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A comparison of co-current and counter-current modes for Fischer–Tropsch synthesis in two consecutive reactors of oxidative coupling of methane and Fischer–Tropsch

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ABSTRACT

The results of three cases of two consecutive reactors are studied in two types of co-current and counter-current flow in second reactor where two consecutive reactors are oxidative coupling of methane (OCM) and Fischer–Tropsch (FT) reactors. FT reactor can be fixed bed or membrane fixed bed reactor with a hydrogen perm-selective membrane. Effect of CH_4/O_2 ratio, contact time, inlet temperature, and amount of N_2 in OCM feed on C_2 to C_{5+} hydrocarbons produced in FT reactor were studied. Results show that use of counter-current hydrogen-perm selective membrane FT reactor that sequenced after OCM reactor improves the C_{5+} yield as a desirable product and reduces the amount of CH_4 and CO_2 as byproducts of FT reactor in comparison to co-current and conventional reactor. This phenomenon can be explained with more H_2 diffusion through the membrane and more CO conversion and more hydrocarbons productions, briefly. As compared to the conventional reactor, in co-current and counter-current reactors, yield of C_{5+} has increased almost 3% and 4% alternatively when using these systems.

1. Introduction

A great part of the world energy source is liquid hydrocarbons such as gasoline, diesel and etc. Liquid fuels can be produced from available sources such as natural gas. The Fischer–Tropsch synthesis (FTS) is a method for production of fuels not based on oil. Natural gas is converted to synthesis gas via a combination of non-catalytic partial oxidation and steam reforming. This synthesis gas is then converted to liquid hydrocarbons in a two stage, Fischer–Tropsch (FT) slurry bed reactor system. The FT wax and liquid hydrocarbons are upgraded to high quality naphtha and diesel blending stocks by conventional petroleum refinery processes. Though large number of efforts has been invested in improving FTS technology, converting methane to longer chained hydrocarbon compounds remains an energy intensive process. As a result, the number of commercial FTS plants is limited. However, the potential of producing liquid fuel without any of the impurities associated with oil derived fuels continues to be a good interest.

Main reaction of FT process is:

$$(2n+1)H_2 + nCo \rightarrow C_nH_{(2n+2)} + nH_2O \quad (1)$$

where n is a positive integer that shows the number of carbon atoms in hydrocarbon product.

Variable grades of synthetic hydrocarbon fuels (e.g., gasoline; C_5–C_{12}, diesel; C_{13}–C_{18}, soft wax; C_{19}–C_{23}, medium wax; C_{24}–C_{35}, hard wax; C_{35+}) can be produced depending on temperature, pressure and catalyst used in FT process (Dry, 1999). C_{5+} fuel is more favorable because of its higher price and demand. C_{5+} that obtained from FT process mainly consists of n-paraffin and leads to lower octane number compared to crude oil C_{5+}. Bifunctional catalysts promote yield and octane number of FT C_{5+} (Cagnoli et al., 2002).

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Table 1
FTS pilot plant characteristics (RIPI-No, 2004).

Parameter	Value
Tube dimension (mm)	Ø38.1 × 3 × 12,000
Feed temperature (K)	569
Cooling temperature (K)	566.2
Reactor pressure (kPa)	1700
Catalyst density (kg m^{-3})	1290
Catalyst sizes (mm)	Ø2.51 × 5.2
Bulk density (kg m^{-3})	730
Tube length (m)	12
Number of tubes	1
GHSV (h^{-1})	235
Feed molar flow rate (gmol s^{-1})	0.0335
Bed voidage	0.488

FT reaction has side reactions that decrease the yield of hydrocarbon fuels. Most important side reaction is water gas shift reaction:

$$H_2O + CO \rightarrow H_2 + CO_2 \quad (2)$$

and, second side reaction is reverse of steam reforming reaction:

$$CO + 3H_2 \rightarrow H_2O + CH_4 \quad (3)$$

Many investigations have been done to increase the gasoline production and decrease the CH_4 and CO_2 formation during this FT process. Synthesizing new catalysts and modification of synthesized catalysts and changing the structure of FT reaction reactor are the main efforts in this way. Using hydrogen perm-selective membrane fix bed and fluidized bed reactors are one of the major ways to increase C_{5+} and decrease major by-products. Tosti et al. (2008) classified catalytic membrane reactors according to the type of membrane (perm-selective/non perm-selective) and the location of the catalyst (within/outside the membrane). Also, Rohde et al. (2005) proposed four concepts to use membrane reactors in Fischer–Tropsch synthesis (FTS): distributed feed of reactants, in situ removal of water, forced through membrane contactor and zeolite encapsulated catalysts. Forghani et al. (2009) showed that by using hydrogen perm-selective membrane reactor the yield of gasoline fuel must be increased. Rahimpour and Elekaei (2009a,b) and Rahimpour et al. (2009) used many types of membrane reactor like: H_2 perm selective and H_2O removal membrane reactor in co-current and counter-current modes. They mentioned that this reactor resulted in higher CO and H_2 conversion and gasoline production. Using hydrogen selective membrane in the FT reactor improves the reaction's yield and selectivity by shifting the thermodynamic equilibrium and increasing the reactants conversion (Sanchez and Tsotsis, 1996). Silver alloyed palladium has very good permeability of hydrogen (Buxbaum and Kinney, 1996; Lin and Rei, 2001).

Syngas is the feed of FT process. However, the product of oxidative coupling of methane (OCM) process can also be fed to FT process to convert syngas to high value hydrocarbons, because OCM products contain large amount of H_2 and CO as byproduct. The OCM is a straight method to upgrade natural gas and convert methane to C_{2+}, but, it has low selectivity and low yield (Labinger, 1988). Various types of reactors with various configuration and operational condition have been used to improve the yield of ethylene production in OCM reaction (Mortazavi et al., 1996; Coronas et al., 1997).

Table 2
OCM reactor parameters and constants.

Parameter	Dimension
Inner diameter (mm)	38.1
Pressure (kPa)	110
Length of catalyst bed (mm)	12,000
Catalyst weight, m_{cat} (g)	0.007–1.000
Flow rate (STP), υ_{STP} (m^3 s^{-1})	4×10^{-6} to 13×10^{-4}
Catalyst size (mm)	0.25–0.35
Catalyst density (kg m^{-3})	3600

Table 3
Catalyst and specifications of membrane FT system.

Parameter	Value
Tube dimension (mm)	Ø38.1 × 3 × 12,000
Inner radius of Pd–Ag layer (mm)	19.05
Outer radius of Pd–Ag layer (mm)	19.065
Reactor radius (mm)	27
Feed temperature (K)	565
Cooling temperature (K)	555
Reactor inlet pressure (kPa)	1700
Catalyst density (kg m^{-3})	1290
Catalyst equivalent diameter (m)	3.83×10^{-3}
Bulk density (kg m^{-3})	730
Tube length (m)	12
Number of tubes	1
GHSV (h^{-1})	235
Feed molar flow rate (gmol s^{-1})	0.0335
Catalyst thermal conductivity (kJ m^{-1} s^{-1} K^{-1})	0.00625
Bed voidage	0.488

In this paper, OCM and FT reactors were used consecutively. In FT reactor two cases of counter-current and co-current flow of OCM exiting gas are discussed. FT reactor was equipped with hydrogen perm-selective membrane reactor with Pd–Ag membrane in one case. We discuss the amount of C_{5+} as desirable product in different conditions of FT reactor. Moreover, in this article we discuss yield of CO_2 and CH_4 as byproducts in each condition. According to observed results, counter current flow in FT reactor causes more yield of C_{5+} and lower CO_2 and CH_4 yield than co-current flow.

2. Process description

As will be described in the later sections, methane is converted to heavy hydrocarbons in two reactors. The OCM reactor is first one in which synthesis gas and C_{2+} is produced for second reactor where it converts CO and H_2 to heavy hydrocarbons. In an

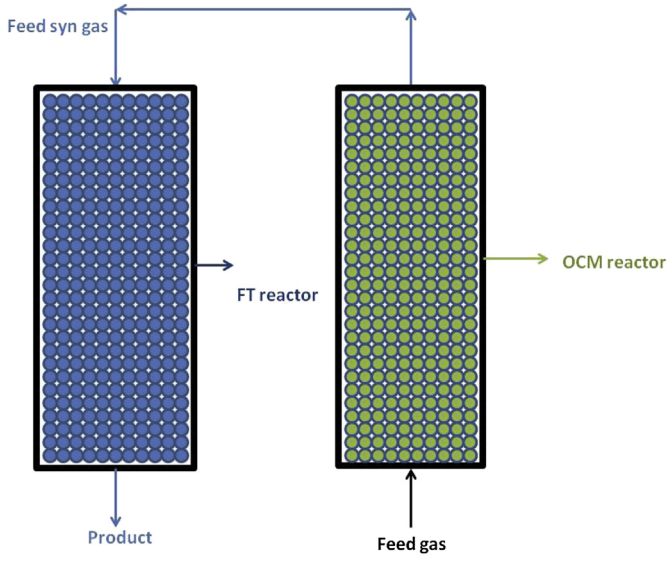

Fig. 1. Schematic diagram of two consecutive reactors: OCM and FT reactors.