Fischer-Tropsch Synthesis in a Two-Phase Reactor with Presaturation

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Abstract

In industry, the Fischer-Tropsch (FTS) synthesis is mostly carried out in multiphase slurry or multitubular reactors (MTR), where gaseous reactants and liquid products (hydrocarbons up to waxes) are contacted in the presence of a solid catalyst. Such reactors are characterized by a complex temperature control, necessity of gas recycling, complicated design and problematic scale-up.

A new alternative to conventional FTS-processes is the presaturated-one-liquid-phase (POLF) technology. The basic principle of this concept is a recirculation of the liquid phase, in which a gaseous reactant(s) is (are) solved before entering the fixed-bed reactor. In a simple column reactor, this technology ensures the effective heat removal and intensive fluid-solid mass transfer. In comparison to conventional reactors, the plant design is very simple, the temperature control is uncomplicated and there is no danger of any runaways. That results in lower investment and operation costs as well as in higher reliability.

The experiments show that the conversion of CO and the product distribution of hydrocarbons are practically independent on the mode of operation (two- or three-phase system). However, in the lab-scale apparatus, water is accumulated in the loop, which leads to a loss of the catalyst activity (due to Fe-carbonate). In a technical process, the water accumulation in a loop can be eluded by taking an oil free of water from the oil work-up unit. Our experiments with the removal of water from the stream by a zeolite demonstrate a much promising applicability of the POLF process to the industrial FTS.

Introduction

The manufacture of gasoline and diesel oil from natural gas (or other fuels like coal or biomass) by FTS is a perspective alternative to today’s fuels produced from crude oil.

On the one hand, diesel and gasoline derived from the FTS products have a great advantage compared to those produced from crude oil since they are free of sulphur nitrogen and metal compounds. Over the last three decades, much attention has been given to desulfurization of fuels because of air pollution and acid rain. The S-limit was gradually decreased, e.g. in Germany from 5000 ppm in 1975 down to today’s 50 ppm (including many European countries). Fuels with even lower S-contents are already available due to tax benefits (In Sweden, Germany the majority of fuels is “S-free” i.e. below 10 ppm). In many countries by 2010, the S-limit for both gasoline and diesel oil is expected to be 10 ppm (or even less with respect to technologies based on fuel cells).

On the other hand, about 50% of the conventional natural gas reserves are located in countries far away from consumers, for example in the Middle East. Moreover, there are large unconventional gas resources like methane hydrate or aquifer gas, the estimated reserves of which exceed the capacity of natural gas over ten times. In order to enable the exploitation of these so-called stranded gas fields, several companies are developing and building FTS-plants for converting gas to liquid in order to ship it to consumers.

Industrial FTS plants of about 8 million tons per year utilizing syngas from coal and to a lower extent from natural gas are mainly encountered in South Africa and Malaysia. The biggest single plant that will consume only natural gas is now being constructed in Qatar. This largest gas-to-liquid plant of 6 bln € invest will produce around 8 mln tons of distillate liquids by 2011 [1].

In spite of the tenacious efforts in the process development and already existing industrial FTS units, a real breakthrough has not been accomplished. The operation costs of these capital-intensive processes are likely to be still above the break-even point, at least considering the current oil prices.

Aim and methods of this work

FTS is the conversion of syngas to liquid hydrocarbons (up to waxes). The industrial processes are carried out in multiphase reactors where a gas, liquid and solid phase (catalyst) are contacted. The specific feature of FTS is the tremendous heat evolution demanding thorough arrangements for the temperature control that is chiefly ensured by gas recycling. In MTR, generated heat is additionally removed from the numerous tubes (filled with a fixed catalyst) to the water boiled in the free space.

The conventional FTS reactors (fixed-bed MTR, fluidized bed and slurry reactors) are characterized by low productivity (due to intraparticle diffusion in case of a fixed bed or a low catalyst concentration in a slurry reactor) exclusively complex equipment, which imposes high investment and operation costs.

A new approach coping with the above-numerated problems is the presaturated-one-liquid-phase technology (POLF) [2]. The basic principle of this concept is that gas-liquid mass transfer (in other words, the saturation of the gaseous reactant(s) in the liquid) is carried out outside the reactor in a saturator so that the single liquid phase enters the reactor. In order for the gaseous reactants to be sufficiently supplied to the reaction zone, the recirculation of the liquid product through the saturator should be employed.

In the POLF process, the generated heat is taken away in an external heat exchanger on a liquid loop permitting to simplify the technological scheme, including the reactor design: Instead of huge gas recycle compressors, comparatively small recycle pumps are used; there is no necessity of complex and expensive MTRs. In comparison to the conventional technologies, the problem related to the pressure drop does not arise in the case of a single liquid phase flow. As a result, the reactor productivity can be significantly enhanced since liquid-solid mass transfer can be intensified by a higher recycle rate and/or by use of small catalyst particles. It is also important that runaways concerning heat accidence are impossible.

In former studies and PhD theses, the POLF technology has already been proven to be technically applicable for the production of fine chemicals (hydrogenation of β-ionone and 1-octene) and hydrodesulfurization processes [3 -7].

In this work, this concept was tested for FTS that represents a more complex reaction system [8] compared to those investigated earlier. For a reference, experiments in a conventional reactor (3-phase system, no liquid recycle) were also conducted. For the experiments, a Fe-catalyst was used. It is always activated outside the FTS reactor with the following detailed analysis (BET etc.).

In addition, since pressure fluctuations or exceeding pressure drop can cause the destruction of a commercial Fe-catalyst due to its low mechanical stability, the attempt to harden the FTS-catalyst has been undertaken by its treatment with different gaseous Si compounds. New Fe/Si catalysts demonstrate a far higher mechanical and thermal stability as well as a more stable activity (details in [8]) and are deserved to be investigated in the near future to realize their promising features.

It is usual for a Fe catalyst in FTS that the time to reach the stationary regime is several days of operation during which the catalyst activity becomes less. The pores of the catalyst are completely filled with liquid hydrocarbons during the initial phase of the synthesis, which leads to a mass transfer resistance by pore diffusion. In addition, the active sites of the pure Fe spots obtained initially by reduction are partly converted to Fe_5C_2 that further serves as an active phase for FTS. By contrast, the silicided catalyst shows a higher activity from the very reaction beginning, which can probably be explained by the fact that the formation of Fe carbide is partly inhibited by silicide so that α-iron remains in an active state facilitating FTS. The more detailed investigations on this field are needed but beyond the scope of this work.

A schematic experimental POLF unit is shown in Fig. 1. For the sufficient supply of syngas, the liquid (saturated with gas) is pumped through the saturator and fed into FTS reactor. The gaseous and volatile products are continuously discharged in the separator while the liquid products are concentrated in the liquid loop (at the beginning of the operation, the reactor is filled with pure dodecane).

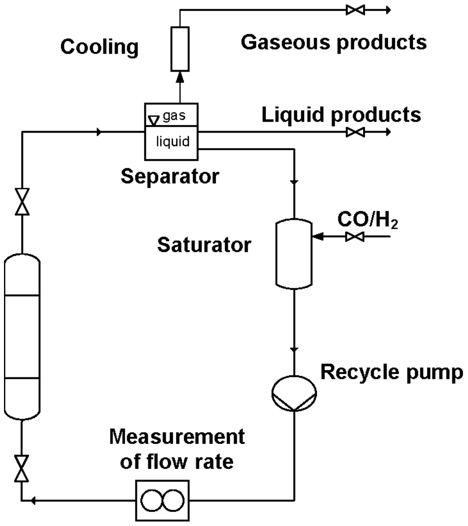

Fig. 1. Experimental set-up for FTS

Results and discussion

The experiments show the advantages of the POLF process with respect to the heat withdrawal and hence to the temperature control. That permits to carry out the reaction at higher temperatures compared to the existing FTS reactors. (The impact of the temperature on conversion (activation energy is about 50 kJ/mol) is presented in Fig. 2.) The reaction rate and selectivity are similar to those in the conventional FTS technologies [8 - 11] if the same catalyst is applied.

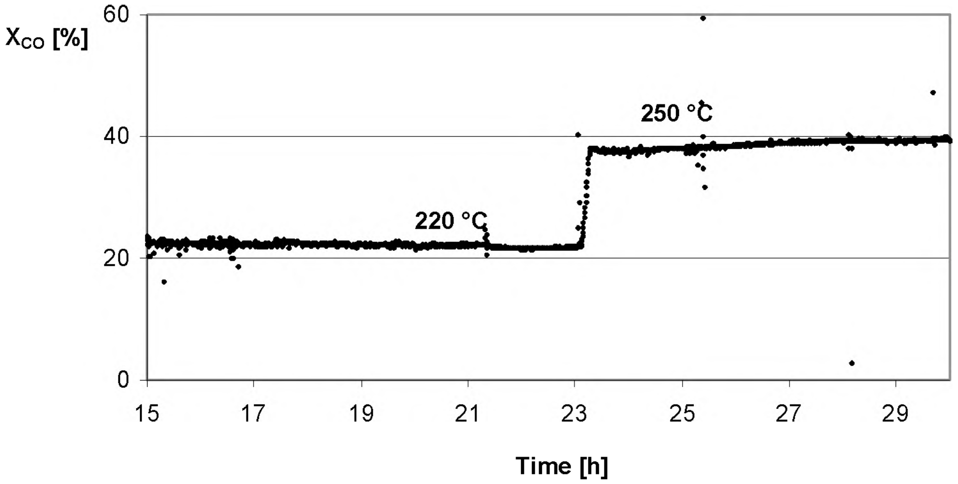

Fig. 2. CO-conversion vs. time on stream
(classical three-phase system, 2 MPa, $CO/H_2/N_2$ ratio (molar): 1/2/7, 100 l $_{NTP}$/h, modified residence time: 8 kg_{cat} h/kg_C)

Fig. 3 and 4 indicate that CO conversion, CO_2 yield and product distribution of hydrocarbons do not depend on the mode of operation (POLF or conventional three-phase systems).

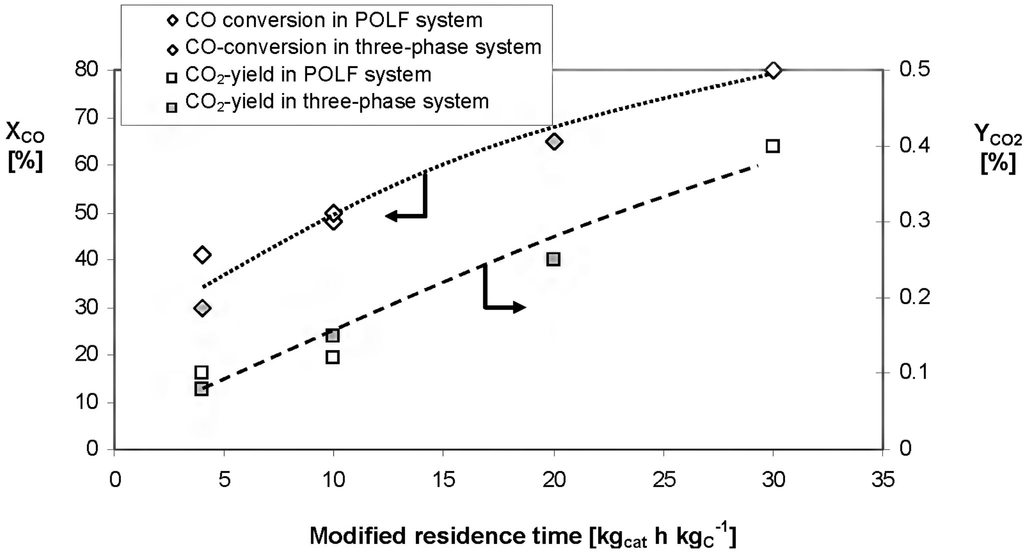

Fig. 3. Influence of residence time on CO conversion and CO_2 yield in POLF and conventional (three-phase) system (250°C, 2 MPa and 2.5 mm catalyst)

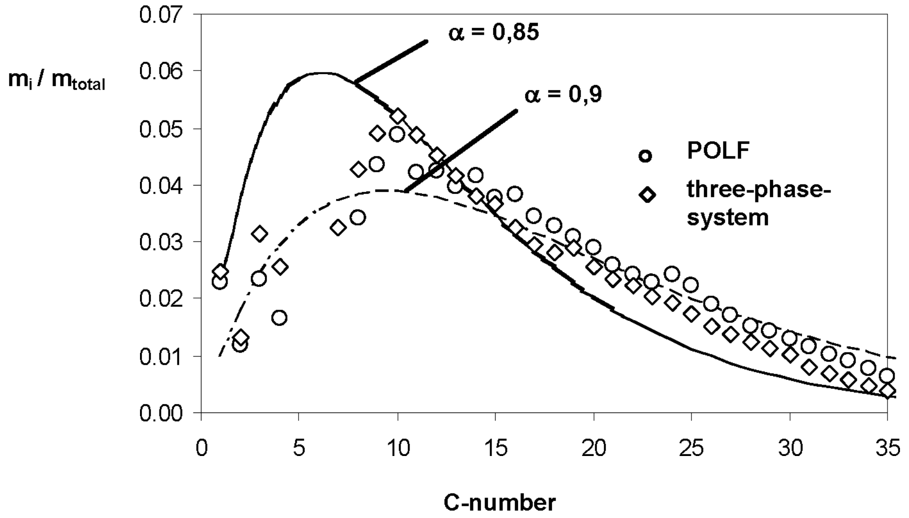

Fig. 4. C-number distribution in the POLF and conventional (three-phase) systems (250 C, 2 MPa and 2.5 mm catalyst).

Despite the first promising result, a serious problem arises from an unavoidable side-product water that exerts a severe impact on the reaction (Fig. 5).

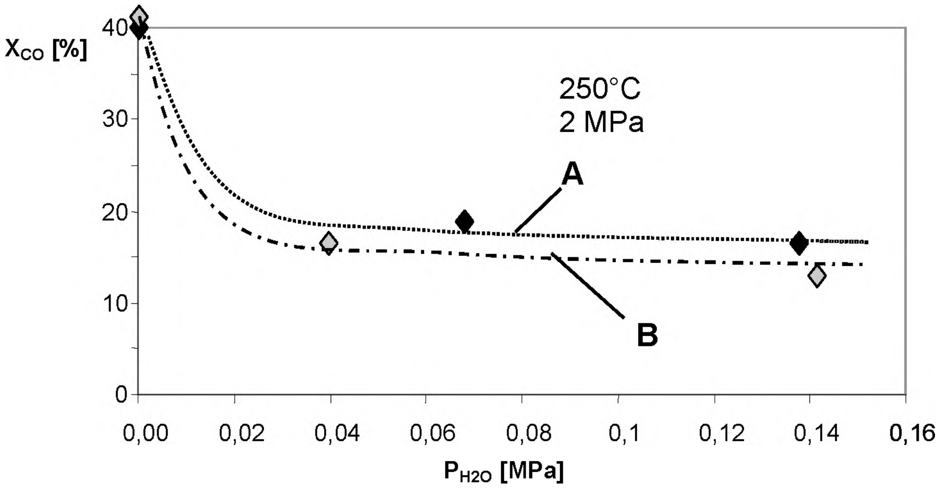

Fig. 5. Influence of partial pressure of water on CO conversion in the conventional three-phase reactor (modified residence time: 8 kg_{cat} h/kg_C, 100l_{NTP}/h **A:** p_{CO}=0,21 MPa, p_{H2}=0,51 MPa, **B:** p_{CO}= 0,21 MPa, p_{H2}=0,76 MPa)

In the lab-scale apparatus, water is accumulated in the liquid phase resulting in the catalyst deactivation as soon as its critical concentration (~200 ppm) is reached (Fig. 6). The cause of this collapse is a Fe-carbonate formation, which is not a case in the common three-phase system. In order to avoid such a strong effect on a Fe catalyst, water should be removed from a loop. In our experimental set-up, water adsorption by a zeolite demonstrates the promising results. In a technical process, the liquid recycle free of water can be organized taking the oil from the oil work-up unit.

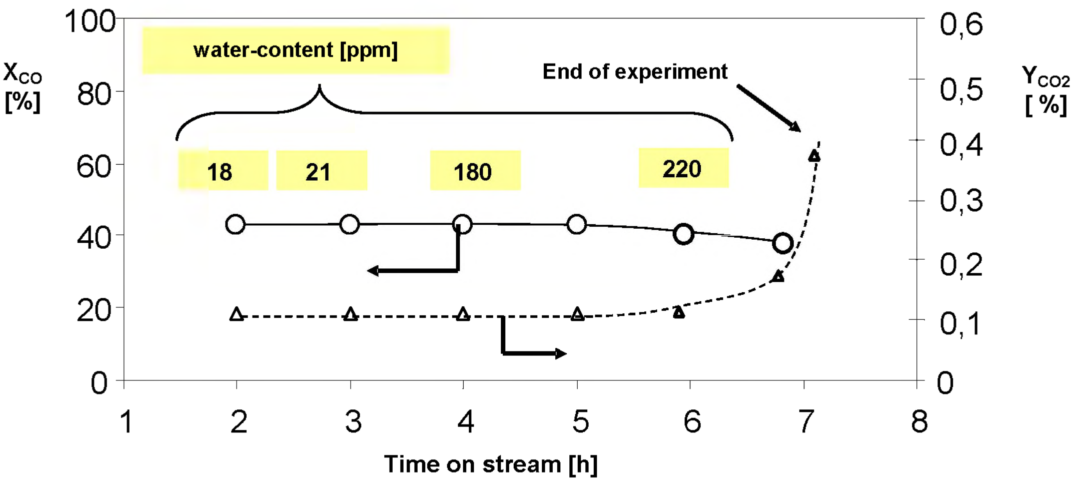

Fig. 6. Course of reaction in POLF system
(250°C, 2 MPa and modified residence time: 10 kg_{cat} h/kg_C, 2.5 mm)

Summary and outlook

The POLF concept is an encouraging method for carrying out FTS, but has to be combined with water removal. The future work should concentrate on this aspect and/or on the use of catalysts that are more stable to water.

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