



Differences between Fisher–Tropsch synthesis of either gasoline or diesel based on changes of entropy and free energy



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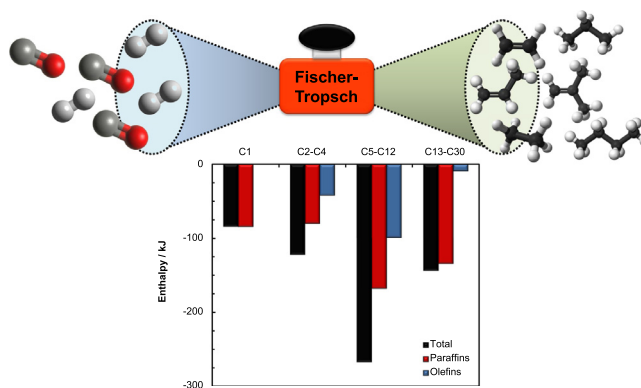
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HIGHLIGHTS

- Fisher–Tropsch synthesis of fuels is analyzed evaluating energy release as consequence of heat of reaction.
- Experimental products distributions obtained using different kinds of catalysts are compared.
- Prevision of energy management during Fisher–Tropsch synthesis is used as criterion for production objectives.
- Lighter liquid fuels, such as gasoline, are found to be more favoured to be produced than diesel.

GRAPHICAL ABSTRACT



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ABSTRACT

Synthesis of liquid fuels, mainly gasoline and diesel, by Fisher–Tropsch reactions is a complex process. Prediction of products distribution as function of carbon number has been under discussion for many years and, currently, it has not been possible to perform without a comprehensive description of catalyst properties/formulation; therefore, usually experimental data are necessary to study this process. In this work, analysis of experimental data obtained from several literature references is performed by evaluating the total energy release, as consequence of heat of reaction, and entropy and free energy generated during the experiments. It is found that depending on the production objectives and the catalyst used, energy management during hydrocarbons synthesis, mainly paraffins and olefins, could be a criterion to decide how long the hydrocarbons chain should be. Additionally, since total Gibbs' free energy becomes less negative as hydrocarbons are longer, it is assessed that production of gasoline and LP gas could be more attractive as target than production of diesel.

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1. Introduction

Interest in alternative, clean technologies to obtain synthetic fuels, such as the Fisher–Tropsch (FT) synthesis, has been steadily growing in the last 30 years. Fuels are indispensable, but the fossil

sources from which they currently come are not. It is feasible to replace fossil sources while keeping renewable fuels as important energy vectors. Additionally, liquid fuels dominate energy trade because they are bottled lightning: it is the best way to transport and store energy, and thus to trade it [1]. It has been said that diesel production should be the preferred option as the efficiency of a diesel fuel engine is higher than that of a gasoline fuel engine [e.g. 1,2]. This proposition is based on the 'fuel yield', usually

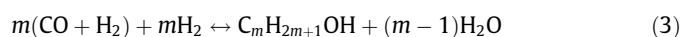
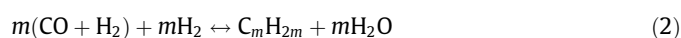
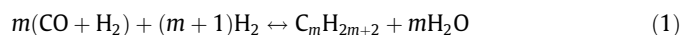
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measured as kilometers per liter or miles per gallon run by a fuel-powered engine; however this comparison is not adequate because of the difference between gasoline and diesel densities (Table 1). There are other measures that can help to compare efficiency of the use of gasoline and diesel as fuels, such as the low heat power and the carbon intensity; the first one related to the energy released during complete combustion of the fuel, and the second one is a measure of the life cycle of green-house gases (GHG) emission per unit of energy in the fuel. For this comparison, GHG emissions include CO₂, CH₄ and N₂O. Life cycle of fossil fuels includes feedstock extraction/preparation, refining activities to produce a finished fuel, and any transportation/transmission of the feedstock or refined fuel to the conversion plant or end user [3] (Table 1).

In addition to equivalent motoristic performances (Table 1), alternative fuels obtained from syngas have the further advantage that do not contain unwanted heterocompounds, such as molecules containing sulfur and nitrogen. An option to obtain a variety of fuels by synthesis that has been recovering importance is the Fisher–Tropsch (FT) synthesis reactions, based on the catalytic conversion of syngas (CO + H₂) followed by oligomerization of –CH– and –CH₂– groups, in order to generate gaseous (methane and dry gas) and liquid fuels (liquid pressure gas, C₃–C₄; gasoline, C₅–C₁₂; and diesel, C₁₃–C₃₅).

Stoichiometry of FT synthesis of paraffins (1), olefins (2) and alcohols (3) is well known, it also determines the (H₂/CO) ratio required for synthesis reactions (Fig. 1). It is important to notice that, as consequence of water formation, water-shift reaction (4) becomes a competitor for the carbon monoxide in catalytic systems containing iron. It has been proposed that oligomerization and water-shift reactions take place in different catalyst sites; therefore there is not competition for the active sites on iron catalysts [5]; moreover water-shift and synthesis of olefins and alcohols is neglectable during synthesis of hydrocarbons on cobalt catalysts [6].



Some main characteristics of FT synthesis are the unavoidable production of a wide range of hydrocarbon products, liberation of large amounts of heat from the highly exothermic synthesis reactions [7] and that FT yields high amounts of waxes and minor amounts of liquid fuels, that forces downstream upgrading [8]. FT synthesis exhibits a variety of reaction steps, such as chain propagation, chain branching, olefins and paraffins desorption, methanation and olefin secondary reactions of double bond shift and hydrogenation [9], which trouble the evaluation of changes of energy and entropy. In addition, product distributions have been difficult to predict; for example Visconti and Mascellaro [10] found that methanation was underestimated and ethylene and propylene formation were overestimated, as well as products of more than nine carbons. This situation suggests that experimental data are

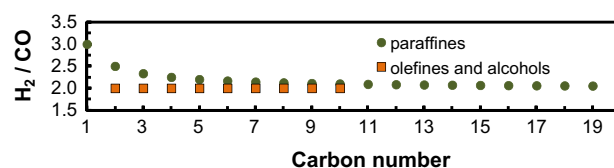


Fig. 1. (H₂/CO) ratio required during FT synthesis reactions.

necessary to analyze changes of energy and entropy during FT synthesis instead of ideal Anderson–Schulz–Flory stochastic distribution.

Comparing two typical FT catalysts, Schulz [9] has pointed out that iron exhibits static growth sites at high temperature favoring high yields to olefins, in contrast cobalt catalysts exhibit a dynamic changing surface that favors secondary reactions of olefins; in the last case yield to paraffins can be favored as function of operating conditions. Therefore, it is necessary to use experimental results to analyze energy and entropy production by FT reactions taking place over different catalysts and at different operating conditions.

In contrast, using a mixed catalyst of three metals and silica (Fe–Cu–Si–La), Pour et al. [11] found high yield of paraffins and almost none olefins. They controlled conversion by limiting the H₂/CO ratio in the range (0.5, 1.5), below the requirements of hydrogen for FT synthesis (Fig. 1).

In a theoretical/experimental work, Stenger and Askonas [12] produced normal alcohols (C₁–C₈), methane, normal paraffins and primarily olefins (both C₂C₁₅), water and carbon dioxide. They found that thermodynamic predictions at equilibrium conditions exhibit two main deviations, the first one for ethylene and propylene (produced in larger amounts than expected) and the second one for alcohols. In fact, alcohols and CO₂ formation (mainly because of the water-shift reaction) is unlikely at high CO conversions. Although they did not mention the catalyst used for the experiments, they conclude that their thermodynamic product distributions can be considered ‘generic’; hence they confirmed the necessity of experimental data for each set of reaction operating conditions.

Yakubovich and Strizhak [6] performed nine experiments, varying pressure (2.5–10 MPa), low-temperature (237–272 °C), maintaining the (H₂/CO) ratio around 2.4, and using a catalyst based on cobalt. They recorded results dividing the production into paraffins from one (CH₄) up to 17+ carbons and olefins from C₂ to C₅ hydrocarbons. In a later work, [13], these authors confirm the possibility of secondary reactions by ethylene and propylene, which would yield iso-paraffins and iso-olefins, in catalytic systems based on cobalt added with aluminum, chromium and zirconium.

Another interesting thermodynamic evidence was pointed out by Lu et al. [14], who used a cobalt catalyst supported on titanium oxide; operating conditions were fixed at 2 MPa and low-temperature (210–250 °C). They found that olefins/paraffins ratios of short-chain hydrocarbons (C₂–C₅) change along experimental runs, nevertheless ratios of adjacent olefins (C_nH_{2n}/C_{n-1}H_{2(n-1)}) remained unchanged. This behavior was explained by introducing a pseudo-equilibrium model for oligomerization of olefins; then calculated equilibrium constant matched the thermodynamic data in [15]. Consequently, authors suggest that a thermodynamic approach for the unique product distribution of FT synthesis is promising.

Visconti [16] performed low-temperature (220–230 °C) FT synthesis, at 2.5 MPa, over a cobalt supported on gamma alumina catalyst. They obtained methane, normal paraffins and primarily olefins (both C₂–C₂₅), alcohols, water and carbon dioxide; the highest selectivity was observed for C₅₊ paraffins. Their experimental

Table 1
Some properties of gasoline and diesel.

Property (units)	Gasoline	Diesel
Density (kg/m ³) [4]	0.705–0.778	0.865
Low heat power (kJ/kg) [4]	43,550	41,868
Carbon intensity/CO _{2eq} emissions/MJ [3]	93.0	93.1

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