys soot precursors. All of these components are contained in a refractory lined pressure shell [21]. Typical conditions of the ATR reactor are described in Table 2.3. The usual catalyst for autothermal reforming is a nickel-based catalyst supported on either alumina ($\alpha$-$\text{Al}_2\text{O}_3$) or magnesium alumina spinel (MgAl$_2$O$_4$). The oxygen, from an air separation unit, is quantitatively consumed by the combustion reactions; however, even though non-catalytic steam reforming and water gas shift reaction occur in the combustion chamber, the methane conversion is not complete. The final conversion of hydrocarbons takes place in the catalyst bed through heterogeneous steam reforming and water gas shift reactions [21, 24].

The main advantages of the POX and ATR technologies are the following [16]:

a) Much larger single stream units are possible compared with steam reforming.

b) Adiabatic reformers are more compact in size.

c) Higher outlet gas temperatures than for steam reforming can be achieved, this means higher methane conversion at lower steam-to-methane ratios.
Table 2.3. Comparison of gas reforming technologies that are industrially applied in combination with Fischer–Tropsch synthesis. Adapted from [16, 21].

<table>
<thead>
<tr>
<th>Description</th>
<th>Steam Reforming</th>
<th>Partial Oxidation</th>
<th>Autothermal Reforming</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrocarbon feed</td>
<td>Natural gas</td>
<td>Natural gas</td>
<td>Process gas&lt;sup&gt;a&lt;/sup&gt; Natural gas</td>
</tr>
<tr>
<td>Feed O&lt;sub&gt;2&lt;/sub&gt;/C [mol/mol]</td>
<td>0</td>
<td>0.55 – 0.65</td>
<td>0.30 – 0.60</td>
</tr>
<tr>
<td>Feed H&lt;sub&gt;2&lt;/sub&gt;O/C [mol/mol]</td>
<td>2.5 – 5.0</td>
<td>0.0 – 0.15</td>
<td>1.2 – 2.5</td>
</tr>
<tr>
<td>Outlet temperature [°C]</td>
<td>820 – 880</td>
<td>1300 – 1400</td>
<td>950 – 1050</td>
</tr>
<tr>
<td>Flame peak temp. [°C]</td>
<td>–</td>
<td>2500 – 3500</td>
<td>Up to 2500</td>
</tr>
<tr>
<td>Outlet CH&lt;sub&gt;4&lt;/sub&gt; content [mol%]</td>
<td>3 – 5</td>
<td>0.1</td>
<td>0.5 – 1.0</td>
</tr>
<tr>
<td>Product H&lt;sub&gt;2&lt;/sub&gt;/CO [mol%]&lt;sup&gt;b&lt;/sup&gt;</td>
<td>4 – 7</td>
<td>1.6 – 1.9</td>
<td>2.5 – 3.5</td>
</tr>
<tr>
<td>Product CO&lt;sub&gt;2&lt;/sub&gt;/CO [mol%]&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.5 – 1.0</td>
<td>0.05 – 0.10</td>
<td>0.2 – 0.3</td>
</tr>
</tbody>
</table>

<sup>a</sup> Partly converted process gas from a primary reformer.
<sup>b</sup> Product compositions with no additional CO<sub>2</sub> co-feed to the reformer.

It is important to remark that the commercial large-scale technologies described above (pre-reforming and reforming) are currently applied in combined fashion in GTL plants, either in series (SR+ATR) or in parallel (SR–POX, SR–ATR) [16, 21]. Although the SR–POX technology is used at commercial scale, it seems that today the most economically attractive technologies for a large-scale Fischer-Tropsch complex are the ATR-based processes [18].

A simplified process scheme for synthesis gas production for a low temperature Fischer-Tropsch process (for the production of middle distillates) is shown in Figure 2.6. In this scheme, the process heat from the exit stream of the ATR reactor is recovered in boilers resulting in surplus steam in the plant. However, a number of alternative process schemes has also been proposed, in which the process heat is used for steam reforming in heat exchange reforming (chemical recuperation) as well as for pre-heating the gas stream for the ATR reactor [15, 21].

**Alternative routes**

There are substantial efforts to develop new technologies. They are mainly focused on reducing, or even eliminating, the use of pure oxygen and/or reducing the size of the main reforming reactor in the SGU [20, 21].
One alternative might be catalytic partial oxidation (CPO) where reactants are premixed and all the chemical conversions take place in a catalytic reactor without a burner. This technology is the main focus of this thesis and will be described in Section 3. Additionally, less expensive technologies for oxygen manufacture might be interesting routes for reducing the costs of the SGU. One approach is the ceramic membrane reforming (CMR); this technology eliminates the oxygen plant using a reactor concept with oxygen addition through a membrane [24, 26]. In order to be considered as competitors for large scale production of synthesis gas, both CPO and CMR technologies should demonstrate their feasibility to find widespread commercial application [21, 27].

### 2.5. Fischer-Tropsch synthesis

The Fischer-Tropsch synthesis is the catalytic polymerization and hydrogenation of carbon monoxide to give a wide range of hydrocarbons as well as water. This product mixture is often called synthetic crude oil or
“syncrude”. In general, syncrude can be used for the production of high quality diesel fuel, gasoline and linear chemicals such as 1-alkenes, alkenes and oxygenated hydrocarbons [28].

The Fischer-Tropsch reaction is highly exothermic; as a result, all FT reactors are designed to maximize heat removal [29]. Insufficient heat removal would otherwise result in increased catalyst deactivation, decreased selectivity to desired products, and, at worst, may induce thermal runaway [30]. The operating pressure of the FT processes is in the range of 18–45 bar. Temperature is an important parameter for classifying the FT processes. Thus, they are classified as high temperature and low temperature Fischer-Tropsch synthesis (HTFT and LTFT, respectively) [29-31]. Currently, LTFT synthesis is performed in both fixed bed and slurry bubble column reactors; fluidized bed reactors are used for HTFT synthesis. The commercial catalysts available for Fischer-Tropsch syntheses are promoted cobalt catalyst (Co-LTFT), fused iron (Fe-HTFT), and precipitated iron (Fe-LTFT). Because of a lower generation of CO$_2$ during reaction (absence of water gas shift activity), higher activity, very good selectivity to long chain paraffins, and low selectivity to oxygenates and olefins, the preferred choice for LTFT in GTL applications is cobalt-based catalysts [30, 32].

2.5.1. Fischer-Tropsch gas loop
The gas loop refers to the way in which the synthesis gas flows around the Fischer-Tropsch synthesis. Since the gas loop controls the flow and destination of the carbon contained in the syngas, it has a marked influence on the carbon efficiency of the GTL plant. Furthermore, the gas loop has an enormous impact on the product work-up section of the plant, and the gas reforming technology cannot be selected in isolation because it has to be matched to the gas loop design of the Fischer-Tropsch process [16]. Both the inlet and the outlet streams of the Fischer-Tropsch influence and are influenced by the gas loop. Therefore, gas loop design is an optimization problem which involves per pass conversion in the FT reactor, synthesis gas conditioning, fate of unconverted syngas in the FT reactor, light products recovery (mainly C$_1$ and C$_2$), and syncrude cooling and separation.
Figure 2.7. Fischer-Tropsch gas loop configurations: (a) open gas loop and (b) closed gas loop. Adapted from [15, 16].

The gas that remains after the recovery section of the Fischer-Tropsch products (see Figures 2.7) is frequently called “tail gas” (which may still contain syngas).

Generally, the configuration of the gas loop can be either open (tail gas is not recycled) or closed (tail gas is recycled). Depending on the design, the closed gas loop might involve one or more separation steps and/or conversion units before being recycled to the FT synthesis [16]. Additionally, tail gas, i.e. non-converted syngas and light synthesis products, may be recycled to the synthesis gas generation unit or used as fuel gas. In order to avoid the buildup of inert compounds (e.g. Ar and N₂), closed gas loops must contain a purge gas stream. As shown in Figure 2.6, in ATR-based processes for synthesis gas generation, tail gas is commonly recirculated.

2.6. Product work-up

The refining of Fischer-Tropsch products is comparable but different from crude oil refining in terms of feed composition, refining focus, and heat management. Unfortunately, the refining of syncrude is not widespread enough to have attracted the development of specific refining technologies. For this reason, the same basic technologies and commercial catalysts as used in crude oil refining have been adapted for syncrude refining [33]. It is
important to notice the difference between upgrading and refining; while refining produces final products, upgrading only produces intermediate products that still need to be refined to produce final products.

The design of the FT refinery depends on the nature of the feed to be processed (HTFT or LTFT products). In the case of the LTFT synthesis over promoted cobalt catalyst, it leads to the formation of paraffinic wax which is converted into high quality middle distillates, with linear naphtha as a main by-product, by mild hydrocracking. Alternatively, hydrotreating is also applied to obtain paraffins and waxes. In some GTL facilities, the lighter hydrocarbons are fractionated into sharp cuts of: C\textsubscript{5}–C\textsubscript{10} for use in solvents, C\textsubscript{10}–C\textsubscript{13} for detergents and C\textsubscript{14}–C\textsubscript{17} for flame-retardant materials. However, in current GTL plants, the fuel-related products are only blending materials and not final fuels [16].

### 2.7. Commercial GTL plants

Several commercial GTL and CTL plants have been operating successfully for many years in various parts of the world.

**Table 2.3.** Commercial GTL plants. Adapted from [34, 35].

<table>
<thead>
<tr>
<th>Plant name</th>
<th>Main products</th>
<th>Capacity [bpd]</th>
<th>Plant owner</th>
<th>Start of production</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sasolburg GTL, South Africa</td>
<td>Waxes, paraffins. LPG, ammonia, hydrogen.</td>
<td>5600 17000</td>
<td>Sasol</td>
<td>CTL: 1955</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>GTL: 2004</td>
</tr>
<tr>
<td>Mossgas GTL, Mossel Bay, South Africa</td>
<td>Gasoline, diesel, LPG, oxygenates.</td>
<td>47000</td>
<td>PetroSA: 37.5% Statoil: 37.5% Lurgi: 25%</td>
<td>1992</td>
</tr>
<tr>
<td>Bintulu GTL, Malaysia</td>
<td>LPG, naphtha, kerosene, Distillates.</td>
<td>14700</td>
<td>Shell</td>
<td>1993</td>
</tr>
<tr>
<td>Oryx GTL, Qatar</td>
<td>LPG, naphtha, Distillates.</td>
<td>34000</td>
<td>Qatar Petroleum: 51% Sasol: 49%</td>
<td>2007</td>
</tr>
<tr>
<td>Pearl GTL, Qatar</td>
<td>Naphtha, kerosene, distillates, paraffins, waxes.</td>
<td>140000</td>
<td>Qatar Petroleum Shell</td>
<td>2011</td>
</tr>
<tr>
<td>Escravos GTL, Nigeria</td>
<td>LPG, naphtha, Distillates.</td>
<td>34000</td>
<td>Chevron Nigeria Ltd.: 75% Nigeria National Petroleum Co.: 25%</td>
<td>2015 (Forecast)</td>
</tr>
<tr>
<td>Oltin Yo’l GTL, Shurtan, Uzbekistan.</td>
<td>Naphtha, kerosene, distillates.</td>
<td>38000</td>
<td>Uzbekneftegaz: 44.5%, Sasol: 44.5%, Petronas: 11%</td>
<td>2017 (Forecast)</td>
</tr>
</tbody>
</table>
Table 2.3 provides information on some commercial GTL facilities. Currently, the world’s largest facility is *Pearl GTL* owned by Royal Dutch Shell; this facility uses a POX-based technology for syngas manufacture. Other important GTL facilities are *Oryx GTL, Escravos GTL,* and *Oltin Yo’l GTL;* these facilities use an ATR-based process for syngas production (similar as that shown in Figure 2.6). At present, there are also new large-scale GTL projects still waiting for approval (e.g. in Mozambique, and Louisiana, US). Also, small-scale GTL developments are planned in the US, Kazakhstan, Russia, Canada, and Brazil [36].
3. Catalytic partial oxidation of methane

3.1. Introduction

In general terms, the catalytic partial oxidation (CPO) of methane is the reaction between methane and oxygen to obtain hydrogen and carbon monoxide (synthesis gas). The principle of CPO is illustrated in Figure 3.1. The oxidant source (i.e. pure oxygen or air) and the methane (or another hydrocarbon feed) are mixed in an inlet zone upstream the catalyst bed. Then, the mixture reacts by heterogeneous reactions along the catalytic section. The space velocity is normally high and metal-based catalyst in the form of pellets, monoliths or foams have been used to perform the reaction [21, 37].

The partial oxidation reaction (R1 in Table 3.1) appears to be a moderately simple reaction; however, due to the presence of a catalyst, several other reactions (irreversible and reversible, exothermic and endothermic) will also take place along the catalyst bed including total oxidation, steam reforming, CO\textsubscript{2} reforming and water gas shift (R2 to R6 in Table 3.1). This is commonly called the “indirect mechanism” and, as a result, a temperature profile along the reactor, with a peak temperature close to the entrance, is typically observed [15, 38, 39].

Figure 3.1. Principle of catalytic partial oxidation (CPO). Adapted from [15].
Table 3.1. Main reactions in the partial oxidation of methane [37, 40].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Process</th>
<th>$-\Delta H_{298}^{\circ}$ [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation</td>
<td>R1: CH₄ + ½O₂ → CO + 2H₂</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>R2: CH₄ + 2O₂ → CO₂ + 2H₂O</td>
<td>802</td>
</tr>
<tr>
<td>Reforming and WGS</td>
<td>R3: CH₄ + H₂O ↔ CO + 3H₂</td>
<td>–206</td>
</tr>
<tr>
<td></td>
<td>R4: CH₄ + 2H₂O ↔ CO₂ + 4H₂</td>
<td>–165</td>
</tr>
<tr>
<td></td>
<td>R5: CH₄ + CO₂ ↔ 2CO + 2H₂</td>
<td>–247</td>
</tr>
<tr>
<td></td>
<td>R6: CO + H₂O ↔ CO₂ + H₂ (WGS)</td>
<td>41</td>
</tr>
</tbody>
</table>

3.2. Thermodynamics

In practice, the product gas of the partial oxidation process will typically be at or very close to the equilibrium of the reforming and WGS reactions [21]. As can be observed, all reactions listed in Table 3.1, except total oxidation and the WGS reaction, lead to the formation of more molecules; this implies that the overall CPO process is favored by low pressures, as illustrated in Figures 3.2a and 3.2b. Additionally, since the amount of oxygen is typically low (e.g. O₂/CH₄ ≈ 0.5 for R1), it seems that for methane conversion the endothermic and reversible reforming reactions (and WGS) prevail to some extent over the irreversible and exothermic combustion reactions; therefore, higher temperatures will also favor the production of synthesis gas.

In general, product yields are greatly influenced by the direct and reverse WGS reaction (R6). For example, as shown in Figures 3.2c and 3.2d, since the latter is exothermic, the CO₂ yields decline at high temperatures while the CO yields will be increased, this in turn will influence the H₂/CO ratio of the synthesis gas.

Addition of steam not only increases methane conversion but also influences product distribution (according to the reforming and WGS reactions). Furthermore, the relative amounts of steam and oxygen (i.e. O₂/CH₄ and H₂O/CH₄ ratios) determine the exothermicity or the endothermicity of the overall process [40].
From Figures 3.2a and 3.2b, it is important to notice that at moderately elevated pressures (e.g. 25 bar) high methane conversions can only be obtained at high temperatures (>1000 °C) and/or at high contents of oxygen (e.g. O₂/CH₄ > 0.5); addition of steam could increase methane conversion but will inevitably be accompanied by increased CO₂ and H₂ yields due to the WGS reaction.

### 3.3. Catalysts

Partial oxidation reactions are normally catalyzed by Group VIII metals. Theoretical and experimental observations have demonstrated that catalyst activity is higher for noble metal-based catalysts, particularly Rh and Ru, followed by Ni, Os, Ir, Pt and Pd [41-43]. It is interesting to notice that...
similar activity trends have been found in the methane steam reforming reaction [15, 44], which, as explained in Section 3.1, also takes place during the CPO process. Many studies have also focused on nickel (a non-noble metal) as active phase for the CPO reaction; however, this kind of catalyst is more sensitive to deactivation, especially by carbon formation and phase transitions, than those based on noble metals [40, 45]. Due to their higher activity and good stability, utilization of noble metals would mean small and/or high-capacity CPO reactors; however, considerably large amounts of noble metal-based catalyst may still be required for a commercial-scale reactor. Thus, the use of less expensive metals, or at least a reduced amount of noble metals, is preferable for catalyst preparation.

3.3.1. Nickel-based catalysts

Nickel has been extensively employed as active metal in catalytic processes, and is currently the preferred choice for the commercial steam reforming of hydrocarbons [21, 22]. In partial oxidation of methane, nickel-based catalysts present a good activity towards synthesis gas production [40]; however, under certain operating conditions, catalyst deactivation may take place [46, 47]. Since most of the CPO reactor will be operated above the Tamman temperature ($T_{\text{Tamman}} = \frac{1}{2} \cdot T_{\text{melt}} = 581$ °C) in order to obtain a fair methane conversion (see Figure 3.2a-b) metal agglomeration or sintering is favored; this involves a decrease in metal surface area which leads to a reduction in activity with time on stream [46]. In addition, surface oxidation of the Ni to NiO may also occur due to the presence of oxygen in the feed stream. The NiO formation during reaction may not only enhance combustion reactions but also interact with the catalyst support to form, for example, nickel aluminates when alumina is used as support or NiO-MgO solid solutions with MgO as support [40, 45, 46]. Additionally, operation under low $O_2/CH_4$ and $H_2O/CH_4$ ratios (required to obtain a synthesis gas with a $H_2/CO$ ratio $\approx 2$) could result in carbon formation (this is described in Section 3.4).

Several strategies have been utilized to improve both the activity and the resistance of nickel-based catalysts against deactivation; they were mainly focused on stabilizing and preserving small nickel particles (which afford
high activity at the same time as reducing deactivation by carbon formation). Some of these strategies include preparing catalysts with different methods [40], selecting appropriate catalyst supports [40, 41, 48-50], promoting the catalysts with noble metals and non-noble metals [51-54], improving the oxygen-storage properties of the catalysts by promotion with rare earth metal oxides [41, 55, 56], addition of promoters with basic properties [57-59], and utilization of supports with high thermal conductivities [60, 61].

3.3.1.1. Nickel catalysts promoted by noble metals

It has been reported that the activity and stability of nickel catalysts can be increased with the addition of low amounts of noble metals. These promoting effects have been attributed to several factors [51, 54, 62, 63]: formation of an alloy, causing electronic changes in nickel; exposure of the noble metal by migration to the nickel surface; multi-functionality of the catalyst (the noble metal catalyzing partial oxidation and nickel catalyzing steam reforming); and a higher amount of metallic nickel exposed to the reaction, resulting from the promotion of nickel reduction by spillover.

Even though most of the strategies for reducing catalyst deactivation in nickel-based catalysts mentioned above have its own merits, they also have shortages (e.g. complicated preparation processes, or some type of deactivation). Additionally, only a few studies have been focused on the deactivation phenomena of nickel-based catalysts under realistic operating conditions and during extended periods of time (e.g. > 1000 h) [45].

3.3.2. Noble metal-based catalysts

The use of noble metals in the CPO catalysts is the object of extensive studies because, despite their high cost, they have higher activity and are more resistant to catalyst deactivation than nickel [40, 64]. In order to have an idea of the difference in prices, during the last 5 years price ratios were approximately Ni : Ru : Pd : Ir : Pt : Rh = 1 : 150 : 1200 : 1300 : 2500 : 3000 [65]; therefore, the higher catalytic activity and stability of noble metals should compensate their higher prices.
Several studies focused on Rh-based catalysts; some of them were investigating catalysts with considerable concentration of noble metal (e.g. 4 wt% Rh) [39, 66-68]. These studies were useful for investigating the mechanism and kinetics; the results supported the indirect mechanism (combustion and then WGS + reforming reactions, as presented in Table 3.1). In the case of Pt, stability at high temperature could be an issue since sintering was observed at high temperatures (800–1000 °C) [69, 70].

In general, low metal loadings have been applied when using noble metals; however, in some cases, a low metal loading usually means small metal particles and consequently the metal might easily be oxidized; this might produce an oscillatory behavior (in temperature and conversion) during operation as well as a higher interaction with the catalyst support [71]. Furthermore, metal oxides also enhance combustion reactions. As previously described for nickel, noble metals can also benefit from the addition of promoters such as ceria, zirconia or other oxides.

### 3.4. Carbon formation on nickel catalysts

As described above, major challenges for the development of nickel catalysts are related to “secondary phenomena”, e.g. carbon formation. The potential for carbon formation is higher when the O₂/CH₄ and H₂O/CH₄ ratios are low (see Section 4). The reactions leading to carbon formation are summarized in Table 3.2.

Reaction Rc1 is commonly referred to as “methane decomposition” or “methane cracking”, reaction Rc2 as “the Boudouard reaction” or “CO decomposition”, and Rc3 as “CO reduction”; reaction Rc4 describes the formation of carbon from higher hydrocarbons [21].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>- ΔH²⁹⁸ [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rc1</td>
<td>CH₄ ↔ C + 2H₂</td>
</tr>
<tr>
<td>Rc2</td>
<td>2CO ↔ C + CO₂</td>
</tr>
<tr>
<td>Rc3</td>
<td>CO + H₂ ↔ C + H₂O</td>
</tr>
<tr>
<td>Rc4</td>
<td>CₘHₙ → carbonaceous deposits</td>
</tr>
</tbody>
</table>
Figure 3.3. Micrograph showing different forms of carbon deposited on the surface of a nickel-based catalyst during the CPO of methane. Adapted from [64].

Different kinds of carbon which vary in morphology and reactivity can be formed from these reactions; however, they are usually classified in three main species, whisker, gum, and pyrolytic [15, 21, 46, 72].

3.4.1. Whisker carbon

Whisker carbon is the most destructive form of carbon. It is formed as characteristic fibers (carbon nanotubes) from the decomposition of CH$_4$, CO and higher hydrocarbons on the nickel particles (Figure 3.3). In general, carbon whiskers grow by reaction of hydrocarbons on one side of a nickel particle and nucleation of carbon on the other side of the particle; continued growth may cause catalyst disintegration when the whisker hits the pore wall. Whisker carbon is also observed on cobalt and iron catalysts [73].

Since the carbon whisker has a higher energy than graphite [22, 74], operation under conditions at which thermodynamics predict formation of graphite may be feasible without carbon formation. Additionally, the carbon limits depend on the nickel crystal size, i.e. smaller particles are more resistant towards carbon formation [75]. These observations are consistent with recent in-situ electron microscopy studies and density functional (DFT) calculations [76-78] which indicate that adsorbed atomic carbon is much more stable at the steps sites than at terrace sites of the nickel particle;
therefore, steps are much better nucleation sites for carbon. When carbon atoms cover the step sites, a single graphite layer can grow from the step. Depending on the operating conditions, a graphene island may nucleate, encapsulating the nickel particle, or alternatively new layers may nucleate below the first graphene layer and grow by addition of carbon atoms. This growth is accompanied by surface diffusion (and perhaps diffusion through the sub-surface layer of nickel) of carbon atoms (Figure 3.4); surface transport of the metal atoms from the step to the free metal surface also takes place resulting in the growth of carbon whiskers from the nickel particle. Additionally, calculations showed that graphene islands below approximately 2.5 nm should not be stable; this is consistent with earlier experimental observations that carbon is not formed on catalysts with small nickel crystals [76, 79].

### 3.4.2. Gum carbon

Gum formation is a low-temperature phenomenon which involves blockage of the metal surface by a thin film of polymerized carbonaceous material which covers the nickel particles. Since gum is mainly formed in reforming of heavy feeds with a high content of aromatic compounds, it is hardly possible that this type of carbon may form if the feedstock is natural gas.

![Figure 3.4](image)  
**Figure 3.4.** Formation of whisker carbon at the nickel particle. (a) Illustration of a graphene island nucleated from a Ni step. (b) Schematic illustration of whisker formation. Adapted from [15, 76].
3.4.3. Pyrolytic carbon

Pyrolytic carbon is the result of thermal cracking (pyrolysis) of higher hydrocarbons at temperatures typically above 600–650 °C [22] as experienced in steam crackers. When the catalyst activity is low, the pyrolysis route may take over; the ethylene formed by pyrolysis may result in rapid carbon formation on nickel. This kind of carbon might encapsulate the catalyst pellet or might be deposited on the tube walls of the reactor and heat exchangers [76, 79].

3.5. Some obstacles to the commercialization of the CPO technology

As described in Section 3.1 the CPO of methane is extensively documented and considerable work has been carried out in recent years. However, the technology is not being applied currently at commercial scale. Fluidized bed reactors, hydrogen membranes, and millisecond fixed-bed reactors have been explored [80-82]. Furthermore, the fixed-bed CPO technology has been studied at pilot scale at different pressures and inlet compositions; in these tests stable conversions close to the thermodynamic equilibria were achieved [21, 83, 84].

In GTL applications, probably the main challenge for the CPO reactor has been to replace the ATR reformer (Section 2.4.2.3). It is important to notice that, essentially, the same reactions occur in a CPO reactor as in an ATR reactor. For adiabatic operation, in both types of reactors, the composition of the exit gas will be practically at equilibrium at the exit temperature (which is in turn determined from a heat balance based on inlet flows and temperatures). This actually implies that with similar inlet streams (amounts and properties) the composition of the exit gas from a CPO reactor may be identical to that of the exit gas of an ATR reactor [85]. Based on this, the ATR reactor might probably be easily replaced by a CPO reactor; however, as described below, there are some important issues or obstacles.
3.5.1. High catalyst temperatures
Since the CPO reactor does not have either a burner or a combustion chamber, the highly exothermic total oxidation reaction takes place, at least to some extent, in the first part of the catalytic bed of the CPO reactor; this produces a hot spot which, at high oxygen contents (e.g. a $O_2/CH_4$ ratio of about 0.5) may be as high as 1100–1300 °C [38, 83, 84, 86]. These high temperatures might lead to the detrimental sintering and/or weakening of the catalysts.

3.5.2. The low inlet temperature of the CPO reactor
As already mentioned, in order to obtain the same exit temperature and therefore similar synthesis gas compositions for a given feed gas stream, the ATR and the CPO would require the same inlet temperature. A typical inlet feed temperature for the ATR reactor is 650 °C [15].

Unfortunately, the inlet feed temperature of a CPO reactor must be kept low (approx. 250 °C) since the reactive mixture present in the inlet zone, upstream the CPO catalyst bed, may spontaneously ignite at temperatures above the autoignition temperature, especially at pressures relevant for GTL. For example, while at low pressures the autoignition temperature of natural gas in air is moderately high (approx. 465 °C, at 1 bar), at higher pressures it is much lower (approx. 267 °C, at 20 bar) [21, 87]; when pure oxygen is used as oxidant the autoignition temperatures are even lower. Additionally, flammability limits (both low and high) are much wider at high pressures [88].

A lower inlet temperature for the CPO reactor means higher oxygen and natural gas consumption compared to the ATR reactor; this is because a larger part of the natural gas feed should be combusted, hence using a larger amount of oxygen, to generate the heat to reach the same exit temperature [85]. As described in Section 2.3, synthesis gas generation in large scale GTL plants suffer from the necessity of an expensive oxygen plant; therefore, a higher consumption of oxygen increases the costs of the air separation unit. An alternative for CPO could be to use air as oxidant; however, the amount of nitrogen in the syngas is prohibitive for closed gas
loops (see Section 2.5.1) due to an enormous accumulation of nitrogen. Also, the larger nitrogen-containing gas volumes will require larger heat exchangers and compressors [89].

An alternative approach in order to overcome the above mentioned issues and obstacles is to operate the CPO reactor upstream and in combination with another reforming technology (i.e. ATR as a primary reformer) [90]. In such an arrangement (CPO + ATR) the inlet temperature of the CPO reactor can be kept low (around 200 °C) since this reactor acts as a pre-reformer at low O₂/CH₄ ratios; consequently, the temperature on the surface of the catalyst is reduced as well. A more detailed analysis and description of such an arrangement, mainly focused in the CPO reactor, is presented and discussed in Section 4.
4. Opportunities of a CPO-reactor in the GTL context: a CPO pre-reformer

4.1. Introduction

As described in Sections 2 and 3, synthesis gas generation for GTL applications is particularly challenging because, in order to obtain an appropriate synthesis gas for the low temperature Fischer-Tropsch synthesis (i.e. $H_2/CO$ ratio of about 2.0), the conditions at which the main reactors operate (pre-reforming and primary reforming) should be carefully chosen in order to avoid the risk of carbon formation. Consequently, conventional process configurations are usually designed and operated close to (but outside) the thermodynamic limit for carbon formation [15, 91, 92].

A promising process configuration comprising a CPO reactor upstream in combination with an ATR reactor has been suggested in the literature [90]. As illustrated in Figure 4.1, the main inlet stream of oxygen is separated in two predetermined fractions. Initially, natural gas, steam and one of these oxygen fractions are fed into a CPO reactor in which, after reaction, a pre-reformed stream is obtained. Then, the pre-reformed stream and the other fraction of oxygen are introduced into an ATR reformer at a lower steam-to-carbon ratio than normally applied.

Some of the advantages of this configuration over a typical process (for example the one shown in Figure 2.6) are reduced steam consumption, reduced pre-heating duty for the inlet stream of the pre-reformer and for the inlet stream of the ATR reactor, and enhanced production of carbon monoxide which favors the $H_2/CO$ ratio for the Fischer-Tropsch synthesis. However, since the amounts of steam and oxygen fed to the CPO reactor are moderately low (see Section 4.2), some difficulties may appear in operating the CPO reactor without carbon formation.
In this section, a synthesis generation unit (SGU) comprising a CPO reactor followed by an ATR reactor is subjected to analysis by adjusting some of the operating conditions and compositions in order to meet the requirements of the low temperature FT synthesis ($H_2/CO = 2$). The risk of carbon formation in the CPO reactor is also addressed by using the equilibrated gas principle. The results obtained are briefly discussed and summarized in this section. For more details and an extensive discussion, the reader is referred to Paper III.

### 4.1.1. Some considerations for the thermodynamic analysis

In order to investigate the performance of the CPO + ATR configuration, the exit stream of both reactors were assumed to be at thermodynamic equilibrium (determined by the Gibbs free energy minimization method); also, both reactors were simulated as adiabatic. It means that the product composition (at equilibrium) is independent of the reactor design and determined from a heat balance based on inlet flows and temperatures. The species involved in the calculations were $CH_4$, $O_2$, $H_2O$, $H_2$, $CO$, $CO_2$, $C_2H_6$, $C_3H_8$, and $C_{(graphite)}$. The calculated results were compared with experimental
data from experiments at pilot scale [90] and there was good agreement between them, with relative errors of around 0.5 %. Further details of the thermodynamic method and operating conditions are given in section 2 of Paper III.

4.2. Effect of the operational variables in the CPO + ATR configuration

As introduced before (Section 2.5.1), in a closed Fischer-Tropsch gas loop, some gas (i.e. tail gas) can be recirculated to the syngas generation unit (SGU) and its composition varies depending on the configuration of the gas loop. Therefore, two types of tail gas have been included in the simulations: a CO-rich tail gas (TG1) and a CO₂-rich tail gas (TG2); see Section 3.2 of Paper III for tail gas composition. In the simulations, the feed streams of hydrocarbons, oxygen, steam, and tail gas were analyzed according to the process scheme shown in Figure 4.1; thus, the H₂O/C ratio was varied in order to obtain a synthesis with a ratio of H₂/CO = 2.0 at the exit of the ATR reactor.

The results showed that a reduction of the total oxygen-to-carbon ratio (O₂/C) produces a reduction in the adiabatic exit temperature and consequently in the conversion at the exit of the ATR reactor; also, in order to obtain a H₂/CO = 2.0, a reduction of the steam-to-carbon ratio (H₂O/C) is needed. Even though the amount of syngas generated per unit of oxygen is similar in all cases, the low conversions also imply a higher yield of species that are not reactive in the Fischer-Tropsch synthesis (i.e. CO₂ and CH₄); this would imply a larger recycle ratio and a reduced partial pressure of syngas for the synthesis. For a targeted H₂/CO ratio of 2.0, it seems that a CO-rich tail gas (TG1) is more beneficial than a CO₂-rich tail gas (TG2).

The increase of the inlet temperature of the feed stream of the CPO reactor resulted in increased conversion and syngas yield at the exit of the ATR reactor. The amount of synthesis gas produced per amount of oxygen consumed is also increased. Additionally, the increase of pressure involved a moderate decrease of conversion and syngas yields accompanied by the
need to slightly increase the H₂O/C ratio to achieve the desired syngas composition. The adiabatic exit temperature of the ATR reactor also increases with pressure; this might not be trivial for heat transfer purposes. Finally, the presence of higher hydrocarbons in the feed stream required a higher H₂O/C ratio to obtain a H₂/CO = 2.0. This was accompanied by a higher hydrocarbon conversion; however, the CO₂ yield increased as well.

4.3. Potential of carbon formation

4.3.1. Carbon limits: the equilibrated gas principle

Carbon formation cannot be accepted because it may result in breakdown of catalysts, increased pressure drop, and/or irregular flow distributions along fixed-bed reactors; as stated by Rostrup-Nielsen and Christiansen [15] “the important question is whether or not carbon is formed and not the rate at which it may be formed”. A simple approach to predict the formation of carbon is by using simple thermodynamic calculations.

Since the decomposition reactions of methane and carbon monoxide (Rc1, Rc2, and Rc3 in Table 3.2) are reversible the risk of carbon formation can be determined by thermodynamics employing the principle of equilibrated gas which indicates that carbon formation is to be expected on the catalyst if the gas shows affinity for carbon formation after the establishment of the equilibrium of methane reforming and WGS reactions [22]. The principle is justified by the typically low effectiveness factors of the total oxidation and steam reforming reactions which, as mentioned in Section 3.1, take place during the CPO process [38, 93-95]. This implies that in most of the catalyst particle, or in the washcoat of structured reactors, the gas is nearly at thermodynamic equilibrium [15].

According to the principle, the potential for carbon formation can be expressed in terms of the Gibbs free energy:

\[-\Delta G_{Rc} = RT \ln \left( \frac{K_{eq,rc}}{Q_{r,eq}} \right)\]  

(4.1)
In essence, equation 4.1 can be applied at any axial position of the reactor based on the actual composition, temperature and pressure. In this regard, \( K_{eq, Rc} \) corresponds to the equilibrium constant for a carbon-forming reaction (Rc1, Rc2 or Rc3) and, since it is only a function of the temperature, it is calculated using the actual temperature. The term \( Q_{r, eq} \) is the reaction quotient for the same carbon-forming reaction, for example, \( Q_{r, eq} = \frac{P_{H_2}}{P_{CH_4}} \) is the quotient for the methane decomposition reaction (Rc1). The composition (partial pressures) used in \( Q_{r, eq} \) are obtained after calculating the equilibrium based on the actual or measured composition, temperature and pressure.

The criteria for the potential for carbon formation are the following:

1) If \( Q_{r, eq} < K_{eq, Rc} \) then \( -\Delta G_{RC} > 0 \): carbon is predicted to form.
2) If \( Q_{r, eq} > K_{eq, Rc} \) then \( -\Delta G_{RC} < 0 \): carbon is not predicted to form.

It is important to mention that the principle is not a law of nature because, as explained in Section 3.4, carbon limits also depend on the catalyst composition and properties. Indeed, a catalyst normally has smaller equilibrium constants for the carbon-forming reactions (i.e. \( K_{eq,Rc} \)) than the corresponding equilibrium constants based on graphite [74, 75].

The equilibrated gas principle is a moderately conservative rule of thumb to predict carbon formation; however, there are also other even more conservative criteria (e.g. the principle of actual gas) and their description can be found elsewhere [15].

### 4.3.2. Analysis of carbon formation in the CPO reactor

The potential of carbon formation in the CPO reactor was evaluated at different inlet flow rates of oxygen (\( O_2 / C_{CPO} \)) while the total amount of oxygen fed to the system was kept constant, as well as the amount of steam, in order to obtain a syngas with a \( H_2/CO \) ratio of 2.0 at the exit of the ATR reactor. For the CPO reactor, equilibrium compositions and adiabatic exit temperatures were used to determine \( -\Delta G_{RC} \).
Table 4.1 Potential for carbon formation in the CPO reactor (CPO + ATR configuration), at different O\textsubscript{2}/C ratios. A negative value of $-\Delta G_R$ (here, in kcal/mol) predicts no carbon formation. For more details see Paper III.

<table>
<thead>
<tr>
<th>Case</th>
<th>Remarks</th>
<th>O\textsubscript{2}/C\textsubscript{CPO}</th>
<th>H\textsubscript{2}O/C\textsubscript{CPO}</th>
<th>T\textsubscript{out, CPO} [°C]</th>
<th>$-\Delta G_{R1}$</th>
<th>$-\Delta G_{R1,w}$*</th>
<th>$-\Delta G_{R2}$</th>
<th>$-\Delta G_{R3}$</th>
<th>O\textsubscript{2}/C\textsubscript{ATR}</th>
<th>H\textsubscript{2}O/C\textsubscript{ATR}</th>
<th>T\textsubscript{out, ATR} [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>-</td>
<td>0.16</td>
<td>0.11</td>
<td>715</td>
<td>2.18</td>
<td>1.32</td>
<td>1.95</td>
<td>1.95</td>
<td>0.49</td>
<td>0.18</td>
<td>1020</td>
</tr>
<tr>
<td>2.2</td>
<td>T\textsubscript{in}=350°C</td>
<td>0.16</td>
<td>0.11</td>
<td>740</td>
<td>2.23</td>
<td>1.34</td>
<td>2.00</td>
<td>1.99</td>
<td>0.51</td>
<td>0.17</td>
<td>1043</td>
</tr>
<tr>
<td>2.5</td>
<td>T\textsubscript{in}=350°C</td>
<td>0.28</td>
<td>0.28</td>
<td>812</td>
<td>0.84</td>
<td>-0.12</td>
<td>0.60</td>
<td>0.58</td>
<td>0.54</td>
<td>0.51</td>
<td>1027</td>
</tr>
<tr>
<td>2.5</td>
<td>T\textsubscript{in}=350°C</td>
<td>0.38</td>
<td>0.28</td>
<td>877</td>
<td>0.15</td>
<td>-0.88</td>
<td>-0.10</td>
<td>-0.12</td>
<td>0.53</td>
<td>0.81</td>
<td>1027</td>
</tr>
<tr>
<td>2.5</td>
<td>T\textsubscript{in}=350°C</td>
<td>0.48</td>
<td>0.28</td>
<td>944</td>
<td>-0.96</td>
<td>-2.08</td>
<td>-1.23</td>
<td>-1.25</td>
<td>0.50</td>
<td>1.65</td>
<td>1027</td>
</tr>
<tr>
<td>3.1</td>
<td>P=20 bar</td>
<td>0.28</td>
<td>0.12</td>
<td>807</td>
<td>1.56</td>
<td>0.61</td>
<td>1.33</td>
<td>1.32</td>
<td>0.52</td>
<td>0.30</td>
<td>1042</td>
</tr>
<tr>
<td>3.4</td>
<td>P=30 bar</td>
<td>0.28</td>
<td>0.27</td>
<td>808</td>
<td>0.85</td>
<td>-0.10</td>
<td>0.60</td>
<td>0.59</td>
<td>0.51</td>
<td>0.50</td>
<td>1021</td>
</tr>
<tr>
<td>4.2</td>
<td>-</td>
<td>0.16</td>
<td>0.20</td>
<td>709</td>
<td>1.87</td>
<td>1.01</td>
<td>1.65</td>
<td>1.64</td>
<td>0.51</td>
<td>0.25</td>
<td>1017</td>
</tr>
<tr>
<td>4.3</td>
<td>-</td>
<td>0.16</td>
<td>0.35</td>
<td>686</td>
<td>1.19</td>
<td>0.36</td>
<td>0.97</td>
<td>0.96</td>
<td>0.54</td>
<td>0.40</td>
<td>1014</td>
</tr>
<tr>
<td>4.3</td>
<td>-</td>
<td>0.28</td>
<td>0.35</td>
<td>793</td>
<td>0.74</td>
<td>-0.20</td>
<td>0.50</td>
<td>0.49</td>
<td>0.53</td>
<td>0.59</td>
<td>1014</td>
</tr>
<tr>
<td>4.3</td>
<td>-</td>
<td>0.38</td>
<td>0.35</td>
<td>861</td>
<td>0.05</td>
<td>-0.96</td>
<td>-0.20</td>
<td>-0.22</td>
<td>0.52</td>
<td>0.94</td>
<td>1014</td>
</tr>
<tr>
<td>4.6</td>
<td>T\textsubscript{in}=350°C</td>
<td>0.16</td>
<td>0.20</td>
<td>733</td>
<td>1.90</td>
<td>1.02</td>
<td>1.67</td>
<td>1.66</td>
<td>0.52</td>
<td>0.24</td>
<td>1043</td>
</tr>
</tbody>
</table>

* $-\Delta G_{R1,w}$: Gibbs free energy change for whisker carbon from methane decomposition reaction (R1).
As illustrated in Table 4.1, the higher tendency towards carbon formation in the CPO pre-reformer occurs at low $O_2/C$ and $H_2O/C$ ratios (both approx. lower than 0.3). Carbon (graphite) formation from $CH_4$ decomposition (reaction Rc1) is more difficult to overcome than carbon from CO decomposition (Rc2 and Rc3). Carbon formation is not predicted only at high $O_2/C$ and $H_2O/C$ ratios; these ratios are less severe when whisker carbon, from $CH_4$, is considered ($-\Delta G_{R_{1,w}^*}$ in Table 4.1 was calculated by using $K_{eq,Re}$ data of a nickel-based catalyst [15]).

The diagrams for carbon limits can give us a wider and more general perspective of the conditions for carbon formation. Therefore, Figure 4.2 shows carbon limits for graphite at different $O_2/CH_4$ and $H_2O/CH_4$ ratios as a function of reaction temperature. Since the CPO reforming process is usually carried out adiabatically, the temperature will correspond to the adiabatic exit temperature of the reactor. These diagrams could also be used to roughly predict carbon formation at the inlet of the reactor by using the inlet temperature. From Figure 4.2a, it is clear that high contents of oxygen and/or steam are needed to avoid carbon formation; however, at low temperatures (e.g. below 300 °C) carbon formation seems to be inevitable; this may be disadvantageous for the inlet part of an adiabatic CPO reactor.

![Figure 4.2](image-url)

**Figure 4.2.** Carbon limits for the partial oxidation of methane. (a) Effect of the $O_2/C$ ratio at $P = 25$ bar, (b) Effect of pressure at $O_2/CH_4 = 0.28$. The potential for carbon (graphite) corresponds to conditions which lie on the left side of the curves. (From Paper III).
Additionally, at moderate temperatures (approx. 400–700 °C), the risk for carbon formation is higher at low pressures (Figure 4.2b). This peculiar behavior is mainly attributed to the effect of pressure on Rc1, Rc2 and Rc3, as predicted by Le Châtelier's principle.

Some CPO applications may involve the use of air as oxidant [15]. Unfortunately, dilution with nitrogen (O₂/N₂ ≈ 0.27), or another inert gas, has a minor effect on the carbon limits during the CPO reaction, as illustrated in Figure 4.3. This is mainly because reaction quotients for the carbon-forming reactions (\(Q_{r,eq}\)) are similar when they (with and without dilution) are evaluated at the same reaction temperature.

Evaluation of the potential for carbon formation by assuming thermodynamic equilibrium at the exit of the adiabatic reactors is a useful approach to defining preliminary operating conditions for the CPO reactor. However, a proper evaluation should be made at each position along the axial direction of reactor using the actual temperature, pressure and composition profiles, which, at industrially relevant conditions, can be strongly influenced by the flow regime (Reynolds number) [96].

![Figure 4.3](image-url). Effect of dilution (air as oxidant) on carbon limits. The potential for carbon (graphite) corresponds to conditions which lie on the left side of the curves. (From Paper III).
Furthermore, as described in Section 3.4.1, when a catalyst is used the extent of carbon formation will depend on the deviation from graphite thermodynamics. Therefore, some strategies might be adopted in order to operate a CPO pre-reforming reactor without carbon formation, for example, utilization of an expensive and carbon-resistant catalyst (e.g. based on noble metals) for those reactor zones which present higher potential for carbon formation, and a less expensive catalyst for zones with lower risk of carbon formation. In the next part of this thesis, Section 5, experimental results of the catalytic performance of nickel and ruthenium-based catalysts in the CPO of methane are presented; carbon formation over the catalysts is also discussed.

5.1. Preparation of the catalysts

All the nickel and ruthenium-based catalysts employed in this work were prepared by the incipient-wetness (IW) technique. In general, the method involves the impregnation of a porous material support with an aqueous or non-aqueous solution containing a salt (precursor) of the active catalytic metal(s). The volume of the solution corresponds to the pore volume of the support; therefore, a precise amount of metal(s) is ensured to be deposited in the pores of the catalytic support. The solution is usually added dropwise to the support until an initial indication of humidity is observed; capillary forces draw the liquid into the pores allowing a uniform distribution of the metal salt. Subsequent drying induces growth of crystallites in the pores; a calcination step is usually performed in order to decompose the salt into metal oxide particles [97].

In this work, the metal precursors (salts) of nickel and ruthenium were *nickel nitrate hexahydrate* (Ni(NO$_3$)$_2$·6H$_2$O) and *ruthenium nitrosyl nitrate* (RuNO(NO$_3$)$_3$), respectively. Catalyst supports were obtained from commercial materials: an aluminum oxide (Puralox from Sasol) and a hydrotalcite–type material (Pural MG 30 from Sasol, MgO:Al$_2$O$_3$ $\approx$ 30:70). Prior to the impregnation procedure, these materials were calcined in air at different conditions in order to obtain $\gamma$-Al$_2$O$_3$ or $\alpha$-Al$_2$O$_3$ from the Puralox material, and MgO/MgAl$_2$O$_4$ from Pural MG30. The pore volume of these support materials was determined by N$_2$-adsorption techniques (see Section 5.2.1). Later, the metal precursors were dissolved in purified water to a volume equivalent to the pore volume of the support; for moderately high metal loadings, and/or low pore volume supports, the volume of the solution was twice or three times the pore volume and therefore the impregnation was repeated accordingly. Each impregnation was followed by drying at 120 °C for 3 h. In the case of bimetallic catalysts, consecutive impregnation was performed. The impregnated powder was then calcined in air at 400 °C or
700 °C. In addition, a commercial nickel-based catalyst was included in this work. The resulting catalyst compositions and their denominations are shown in Table 5.1. For more detailed catalyst preparation procedures and conditions, see Papers IV and V.

5.2. Catalyst characterization

In general terms, characterization of a heterogeneous catalyst refers to the measurement of its physical and chemical properties which are assumed to be responsible for its catalytic performance in a given reaction [98]. Currently, many different methods are available for investigating a catalyst’s properties, each having its advantages and limitations. For an appropriate description of the characterization methods, the reader is directed to the relevant literature dealing with the subject, for example [98].

In the following, the characterization methods employed in this work are briefly described and the most significant results are summarized. For details on the instruments, analysis conditions, preparation of the samples, and a more extensive discussion of the results, the experimental sections of Papers IV and V are recommended.

5.2.1. N₂ adsorption

N₂ adsorption, also called N₂ physisorption, is the most common method for determining the internal surface area of a porous material and it is based on the adsorption and condensation of N₂ at its boiling point temperature (−196 °C) using static vacuum procedures. Since it is assumed that each adsorbed molecule of N₂ occupies an area of the surface equivalent to its cross-sectional area, it is possible to calculate internal surface area by measuring the number of N₂ molecules adsorbed at monolayer coverage; in practice, coverage beyond a monolayer also takes place [98]. The method developed by Brunauer, Emmett and Teller [99] is the preferred method for determining the specific surface area of a solid material (i.e. a catalyst) since among other peculiarities it also takes into account multilayer adsorption. The specific surface area calculated by this method is commonly designated as BET surface area.
Table 5.1. Catalysts Properties (From Papers IV and V).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Support</th>
<th>Ni [wt%]</th>
<th>Ru [wt%]</th>
<th>BET surface area [m²/g]</th>
<th>Metal dispersion [%]</th>
<th>Metal surface area [m²/gcat]</th>
<th>H₂-Chem metal particle size [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni–MG30</td>
<td>MgO/MgAl₂O₄</td>
<td>15</td>
<td>-</td>
<td>96</td>
<td>7.9</td>
<td>7.9</td>
<td>13</td>
</tr>
<tr>
<td>NiRu–MG30</td>
<td>MgO/MgAl₂O₄</td>
<td>5</td>
<td>0.3</td>
<td>122</td>
<td>9.0</td>
<td>3.1</td>
<td>11</td>
</tr>
<tr>
<td>Ru–MG30</td>
<td>-</td>
<td>1</td>
<td>1</td>
<td>166</td>
<td>4.1</td>
<td>0.2</td>
<td>31</td>
</tr>
<tr>
<td>Ni–Gamma</td>
<td>γ-Al₂O₃</td>
<td>15</td>
<td>-</td>
<td>97</td>
<td>5.4</td>
<td>5.4</td>
<td>19</td>
</tr>
<tr>
<td>NiRu–Gamma</td>
<td>γ-Al₂O₃</td>
<td>5</td>
<td>0.5</td>
<td>108</td>
<td>9.3</td>
<td>3.3</td>
<td>11</td>
</tr>
<tr>
<td>Ru–Gamma</td>
<td>-</td>
<td>1</td>
<td>1</td>
<td>120</td>
<td>15.2</td>
<td>0.6</td>
<td>8</td>
</tr>
<tr>
<td>Ni–Alpha</td>
<td>α-Al₂O₃</td>
<td>15</td>
<td>-</td>
<td>&lt;10</td>
<td>3.0</td>
<td>3.0</td>
<td>34</td>
</tr>
<tr>
<td>NiRu–Alpha</td>
<td>α-Al₂O₃</td>
<td>5</td>
<td>0.3</td>
<td>&lt;10</td>
<td>6.2</td>
<td>2.1</td>
<td>17</td>
</tr>
<tr>
<td>Ru–Alpha</td>
<td>-</td>
<td>1</td>
<td>1</td>
<td>&lt;10</td>
<td>12.5</td>
<td>0.5</td>
<td>10</td>
</tr>
<tr>
<td>Ni–Com</td>
<td>CaO/Al₂O₃</td>
<td>11</td>
<td>-</td>
<td>12</td>
<td>3.0</td>
<td>2.2</td>
<td>34</td>
</tr>
</tbody>
</table>
Analogously, the method devised by Barret, Joyner and Halenda (BHJ) [100], which assumes cylindrical pores and uses the Kelvin model of pore filling, is widely used for determination of pore size distribution and pore volume from N₂-adsorption measurements. The BHJ method was applied for estimation of the pore volume of the support materials described in Section 5.1.

Table 5.1 shows the BET surface area of the studied catalysts after calcination at 400 °C (MG30 and Alpha catalysts) or 700 °C (Gamma catalysts). In general, the surface area decreased as the weight loading of active metals was increased, probably caused by some blockage of the pores by the metal particles. Because of the low amount of catalyst used during catalytic testing (Section 5.3), it was practically impossible to perform BET surface area measurements after the CPO reaction.

**5.2.2. H₂ chemisorption**

Chemisorption involves the formation of an irreversibly adsorbed monolayer of gas; contrary to physisorption, chemisorption is assumed to take place only on the metal surface by chemical bond formation. Therefore, if the stoichiometry of the chemisorption reaction (i.e. the number of metal atoms with which each gas molecule reacts) is known, the measurement of the amount of gas adsorbed at monolayer coverage gives the metal surface area, the metal dispersion, and the average metal particle size [101]. Chemisorption of hydrogen is widely used for several metallic catalysts since it selectively chemisorbs on metal surfaces. Adsorption of H₂ generally takes place by dissociation of a hydrogen molecule into two hydrogen atoms which are assumed to absorb onto two metal atoms [98].

In this work, H₂ chemisorption was performed at 35 °C; dissociative adsorption of H₂ and spherical particles were assumed for both metals (nickel and ruthenium). Prior to the analysis the catalysts were reduced in pure hydrogen at 900 °C for 0.5 h. As shown in Table 5.1, the Ni catalysts presented a higher metallic surface area than the bimetallic NiRu catalysts; this is reasonably attributed to the higher metal loading in the monometallic Ni catalysts. Among the different types of catalysts, larger particle sizes, and
therefore lower dispersion and metal surface area, were observed for the catalysts supported on α-Al₂O₃. The H₂-chemisorption properties are directly related to catalyst activity in Section 5.

5.2.3. X-ray diffraction
X-ray diffraction (XRD) is commonly used in catalysis for qualitative and quantitative phase analyses of catalytic materials. The material should be sufficiently crystalline to diffract X-rays (i.e. crystallites larger than 3–5 nm) and preferably present in quantities greater than approx. 1%. Additionally, the size of metal the crystals present in the catalyst can be estimated from peak broadening by using the Scherrer equation [98].

In this work, XRD was mainly used for determination of the crystal phases of the supports and calcined catalysts. Accordingly, XRD analysis revealed, for example, that the hydrotalcite structure (used as base material for the MG30 catalysts) is partially reconstructed [102, 103] after impregnation of the calcined support with the aqueous solution (which contains the metal precursors); this reconstruction might be responsible, to some extent, for the large ruthenium particle sizes (See also Section 5.2.4 and 5.2.5) since, in the case of the Ru-containing catalysts, the impregnation was repeated several times. Additionally, after thermal treatments, XRD analyses were useful for identifying the presence of γ-Al₂O₃, α-Al₂O₃ and MgO/MgAl₂O₄; these materials were used later as catalyst supports (Gamma, Alpha and MG30 respectively). The crystal size of nickel oxide was also estimated from XRD, and the same trends as those obtained by H₂ chemisorption for nickel were observed; however, crystal sizes from XRD were moderately smaller, mainly in the bimetallic catalysts (this is further discussed in Section 5.2.5).

5.2.4. Temperature-programmed analysis: TPR and TPO
TPR and TPO are thermoanalytical techniques that are used to understand the gas–solid interactions as well as surface reactivities, for example: to identify metal–support interactions, to understand complex systems (e.g. bimetallic or doped catalysts), to find appropriate reduction conditions, etc. When using these methods, the chemical reaction is monitored (i.e. via continuous analysis of the gas phase) while the temperature is raised linearly
with time [104]. In TPR (temperature-programmed reduction) a reducible solid sample is exposed to a flow of a reducing gas mixture (typically a few % H\textsubscript{2} or CO in N\textsubscript{2}). Likewise, in TPO (temperature-programmed oxidation), an oxidable solid sample is exposed to a flow of an oxidant gas (typically a few % O\textsubscript{2} in N\textsubscript{2}).

Experimental results on H\textsubscript{2}–TPR and O\textsubscript{2}–TPO are presented in Figure 5.1. From the H\textsubscript{2}–TPR profiles shown in Figure 5.1a it could be concluded that the nickel of the catalysts supported on γ-Al\textsubscript{2}O\textsubscript{3} (Ni–Gamma and NiRu–Gamma) has a large interaction with its support by forming nickel aluminates (which is attributed to the high calcination temperature applied in these catalysts); this observation was also supported by XRD analyses. Additionally, in bimetallic catalysts, mainly in NiRu–Gamma, the reduction of the Ni and Ru species seems to take place almost independently, resulting in the occurrence of mainly segregated atom clusters of each species.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.1}
\caption{Temperature-programmed profiles of the catalysts. (a) H\textsubscript{2}–TPR, (b) O\textsubscript{2}–TPO. (From Papers IV and V).}
\end{figure}
On the contrary, in the NiRu–Alpha and NiRu–MG30 catalysts, some Ni-Ru interaction takes place; however, it was not possible to see this effect in the XRD measurements. As shown in the TPO measurements of the reduced catalysts (Figure 5.1b), there is a considerably large fraction of metallic nickel and ruthenium that is separately oxidized which may also support the idea of the formation of segregated and moderately large metal clusters.

Temperature–programmed oxidation (TPO) was also employed to characterize the carbonaceous deposits on some of the spent catalysts (Figure 5.2). Noticeable differences between the different catalysts were observed in the amount and characteristics of the carbon formed during the CPO reaction (see Section 5.4.2). More carbon was formed on the commercial catalyst (Ni–Com) while on the Ru–MG30 none or very little carbon was formed. Carbon formation on the NiRu–MG30 catalyst was moderately low, probably due to the combined effects of the small metal particle size and the presence of a noble metal; this is discussed in more depth in Sections 5.4 and 5.5.

![Figure 5.2. Temperature-programmed oxidation (TPO) of the catalyst after CPO reaction. (From Paper IV).](image-url)
Figure 5.3. TEM images after CH₄ decomposition experiments at ~ 550°C. (a) Ni–Alpha, (b) Ni–MG30, (c) Ni–Gamma, (d) NiRu–Alpha, (e) NiRu–MG30, (f) NiRu–Gamma, (g) Ru–Alpha, (h) Ru–MG30. (From Paper V).
5.2.5. Transmission electron microscopy (TEM)

In transmission electron microscopy, a thin sample is irradiated with a parallel beam of electrons and those electrons that are “transmitted” are diffracted by a lens to be further projected and combined as a two-dimensional image. Therefore, TEM enables the examination of the catalyst surface permitting the determination of particle size distributions and useful information on the structure of the catalyst sample that other characterization techniques can hardly provide; however, only a small portion of the sample is analyzed and not all combinations of materials can easily be analyzed [105].

In this work, TEM analyses were used to identify the type of carbon formed on the catalysts after CH$_4$ decomposition experiments at about 550 °C (Paper V). As shown in Figure 5.3, nickel particles formed whisker-like structures with tubular appearance, while the ruthenium catalysts did not form whisker carbon; this observation is in agreement with literature [15, 73]. Furthermore, from TEM analyses it was also possible to determine the particle size distributions in the catalysts. Nickel particle sizes were in good agreement with the values obtained by H$_2$ chemisorption, mainly for Ni catalysts; however, in the bimetallic catalysts, it was concluded that ruthenium mainly formed large particles which supports the idea of segregated metal clusters of both Ni and Ru. It is important to mention here that the particle sizes obtained by TEM represent very useful information in order to associate the nickel particle size with the extent of carbon formation during equilibrium experiments on CH$_4$ decomposition (Section 5.5).
5.3. Catalytic tests: equipment and experimental procedures

During the course of this work two reaction systems were used. One system was designed, built and exclusively used for performing the CPO activity tests in the presence of steam (Paper IV). The other system was an already existing unit which was suitably modified for assessing the equilibrium of the methane decomposition as well as for some CPO activity tests (Paper V). In the following, a brief description of these systems, including the procedures employed for performing the reaction tests, is provided.

5.3.1. CPO activity tests in the presence of steam

5.3.1.1. Experimental setup

The CPO activity tests in the presence of steam were carried out in a continuous flow quartz reactor. The reactor tube consisted of a 1/2-inch quartz tube with a total length of 50 cm and an internal diameter of 9.5 mm. The reaction zone of the reactor tube was externally heated by using an electric cylindrical furnace equipped with a digital PID controller. The temperature of the furnace, i.e. outside the reactor tube, could be conveniently regulated from ambient to 900 °C.

In a typical experiment a monolithic catalyst (9.3 mm diameter, 30 mm length, and 400 cells per square inch) was surrounded by two blank monoliths and placed inside the reactor tube. In order to measure the temperature profile in the flow direction, a thermowell with an external diameter of 1.6 mm was placed along the reactor and passed through the center of the three monoliths (see Figure 5.4); inside the thermowell, a movable K-type thermocouple (OD = 0.5 mm) was used to monitor the temperature.

Gaseous reactants (usually CH₄, O₂, and N₂; 99.999 vol% purity) were fed to the reactor by using thermal mass flow controllers (Bronkhorst High-Tech B.V, EL-FLOW ®). Water was purified by ion exchangers and was then fed to the reactor by a HPLC dosing pump (Scientific Systems, Inc.) followed by an evaporator equipped with a temperature controller. After cooling the
product stream from the reactor, liquid water was separated in a cold trap (at about 0 °C). A backward electronic pressure controller (Bronkhorst High-Tech B.V, EL-PRESS) was placed downstream the cold trap in order to control the pressure. The product gases leaving the system as well as the gas reactive mixture were analyzed on-line using a Master GC gas chromatograph (DANI Instruments SpA) equipped with two flame ionization detectors (FID) and a thermal conductivity detector (TCD). A detailed description of the chromatographic method can be found in Andersson et al. [106].

Figure 5.4. Schematic overview of the catalytic testing system for CPO experiments (oven is not shown, for clarity). From Paper IV.
5.3.1.2. Experimental methodology

The aim of this set of experiments was to evaluate the influence of catalyst properties and composition on the catalytic activity, temperature profile and carbon formation during the CPO of methane at low O₂/CH₄ and H₂O/CH₄ ratios. The catalysts supported on MgO/MgAl₂O₄ (Ni–MG30, NiRu–MG30 and Ru–MG30) were chosen for this purpose as well as the commercial Ni-based catalyst (Ni–Com).

Prior to the experiments, the catalyst powders were ball-milled and then wash-coated onto cordierite monoliths. The amount of catalyst deposited onto the monoliths was in the range of 180–200 mg. The composition of the reactive mixture was kept constant at O₂/CH₄ = 0.2 and H₂O/CH₄ = 0.3 (on a molar basis). These experiments were carried out at a constant exit temperature of 700 °C (set 2 mm downstream the monolithic catalyst); the operating pressure was 1.0 bar (gauge). At these conditions, thermodynamic calculations based on graphite predict carbon formation (see Figure 4.3). The space velocity (SV) was 100 Nl(CH₄)gcat⁻¹:h⁻¹, equivalent to GHSV(CH₄) = 8830 h⁻¹ (based on monolith volume) and WHSV(CH₄) = 71 h⁻¹ (based on catalyst loading); typical CH₄ inlet flow rates were 300 Nml/min.

Furthermore, in order to study the effect of operating conditions on the catalytic performance, the Ru–MG30 catalyst was tested at different space velocities (SV = 90, 150 and 210 Nl(CH₄)gcat⁻¹:h⁻¹) and O₂/CH₄ and H₂O/CH₄ ratios (H₂O/CH₄ = 0, 0.3 and 0.5; O₂/CH₄ = 0.2 and 0.4). This catalyst was chosen because it was the only catalyst able to withstand carbon formation during the previous tests.

Before all reaction tests, the washcoated catalysts were reduced in situ with pure hydrogen (50 ml/min) from ambient temperature to 850 °C and held at this temperature for about 1 hour. Then, the furnace temperature was lowered to about 700 °C and at this temperature the system was flushed with N₂. Afterwards, the feed was switched to the reactive mixture while the furnace temperature was properly modified to obtain 700 °C at the catalyst bed exit. In all the experiments, the total reactive mixture contained 10 mol% N₂ as internal standard for the chromatographic analysis.
Additional CPO tests were performed in another test rig (the same as described in Section 5.3.2.1) using similar washcoated monolithic catalysts. The Ni and bimetallic NiRu catalysts supported on $\alpha$-Al$_2$O$_3$ (Ni–Alpha and NiRu–Alpha), $\gamma$-Al$_2$O$_3$ (Ni–Gamma and NiRu–Gamma) and MgO/MgAl$_2$O$_4$ (Ni–MG30 and NiRu–MG30) were tested. These tests were carried out in a reactor tube of 15 mm of inner diameter at atmospheric pressure and at a constant catalyst bed exit temperature of 700 °C. The space velocity was kept constant at 105 Nl$_{\text{CH}_4}$·g$^{-1}$·h$^{-1}$ (i.e. GHSV$_{\text{CH}_4}$ = 1380 h$^{-1}$, based on monolith volume, or WHSV$_{\text{CH}_4}$ = 70 h$^{-1}$, based on catalyst loading). In these tests, the reactive mixture composition was kept constant at O$_2$/CH$_4$ = 0.25 and diluted with nitrogen (89 % N$_2$). For further details about this set of reactions, the reader is directed to Paper V.

5.3.2. CH$_4$ decomposition tests

5.3.2.1. Experimental setup

The equilibrium tests on the CH$_4$ decomposition reaction were carried out in a U-shape quartz reactor (ID ≈ 5 mm) in which the catalyst powder was placed between two quartz wool plugs. A cylindrical furnace equipped with a digital PID controller was employed to heat the reactor. A thermocouple was placed outside the quartz reactor with its tip located at the same level as the catalyst bed. In order to check for pressures drops, a manometer was placed upstream the catalyst bed. Thermal mass flow controllers (Bronkhorst High-Tech B.V) were used for feeding gaseous reactants into to the reactor. After cooling the product stream from the reactor, liquid water (if present) was separated in cold traps. The gas reactive mixture and the product gases (i.e. CH$_4$, CO, CO$_2$, O$_2$ and H$_2$) were analyzed on-line by paramagnetic (O$_2$), IR spectroscopy (CH$_4$, CO, CO$_2$) and thermal conductivity (H$_2$) techniques in a combined system (NGA 2000 MLT-Analyzer and HYDROS 100, from Rosemount Analytical) which is described elsewhere [107]; this analytical system is able to detect reactant concentrations at ppm levels continuously (time response < 1 s).
5.3.2.2. Experimental methodology

The aim of this set of experiments was to gain more insights about the influence of the catalyst properties and composition on carbon formation, more specifically, through the analysis of the equilibrium of the methane decomposition reaction (Rc1 in Table 3.2). The Ni and bimetallic NiRu catalysts supported on α-Al₂O₃ (Ni–Alpha and NiRu–Alpha), γ-Al₂O₃ (Ni–Gamma and NiRu–Gamma) and MgO/MgAl₂O₄ (Ni–MG30 and NiRu–MG30) were chosen for this purpose.

Before each test, the catalyst powder, typically 200 mg, was reduced in situ with 5% H₂ in N₂ (200 ml/min) from ambient temperature to 850 °C and held at this temperature for 0.5 h. Then, the system was flushed with N₂ and the catalyst temperature was decreased to about 350 °C. Subsequently, H₂ and then CH₄ were added until a desired gas composition was obtained, and once it was constant, the temperature was raised at a rate of 3 °C/min until an increase in the H₂ concentration, accompanied with a decrease in the CH₄ concentration, was indicated in the gas analyzer; this situation indirectly indicated the formation of carbon on the catalyst. Then, the temperature was allowed to increase by about 20 °C and then the ramp was stopped; immediately after, the temperature was decreased at about 3 °C/min until the initial H₂ and CH₄ concentrations were again obtained. To form each equilibrium point (Kₚ and T), the equilibrium quotient, \( K_p = \frac{P_{H_2}^2}{P_{CH_4}} \), was calculated using the H₂ and CH₄ concentrations, with “T” corresponding to the lower temperature at which carbon starts to form. The same procedure was followed for other H₂ and CH₄ concentrations corresponding to each equilibrium point. All the equilibrium tests were carried out at atmospheric pressure. The equilibrium points were obtained in the following order of molar ratios H₂:CH₄ = 8.0:1.0, 5.6:1.0, 1.6:1.0, and 1.0:2.2. Tests varying the former order were also performed, as well as adding some intermediate points, and no significant deviations were observed.
5.4. Catalytic performance in the CPO reaction.

5.4.1. Activity

As mentioned in Section 3, catalytic partial oxidation involves both exothermic and endothermic reactions. Since several reactions take place, reversible and irreversible, variations of the composition of the feed stream, for instance the incorporation of H$_2$O, will change the extent of these reactions as well as methane conversion and product distribution. For example, at a feed molar ratio of O$_2$/CH$_4$ = 0.2 and a constant exit temperature of 700 °C, methane equilibrium conversion for total oxidation only (R2 in Table 3.1) is barely 10 %; however, if partial oxidation, reforming and WGS reactions (R1 and R3–R6 in Table 3.1, respectively) are also included in the calculations, the conversion increases to about 35 %. Furthermore, when H$_2$O is also added as reactant (i.e. O$_2$/CH$_4$ = 0.2 and H$_2$O/CH$_4$ = 0.3) and all reactions are taken into account in the calculations, methane conversion is further increased to about 52 %; this is shown in Figure 5.5. Also, initial experimental methane conversion as function of the metallic surface area of the Ni–MG30, NiRu–MG30, Ru–MG30 and Ni–Com catalysts are reported in Figure 5.4.

![Figure 5.5. Activity of the catalysts during the partial oxidation of methane at O$_2$/CH$_4$ = 0.2, H$_2$O/CH$_4$ = 0.3, T$_{exit}$ ≈ 700 °C. Equilibrium conversions are included for comparative purposes (See Table 3.2). (From Paper IV).](image-url)
The moderately thick line for the equilibrium conversions at \( \text{O}_2/\text{CH}_4 = 0.2 \) and \( \text{H}_2\text{O}/\text{CH}_4 = 0.3 \) intends to take into account the small differences between \( 700 \) °C and the experimental exit temperatures.

The initial methane conversions followed the order \( \text{Ni–MG30} > \text{NiRu–MG30} > \text{Ru–MG30} \approx \text{Ni–Com} \); however, regarding methane molecules converted per amount of active metal sites, the Ru–MG30 catalyst was found to be the most active; on the contrary the Ni–MG30 catalyst had the lowest activity. It is interesting to see that the bimetallic NiRu–MG30 catalyst exhibited an intermediate behavior (see Figure 5.5, the diagonal dotted lines point to zero conversion at zero metal surface area). For comparative purposes, activity results for the Ni–Gamma, NiRu–Gamma and Ru–Gamma catalysts were also included in Figure 5.5; these catalysts also followed similar trends. Therefore, at the conditions applied in this set of experiments, it seems that methane conversion not only increases with the metallic surface area of the catalyst, but also in accordance with the type of metal present in the catalyst (Ni and/or Ru).

![Graph](image)

**Figure 5.6.** Activity of the catalysts for partial oxidation of methane (\( \text{O}_2/\text{CH}_4 = 0.25 \), \( T_{\text{exit}} = 700 \) °C). (From Paper V).
In another set of experiments (Paper V), catalyst activity was related to catalyst properties by using the number of molecules of methane or a specified product converted per catalytic active site per time, i.e. the turnover frequency (TOF); the results are illustrated in Figure 5.6. Even though this approach for comparing catalyst activities might be doubtful, it was helpful in order to roughly explain the different activities demonstrated by the catalysts. For example, it is clear that ruthenium is intrinsically much more active than nickel not only for partial oxidation but also for steam reforming, in agreement with previous literature [41, 42, 44]. The linear trends in the relationship between TOF and metal dispersion usually suggest, at least for steam reforming, that the activity of each kind of metal is dominated by steps sites rather than terrace and corner sites [44]. Therefore, the linear trends shown by the Alpha and Gamma catalysts, might suggest that either the presence of ruthenium affects catalyst performance very little or that large ruthenium particle obscures its intrinsic higher activity. The latter affirmation seems to conform better to the characterization results which showed large ruthenium particles mainly in the bimetallic catalysts. In the case of the NiRu-MG30 catalyst, it seems that the presence of ruthenium enhances activity by either promoting smaller nickel particle sizes (with more corners) or by its intrinsically higher activity. Additionally, the higher activity presented in the catalysts supported on α-Al₂O₃ (Ni–Alpha and NiRu–Alpha) catalysts was suggested to be related to a lower impact of internal mass transfer as inferred from their low BET surface area. From the results shown in Figures 5.5 and 5.6, it can be deduced that the use of a hydrotalcite-derived material as catalyst support is more beneficial when both nickel and ruthenium metals are present in the catalyst.

5.4.2. Temperature profiles
As mentioned in Section 3.5, during CPO, an important issue is the formation of a hot spot in the first part of the catalytic bed produced by the exothermic oxidation reactions; this might have detrimental consequences for the catalyst. However, when the activity of the catalyst for the endothermic reforming reactions is sufficiently high, these may probably
compete with the exothermic oxidation reactions and therefore reduce the hot spot formation [103].

Figure 5.7 shows the temperature profiles along the reactor for the Ru–MG30, Ni–MG30, NiRu–MG30, Ni–Com catalysts at an initial time of 0.5 h and after 8 h of operation. Higher temperatures close to the reactor inlet were observed in the case of Ru–MG30 and Ni–Com catalysts suggesting an important contribution of the exothermic reactions (see Table 3.1). Additionally, because of the endothermic reactions, the temperature along the reactor decreased; this effect was more relevant for the Ru–MG30 and NiRu–MG30 catalysts.

![Temperature profiles of the catalysts during the partial oxidation of methane](image)

**Figure 5.7.** Temperature profiles of the catalysts during the partial oxidation of methane (O₂/CH₄ = 0.2, H₂O/CH₄ = 0.3). (From **Paper IV**).
The differences in the temperature profiles were attributed to the influence of the metallic surface area of the catalysts on the extent of the exothermic and endothermic reactions. When the amount of active metal is high enough, a fraction of it will catalyze the exothermic reactions while the other fraction will catalyze, almost in parallel fashion, the endothermic reactions; therefore the heat generated by exothermic reactions is partially absorbed by the endothermic reforming reactions resulting in a modest temperature peak. On the contrary, if the metallic surface area is low, there will not be enough active metal to catalyze both types of reactions in parallel and, since oxidation reactions proceed faster, the endothermic reactions will preferably be consecutive to the exothermic reactions; this results in a more pronounced maximum peak temperature.

The temperature profiles shown in Figure 5.7 presented a slight movement towards higher temperatures with time; this was also accompanied by a reduction in methane conversions, except for the Ru–MG30 catalysts. The movement of the temperature profiles was attributed to catalyst deactivation. Regarding carbon formation, the potential for forming carbon, calculated by the equilibrated gas principle (as described in Section 4.3), existed all along the catalyst bed, but the highest risk is found close to the inlet of the reactor, in agreement with the analysis performed in Section 4.3.2. The Ni–Com catalyst presented a higher potential for carbon formation than the other catalysts and this was attributed to the shape of its temperature profile. In addition, TPO analyses of the catalysts after CPO reaction (Section 5.2.4) also showed that more carbon is formed on the Ni–Com catalyst. Additionally, sintering and phase transitions might also take place; however, experimental limitations made difficult to analyze their occurrence in depth (see Papers IV and V for further discussion).

5.4.2. Effect of operating conditions

The effect of space velocity on the CPO of methane is shown in Figure 5.8a; in these tests, the temperature of the furnace was the same for all experiments and the $O_2/CH_4$ ratio was 0.4, no water was added to the feed. It is evident that the increment of space velocity not only produced higher temperatures at the inlet of the bed but also a slight movement of the
temperature profiles downwards the catalytic bed; as a consequence, the exit temperature was also higher. However, methane conversions and selectivity of products did not increase proportionally to the exit temperatures; consequently, it seems that at high space velocities there was not enough catalyst available for further methane conversion and product formation.

The addition of steam at H$_2$O/CH$_4$ ratio of 0.4 (dotted line in Figure 5.8a) produced a reduction in the maximum temperature; probably driven by enhancement of the reforming and WGS reactions. Also, methane conversion and selectivity of products were closer to those expected from thermodynamic equilibrium.

![Figure 5.8](image)

**Figure 5.8.** Temperature profiles of the Ru–MG30 catalyst during the partial oxidation of methane: (a) Effect of space velocity, (b) Effect of H$_2$O/CH$_4$ ratio. (From Paper IV).

Additionally, the results shown in Figure 5.8b, obtained at constant exit temperature, indicate that addition of steam modifies the temperature profile. However, because of the low O$_2$/CH$_4$ ratio, methane conversions were lower than the values expected from equilibrium and the difference increased with the H$_2$O/CH$_4$ ratio.

### 5.5. CH$_4$ decomposition tests

In this work, the conditions at which the CPO tests were performed involved the risk for carbon formation (graphite) as predicted by thermodynamics (See Section 4); however, when catalysts are used the limits predicted by
thermodynamics may vary depending on the catalyst composition and properties (see Section 3.4).

Preliminary tests for CH$_4$ decomposition were carried out by means of temperature programmed analysis (Figure 5.9). The ruthenium catalyst, Ru–MG30, did not present any appreciable amount of carbon; on the contrary, the Ni–MG30 catalyst formed considerably large amounts while the bimetallic NiRu–MG30 formed little carbon. This was in agreement with TEM analyses (Section 5.2.5) which showed that nickel particles formed whisker carbon and ruthenium did not. In addition, it was interesting to see in Figure 5.9 that the temperature at which carbon started to form was slightly higher in the case of the monometallic Ni catalyst compared to the NiRu bimetallic catalyst. The latter observation originated the next set of tests, i.e. the equilibrium experiments.

Determining the deviations of the equilibrium for carbon formation from graphite data could be very useful for understanding the role of the catalytic supports as well as the presence of ruthenium in the bimetallic catalysts. For this purpose, equilibrium tests on the CH$_4$ decomposition reaction were performed over Ni and the bimetallic NiRu catalysts.

![Figure 5.9. Temperature-programmed CH$_4$ decomposition of the Ni–MG30, NiRu–MG30, and Ru–MG30 catalysts. (From Paper IV).](image-url)
The relationship between the equilibrium constant and the temperature is illustrated in Figure 5.10. Furthermore, earlier published data have been included in this figure corresponding to a nickel catalyst (Ni-a) with a maximum nickel particle size of 300 nm [15, 75]. For all catalysts, the equilibrium constants were smaller than the corresponding values for graphite; this difference is ascribed to the formation of a more disordered structure of carbon [74].

The main difference found among the data of the catalysts was that the equilibrium constants for the NiRu-MG30 catalyst were moderately smaller than those for the other catalysts. The new question was if this difference could be ascribed to the interaction of nickel with ruthenium and/or with the catalyst support, or simply related to the particle size of nickel. Therefore,
the deviation of the free energy from graphite data, $\Delta G_C = RT \ln \frac{K_p(\text{graphite})}{K_p(\text{catalyst})}$, was calculated from the data presented in Figure 5.10 and was used jointly with the maximum nickel particle size obtained by TEM (see Section 5.2.5) to plot Figure 5.11.

![Figure 5.11. Deviation of the free energy ($\Delta G_C$) from graphite data and nickel particle size (CH$_4$ decomposition at 600 °C). (From Paper V).](image)

The deviation of graphite thermodynamics with maximum nickel particle size is evident. All catalysts seem to fit well with a linear relationship ($\Delta G_C = 2k \cdot \frac{1}{D_{\text{max}}} + \mu^*$) well documented in previous literature [15, 22, 74]. The deviations from graphite data could be attributed to the additional contribution of surface energy which increases with decreasing whisker diameter and hence with nickel particle size. However, the bimetallic NiRu–MG30 catalyst has a moderately higher value of $\Delta G_C$ compared with the Ni–MG30 catalyst. This would be in agreement with the higher activity presented during activity tests and probably be related to an enhancement of the Ni-Ru interactions as well as a beneficial effect of the catalyst support. Nonetheless, this subject deserves more careful attention and still needs to be investigated.
6. Conclusions and future work

The aim of this work was to gain increased knowledge concerning the utilization of a catalytic partial oxidation (CPO) reactor as pre-reforming step in synthesis gas production process in Gas to Liquids (GTL) applications. The aim was also to gain a deeper understanding of nickel and ruthenium based catalysts of different compositions on catalytic behavior and carbon formation during the CPO reaction. A thermodynamic equilibrium approach was used to analyze a process configuration consisting of a CPO reactor followed by an autothermal reforming (ATR) reactor as well as to determine the limits and conditions for carbon formation. Catalysts based on nickel, ruthenium and bimetallic nickel-ruthenium on α-Al₂O₃, γ-Al₂O₃, or MgO/MgAl₂O₄ supports were prepared, characterized and tested in the CPO reaction; for this purpose, an experimental reaction system was designed and constructed. The prepared catalysts were also tested in the CH₄ decomposition reaction.

6.1. Main conclusions of this work

Results from thermodynamic analysis of the catalytic system consisting of a CPO reactor followed by an ATR reactor showed that synthesis gas production can be strongly influenced by changes in operating conditions such as the oxygen-to-carbon (O₂/C) and the steam-to-carbon (H₂O/C) ratios, recycled gas (tail gas) compositions, and operating pressures and temperatures. It was found that an effective operation of the process (CPO + ATR) requires a correct combination of these operating conditions in order to accomplish the synthesis gas requirements of the Fischer-Tropsch synthesis. Additionally, it was shown that operation of the CPO pre-reformer demands low oxygen-to-carbon and steam-to-carbon ratios, both approximately lower than 0.3. Furthermore, it was shown that the risk for carbon formation in the CPO reactor can be reduced by a proper combination of the operating conditions; however, the inlet part of the CPO reactor inevitably showed a high potential for carbon formation.
During experimental tests of the CPO reaction, at feed molar ratios of \( \text{O}_2/\text{CH}_4 = 0.2 \) and \( \text{H}_2\text{O}/\text{CH}_4 = 0.3 \), over catalysts based on Ni, Ru and bimetallic Ni-Ru supported on a MgO/MgAl\(_2\)O\(_4\) material, it was found that the methane conversion increased with the metallic surface area of the catalyst, in accordance with the relative intrinsic activity of the type of metal present in the catalyst (Ni and/or Ru). Additionally, the metallic surface area of the catalysts was found to be related to the extent and thermal effects of the exothermic oxidation reactions and the endothermic reforming reactions which are in turn responsible for the “shape” of the temperature profile and consequently for the potential for carbon formation along the catalytic bed. Furthermore, it was possible to examine and analyze catalyst deactivation from the change in shape of the temperature profile of each catalyst. Even though all the prepared catalysts showed good initial performances, the only catalyst able to withstand carbon formation was the monometallic Ru catalyst; the bimetallic Ni-Ru catalyst showed a higher resistance to carbon deposition than the monometallic Ni catalysts.

Experiments with different catalytic supports, i.e. \( \alpha\)-Al\(_2\)O\(_3\), \( \gamma\)-Al\(_2\)O\(_3\), and MgO/MgAl\(_2\)O\(_4\), at \( \text{O}_2/\text{CH}_4 \) ratio of 0.2 confirmed that catalyst performance during the CPO of methane is also affected by support morphology, either by influencing catalyst properties or by probably affecting the extent of internal mass transfer restrictions. From these results, it was concluded that the use of a hydrotalcite-derived material, i.e. MgO/MgAl\(_2\)O\(_4\), as catalyst support is more beneficial when both nickel and ruthenium are present in the catalyst.

From experiments regarding the equilibrium of the methane decomposition reaction (\( \text{CH}_4 \leftrightarrow 2\text{H}_2 + \text{C} \)), all tested catalysts, i.e. catalysts based on Ni and Ni-Ru supported on \( \alpha\)-Al\(_2\)O\(_3\), \( \gamma\)-Al\(_2\)O\(_3\), and MgO/MgAl\(_2\)O\(_4\), presented smaller equilibrium constants than those calculated on the basis of graphite. It was found that the deviations from graphite data are mainly associated with the maximum particle size of nickel regardless of whether ruthenium is present in the catalyst or not. However, once again, in this set of experiments the bimetallic Ni-Ru catalyst supported on hydrotalcite-derived material showed an interesting enhanced behavior compared with the other
bimetallic Ni-Ru catalysts; therefore, this type of catalyst deserves further attention and investigation.

6.2. Future work

It should be evident from the results presented in this work that several aspects have to be included in future investigations. There is much that can be done with data obtained from CPO tests under adiabatic conditions; in particular, temperature profiles at high mass velocities (high Reynolds numbers) and their relationship to catalyst properties and composition. Additionally, an appropriate reactor model might provide the information that otherwise would not be possible to obtain experimentally, e.g. temperature and gas concentrations gradients in a catalyst pellet or in the washcoat which can be used to evaluate the potential of carbon formation as well as optimizing reactor design. Furthermore, a proper evaluation on the effect of co-feeding higher hydrocarbons and tail gas-like gases on the reactor performance is also required.

Additionally, there is a critical need for basic evaluation of catalyst deactivation during CPO by mechanisms that were not studied in depth during this work, i.e. sintering and phase transitions. In particular, more experiments are needed to understand both the catalytic behavior and catalyst deactivation of the bimetallic nickel-ruthenium catalyst over hydrotalcite-derived materials. Preparation of uniform metal particles with controlled particle size by using, for example, the microemulsion method, could help to clarify and complement the current studies on the deviations of carbon formation from graphite data.

Based on the information provided in this work, the dual bed approach, i.e. the first part of the reactor having a noble metal catalyst and downstream a nickel-based catalyst, could be a valid alternative for overcoming the high tendency for carbon formation in the inlet region of the CPO pre-reformer; therefore, proper theoretical and experimental evaluations are needed.
Addressing the aspects mentioned here would constitute important contributions to scientific knowledge and technological development of the CPO technology.
List of abbreviations

a.u.       Arbitrary units
ASU       Air separation unit
ATR       Autothermal reforming
BET       Brunauer-Emmett-Teller
BHJ       Barret-Joyner-Halenda
bpd       Barrels per day
BTL       Biomass-to-Liquids
BWF       Boiler feed water
CMR       Ceramic membrane reforming
CPO       Catalytic partial oxidation
CTL       Coal-to-Liquids
FID       Flame ionization detector
FT        Fischer-Tropsch
GC        Gas chromatograph
GHSV      Gas hourly space velocity
GTL       Gas-to-Liquids
H₂O/C     Steam-to-carbon ratio (based on total hydrocarbons)
H₂O/CH₄   Steam-to-carbon ratio (based on methane)
HP        High pressure
HTFT      High-temperature Fischer-Tropsch
IW        Incipient-wetness
LPG       Liquefied petroleum gas
LTFT      Low-temperature Fischer-Tropsch
MP        Low pressure
NGL       Natural gas liquids
O₂/C      Oxygen-to-carbon ratio (based on total hydrocarbons)
O₂/CH₄    Oxygen-to-carbon ratio (based on methane)
PID       Proportional-integral-derivative
POX       Partial oxidation
SGU       Syngas generation unit
SR        Steam reforming
SV        Space velocity
TCD       Thermal conductivity detector
TEM       Transmission electron microscopy
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOF</td>
<td>Turnover frequency</td>
</tr>
<tr>
<td>TPO</td>
<td>Temperature-programmed oxidation</td>
</tr>
<tr>
<td>TPR</td>
<td>Temperature-programmed reduction</td>
</tr>
<tr>
<td>WGS</td>
<td>Water-gas shift</td>
</tr>
<tr>
<td>WHSV</td>
<td>Weight hourly space velocity</td>
</tr>
<tr>
<td>WTL</td>
<td>Wire-to-Liquids</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>XTL</td>
<td>X(any carbon source)-to-Liquids</td>
</tr>
</tbody>
</table>
Acknowledgments

I am indebted to many people for their inspiration and support throughout this journey.

First and foremost, I would like to thank my supervisors Associate Professor Magali Boutonnet and Professor Sven Järås for giving me the opportunity to carry out doctoral studies at the division of Chemical Technology. I appreciate their patience, support and confidence in me and my work. Likewise, I am grateful to Dr. Saul Cabrera for his supervision, support and friendship. Thanks also to Associate Professor Henrik Kušar for his interest and supervision during the last years of my studies.

I would also like to acknowledge the Swedish International Development Cooperation Agency (SIDA) for financial support, thus making this work possible.

I would like to thank Professor Lars J. Pettersson for his cordiality and good humor. I am indebted to Roberto Lanza for guidance and constant help with experimental work. I want to express my sincere gratitude to Rolando Zanzi, I really appreciate his willingness to help and friendship during all these years. Also, thanks to Yohannes Kiros for his kindness and support.

Very special thanks to Luis Lopez, Adhemar Araoz and Mauricio Ormachea for putting up with me during these years. I appreciate your continuous support and sustaining friendship (por tantas cosas... gracias de verdad amigos!).

I had the fortune to be surrounded by a nice group of colleagues at Chemical Technology. Thanks especially to Robert Andersson, Sara Lögdberg, Francesco Regali, Matteo Lualdi, Xanthias Karatzas, Moa Zietheń Granlund, Vera Nemanova, and Angelica González for very good times and nice experiences (I have learned a lot from you guys!). Many thanks to Fatima Pardo, Javier (Barri) Barrientos, Rodrigo Suárez, Pouya Haghighi, Francesco Montecchio, Jonas Granestrand, Alagar Raj Paulraj, Jerry Solis, Sandra Dahlin, Lina Norberg Samuelsson and Zari Musavi for interesting
discussions, jokes, advise, help and support. Furthermore, I would like to thank Silvia Tomé T. and Raquel Rodríguez for your kindness and friendship. Special thanks to Otto von Krusenstierna for his great enthusiasm about science; social events at the Chemical Technology Division would not be the same without him. I am also very grateful to Christina Hörnell for improving the linguistic quality of my publications and this thesis.

I wish to thank to my “temporary” office mates and good friends Oscar Laguna, Vicente Montes, and Victoria Garcilaso de la Vega; even though their research stays in Sweden were short, they certainly won my admiration and affection.

Many thanks to my colleagues and friends at the Natural Gas Institute (IGN), La Paz, Bolivia, for their support and friendship. In particular, I want to thank Cristhian Fernandez and Ronald Escobar for their enthusiasm, hard work, friendship and good times. Furthermore, I would like to thank my old Bolivian friends; your question: “when are you finishing your PhD?” probably repeated hundreds of times, was always a source of motivation. Your support during these years has been very important, Gracias!

Last, but absolutely not least, I would like to thank all my family, especially my wife Magaly and my little son Javier, for your love, patience and understanding. You have been a steady support throughout these years and without you nothing of this would have been possible.
References


