KINETICS OF SLURRY PHASE FISCHER-TROPSCH SYNTHESIS

Second Annual Technical Progress Report

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Abstract

This report covers the second year of this three-year research grant under the University Coal Research program. The overall objective of this project is to develop a comprehensive kinetic model for slurry phase Fischer-Tropsch synthesis on iron catalysts. This model will be validated with experimental data obtained in a stirred tank slurry reactor (STSR) over a wide range of process conditions. The model will be able to predict concentrations of all reactants and major product species (H_2O, CO_2, linear 1- and 2-olefins, and linear paraffins) as a function of reaction conditions in the STSR.

During the second year of the project we completed the STSR test SB-26203 (275-343 h on stream), which was initiated during the first year of the project, and another STSR test (SB-28603 lasting 341 h). Since the inception of the project we completed 3 STSR tests, and evaluated catalyst under 25 different sets of process conditions. A precipitated iron catalyst obtained from Ruhrchemie AG (Oberhausen-Holten, Germany) was used in all tests. This catalyst was used initially in commercial fixed bed reactors at Sasol in South Africa. Also, during the second year we performed a qualitative analysis of experimental data from all three STSR tests. Effects of process conditions (reaction temperature, pressure, feed composition and gas space velocity) on water-gas-shift (WGS) activity and hydrocarbon product distribution have been determined.

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Executive Summary

During three STSR tests 25 sets of different process conditions were employed. Following values (or ranges) of process conditions were utilized in these three STSR tests:

Reaction temperature (T):   220, 240 and 260°C
Reaction pressure (P):   8, 15 and 25 (22.5) bar
Feed composition (H_2/CO ratio):   2/3 or 2/1
Gas space velocity (NL/g-Fe/h): 0.5 – 23.5

Catalyst deactivation was moderate in run SB-21903 (694 h on stream) but more severe in the other two STSR tests (terminated after approximately 340 h on stream). Deactivation did not have significant effect on hydrocarbon selectivity in runs SB-21903 and SB-26203. Lower methane and higher C_5^+ selectivity (C-atom basis) were obtained in run SB-28603 at 340 h in comparison to results at 70 h on stream.

Increase in the extent of WGS reaction, manifested in increase of CO_2 selectivity and decrease in UR, with increase in conversion of the limiting reactant, is consistent with the concept that the WGS is a consecutive reaction with respective to water that is formed in FTS reaction. Increase in the extent of WGS reaction with increase in temperature, decrease in total pressure, or decrease in H_2/CO feed ratio (i.e. decrease in CO partial pressure) is due to kinetic effects.

The observed decrease in 1-olefin content and increase in 2-olefin and n-paraffin contents with increase in conversion are consistent with the concept that 1-olefins participate in secondary reactions, whereas 2-olefins and n-paraffins are formed in these reactions (e.g. 1-olefin hydrogenation, isomerization and readsorption).

Methane selectivity decreased (and that of C_5^+ hydrocarbons increased) with decrease in temperature, increase in reaction pressure, and/or decrease in H_2/CO feed ratio. Carbon number product distribution could be described by so-called "double alpha" model (two distinct chain growth probabilities, one for lower MW products and the second one for higher MW products).

Introduction

The overall objective of this project is to develop a comprehensive kinetic model for slurry phase Fischer-Tropsch synthesis on iron catalysts. This model will be validated with experimental data obtained in a stirred tank slurry reactor (STSR) over a wide range of process conditions. This model will be able to predict concentrations of all reactants and major product species (H_2O, CO_2, linear 1- and 2-olefins, and linear paraffins) as a function of reaction conditions in the STSR. Kinetic model will be useful for preliminary reactor design and process economics study.

The overall program is divided into several tasks, and their timetable and brief descriptions are:

Task 1. Development of Kinetic Models (November 1, 2002 - March 31, 2005)

Kinetic models will be formulated utilizing the current state-of-the-art understanding of reaction mechanisms for formation of reaction intermediates and hydrocarbon products. Models will be based on adsorption/desorption phenomena for reactants and product species. These models will be continually updated on the basis of experimental data obtained in Task 3, and subsequent data analysis in Task 4.

Task 2. Catalyst Synthesis (August 1, 2003 - October 30, 2003)

A precipitated iron catalyst with nominal composition 100 Fe/3 Cu/4 K/16 SiO_2 (in parts per weight) will be synthesized utilizing equipment and procedures developed in our laboratory at Texas A&M University (TAMU). As an alternative we may utilize a robust commercially available catalyst with similar performance characteristics to TAMU's catalyst.

Task 3. Experiments in a Stirred Tank Slurry Reactor (January 15, 2003 - March 31, 2005)

Experiments will be conducted in a 1 dm^3 stirred tank slurry reactor (STSR) over a wide range of process conditions of industrial significance. Synthesis gas feed H_2/CO molar ratio will vary from 0.67 (coal derived syngas) to 2 (natural gas derived syngas). Baseline conditions will be repeated periodically to assess the extent of catalyst deactivation.

Task 4. Model Discrimination and Parameter Estimation (March 1, 2004 – August 31, 2005)

Langmuir-Hinshelwood-Hougen-Watson (LHHW) approach and the concept of rate limiting step result in a large number of competing kinetic models. Discrimination between the rival models will be based upon the goodness of fit, supplemented with statistical tests on parameter values and the physicochemical meaningfulness of the estimated parameter values.

Current Status

Task 1. Development of Kinetic Models

The work on this task has been initiated in June 2004. The main focus of this work has been to adopt the kinetic model of Lox and Froment [5,6] to a stirred tank slurry reactor. This work is still in progress.

Task 2. Catalyst Synthesis

Instead of synthesizing a new batch of TAMU's precipitated catalyst 100 Fe/3 Cu/4 K/16 SiO_2 (in parts by weight) we have decided to use a precipitated iron catalyst prepared by Ruhrchemie AG (Oberhausen-Holten, Germany). This catalyst (LP 33/81) has a nominal composition 100 Fe/4.3 Cu/4.1 K/25 SiO_2 (in parts by weight) and it was used initially in fixed bed reactors at Sasol in South Africa. It has been tested extensively at TAMU [1-4], and was used in previous study of kinetics of Fischer-Tropsch (F-T) synthesis by Lox and Froment [5,6]. It is a robust catalyst and its selectivity is similar to that of TAMU's catalyst.

Task 3. Experiments in a Stirred Tank Slurry Reactor

The work on this task was initiated in January 2003 and three tests were completed by the end of October 2003. Detailed information on these experiments including data analysis is presented in other sections of this report (Experimental and Results and Discussion).

Task 4. Model Discrimination and Parameter Estimation

The work on this task has not been initiated during the reporting period.

Experimental

Three tests (runs SB-21903, SB-26203 and SB-28603) were conducted in a 1 dm^3 stirred tank slurry reactor (Autoclave Engineers). A schematic of the experimental apparatus is shown in Figure 1. The feed gas flow rate was adjusted with a mass flow controller and passed through a series of oxygen removal, alumina and activated charcoal traps to remove trace impurities. After leaving the reactor, the exit gas passed through a series of high and low (ambient) pressure traps to condense liquid products. High molecular weight hydrocarbons (wax), withdrawn from a slurry reactor through a porous cylindrical sintered metal filter, and liquid products, collected in the high and low pressure traps, were analyzed by capillary gas chromatography. Liquid products collected in the high and atmospheric pressure traps were first separated into an organic phase and an aqueous phase and then analyzed using different columns and temperature programmed methods. The reactants and noncondensible products leaving the ice traps were analyzed on an on-line GC (Carle AGC 400) with multiple columns using both flame ionization and thermal conductivity detectors. Further details on the experimental set up, operating procedures and product quantification can be found elsewhere [1,2,5,8].

Ruhrchemie catalyst (15 g in run SB-21903, 11.2 g in run SB-26203 and 25 g in run SB-28603) was calcined in air at 300°C and a fraction between 140-325 mesh was loaded into the reactor filled with 300-320 g of Durasyn 164 oil (a hydrogenated 1-decene homopolymer, ~ C$_{30}$

obtained from Albemarle Co.). The catalyst was pretreated in CO at 280°C, 0.8 MPa (100 psig), and 3 NL/g-cat/h for 12 hours. After the pretreatment the catalyst was tested initially at 260°C, 1.5 MPa (200 psig), 4 NL/g-Fe/h (where, NL/h, denotes volumetric gas flow rate at 0°C and 1 bar) using CO rich synthesis gas (H_2/CO molar feed ratio of 0.67). After reaching a stable steady state value (~60 h on stream) the catalyst was tested at different process conditions. A minimum length of time between changes in process conditions was 20 h.

Results and Discussion

Process conditions and selected results (from online gas analysis of inorganic species and C_1-C_5 hydrocarbons) for all three tests are summarized in Table 1. Run SB-21903 (15 mass balances) and the first 275 h of testing in run SB-26203 (6 mass balances) were completed during the first year of the project. However, the data from these two tests have not been analyzed in our first annual report. Before discussing results from stirred tank slurry reactor (STSR) tests in detail, we provide definitions of conversions and selectivities used in this report.

H_2 conversion (%) = 100 x ((Moles of H_2)$_{in}$- (Moles of H_2)$_{out}$)/(Moles of H_2)$_{in}$ (1)

CO conversion (%) = 100 x ((Moles of CO)$_{in}$- (Moles of CO)$_{out}$))/(Moles CO)$_{in}$ (2)

(H_2+CO) conversion (%) = 100 x ((Moles of H_2+CO)$_{in}$- (Moles of H_2+CO)$_{out}$))/(Moles of H_2+ CO)$_{in}$ (3)

Usage ratio (UR) and CO_2 selectivity are defined as:

UR (-) = (Moles of H_2 consumed)/(Moles of CO consumed) (4)

$$CO_2 \text{ selectivity (\%)} = 100 \times \frac{(n_{CO_2})_{out}}{(n_{CO})_{in} - (n_{CO})_{out}} \qquad (5)$$

Hydrocarbon selectivity on carbon atom basis is calculated from:

$$S_{ij}(\%) = \frac{100 \times (in_{ij})}{(n_{CO})_{in} - (n_{CO})_{out} - (n_{CO_2})_{out}} \qquad (6)$$

where: S_{ij} is the selectivity of hydrocarbon species j containing i carbon atoms, n_{ij} is molar flow of compound j in the gas phase, $(n_{CO})_{in}$ and $(n_{CO})_{out}$ are molar flow rates of CO in and out of the reactor, and $(n_{CO_2})_{out}$ is the molar flow rate of carbon dioxide out of the reactor. The above formulas assume that there is no carbon dioxide in the feed, and neglect formation of oxygenates.

Olefin and paraffin selectivities (contents), based on molar flow rates of the corresponding hydrocarbons of the same carbon number, are calculated as:

1-olefin content (%) = 100 x (1-olefin)/(1-olefin + 2-olefin + n-paraffin)   (7)

2-olefin content (%) = 100 x (2-olefin)/ (1-olefin + 2-olefin + n-paraffin)   (8)

n-paraffin content (%) = 100 x (n-paraffin)/ (1-olefin + 2-olefin + n-paraffin)   (9)

Reproducibility of Results and Catalyst Deactivation

In runs SB-21903 and SB-26203 after the CO pretreatment, the catalyst was tested initially at the baseline conditions (260°C, 1.5 MPa, 4 NL/g-Fe/h, H_2/CO = 2/3), whereas in run SB-28603 the catalyst was tested initially (up to 46 h on stream) at 220°C (the other process conditions were the same as the baseline conditions) and then the temperature was increased to 260°C (baseline conditions from 50-73 h on stream). Results from all three tests at the baseline conditions are shown in Figures 2 and 3.

Syngas conversion (Fig. 2a) and methane and C_5^+ hydrocarbon selectivities on carbon atom basis (Fig 2b) during the first 80 h of testing were remarkably similar in all three tests, indicating that the CO activation procedure was reproducible and that the use of different amounts of catalyst

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(11.2-25 g) did not have any impact on the initial catalyst activity and selectivity. Activity (syngas conversion) increased with time reaching a constant value at about 50 h on stream.

After testing at the baseline conditions the catalyst was tested at different process conditions in all three tests (see Table 1). In order to assess the extent of catalyst deactivation the baseline conditions were repeated throughout the test (run SB-21903) or at the end of the test (runs SB-26203 and SB-28603). These results are shown in Figure 3.

Catalyst activity (measured by syngas conversion) decreased in all three tests (Fig. 3a). Average deactivation rate (expressed in terms of loss of conversion per hour) ranged from 0.018 %/h in run SB-21903 to 0.054 %/h in run SB-26203. Methane selectivity increased whereas C_5^+ selectivity decreased slightly with time in runs SB-21903 and SB-26203. The opposite trend (decrease in methane selectivity and increase in C_5^+ selectivity) was observed in run SB-28603.

Effect of time on stream (i.e. catalyst deactivation) on olefin selectivities (obtained from complete analysis of all products) in run SB-21903 is shown in Figure 4. As can be seen, the olefin selectivity did not change much with time, which is consistent with results shown in Fig. 3b (methane and C_5^+ selectivities).

Effects of Process Conditions and Conversion on Water-Gas-Shift Reaction and Hydrocarbon Product Distribution
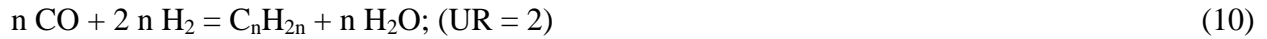
The catalyst was tested under 25 sets of different process conditions. The following values (or ranges) of process conditions were utilized in these three STSR tests:

Reaction temperature (T):	220, 240 and 260°C
Reaction pressure (P):	8, 15 and 25 (22.5) bar
Feed composition (H_2/CO ratio):	2/3 or 2/1
Gas space velocity (NL/g-Fe/h):	0.5 – 23.5

Effects of temperature, pressure, feed composition and gas space velocity (i.e. limiting reactant conversion) on the extent of water-gas-shift (WGS) reaction (in terms of usage ratio –UR and CO_2 selectivity), and hydrocarbon selectivity (CH_4 and C_5^+) are shown in Figures 5-13.

Effect of temperature and conversion of the limiting reactant (H_2 for $H_2/CO = 2/3$ feed gas, CO for $H_2/CO = 2/1$ feed gas) is shown in Figures 5-7. As shown in Figure 5 the usage ratio (UR) decreases whereas the CO_2 selectivity increases with increase in conversion (at constant temperature) or with increase in temperature (at constant conversion of the limiting reactant). This trend is the same regardless of feed composition ($H_2/CO = 2/3$ in Fig. 5a, or $H_2/CO = 2/1$ in Fig. 5b). The effect of conversion is consistent with a concept that the WGS reaction is a consecutive reaction according to the following stoichiometric equations.

Hydrocarbon formation (Fischer-Tropsch synthesis - FTS) reaction

$$n\ CO + 2\ n\ H_2 = C_nH_{2n} + n\ H_2O;\ (UR = 2) \tag{10}$$

Water-Gas-Shift (WGS) reaction

$$CO + H_2O = CO_2 + H_2 \tag{11}$$

Overall reaction (high WGS activity)

$$2\ n\ CO + n\ H_2 = C_nH_{2n} + n\ CO_2;\ (UR = 0.5,\ CO_2\ selectivity = 50\%) \tag{12}$$
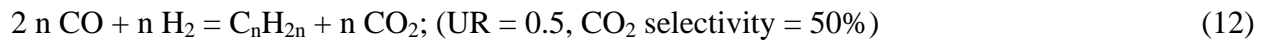
In the absence of WGS reaction, the usage ratio is 2 (Eq. 10), whereas if all water produced by FTS is consumed by WGS reaction the usage ratio is 0.5 and the CO_2 selectivity is 50% (assuming that CO is not consumed in any other reactions). From the above stoichiometry it is expected that the extent of WGS reaction (secondary or consecutive reaction) will increase with increase in conversion, which is manifested in decrease of the usage ratio and increase in CO_2 selectivity.

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The increase in WGS activity (higher CO_2 selectivity and lower UR) with increase in temperature (at constant conversion) is a kinetic effect (Fig. 5).

As shown in Figures 6 and 7, methane selectivity increases whereas the selectivity of high molecular hydrocarbons (C_5^+) decreases with increase in temperature. Experimental data at 220°C and 240°C in Fig. 6 (H_2/CO = 2/3, P =15 bar) do not follow this trend, due to experimental errors. At a given temperature methane conversion increases with increase in conversion (H_2/CO = 2/3 feed in Fig. 6a) whereas C_5^+ selectivity decreases. However, this trend was not observed with H_2/CO = 2 feed gas (Fig. 7a) at 220°C and 240°C.

Effect of reaction pressure and conversion of the limiting reactant is shown in Figures 8-10. The extent of WGS reaction increases (lower UR and higher CO_2 selectivity) with increase in conversion or with decrease in total pressure (Fig. 8). Conversion effect on the extent of WGS reaction was discussed previously (Fig. 5) whereas the effect of pressure is the kinetic effect. Methane selectivity decreases with increase in pressure (Figures 9a and 10a), whereas the pressure does not have significant effect on C_5^+ selectivity (Figs. 9b and 10b). Methane selectivity increases with conversion at constant pressure (Fig. 10a with H_2/CO = 2, and at 15 bar with H_2/CO = 2/3 in Fig. 9a).

The extent of WGS reaction is higher with the CO rich feed gas (H_2/CO = 2/3) relative to syngas derived from natural gas (H_2/CO = 2) as illustrated in Figure 11. Methane selectivity is lower, and C_5^+ selectivity higher with the CO rich feed gas (Figs. 12 and 13). This is related to partial pressures of H_2 and CO. Methane selectivity increases and C_5^+ selectivity decreases with increase in partial pressure of H_2, i.e. with increase in H_2/CO ratio inside the reactor.

Effects of Conversion (gas space velocity) and Carbon Number on Olefin and Paraffin Selectivities

As shown in Figures 14-16, 1-olefin content decreases, whereas 2-olefin content and n-paraffin content increase with increase in conversion of the limiting reactant. This trend is less pronounced for the CO rich feed gas at conversions of 40-65%, but is clear at higher conversions

(Figs. 15 and 16). This indicates that 1-olefins are consumed in secondary reactions, whereas n-paraffins and 2-olefins are formed in part in secondary reactions.

Carbon number dependences of selectivities (at constant conversion) show the following trend: 1-olefin selectivity passes through a maximum and n-paraffin selectivity passes through a minimum at C_3, whereas 2-olefin selectivity increases with carbon number. It is well known that ethylene is more reactive than other 1-olefins and it can initiate chain growth or be incorporated into the growing chains, and thus its selectivity is lower than that of 1-propene and other low molecular weight (MW) 1-olefins [9-13]. Described carbon number effects have been ascribed [14-19] to secondary reactions of 1-olefins (1-olefin readsorption, hydrogenation and/or isomerization) and increase in residence time with increase in molecular weight.

Carbon Number Product Distribution

Typical carbon number product distributions at different process conditions are shown in form of Anderson-Schulz-Flory (ASF) plots (Figures 17 and 18). Carbon number distributions could not be described by uniform chain growth probability factor α, which would result in a straight line (ln x_n vs C_n). Experimental data were fitted using a three-parameter model of Huff and Satterfield [20]:

$$x_n = \beta (1-\alpha_1) \alpha_1^{n-1} + (1 - \beta) (1 - \alpha_2) \alpha_2^{n-1} \tag{13}$$

where: x_n = mole fraction of products containing n carbon atoms (hydrocarbons and oxygenates), β = fraction of type 1 sites, α_1 = chain growth probability on type 1 sites, and α_2 = chain growth probability on type 2 sites.

Experimental data are reasonably well represented by this type of model. The model parameters were estimated using a nonlinear regression.

Conclusions

During the second year of the project we completed the STSR test SB-26203, which was initiated during the first year of the project, and another STSR test (SB-28603 lasting 341 h). Since the inception of the project we completed 3 STSR tests, and evaluated catalyst under 25 different sets of process conditions. Also, during the second year we performed a preliminary analysis of experimental data.

Catalyst deactivation was moderate in run SB-21903 (694 h on stream) but more severe in the other two STSR tests (terminated after approximately 340 h on stream). Deactivation did not have significant effect on hydrocarbon selectivity in runs SB-21903 and SB-26203. Lower methane and higher C_5^+ selectivity (C-atom basis) were obtained in run SB-28603 at 340 h in comparison to results at 70 h on stream.

Increase in the extent of WGS reaction, manifested in increase of CO_2 selectivity and decrease in UR, with increase in conversion of the limiting reactant, is consistent with the concept that the WGS is a consecutive reaction with respective to water that is formed in FTS reaction. Increase in the extent of WGS reaction with increase in temperature, decrease in total pressure, or decrease in H_2/CO feed ratio (i.e. decrease in CO partial pressure) is due to kinetic effects.

Decrease in 1-olefin content and increase in 2-olefin and n-paraffin contents with increase in conversion are consistent with the concept that 1-olefins participate in secondary reactions, whereas 2-olefins and n-paraffins are formed in these reactions (e.g. 1-olefin hydrogenation, isomerization and readsorption). Secondary hydrogenation and isomerization reactions increase with increase in partial pressure of hydrogen. Gas residence time has pronounced effect on selectivity of ethylene and gaseous 1-olefins, but it is less pronounced for higher MW olefins (C_{10}^+). The residence time of high MW hydrocarbons is much longer than that of gaseous hydrocarbons and is determined by the rate of liquid (wax) removal from the reactor.

Methane selectivity decreases (and that of C_5^+ hydrocarbons increases) with decrease in temperature, increase in reaction pressure, and/or decrease in H_2/CO feed ratio. The effect of

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conversion (i.e. gas space velocity) on hydrocarbon selectivity was relatively small in most cases, and there were no clearly discernible trends. Carbon number product distribution could be described by so-called "double alpha" model (two distinct chain growth probabilities, one for lower MW products and the second one for higher MW products).

Future Work

Our plan for the next period (third year of the project) is to develop kinetic models and estimate kinetic parameters from experimental data.

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Table 1. Process conditions and results (gas phase analysis).

	MB#	TOS	T	P	H_2/CO	SV	X_{CO}	X_{H2+CO}	UR	CO_2	CH_4	C_5^+
		h	°C	bar	(-)	NL/g-Fe/h	%	%	(-)	(%)	(%)	(%)
SB-21903	I/1	71-78	260	15	0.67	4.0	54	57	0.75	43.2	4.0	76.6
	I/2	94-101	260	15	0.67	1.7	84	82	0.64	44.7	4.5	77.0
	I/3	119-126	260	15	0.67	9.2	27	31	0.96	32.8	3.8	76.8
	I/4	152-164	240	15	0.67	2.0	39	45	0.91	32.1	2.7	83.8
	I/5	193-215	240	15	0.67	1.0	56	59	0.75	40.0	3.3	77.9
	I/6	225-238	240	15	0.67	5.5	14	18	1.20	20.2	3.0	81.5
	I/7	263-270	260	15	0.67	4.0	46	50	0.81	41.3	4.3	75.0
	I/8	298-310	240	15	2	4.2	46	36	1.35	24.9	7.2	69.2
	I/9	334-338	240	15	2	2.1	80	64	1.42	22.6	5.5	77.0
	I/10	364-368	240	15	2	10.8	22	18	1.49	17.5	7.1	65.5
	I/11	391-408	260	15	2	3.5	59	48	1.29	27.1	7.2	74.6
	I/12	418-433	260	15	2	8.0	59	48	1.43	24.8	6.7	72.3
	I/13	489-505	260	15	0.67	4.0	46	50	0.79	41.3	4.2	75.8
	I/14	600-606	260	22.5	0.67	6.1	36	43	0.96	38.0	4.2	74.8
	I/15	647-654	260	22.5	0.67	1.0	84	83	0.65	45.3	4.5	75.6
	I/BL	676-694	260	15	0.67	4.0	43	46	0.78	38.8	4.4	75.3
SB-26203	II/0	51-55	260	15	0.67	4.0	54	57	0.77	43.9	4.1	76.4
	II/1	86-92	260	15	2	7.1	77	52	1.08	35.9	9.3	66.3
	II/2	118-122	260	15	2	10.1	66	46	1.15	34.1	8.4	66.8
	II/3	142-146	260	15	2	23.5	41	32	1.37	29.4	7.8	64.0
	II/4	175-191	240	15	2	5.8	55	42	1.32	27.9	6.3	69.9
	II/5	224-240	260	25	0.67	6.7	43	50	0.91	35.1	2.8	79.8
	II/6	264-268	260	25	0.67	17.1	20	27	1.30	26.7	3.6	76.0
	II/7	297-313	260	25	0.67	2.0	70	72	0.73	41.7	3.4	76.9
	II/8	323-337	260	15	0.67	4.0	37	42	0.87	37.4	4.4	73.7
SB-28603	III/BL	50-73	260	15	0.67	4.0	56	59	0.74	46.4	4.3	74.5
	III/1	94-101	220	15	0.67	4.1	11	16	1.57	18.8	7.1	75.9
	III/2	128-143	220	15	0.67	0.5	34	41	1.00	35.1	3.2	75.3
	III/3	166-170	220	15	2	9.5	13	13	1.80	11.6	5.3	72.7
	III/4	192-198	220	15	2	0.6	72	54	1.23	27.6	5.4	96.1
	III/5	224-238	260	8	2	1.5	84	54	0.90	39.5	11.0	64.1
	III/6	262-268	260	8	2	9.0	35	25	1.20	31.1	7.1	69.6
	III/7	287-292	240	8	0.67	5.5	9	13	1.45	28.0	3.2	80.7
	III/8	313-318	240	8	0.67	0.7	50	54	0.78	45.8	2.9	81.7
	III/BL	338-341	260	15	0.67	2.0	41	45	0.86	38.6	3.1	81.5

BL = Baseline process conditions
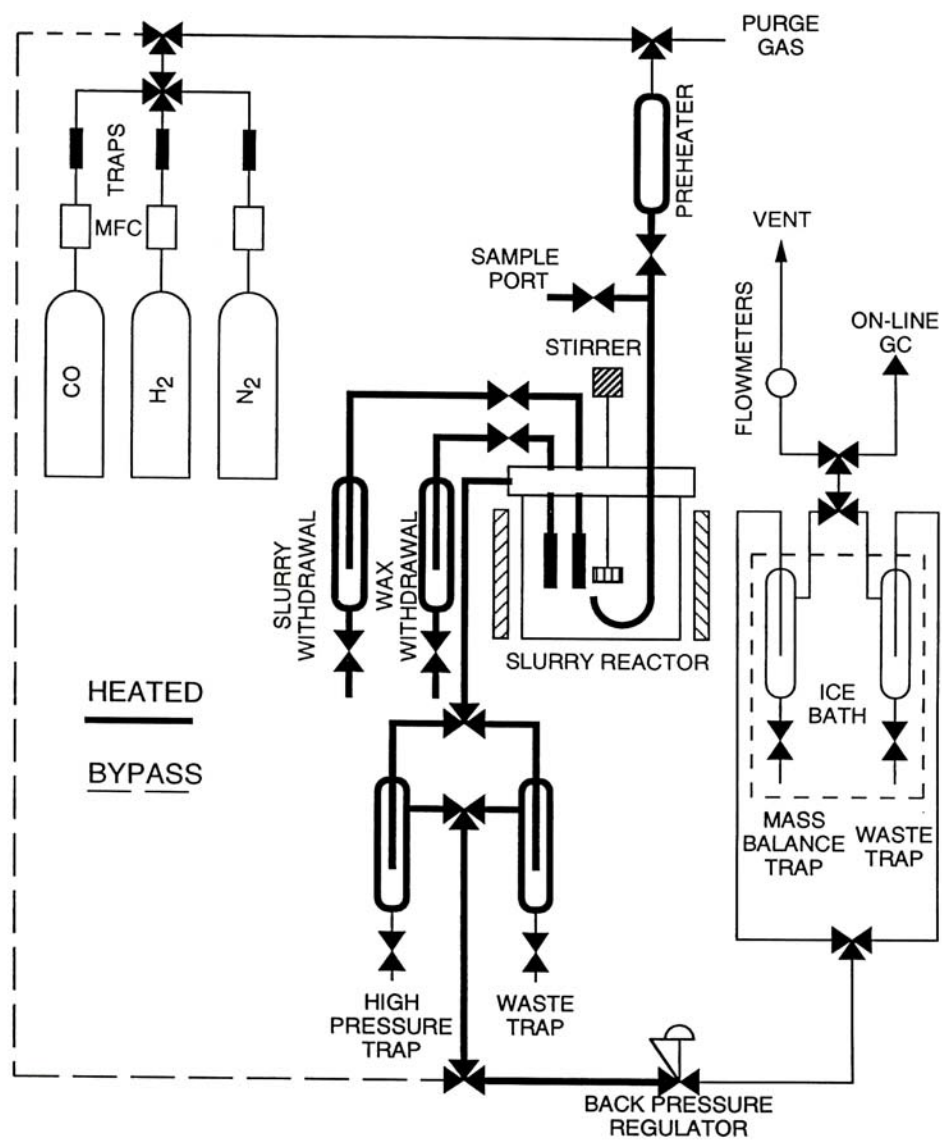
Figure 1. Schematic of stirred tank slurry reactor system.
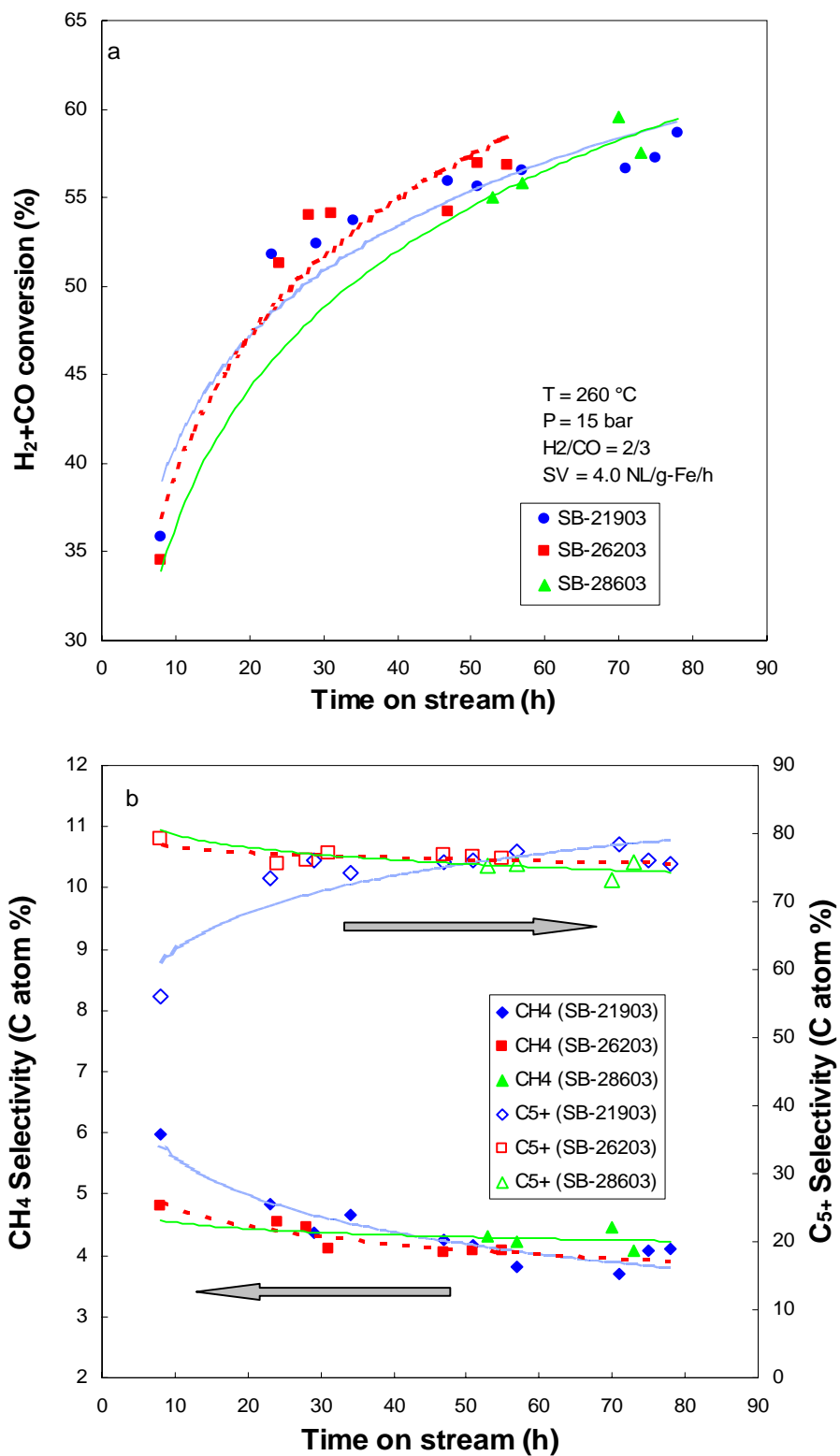
Figure 2. Effect of time at the baseline conditions (initial period).
(a) Syngas conversion, (b) Methane and C_5^+ selectivity.
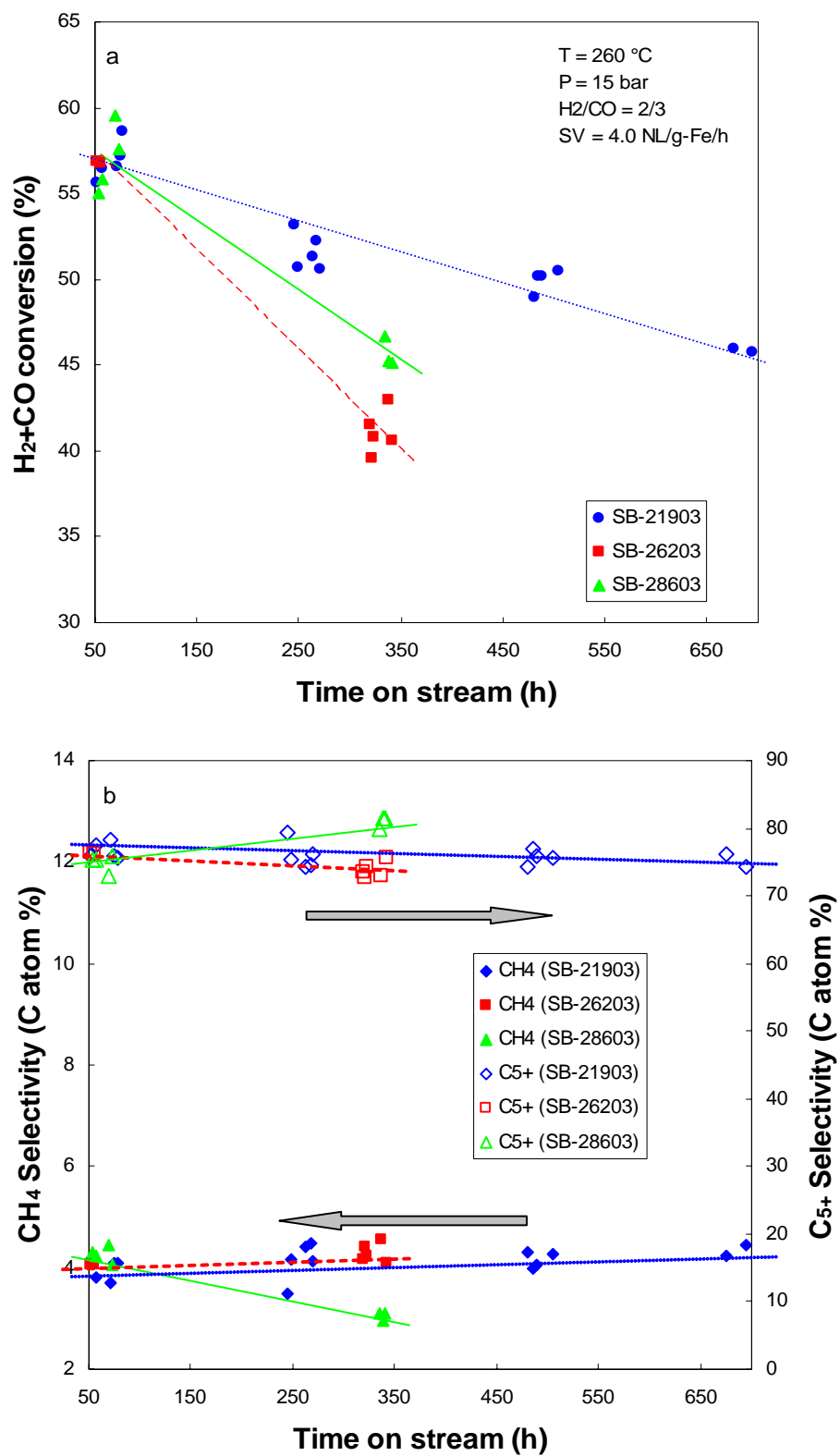
Figure 3. Effect of time at the baseline conditions.
(a) Syngas conversion, (b) Methane and C_5^+ selectivity.
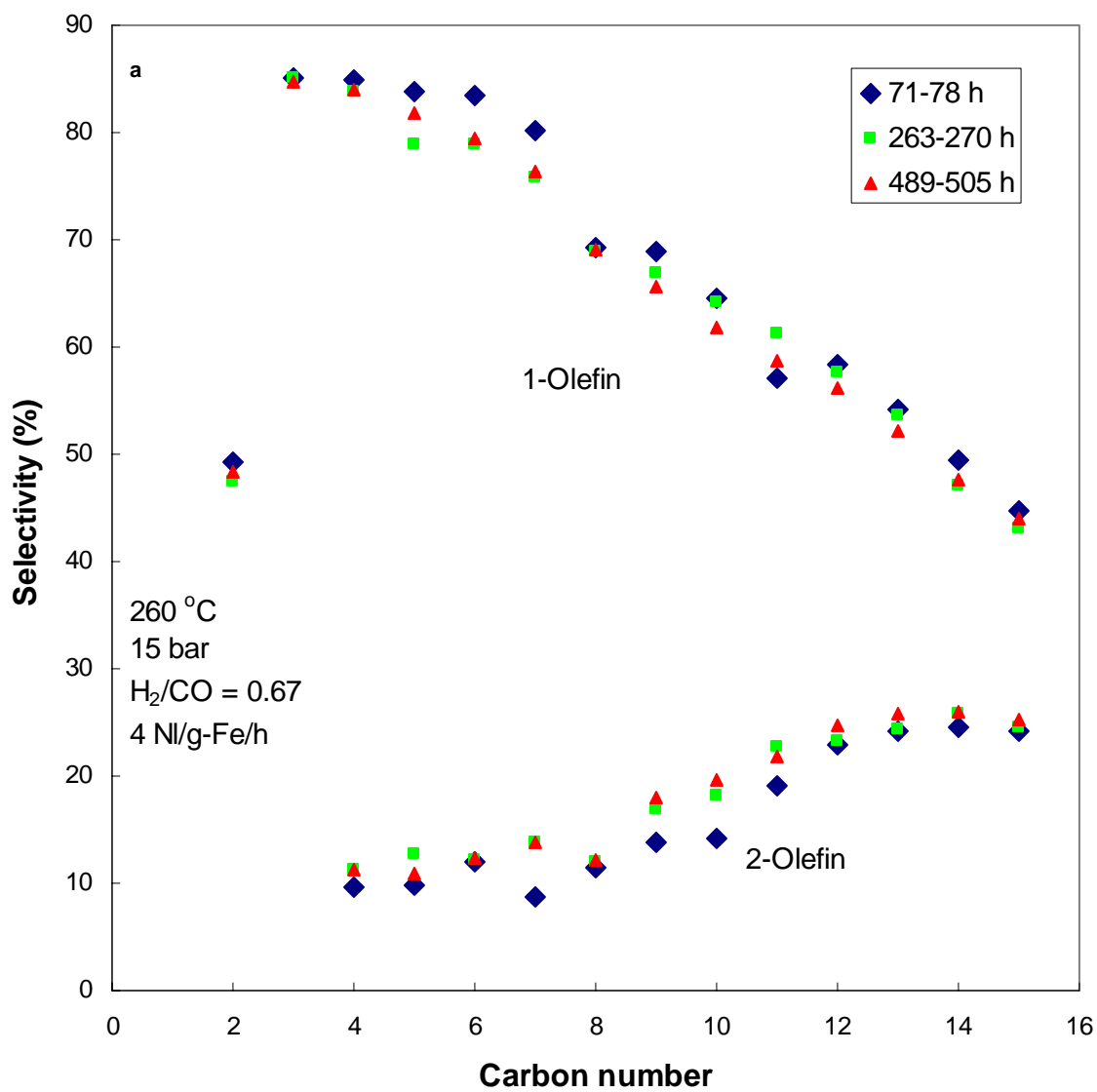
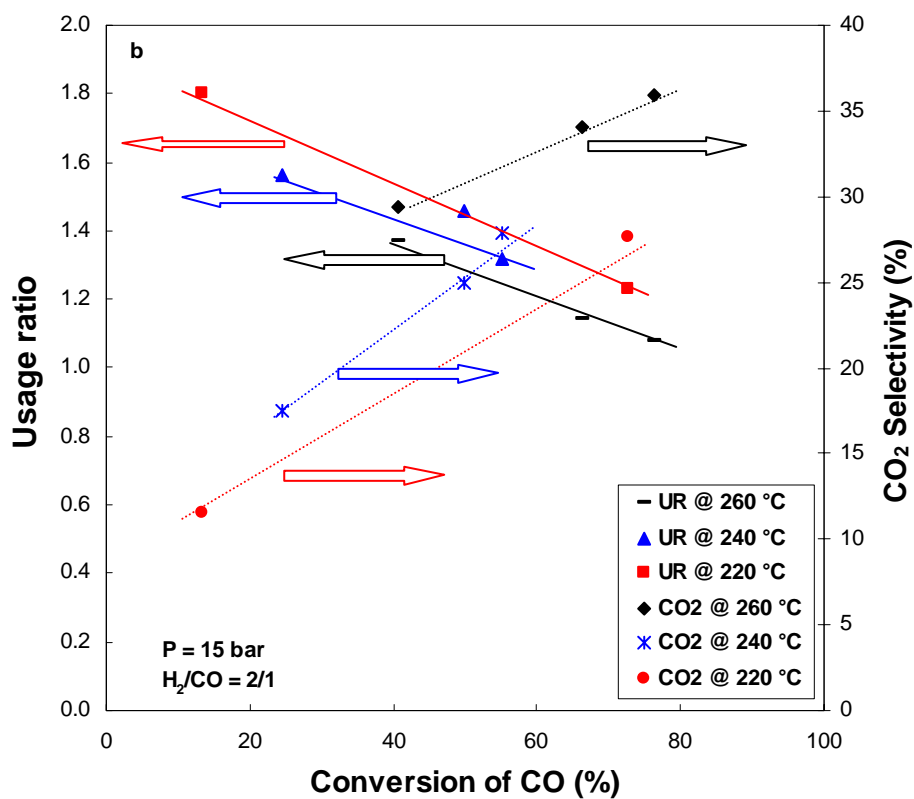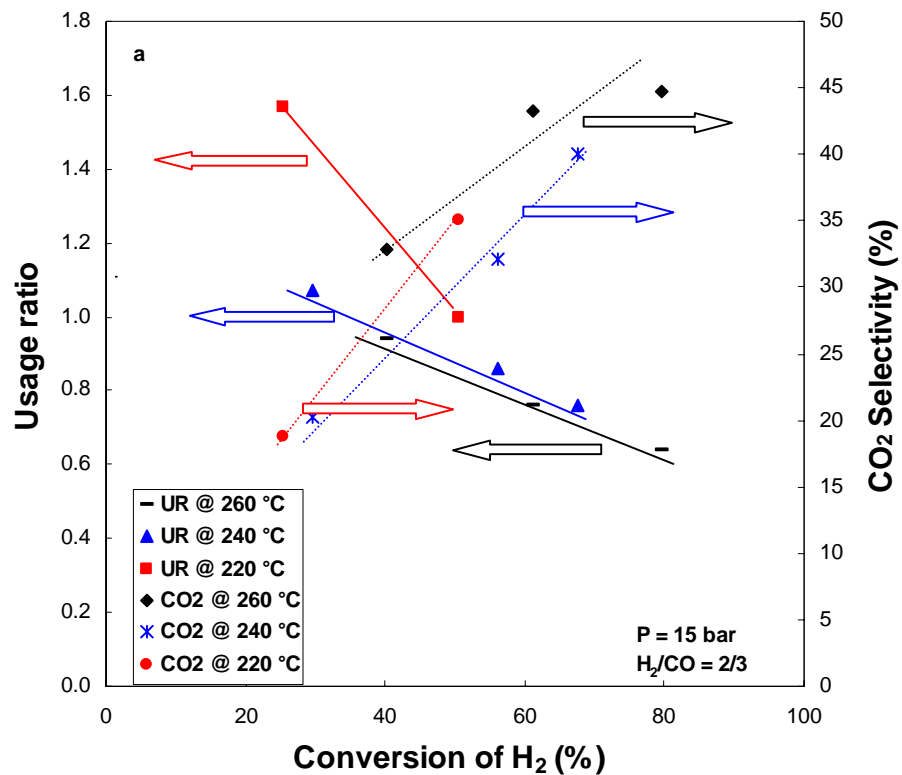Figure 4. Effect of time-on-stream on olefin selectivities.

Figure 5. Effect of temperature on WGS reaction (15 bar)
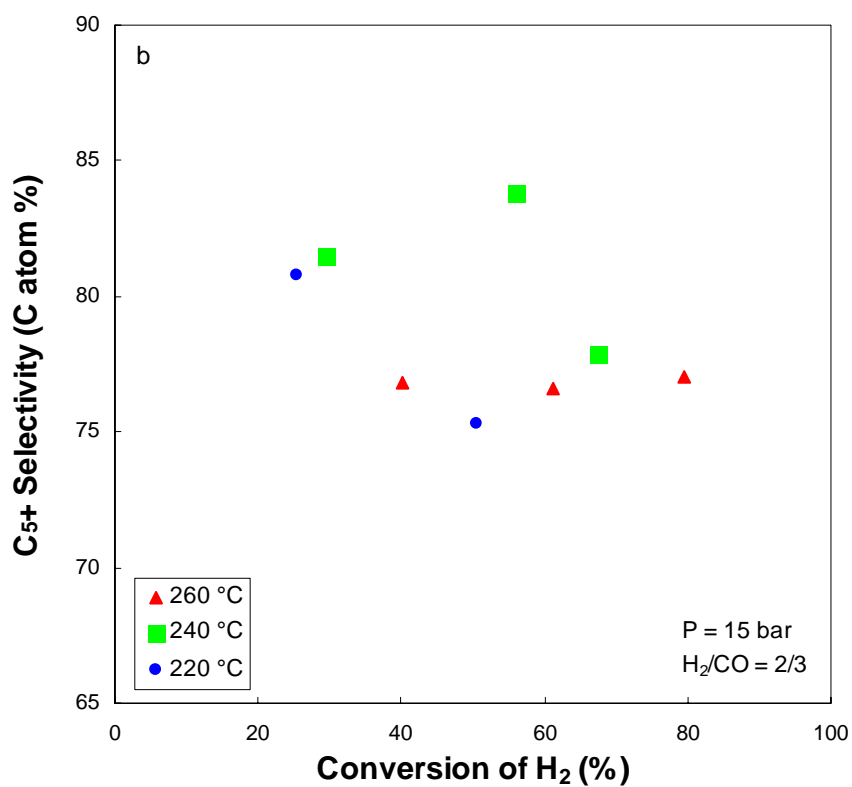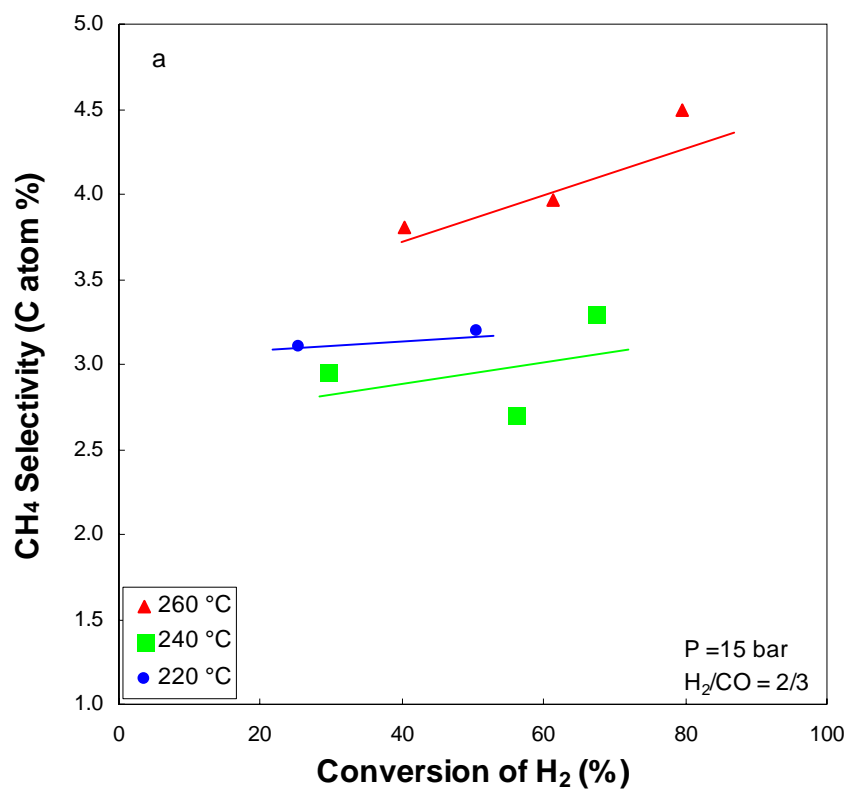(a) feed H_2/CO = 2/3, (b) feed H_2/CO = 2/1.

Figure 6. Effect of temperature on hydrocarbon selectivity (15 bar, $H_2/CO = 2/3$)
(a) Methane selectivity, (b) C_5^+ selectivity.
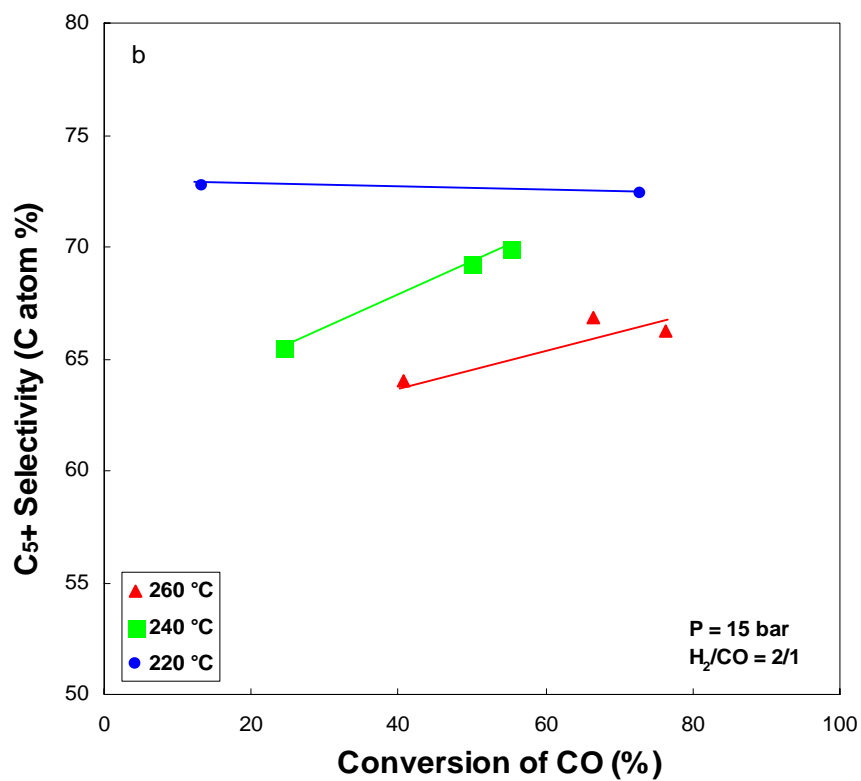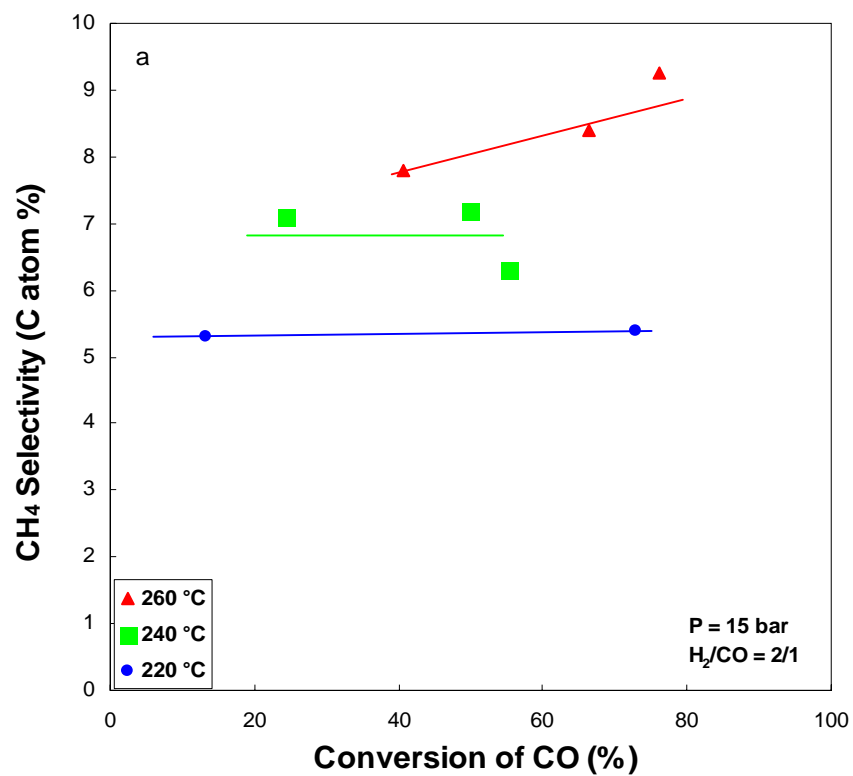
Figure 7. Effect of temperature on hydrocarbon selectivity (15 bar, $H_2/CO = 2/1$)
(a) Methane selectivity, (b) C_5^+ selectivity.
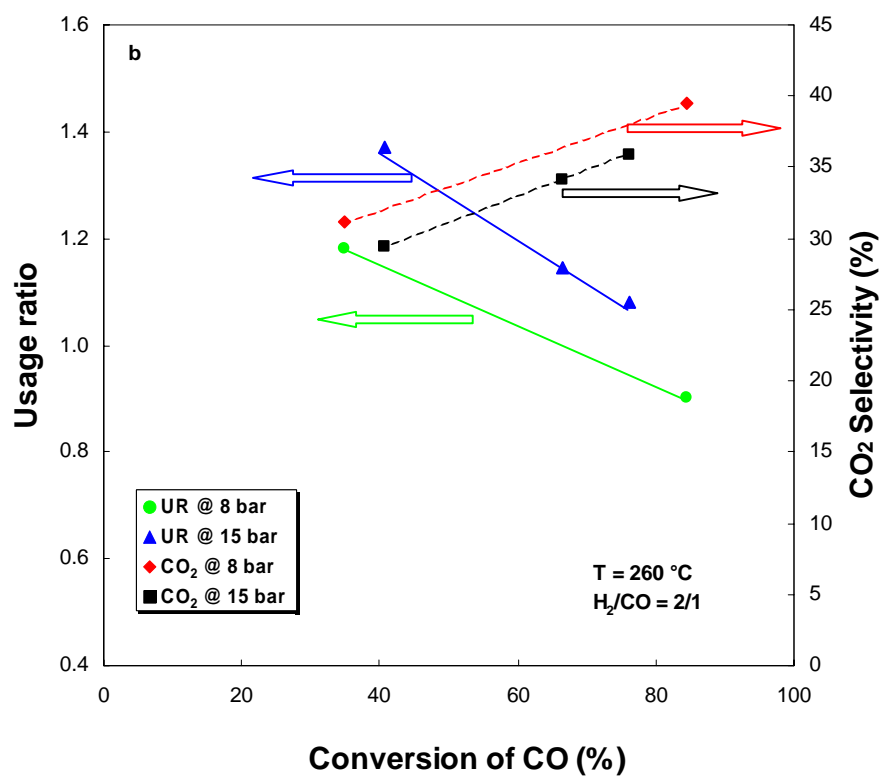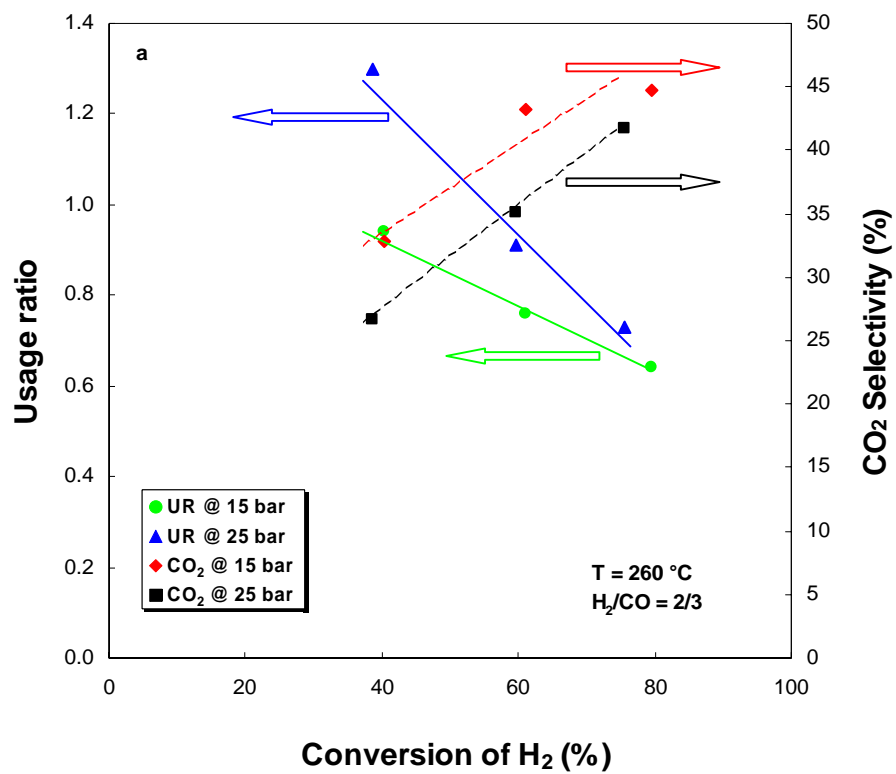
Figure 8. Effect of pressure on WGS reaction (260°C)
(a) feed $H_2/CO = 2/3$, (b) feed $H_2/CO = 2/1$.
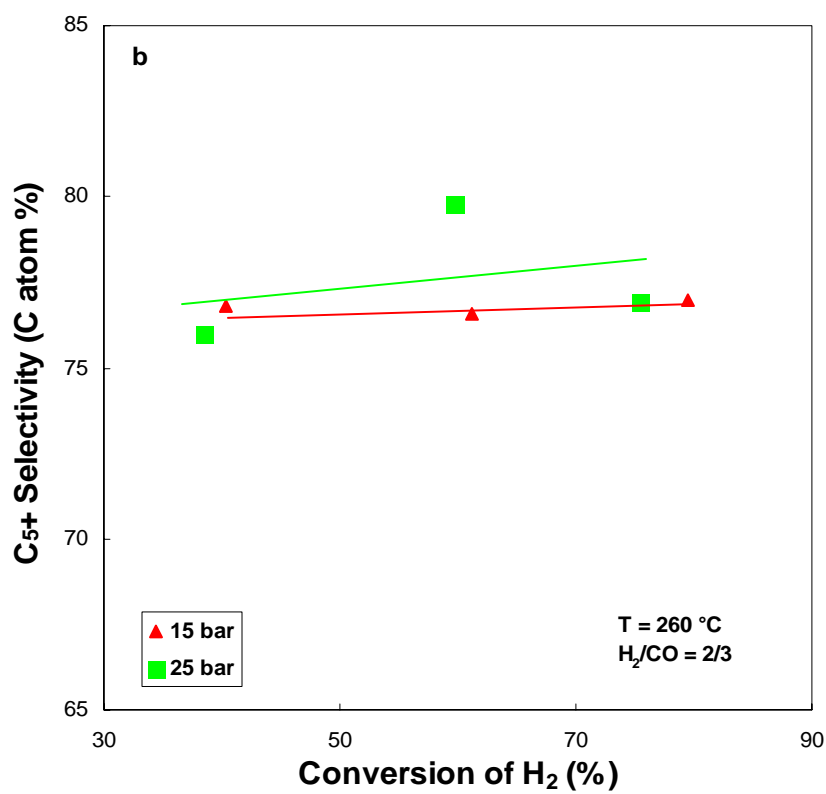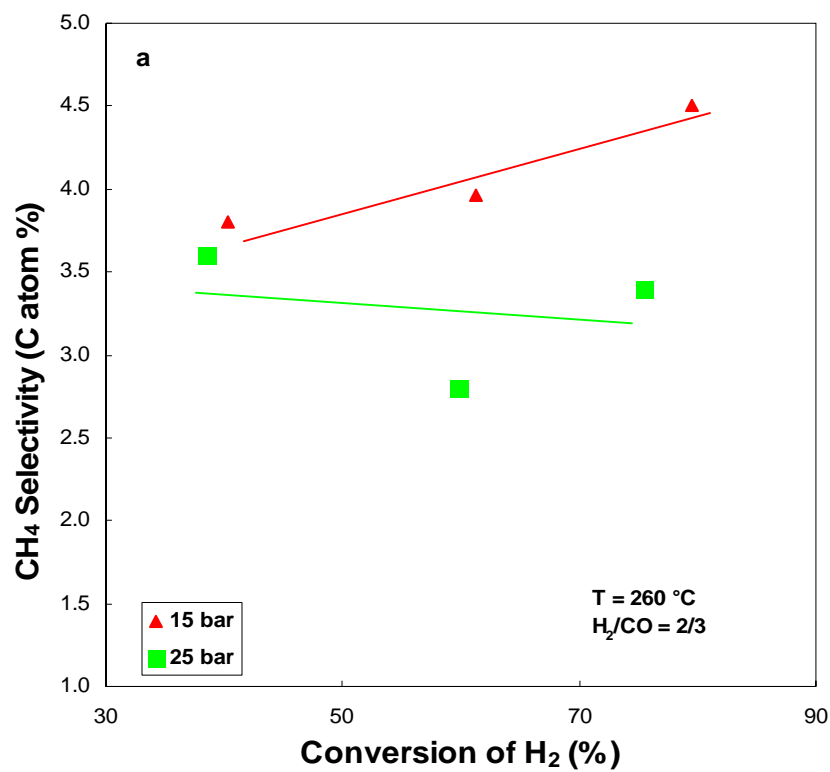
Figure 9. Effect of pressure on hydrocarbon selectivity (260°C, H_2/CO = 2/3)
(a) Methane selectivity, (b) C_5^+ selectivity.
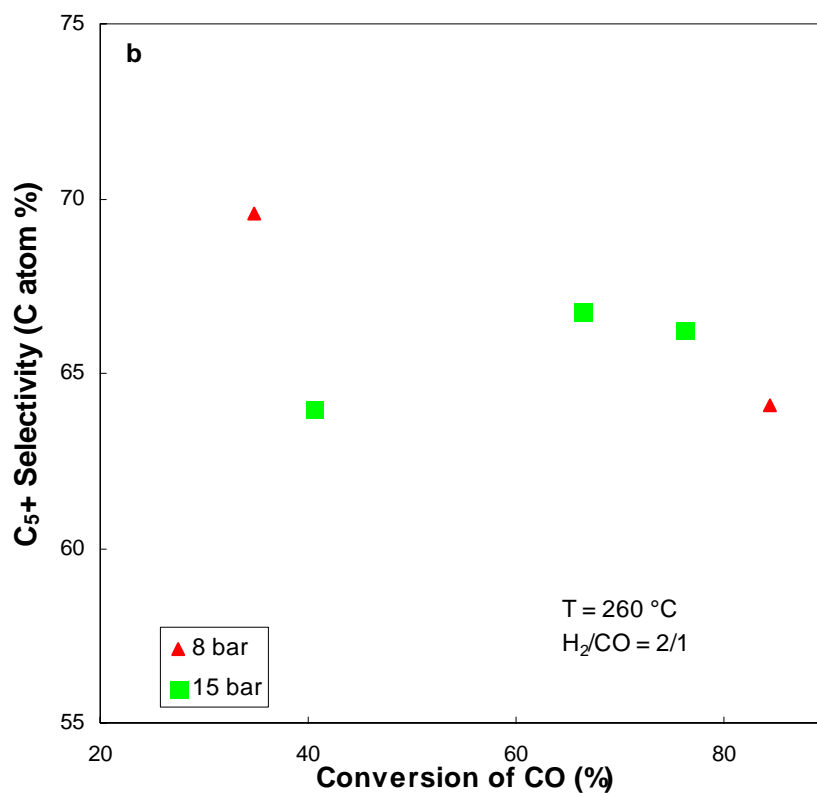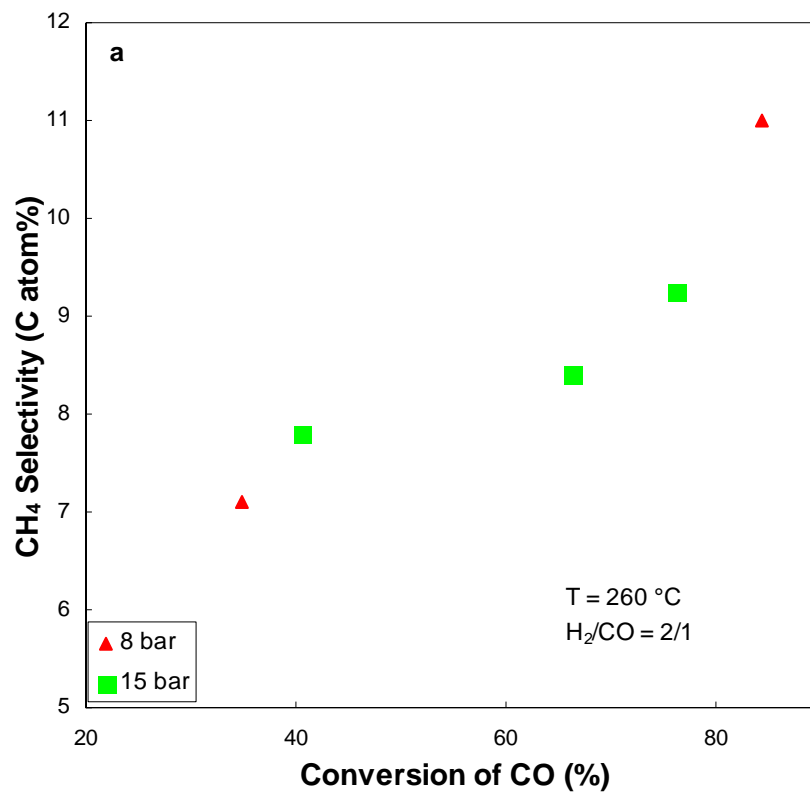
Figure 10. Effect of pressure on hydrocarbon selectivity (260°C, H_2/CO = 2/1)
(a) Methane selectivity, (b) C_5^+ selectivity.
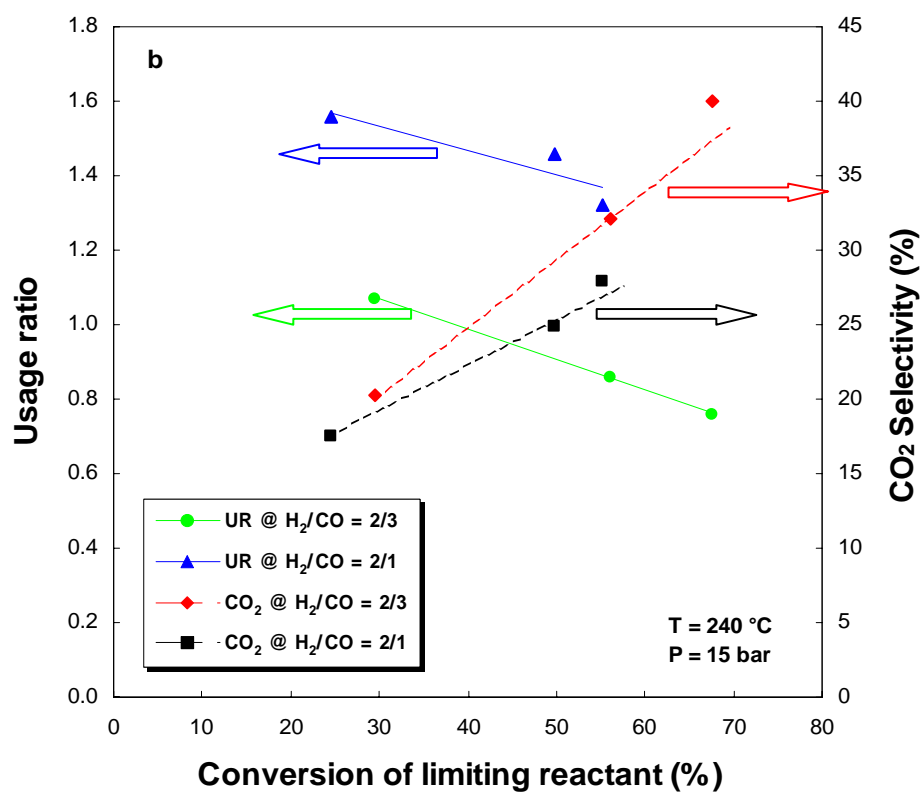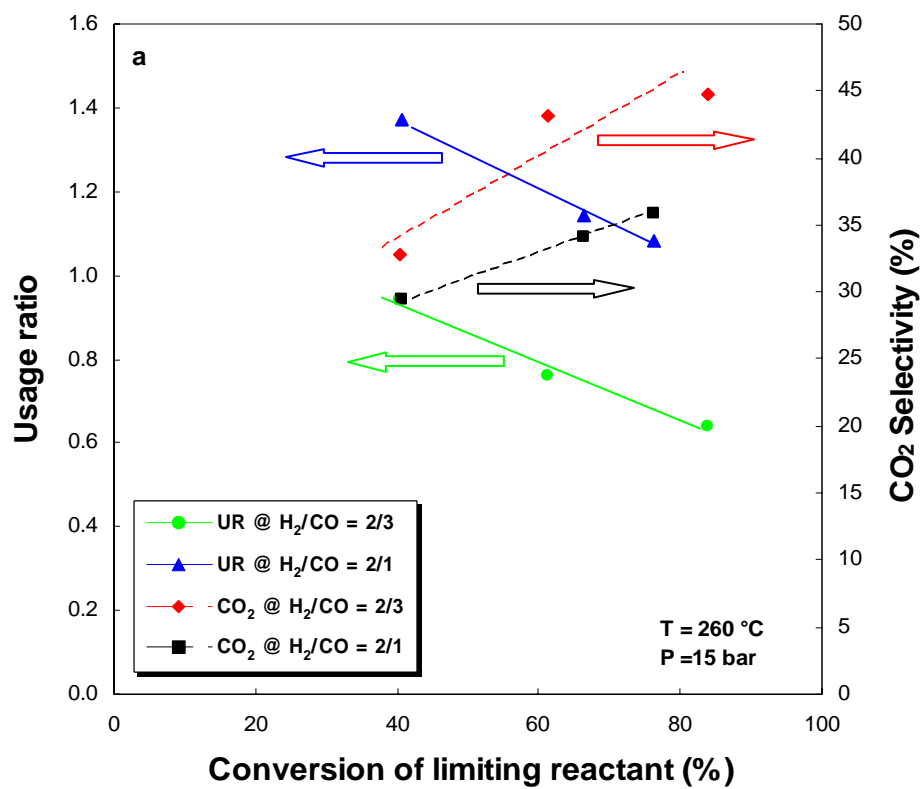
Figure 11. Effect of feed composition on WGS reaction (15 bar)
(a) 260°C, (b) 240°C.
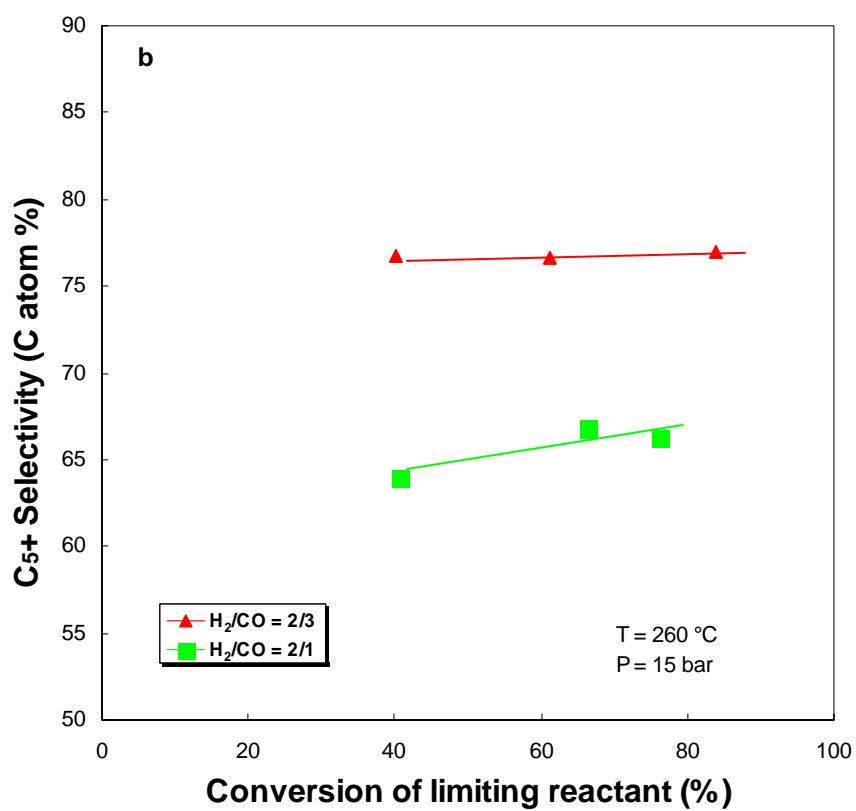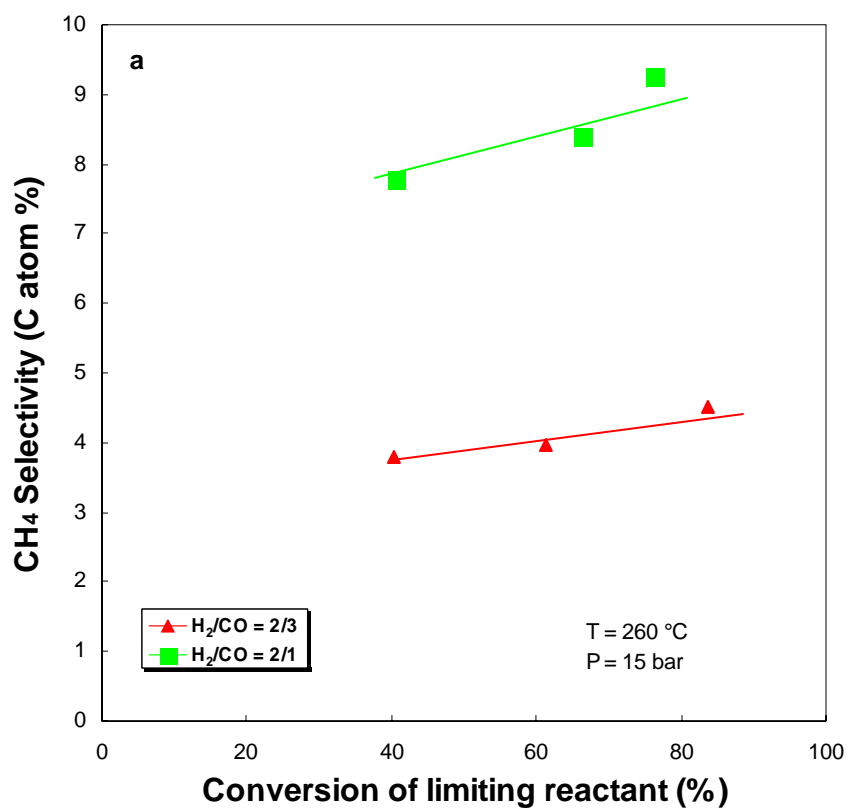
Figure 12. Effect of feed composition on hydrocarbon selectivity (260°C, 15 bar)
(a) Methane selectivity, (b) C_5^+ selectivity.
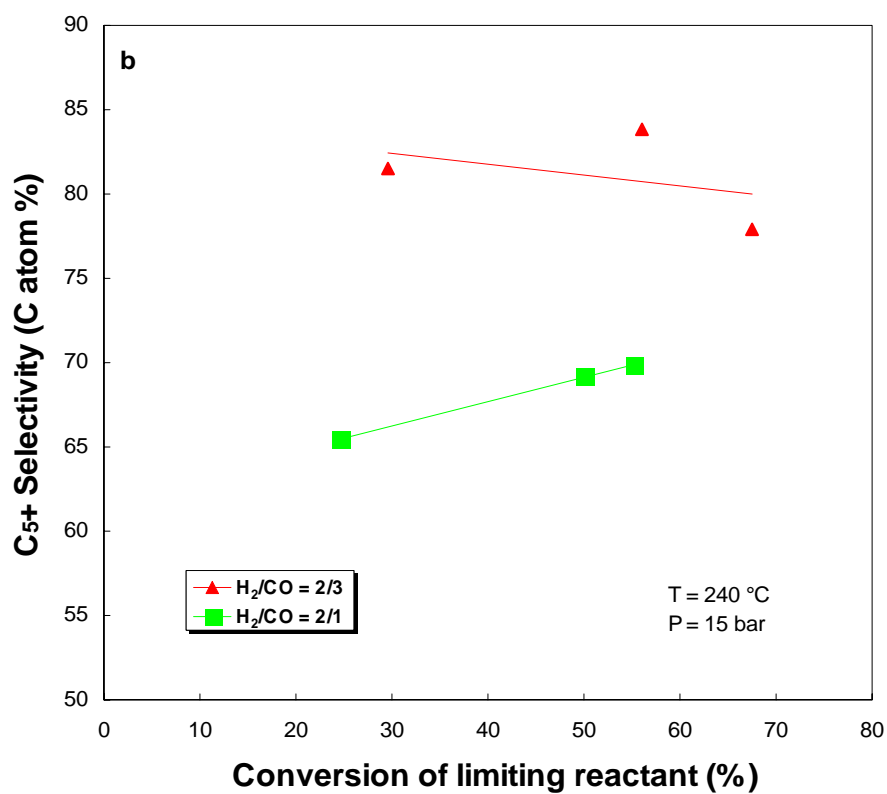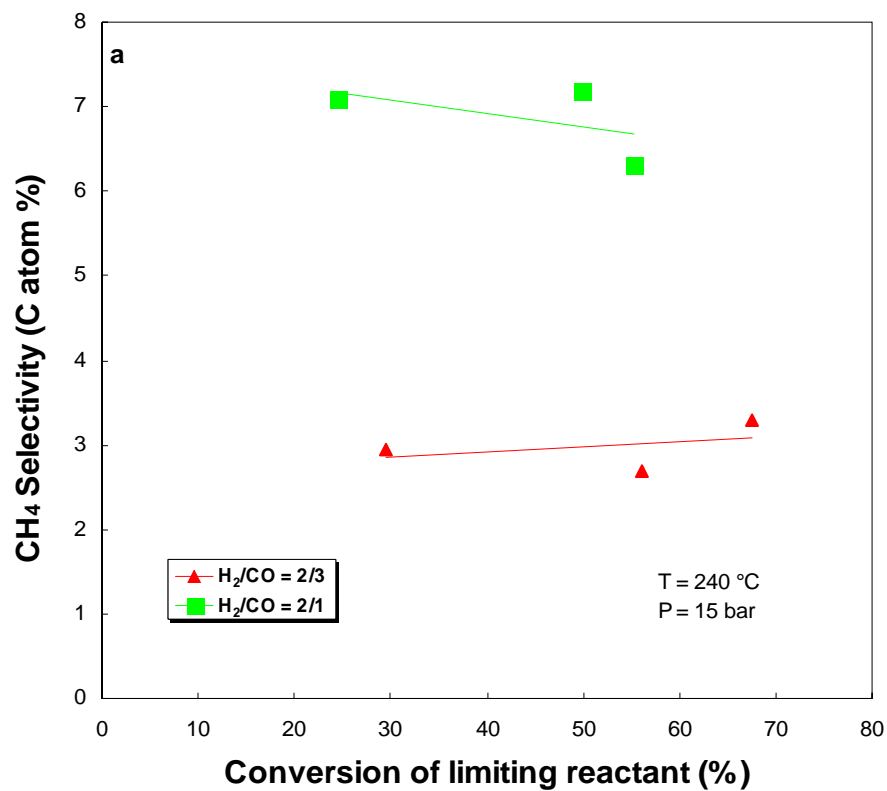
Figure 13.Effect of feed composition on hydrocarbon selectivity (240°C, 15 bar)
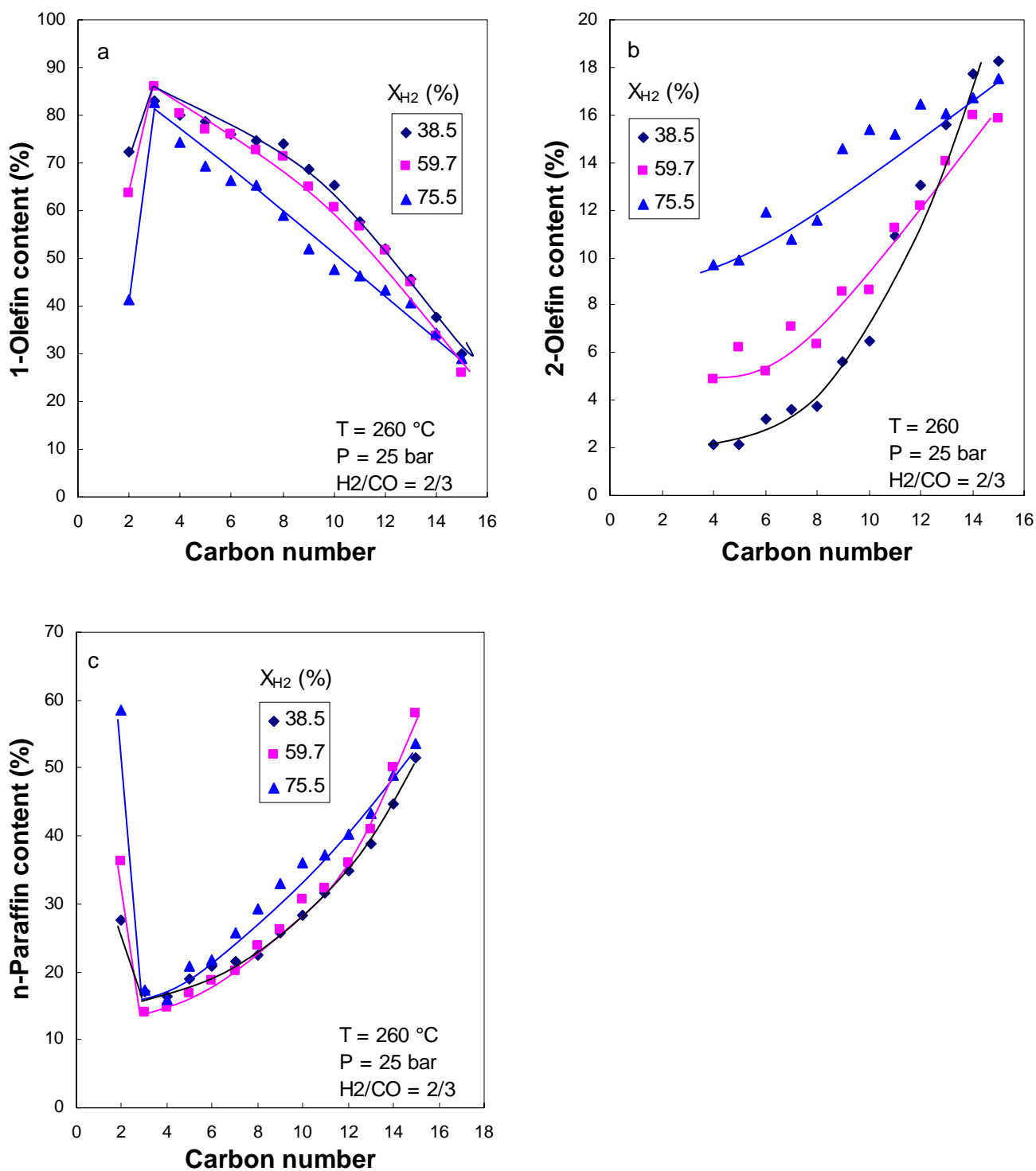(a) Methane selectivity, (b) C_5^+ selectivity.
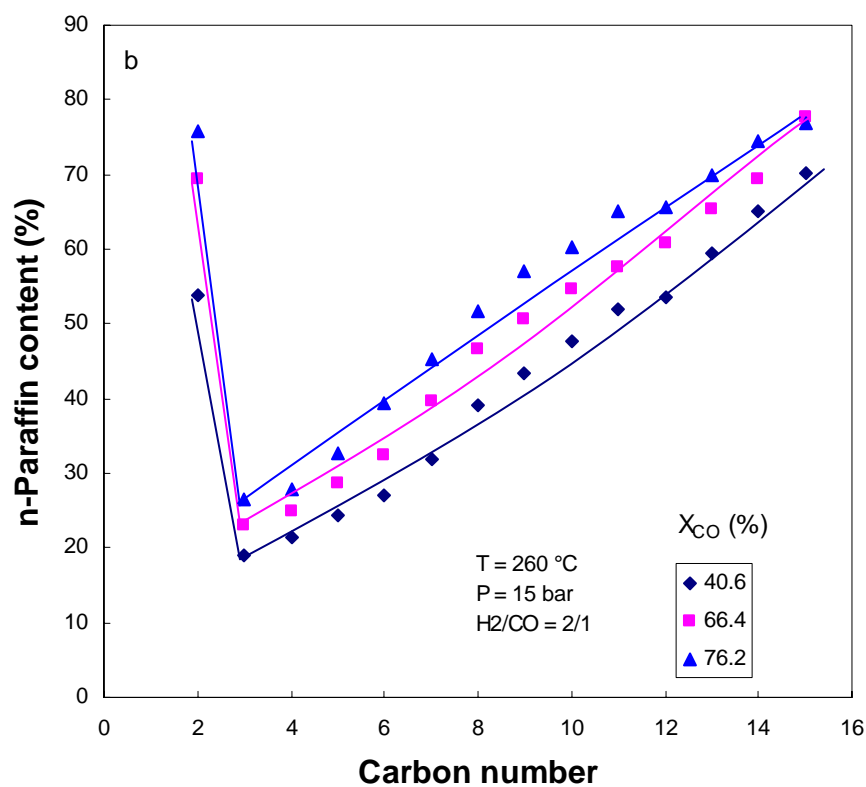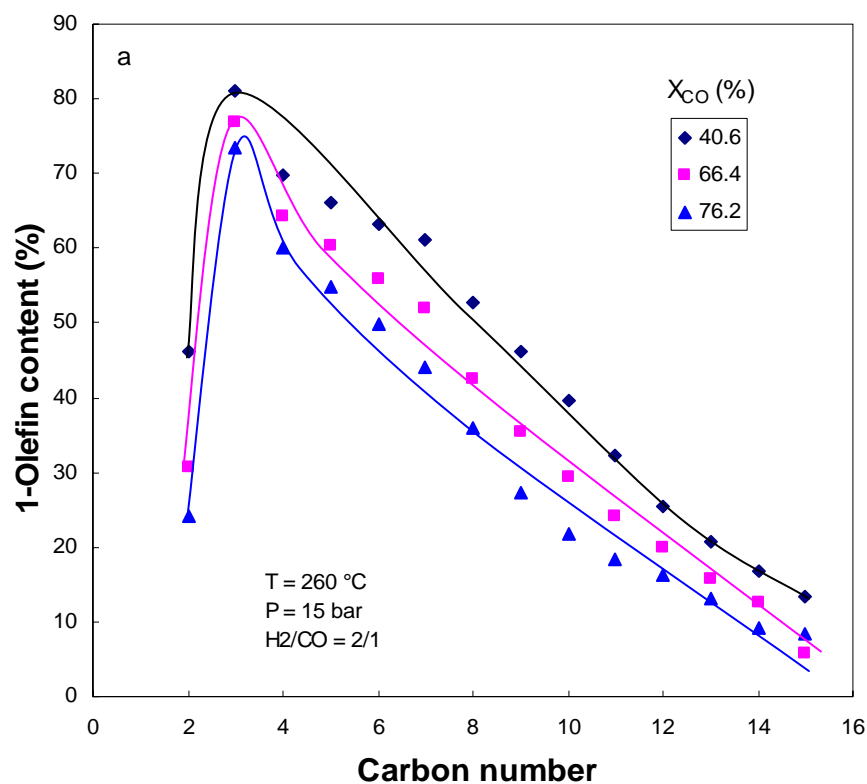
Figure 14. Effect of conversion (260°C, 15 bar, $H_2/CO = 2/1$) on (a) 1-olefin content and (b) n-paraffin content.
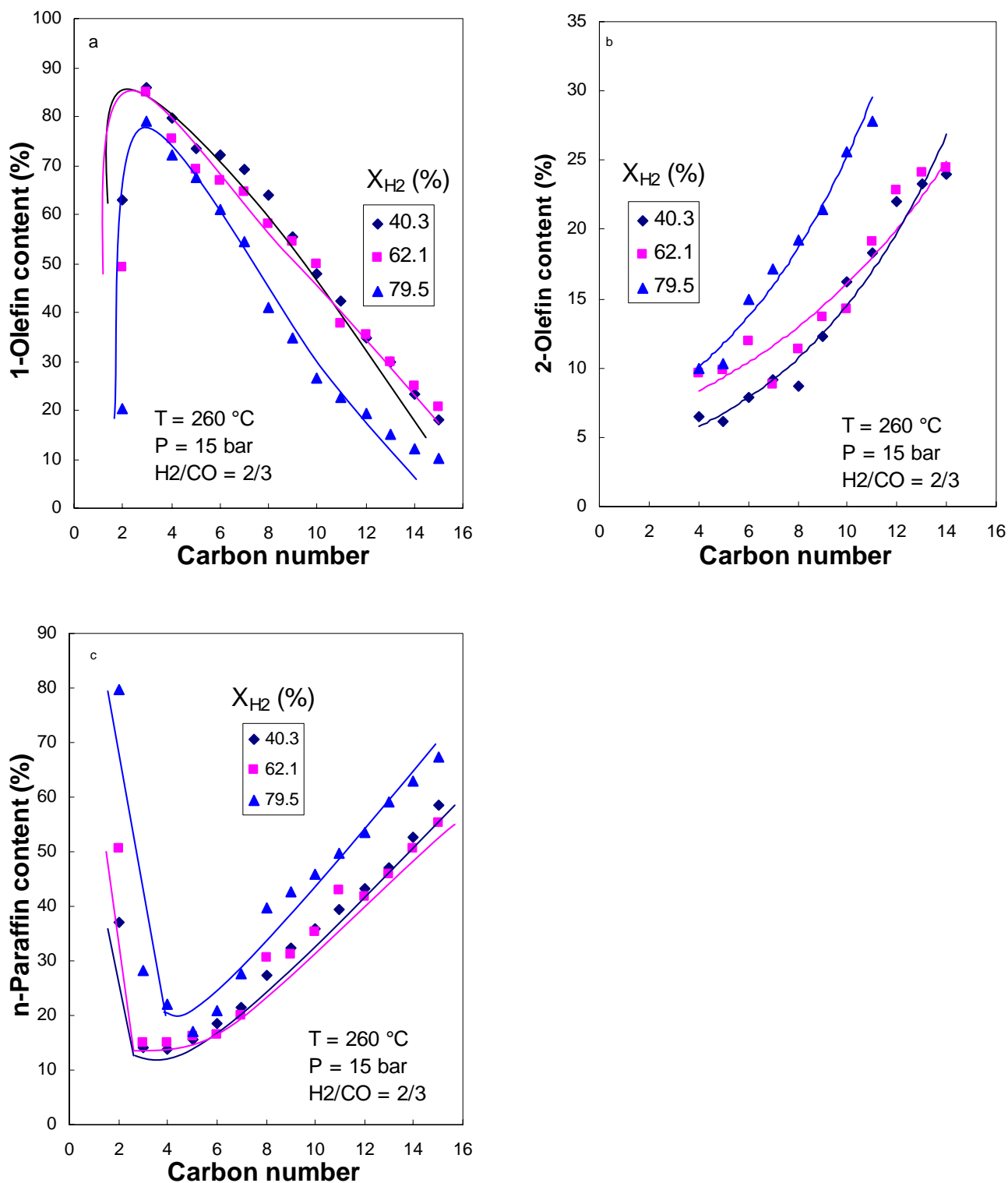
Figure 15. Effect of conversion (260°C, 15 bar, $H_2/CO = 2/3$) on
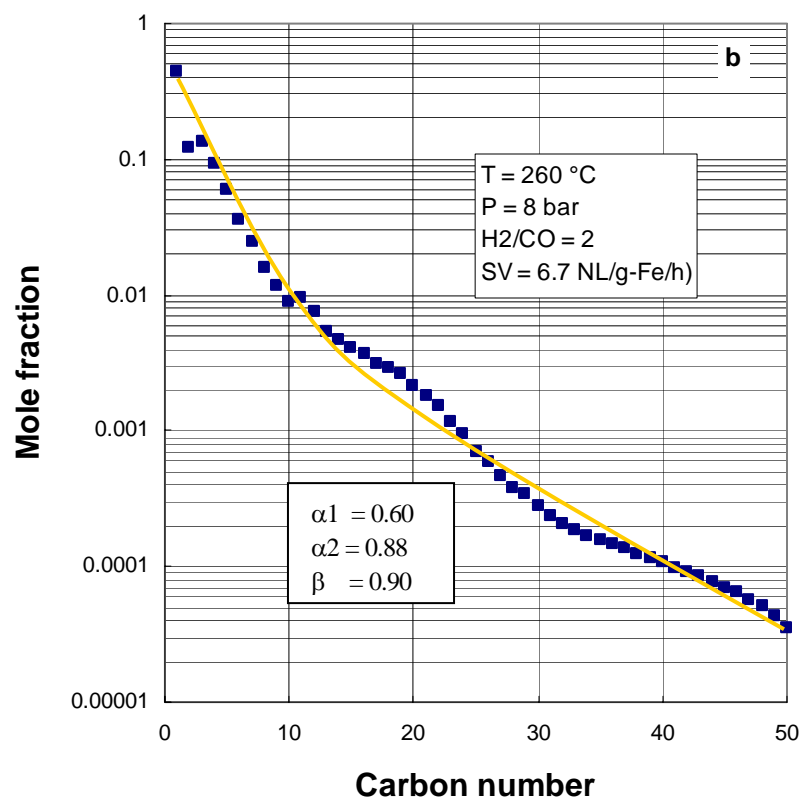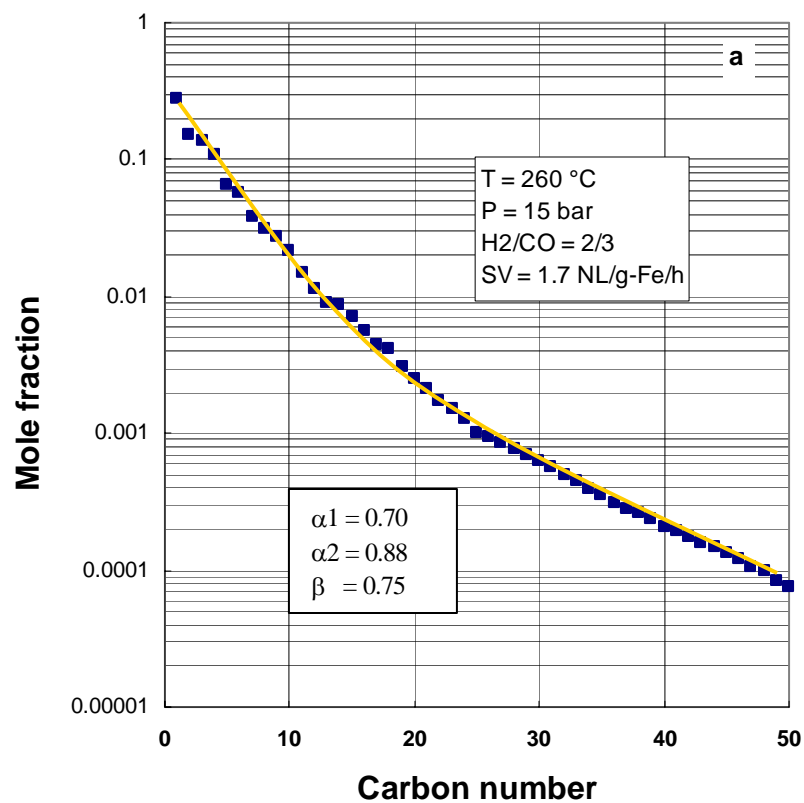(a) 1-olefin content, (b) 2-olefin content and (c) n-paraffin content.

Figure 16.Effect of conversion (260°C, 25 bar, H$_2$/CO = 2/3) on
(a) 1-olefin content, (b) 2-olefin content and (c) n-paraffin content.

Figure 17.Carbon number product distribution according to extended
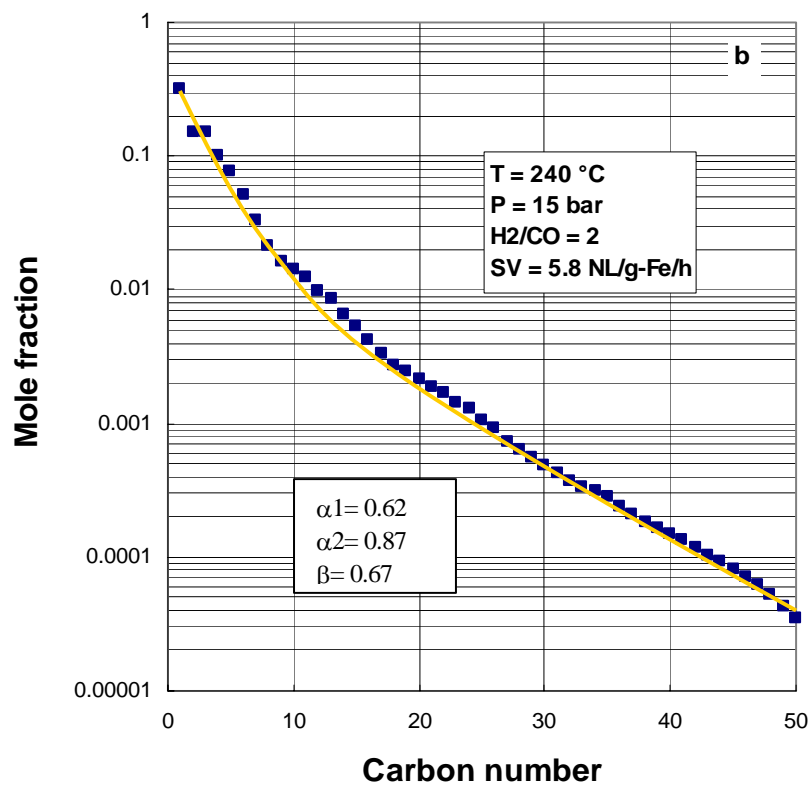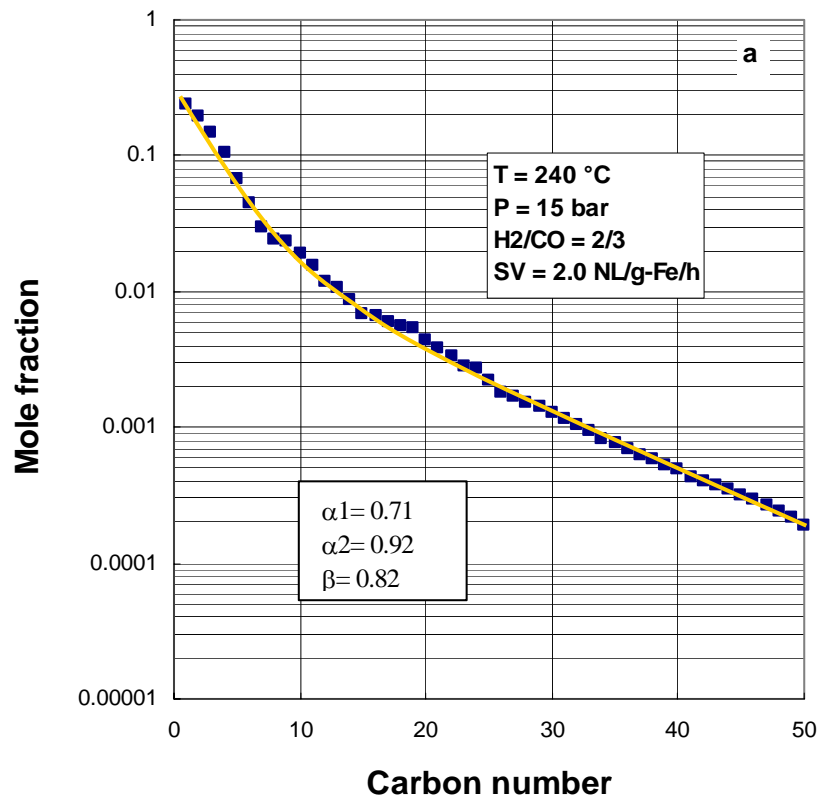Anderson-Schulz-Flory model (T = 260°C).

Figure 18. Carbon number product distribution according to extended Anderson-Schulz-Flory model (T = 240°C).