

HIGHLY EFFICIENT FISCHER-TROPSCH SYNTHESIS USING IONIC LIQUIDS AND SUPERCRITICAL CARBON DIOXIDE AS SOLVENTS

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Fischer-Tropsch synthesis involves production of liquid fuel from hydrogen and carbon monoxide under supercritical conditions. Conventional Fischer-Tropsch processes are intrinsically inefficient as a result of the polymerization nature of the reaction, which yields a product distribution rather than a single product. In the subsequent upgrading step the hydrocarbons that are too long are ‘cracked’ into molecules with shorter chain length, partly destroying what has been produced in the reaction step. This upgrading step is not only energy intensive, but it also accounts for a significant part of the capital expenditure. In this work, a novel highly efficient Fischer-Tropsch process is developed that selectively produces hydrocarbons with the desired chain length (diesel) using an ionic liquid/ supercritical carbon dioxide mixture as solvent. This innovative process employs the phenomenon that the solubility of hydrocarbons in ionic liquids decreases with increasing hydrocarbon chain length. The polymerization reaction takes place in a hydrophobic ionic liquid, which dissolves reactants, catalyst and hydrocarbons shorter than the desired product. However, at the moment the desired chain length is reached, the hydrocarbon is no longer soluble in the ionic liquid, and forms a separate layer that floats on top of the ionic liquid, thus avoiding contact with the catalyst and preventing further reaction. The product can be easily withdrawn from the reactor, abandoning the need for a conventional energy- and capital intensive upgrading section. The function of the supercritical carbon dioxide is to enhance the solubility of the reactants in the ionic liquid phase.

INTRODUCTION

The world energy consumption is continuously increasing. The Energy Information Association expects that the world energy consumption in 2030 will increase with 57 % as compared to 2004 [1]. Despite its finite availability, petroleum is still commonly used as a major source of energy supply and as important feedstock for chemicals. However, in the last decade the petroleum price has increased beyond expectations, making production of liquid fuel from sources other than petroleum attractive. Especially the production of liquid fuels from gas-to-liquids and coal-to-liquids are expected to grow substantially during the coming decades. Environmental legislation is causing a shift from the production of gasoline to the production of diesel in many refineries in Europe and the USA [2]. Given these facts, diesel production using Fischer-Tropsch synthesis is favored because it uses a feedstock different from petroleum (e.g., biomass, natural gas, coal, etc.) and the fuel produced better meets strict environmental legislations compared to conventional fuels [3].

Fischer-Tropsch synthesis involves the production of linear alkanes (diesel) from hydrogen and carbon monoxide (synthesis gas). The most important reactions taking place during the Fischer-Tropsch synthesis are covered by the exothermal Fischer-Tropsch reaction (Eq. 1) and the water-gas-shift reaction (Eq. 2):



The Fischer-Tropsch synthesis takes place at temperatures between 473 K and 593 K, and pressures between 2.5 MPa and 6.0 MPa [4]. The reaction is a polymerization, consisting of chain initiation, chain growth and chain termination steps. Despite a long history of research no definite reaction mechanism has been proposed yet. At the Fischer-Tropsch reaction conditions, the water-gas-shift reaction is an equilibrium reaction so that the reverse reaction has to be taken into account as well [4].

The Fischer-Tropsch reaction is conventionally catalyzed by heterogeneous, metal containing catalysts. The following ranking of descending activity is generally observed: ruthenium (Ru) > iron (Fe) > nickel (Ni) > cobalt (Co) > rhodium (Rh) > palladium (Pd) > platinum (Pt) > iridium (Ir) [5]. Most commonly, catalysts based on Fe and Co are used because of their lower price [4].

Selective production of hydrocarbons with a narrow chain length distribution is impossible with conventional Fischer-Tropsch processes. The polymerization nature of the Fischer-Tropsch reaction leads to formation of a product distribution rather than a single product. A process scheme of the conventional Fischer-Tropsch synthesis is shown in Figure 1. It can be seen that the hydrocarbons that are too short have to be recycled. Moreover, hydrocarbons that are too long have to be ‘cracked’ into molecules with shorter chain length, partly destroying what has been produced in the reaction step. These upgrading steps make the Fischer-Tropsch process a very energy-intensive and capital-intensive process [4].

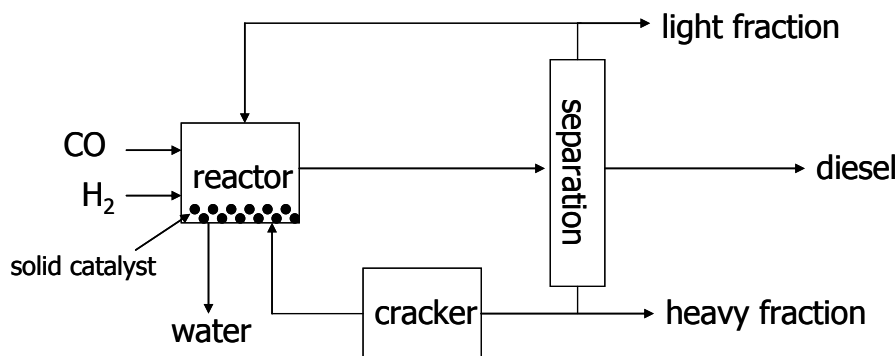


Figure 1: Process scheme of the conventional Fischer-Tropsch synthesis

In this work a novel more energy-efficient Fischer-Tropsch process is developed that selectively produces hydrocarbons with the desired chain length (diesel) using an ionic liquid/

supercritical carbon dioxide mixture as solvent. The ionic liquid 1-hexyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ($[\text{hmpyrrol}^+][\text{NTf}_2^-]$) is chosen due to its hydrophobicity (non-miscible with the water produced), its relatively high thermal stability (up to the Fischer-Tropsch temperature of 493 K) and its relatively high reduction stability (because of the presence of hydrogen in the system). A specifically designed ionic liquid, which contains a cation with Ru, is used as (homogeneous) catalyst.

MATERIALS AND METHODS

In the new process, the following components are present: (i) $[\text{hmpyrrol}^+][\text{NTf}_2^-]$, (ii) Ru-catalyst, (iii) CO_2 , (iv) H_2 , (v) CO , (vi) H_2O , and (vii) linear alkanes with different chain lengths. The phase behavior of this system is determined using available experimental data and estimations using the group contribution equation of state (GC-EoS) as developed by Skjold-Jørgensen [6]. This GC-EoS was used to predict the phase equilibria of linear alkanes and CO_2 in the ionic liquid phase. The ionic liquid $[\text{hmpyrrol}^+][\text{NTf}_2^-]$ was decomposed into one CH_3 group, five CH_2 groups, and one $[-\text{mpyrrol}^+][\text{NTf}_2^-]$ group. Pure group parameters were regressed from liquid density data. Binary interaction parameters were fitted from infinite dilution activity coefficients and vapor-liquid equilibrium data as previously described [7].

On basis of the phase behavior, the conditions for the novel Fischer-Tropsch process were determined. The process was next carried out in a high-pressure batch reactor. The reactor, designed for operating up to 350 bar, consists of a 150 ml pressure vessel connected to a pressure manometer and a needle valve that serves as an inlet and outlet for the gases (hydrogen, carbon monoxide, carbon dioxide). The ionic liquid with catalyst was loaded into the reactor, and the reactor was closed. The gases were added via the needle valve. The reactor is, subsequently, placed in the thermostatic bath settled at a temperature of 493 K. When the reaction time was completed, the reactor was removed from the thermostatic bath and the reaction was stopped by cooling. Afterwards, the reaction mixture was carefully collected in a sample flask via the needle valve. The composition of the sample was immediately determined by HPLC analysis.

RESULTS

The alkane concentration in the ionic liquid phase can be determined using the GC-EoS. Hereby, it is assumed that the organic phase consists solely of alkanes, and no ionic liquid is dissolved in the organic phase. Table 1 and 2 show the predicted pure group and binary interaction parameters.

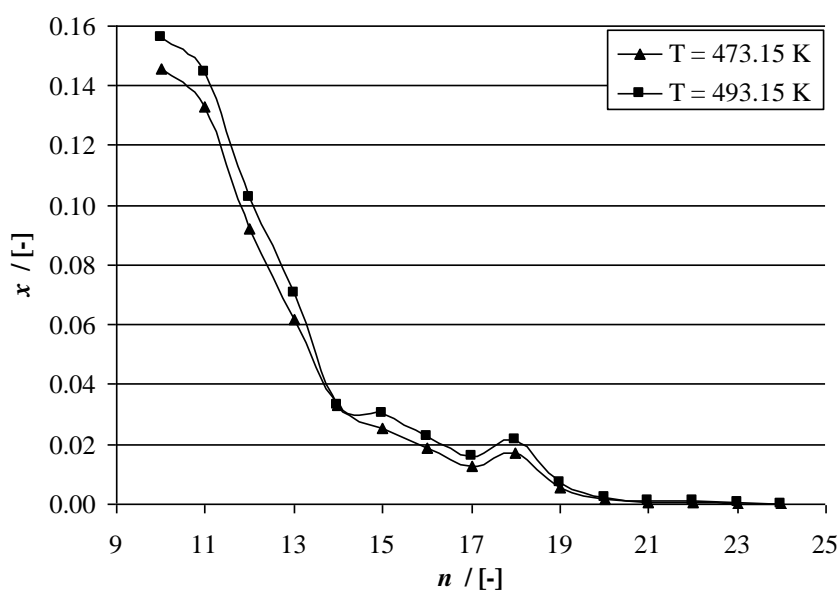
Table 1: Predicted pure group parameters for $[-\text{mpyrrol}^+][\text{NTf}_2^-]$

	$T_c [K]$	q	g_{IL}^*	g'_{IL}	g''_{IL}
$[-\text{mpyrrol}^+][\text{NTf}_2^-]$	600	7.26	1036659	-0.5102	0

Table 2: Predicted binary interaction parameters for $[-\text{mpyrrol}^+][\text{NTf}_2^-]$, CH_3 and CH_2

Group i	Group j	k_{ij}^*	k_{ji}^*	k'_{ij}	k'_{ji}	α_{ij}	α_{ji}
CH_3	$[-\text{mpyrrol}^+][\text{NTf}_2^-]$	0.9814	0.9814	0	0	0	0
CH_2	$[-\text{mpyrrol}^+][\text{NTf}_2^-]$	0.9814	0.9814	0	0	0	0

The results for the solubility of alkanes in $[\text{hmpyrrol}^+][\text{NTf}_2^-]$ as a function of alkane chain length are presented in Figure 2.

**Figure 2:** Plot of the solubility of an alkane in the ionic liquid $[\text{hmpyrrol}^+][\text{NTf}_2^-]$ as function of the carbon chain length, predicted by the GC-EoS

It can be seen that the solubility of alkanes in $[\text{hmpyrrol}^+][\text{NTf}_2^-]$ decreases with increasing hydrocarbon chain length. This phenomenon can be employed in a novel Fischer-Tropsch process.

In this novel process, the polymerization reaction takes place in a hydrophobic ionic liquid, which dissolves reactants, catalyst and hydrocarbons shorter than the desired product. However, at the moment the desired chain length is reached, the hydrocarbon is no longer soluble in the ionic liquid, and forms a separate layer that floats on top of the ionic liquid, thus avoiding contact with the catalyst and preventing further reaction. During the Fischer-Tropsch synthesis water is also produced. Because both the ionic liquid and the organic phase do not mix well with water, the water forms a third phase. It is even possible that there are four phases in equilibrium, because the solubilities of hydrogen and carbon monoxide in the system are rather low, forming a separate vapor phase. Supercritical carbon dioxide can be added to enhance the solubility of hydrogen and carbon monoxide in the ionic liquid phase [8].

The product can be easily withdrawn from the reactor, abandoning the need for a conventional energy- and capital intensive upgrading section. The new Fischer-Tropsch process in an ionic liquid is shown in Figure 3.

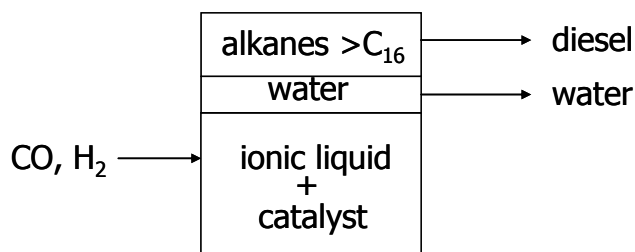


Figure 3: Process scheme of the alternative Fischer-Tropsch synthesis in an ionic liquid/supercritical carbon dioxide mixture

First tests were carried out in an autoclave. For the first time, a homogeneous catalyst is used in a Fischer-Tropsch process. Conventional Fischer-Tropsch processes use heterogeneous catalysts, and are therefore mass transfer limited. The new process does not suffer from this disadvantage. Moreover, because the products form a separate layer, the product can be easily recovered without the problems related to conventional homogeneous catalysis.

Preliminary calculations showed that the capital investment costs of the innovative Fischer-Tropsch process will be more than three times lower than the cheapest commercially used Fischer-Tropsch process.

CONCLUSIONS

The efficiency of conventional Fischer-Tropsch processes can significantly be improved by selectively producing only the preferred products. On basis of the phase behavior of ionic liquid + alkane systems, such a novel process for the Fischer-Tropsch synthesis is developed. The new process in this work combines reactions and separations while selectively only producing the preferred products (diesel). The innovative process utilizes the solubility difference between alkanes of different chain lengths in the ionic liquid phase to separate the alkanes with the preferred chain length from the reaction medium. The product distribution is controlled by the recycle ratio of gaseous products to the reactor. The water produced forms a separate liquid layer on top of the ionic liquid layer due to the high partial pressure of water in the gas phase. This water layer can be withdrawn continuously from the reactor. The desired organic products also form a liquid layer, which will float on top of the water layer, thus being the top layer. Calculations revealed that perfect separation of water and organics can be achieved in the reactor, enabling continuous withdrawal of (by)-products from the reactor. The water and the organic product stream are fed to separate settlers that operate as flash units to remove the gases dissolved. This innovative process design ensures, contrary to conventional Fischer-Tropsch processes, selective production of the preferred products only and continuous separation of water from the organics produced.

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