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# Lab-scale experimental studies of Fischer–Tropsch kinetics in a three-phase slurry reactor under transient reaction conditions

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Dedicated to Prof. Hans Schulz expressing gratitude for his inspiration and support throughout many years of Fischer–Tropsch research.

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## ABSTRACT

Fluctuating electricity can be converted into hydrocarbon fuels via hydrogen as intermediate, thus replacing fossil fuels and possibly be attractive as a long-term storage in excess electricity generation situations. In this context, flexible operation of the chemical synthesis reactor may be motivated by the possibility of reducing the size of the hydrogen storage and the investment needed. The present study has the aim to identify general aspects and limitations of flexible Fischer–Tropsch reactor operation considering catalyst behavior and reactor operation in a three-phase system. In this contribution, methodology and first results of lab-scale experiments with a stirred slurry reactor are presented. Results of step-change experiments can be described by a mathematical model of the lab-scale setup, using steady-state kinetics determined in separate experiments. During periodic-change experiments, average rates of CO consumption and CH<sub>4</sub> formation are not affected by period length. In contrast, analysis of periodic-change experiments with emphasis on hydrocarbon product distribution indicate that long chain hydrocarbon molar flows cannot follow forced oscillation as fast as methane molar flow.

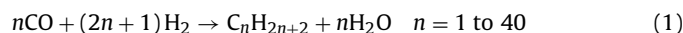
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## 1. Introduction

### 1.1. Integration of renewable electricity with synfuel production

In a future energy system, primary energy supply will be based to a large extent on renewable sources like wind and solar, leading to electricity with fluctuating generation characteristics. As chemical energy carriers will still be needed in mobile and other applications, conversion of electricity into chemical energy may then become important. For example, fluctuating electricity can be converted into hydrocarbon fuels via hydrogen as intermediate, thus replacing fossil fuels and possibly be attractive as a long-term storage in excess electricity generation situations. A general flow diagram of an electricity-to-fuel process is shown in Fig. 1, indicating electrolysis for fluctuating H<sub>2</sub> generation, some H<sub>2</sub> storage and the catalytic synthesis process with CO-rich synthesis gas as carbon source. In this context, flexible operation of the chemical synthesis reactor may be motivated by the possibility of reducing the size of the storage and the investment needed [1].

CO-rich synthesis gas is a product in cases where feedstocks deficient in hydrogen are gasified (e.g., biomass, coal). The required H<sub>2</sub>/CO-ratio for Fischer–Tropsch synthesis cannot be reached in gasification (Eq. (1)). In order to achieve the required higher value, CO is usually converted to H<sub>2</sub> via CO-shift reaction and the resulting CO<sub>2</sub> is removed. As a consequence, part of the carbon of the feedstock is not available for synthesis. If external H<sub>2</sub> from renewable electricity is integrated (as shown in Fig. 1), this carbon loss can be avoided and the yield of hydrocarbon product can be significantly increased (Table 1).



In a recent publication a similar process to produce liquid hydrocarbon fuels is proposed, using CO<sub>2</sub> instead of synthesis gas from biomass as carbon source [3]. However, this process needs a reverse water-gas shift unit at high temperatures to produce CO prior to Fischer–Tropsch synthesis instead of a gasifier.

### 1.2. Flexible operation of catalytic reactors

Flexible operation of catalytic chemical reactors is a field of research, where many aspects may play an important role, with limited knowledge available at present (e.g., catalyst and material behavior, reactor design, control strategies, heat integration, etc.).

Abbreviations: Cpr, cyclopropane; FTS, Fischer–Tropsch synthesis; IR, infrared analyzer; off-GC, offline gas chromatograph; on-GC, online gas chromatograph.

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**Notation**

$a_{FT}$	inhibition parameter
$d_p$	catalyst particle diameter
$E_A$	activation energy
$F$	flow
$F_{V,Gasifier}$	volume flow of synthesis gas produced in gasifier
$k_{FT,0}$	rate constant of chemical reaction in Arrhenius equation
$k_{FT}$	rate constant in reaction equation of Fischer–Tropsch synthesis
$m_{cat}$	catalyst mass
$p$	pressure
$r$	reaction rate
$T$	temperature
$t$	time
$X$	conversion
$y$	molar fraction
$Z_{F_n,S,out}$	normalized molar flow at setup outlet
$\left(\frac{F_{n,S,out}(t)-F_{n,S,out,0}}{F_{n,S,out,\infty}-F_{n,S,out,0}}\right)$	Fig. 4 (left)
$\left(\frac{F_{n,S,out}(t)-F_{n,S,out,\infty}}{F_{n,S,out,0}-F_{n,S,out,\infty}}\right)$	Fig. 4 (right)
$\Delta F_{n,CO,consumption}$	change of CO molar flow at setup outlet due to change of CO consumption rate: $r_{CO,ss(H_2/CO)=2} - r_{CO,ss(H_2/CO)=1.1}$
$\Delta F_{n,CO,flow}$	change of CO molar flow at setup outlet due to change of CO molar flow at setup inlet: $F_{n,CO,in(H_2/CO)=1.1} - F_{n,CO,in(H_2/CO)=2}$
$\tau$	normalized elapsed time within one period
$\tau_{per}$	period length
<i>repeatedly used subscripts</i>	
1	in feed line 1
2	in feed line 2
$\infty$	steady-state value after step-change, $t \rightarrow \infty$
A	at ampoule sampler
in	inlet
m	mean value
n	with respect to molar flow
out	outlet
R	reactor
S	setup
ss	steady-state
V	with respect to volume flow

Flexible operation means operation at varying load with frequent changes between different load situations, variations in syngas composition and flow, and any changes as a consequence (i.e., temperature and pressure).

Catalyst and reactor behavior under variable operating conditions was a field of study in the 1980s and 1990s. Primarily, the aim was to improve catalyst activity and selectivity and to optimize temperature distribution in fixed-bed reactors by reverse flow operation [4,5]. In literature, numerous studies can be found for different reactions. An overview about periodic operation of catalytic reactors is given in the review article by Silveston et al. [6]. A detailed review about periodic operation of Fischer–Tropsch synthesis was presented by Adesina et al. [7]. Periodic experiments are helpful to get a better understanding of the catalytic system, and its interactions with the fluid phase. However, the reported variations of the gas phase are strong (often using a pure reactant flow for some time) and not relevant for the dynamic operation expected in the context of the presented electricity-to-fuel process

(Fig. 1). Recently, several investigations about transient operation of methanation reactors were published connected to an increasing interest in power-to-gas concepts [8,9].

In today practical process applications, examples for intentional or stochastic transient operation of heterogeneous catalytic reactors are rare: cleaning of automotive exhaust gases, NO<sub>x</sub> reduction in thermal power and waste incineration plants. Causes are time-dependent power demand or fluctuation in fuel composition (e.g., municipal waste) [10].

In this context, the present study has the following aims: (i) identify general aspects and limitations of flexible reactor operation considering catalyst behavior and reactor operation in a three-phase system, using the example of a representative catalytic fuel synthesis reaction and a suited slurry bubble column reactor (example reaction: low-temperature FT synthesis to liquid hydrocarbons with Co-based catalyst with mild variations of inlet concentration and volume flow), and (ii) develop a method to study transient processes on catalyst and reactor scale, based on a combination of experimental work and conceptual studies using mathematical models.

## 2. Approach and methodology

### 2.1. General approach

The approach followed comprises two parts: (i) experimental work in a lab-scale setup combined with mathematical modeling of the lab-scale setup to evaluate the restrictions that the catalytic system could impose on attainable reactor flexibility (model-based analysis) and (ii) modeling of an industrial reactor to conduct design studies for part-load and transient operation, respectively (Fig. 2).

In this contribution, methodology and first results of the lab-scale part are presented (Fig. 2, left). Steady-state experiments are conducted in the lab-scale setup to determine reaction kinetics. Furthermore, catalyst behavior under transient conditions is examined. For this purpose, step-change and periodic-change experiments are performed, which are analyzed and designed with the mathematical model of the lab-scale setup, respectively.

In a further step the information derived by experimental work is used to mathematically describe an industrial-scale slurry bubble column reactor considering chemical kinetics, residence time distribution, mass and heat transfer and hydrodynamics. The mathematical model offers the possibility to analyze transient operation of the chemical reactor, and thus gives insights in potential limiting factors for flexible operation. Results of this part of the study will be published in the future.

### 2.2. Lab-scale stirred slurry reactor for steady-state and transient experiments

The lab-scale setup described in this section is based on earlier studies of low-temperature Fischer–Tropsch synthesis under steady-state conditions [11–13]. In order to conduct and evaluate step-change and periodic-change experiments the setup was extended with instrumentation and control equipment (Fig. 3).

Each feed gas line is equipped with two mass flow controllers (one for each synthesis gas component: H<sub>2</sub> and CO). Thus, the synthesis gas composition and the volume flow in the two feed lines can be adjusted separately. Each syngas line is connected to a magnetic valve so that one synthesis gas mixture is fed into the reactor and the other is vented. Both magnetic valves are computer-controlled to enable exact switching times and automation. The pressure in the offgas line and in the reactor is the same to avoid pressure variation during periodic changing between both feed lines. This is possible by means of argon addition and a needle

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