

Kinetic modeling of Fischer – Tropsch Synthesis over Fe – Ce Catalyst in Fixed Bed Reactor

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Abstract

The kinetic modeling of CO hydrogenation over Iron/Cerium catalyst which is constructed by sol-gel method was studied in fixed bed micro reactor under conditions as follows: temperature: 230 – 370 °C; pressure: 1 – 14 bar; H₂/CO feed ratio: 1:1, 2:1 and 3:1 and space velocity of 3600(cm³)/h/gram catalyst. For kinetic model of Fischer – Tropsch synthesis, catalyst seeds are selected smaller than 0.212 mm. On the basis of Langmuir – Hinshelwood kinetic mechanism were tested the sixteen kinetic expressions for CO consumption and interaction between adsorbed CO and molecular H₂ as the controlling step gives the most plausible kinetic model. The CO conversion increases with increasing temperature and pressure in operation conditions. Increasing temperature resulted higher molecular hydrocarbons. The poly math software 6.0 was used to fit the experimental data. At best performance activation energy of 36.110 kJ for CO consumption was obtained.

Keywords: CO hydrogenation, Fischer – Tropsch Synthesis, kinetic model, sol-gel

1. Introduction

Fischer-Tropsch Synthesis (FTS) is include a series of catalytic and chemical reactions that converts natural resources such as coal, natural gas and biomass into an array of various hydrocarbons [1-3]. During this reaction, Carbon-monoxide and hydrogen (syngas) are converted to paraffins and olefins [4]. In general, the FT kinetic is a study of effective parameters on rate of a chemical reactions. Hence, the first step is obtaining rate expressions. The main problem in explaining the FT reaction kinetics is complexity of its reaction mechanism and numerous reactants involved. Accordingly, many kinds of kinetic models have been suggested for this process which suggested mechanisms that are composed of varied surface components and different initial reactants. In order to, some of authors for understanding and modeling this process used of Langmuir-Hinshel-Wood-Hougen-Watson (LHHW) rate expressions [5-10]. The rate expressions are based different mechanisms. But must be aware that every one of this models just in special range are in agreement with results from experiments and are not applicable in wide range of conditions. Most important growth mechanism to forming of hydrocarbons on cobalt, iron and ruthenium catalysts is

surface carbide with entering of CH_2 group [11]. In carbide mechanism, monomer includes some kinds of methylene (CH_2) and it is supposed that H_2 , CO are adsorbed separately. So many types such as CH , CH_2 and CH_3 can be produced with this method. Chain growth is done by entrance of monomer into growing alkyl types. Chain finishing can be done by adsorb of hydrogen over an olefin or with addition of CH_3 types or hydrogen to forming of paraffin. This mechanism is most possible mechanism for hydrocarbon forming reactions on iron, cobalt, and ruthenium. This matter is not clear that monomer forming progress is from hydrogenation of separated CO whether non-separated CO . Other important mechanism is enol mechanism. In this mechanism CO is adsorbed on surface of catalyst and with surface hydrogen atoms produce adsorbed CHOH and water. Chain growth is done through adsorbed two parted $4z$ (CHOH) condensation reaction. In this mechanism key part is enol which is formed through partial hydrogenation of adsorbed CO . This mechanism explain alcohols forming through hydrogenation, aldehydes forming through surface desorption and hydrocarbons forming from hydrogenation and elimination of OH group. Base of mechanism is on this basis that if alcohols enter with feed to FT reaction they will interfere in chain growth process, although in resulted chain there is no effect of containing O parts and in addition, forming of C-C doesn't appear between two parts of electrophilic hydroxy [11-17].

Kinetic model of FTS have been studied by many researchers [18-23] and they have developed the kinetic equations for iron catalyst but because of complexity and different parallel steps with numerous kinds which effects on reaction path, still really kinetic model isn't recognized completely [24]. Hence, main goal in this article is obtaining a good kinetic model for consumption rate of CO in FTS.

2. Experiments

2.1. Catalyst preparation

The catalyst used in this studies was prepared using sol-gel procedure from aqueous solution of 1.6 gr of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 0.4 gr of $\text{Ce}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, then this mixture was solved by addition of Ethanol then Tetra Ethyl Ortho Silicate was added slowly with mixing, after good mixing around 1 hour, 10% HNO_3 and .4 gr Al_2O_3 were added and mixture was put on a mixer and left on the mixer for one and half hours then it was left for 24 hours after it was put inside of oven for 16 hours then it was put inside of furnace for 6 hours in 600 C, Then catalyst is ready just it must be made soft.

2.2. Catalyst tests

A schematic diagram of the experimental set up is shown in figure 1.

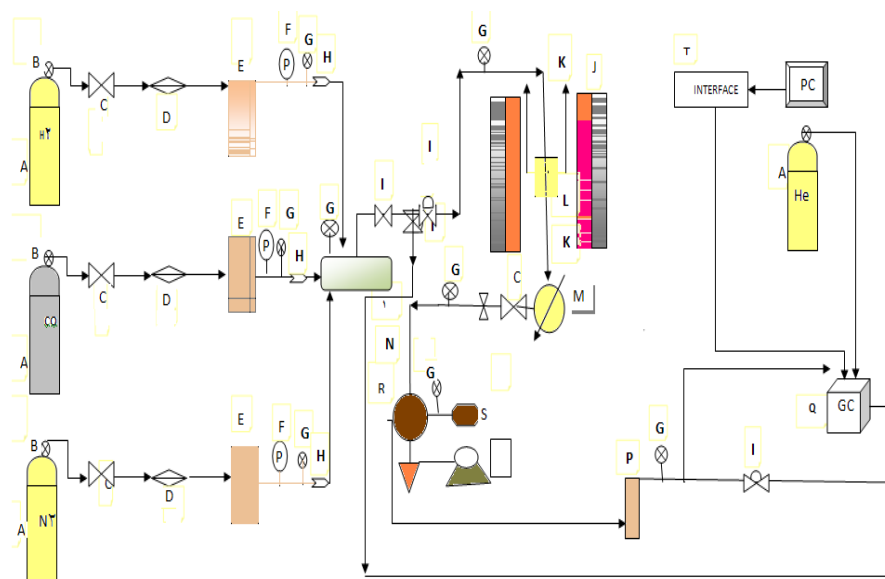


Fig. 1. Schematic of experimental setup:(A)gas cylinders ,(B)pressure regulators ,(C)needle valves ,(D)valves ,(E) mass flow controllers(MFCs) ,(F)digital pressure controllers ,(G)pressure gauges,(H)non return valves ,(I)ball valve,(J)tubular furnace ,(K) temperature indicators ,(L)tubular reactor and catalyst bed ,(M)condenser ,(N)trap,(P)air pump ,(q)silica gel column ,(R)gas chromatograph (GC),(S)mixing chamber ,(T)(BPR)back pressure regulator (U)control panel(CP)

The kinetic data was obtained in a fixed bed micro reactor under condition as same as to industrial operation ($T = 230 - 370$; $P = 1-14$; H_2/CO feed molar ratio, 3, 2 and 1 ; gas space velocity $60 \text{ cm}^3(\text{STP})/\text{min.gr catalyst}$) where high purity gas (H_2 , CO and N_2 99.99%) passed through (1/4)" stainless steel tubing. The synthesis gas was provided from pressurized cylinders (Roham gas) and passed from silica gel traps before entering the process. The gas flows were controlled by three mass flow controllers (Brooks, Model 5850E) and adjust by a central panel (BROOKS0154). The mixed gases were then allowed to flow through a 110 cm length and 9 mm id micro reactor which placed inside a furnace (ATBINE , model ATU 150-15), that capable to produce temperature to 1300 C. A digital programmable controller adjusts temperature of furnace and monitored by computer software. The meshed catalyst which is smaller than $212 \mu\text{m}$ (1gr) was placed in the center of the micro reactor that located in middle of the furnace. Two thermocouples inserted in catalyst bed above region of furnace, controlled temperature of the reaction zone ($\pm 1\text{K}$) and the space of above reactor that act as pre-heater respectively. An electronic back pressure regulate pressure by use of remote central via the TESCCOM software package integration that work on pressure ranging from 1 to 100 bar. The system is capable to divert feed gases and products that leaving reactor to gas chromatograph (GC) analyzer for analysis. Reactant and product were analyzed by an online Varian, model 3400 series gas chromatographic equipped with sampling loop and thermal conductivity detector. A 10 meter long, 1/8 " packed column with particle mesh 100/120 (Hayesep DB, Altech company, USA) were used in the analysis under He carrier gas with flow rate 30 ml/min.

3. Results

It is generally accepted that operation condition variables such as temperature, pressure, H_2/CO feed ratio and gas space velocity effect on production distribution in FTS. After catalyst preparation and characterization steps catalyst was reduced in atmospheric pressure in flow steam of 60 ml/min at 673 K for 2 hours. 48 kinetic tests were carried out on Ce 20% and Fe 80% on the bases of total catalyst weight. In each molar feed ratio 1:1, 2:1 and 3:1, 16 test were done. Experimental data include of experimental velocities are shown in 1 to 6 tables.

Table1. The effect of pressure on experimental velocity in $H_2/CO = 1$.

T= 230 ($^{\circ}C$)		selectivity	$-r_{co} * 10^5$ (mol/grcat.min)'
P (bar)	conversion %	CO ₂	
1	0.124	1.631	6.037
2	0.102	1.974	9.945
4	0.128	1.584	24.955
6	0.122	1.435	35.597
8	0.135	1.415	52.372
10	0.125	1.544	60.471
12	0.119	1.655	69.616
14	0.131	1.366	88.905

3.1. Temperature effect

Effect of temperature on CO conversion is shown figure 2 which shows that conversions increase with increasing of temperature, also effect of temperature on selectivity is shown in figure 3 where selectivities increase with temperature increasing.

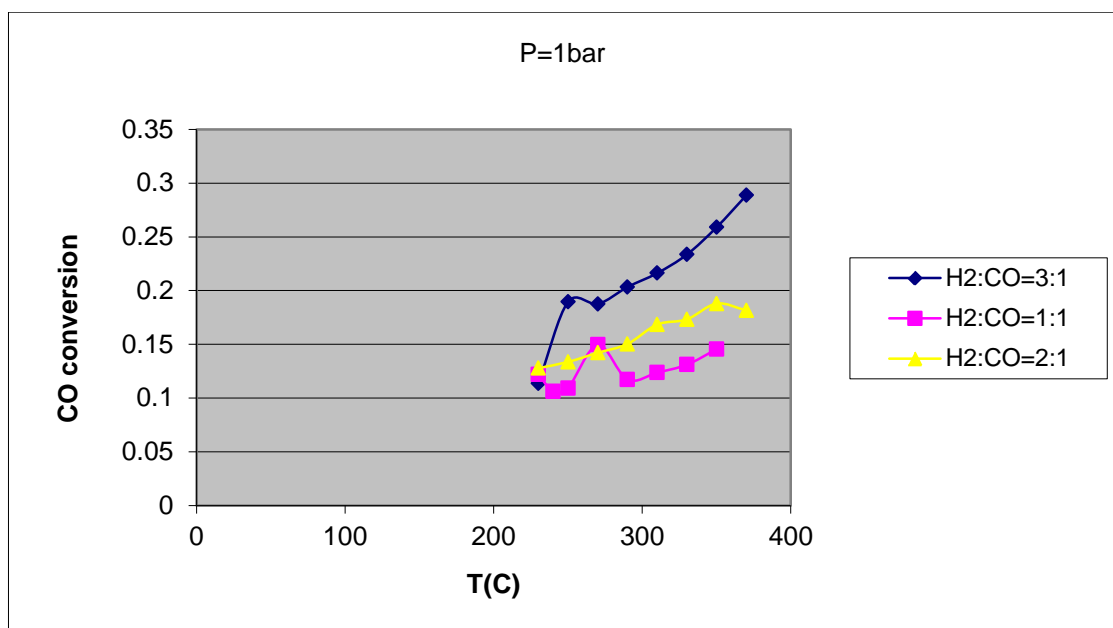
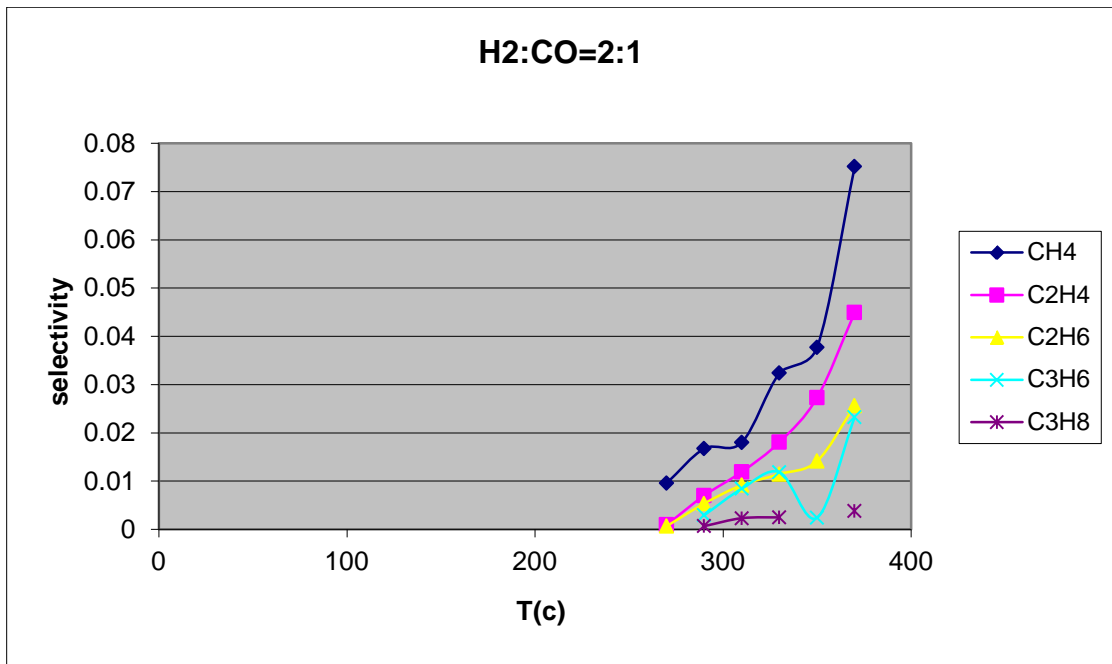
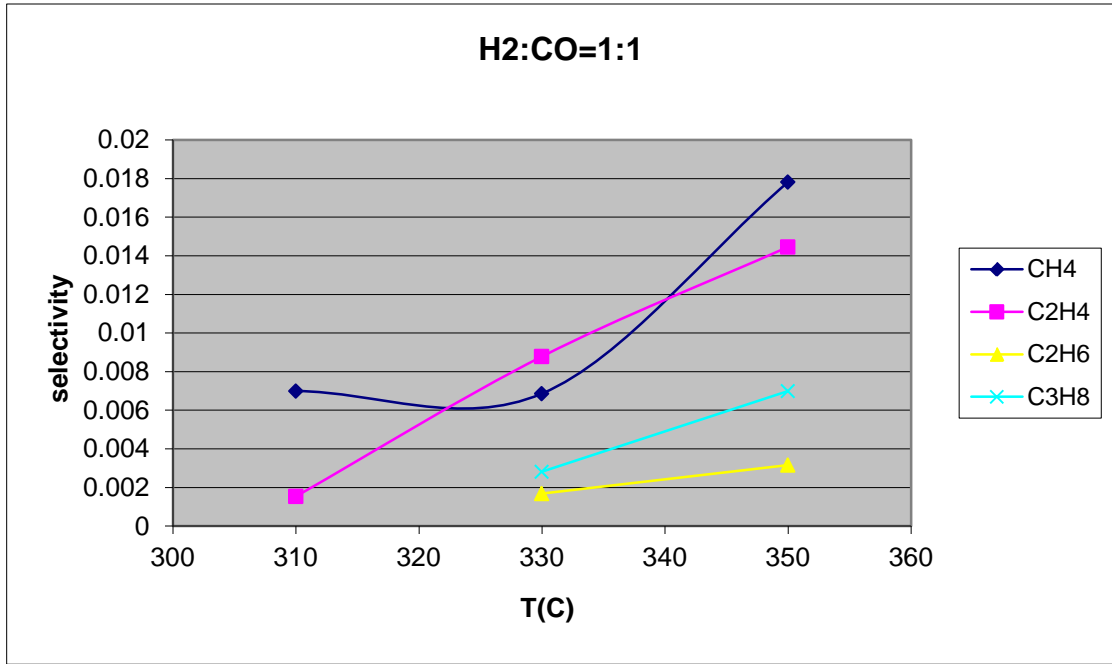


Fig. 2. Conversion changes with temperature increasing



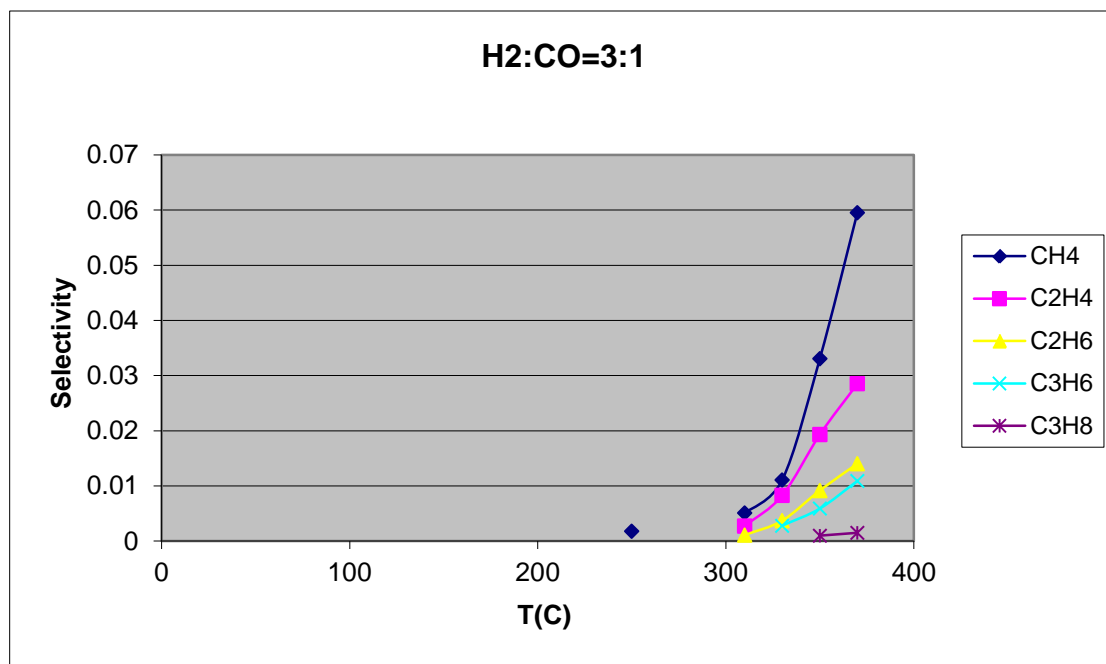


Fig. 3. Change of selectivity with temperature increasing in different feed ratios.

Maximum of selectivity and conversions happen in maximum temperatures. Also increasing in temperature is caused to produce of heavy hydrocarbons.

Table2: The effect of pressure on experimental velocity in H₂/CO =2.

T=230 (°C)		selectivity						-r _{co} *10 ⁵ (mol/grcat.min)'
P (bar)	conversion %	CO ₂	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	
1	0.136	1.237	-	-	-	-	-	4.948
2	0.128	1.062	-	-	-	-	-	9.309
4	0.148	0.974	-	-	-	-	-	21.532
6	0.144	1.031	-	-	-	-	-	31.368
8	0.126	1.202	-	-	-	-	-	36.661
10	0.133	1.126	-	-	-	-	-	48.538
12	0.157	0.664	-	-	-	-	-	68.452
14	0.200	0.717	0.001	-	0.001	-	-	102.179

3.2. Pressure effect

Effect of pressure on conversions is shown in figure 4. Also effect of pressure on selectivity is shown in 5 figures. In each series of figures temperature is fixed on 230 °C and just pressure changes.

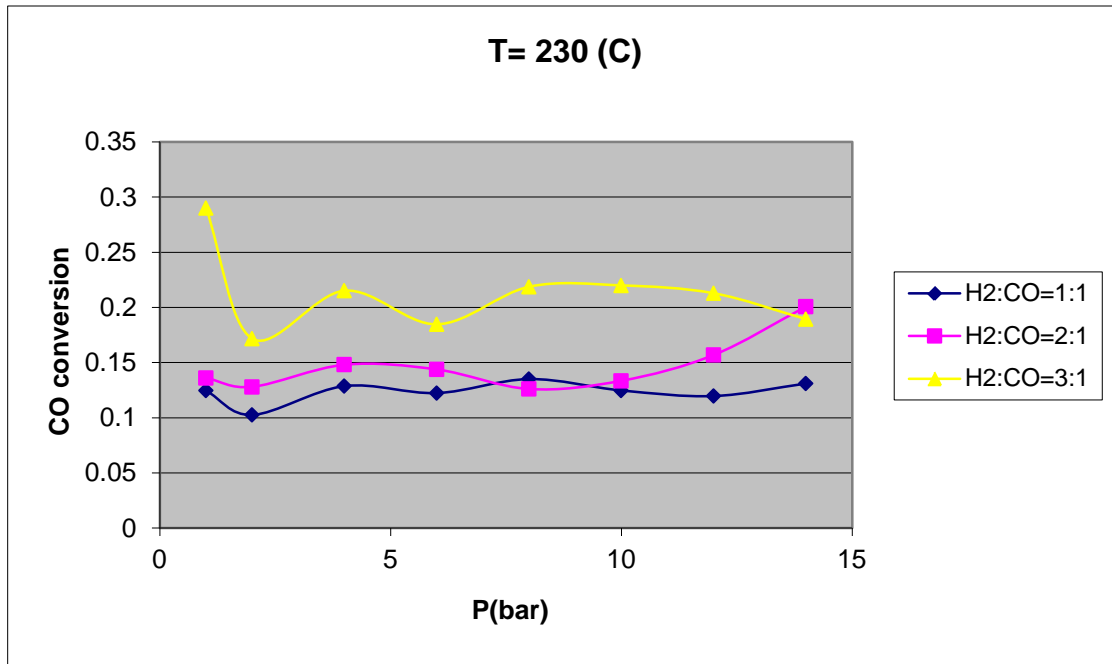


Fig. 4. CO conversion with pressure increasing in constant temperature.

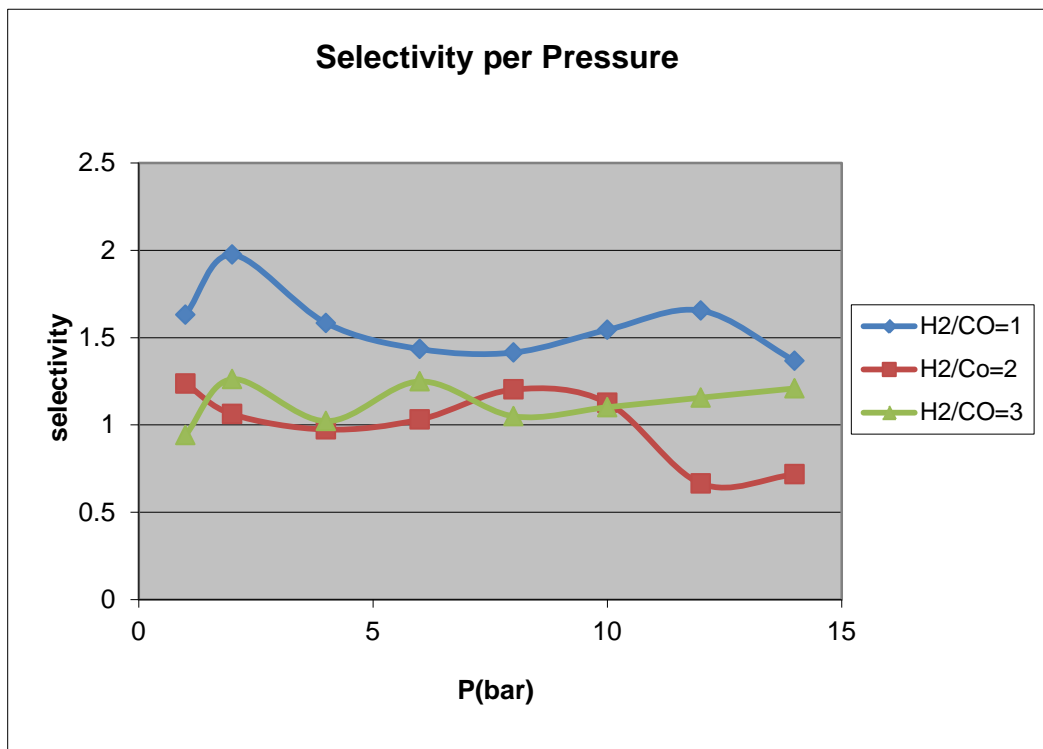


Fig. 5. The effect of pressure on selectivity in T=230 °C in different feed ratios.

Table 3: The effect of pressure on experimental velocity in $H_2/CO = 3$

T= 230 ($^{\circ}C$)		selectivity	$-r_{co} * 10^5$ (mol/grcat.min)'
P (bar)	conversion %	CO_2	
1	0.29	0.942	7.031
2	0.172	1.262	8.323
4	0.215	1.022	20.868
6	0.185	1.249	26.866
8	0.218	1.049	42.432
10	0.219	1.102	53.329
12	0.213	1.156	61.929
14	0.189	1.209	64.292

3.3. Yield

One of important parameters which is studied here is Yield that defines as follows:

$$\text{Yield} = CO_{\text{conj,T,P}} \times \text{selectivity}$$

$CO_{\text{conj,T,P}}$ denote the CO conversion in a certain temperature and pressure. Yield of productions in different temperatures are shown in figure 6. In calculation of yield it is supposed that CO is limiting reactant. Maximum values for yield happen in maximum temperatures.

 Table 4: The effect of temperature on experimental velocity in $H_2/CO = 1$

P= 1 bar	Selectivity							$-r_{co} * 10^5$ (mol/grcat.min)'	
	T ($^{\circ}C$)	conversion %	CO_2	CH_4	C_2H_4	C_2H_6	C_3H_6		C_3H_8
	230	0.122	1.569	-	-	-	-	-	5.905
	240	0.106	1.749	-	-	-	-	-	5.049
	250	0.109	1.768	-	-	-	-	-	5.093
	270	0.149	1.283	-	-	-	-	-	6.716
	290	0.117	1.802	-	-	-	-	-	5.077
	310	0.124	1.788	0.007	0.001	-	-	-	5.172
	330	0.131	1.744	0.007	0.008	0.002	0.003	-	5.298
	350	0.145	1.688	0.017	0.014	0.003	0.007	-	5.693

3.4. Kinetic models

Final goal here is obtaining of a suitable kinetic equation for expression of CO consumption rate. For obtaining an expression for CO consumption and hydrocarbon formation on the 80% Fe and 20% Ce, tests was done in pressure 1-14 bar, temperature among 230 – 370 C and feed ratio of 1:1; 2:1; 3:1.

Table 5: The effect of temperature on experimental velocity in H₂/CO =2

P =1 bar	Selectivity							-r _{co} *10 ⁵ (mol/grcat.min)'	
	T (°C)	conversion %	CO ₂	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆		C ₃ H ₈
	230	0.127	1.337	-	-	-	-	-	4.646
	250	0.134	1.3639	-	-	-	-	-	4.671
	270	0.142	1.405	0.009	0.001	0.001	-	-	4.785
	290	0.150	1.392	0.017	0.007	0.005	0.003	0.001	4.882
	310	0.168	1.338	0.018	0.012	0.009	0.008	0.002	5.282
	330	0.173	1.355	0.032	0.018	0.011	0.012	0.002	5.255
	350	0.188	1.260	0.037	0.027	0.014	0.002	-	5.515
	370	0.181	1.433	0.075	0.045	0.026	0.023	0.004	5.165

Kinetic of FT synthesis has been studied with so many researchers and so many mechanistic designs was presented. Surface carbide and enolic mechanisms are noticed more than others. In carbide mechanism dissociative adsorption of CO and H₂ followed by hydrogenation of adsorbed carbon by adsorbed hydrogen lead to produce of methane and higher hydrocarbons.

 Table 6: The effect of temperature on experimental velocity in H₂/CO =3

T= 230 (°C)		selectivity	-r _{co} *10 ⁵ (mol/grcat.min)'
P (bar)	conversion %	CO ₂	
1	0.29	0.942	7.031
2	0.172	1.262	8.323
4	0.215	1.022	20.868
6	0.185	1.249	26.866
8	0.218	1.049	42.432
10	0.219	1.102	53.329
12	0.213	1.156	61.929
14	0.189	1.209	64.292

In enolic mechanism dissociative adsorption H₂ and molecular adsorption of CO with hydrogenation of adsorbed CO by adsorbed hydrogen lead to oxygenated intermediates which in combination with adsorbed hydrogen produce water and adsorbed carbon.

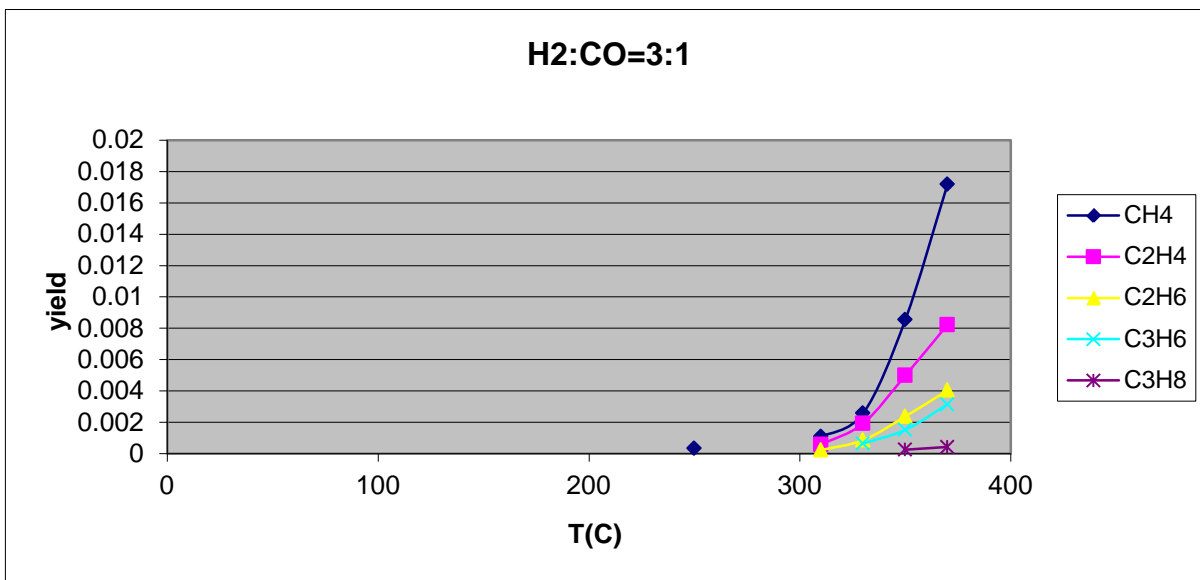
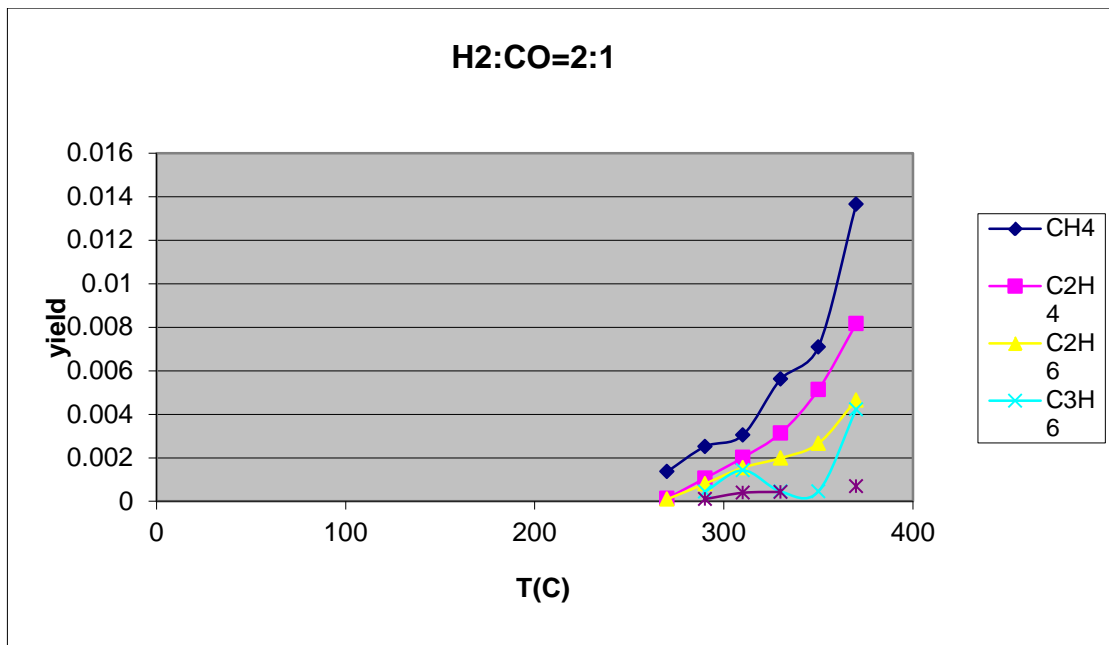
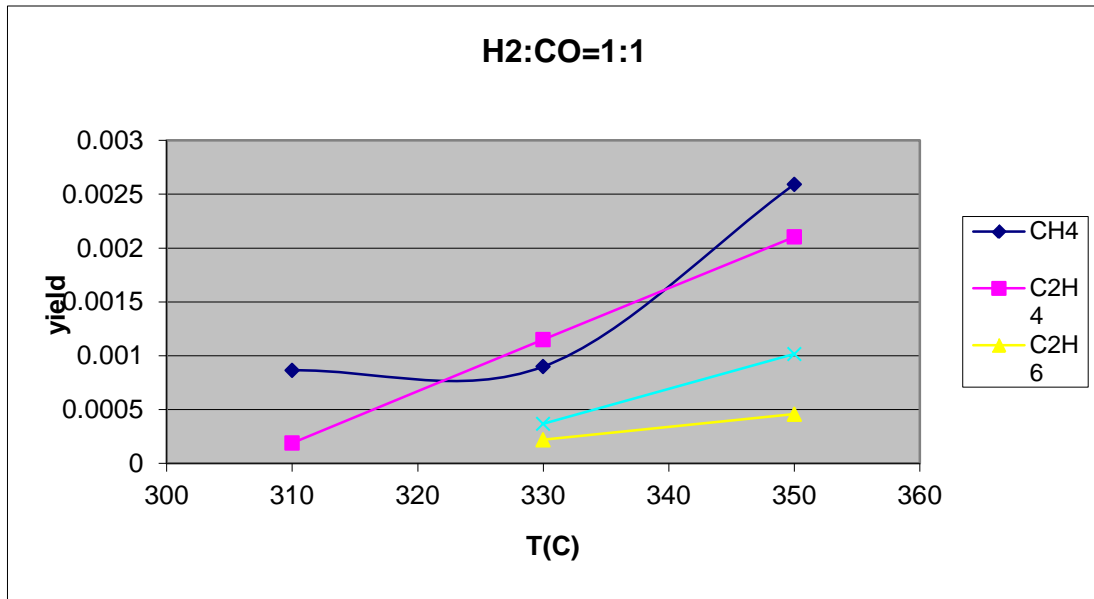


Fig. 6. The effect of temperature on yield on different feed ratios.

In finding of a kinetic model at first 4 mechanism, 2 in base of carbide mechanism and 2 in base of enolic mechanism are obtained. From these 4 mechanism 16 kinetic model are found in base of LHHW (Langmuir-Hinshelwood-Hougen-Watson) theory. Kinetic models are shown in table 7.

For example kinetic model of adsorbed CO and molecular H₂ reaction stage is obtained, reaction equation is like this:



Initial velocity equation of limiting rate stage:

$$-R_{CO} = k_2 \theta_{CO} P_{H_2} \tag{2}$$

Where -R_{CO} rate of disappearance of CO is, K₂ is forward reaction constant coefficient, P_{H₂} is partial pressure of hydrogen in gas phase and θ_{CO} is concentration of adsorbed CO. Empty sites are obtained from this equation:

$$\theta_s + \theta_{CO} + \theta_H = 1 \tag{3}$$

With use of most abundant intermediate reactants, important surface types are noticed which include of CO adsorbed molecules and adsorbed hydrogen atoms plus empty sites.

With suppose that other stages are near to equilibrium and then we can write:

$$K_1 = \frac{k_1}{k_{-1}} = \frac{\theta_{CO}}{P_{CO} \theta_s} \rightarrow \theta_{CO} = K_1 P_{CO} \theta_s \tag{4}$$

With notice to reaction mechanism which hydrogen enter to reaction in molecular shape:

$$\theta_H = 0 \tag{5}$$

After replacement of (4) and (5) equations in sites equilibrium equation we have:

$$\theta_s + \theta_{CO} + \theta_H = 1 \rightarrow \theta_s + K_1 P_{CO} \theta_s = 1 \rightarrow \theta_s = \frac{1}{1 + K_1 P_{CO}} \tag{6}$$

And from substitution of (4), (6) in equation (1) velocity equation will be like this:

$$-R_{CO} = k_2 \theta_{CO} P_{H_2} = k_2 (K_1 P_{CO} \theta_s) P_{H_2} \rightarrow -R_{CO} = \frac{k_2 K_1 P_{CO} P_{H_2}}{1 + K_1 P_{CO}}$$

And finally we have:

$$-R_{CO} = \frac{K P_{CO} P_{H_2}}{1 + \alpha P_{CO}} \tag{7}$$

Which in this equation we have:

$$\alpha = K_1 \quad , \quad K = k_2 K_1$$

Now after examination models in 3 different feed ratios in 2:1 and 3:1 feed ratios FT – III- 2 model is selected as a plausible model. Activation energy for this model is 36.11 kj which has acceptable sign and measurement. Kinetic modeling of these data has been done by POLYMATH 6 software.

Table7: Reaction velocity expressions for fischer- tropsch synthesis

Number of model	Kinetic model
FT-I-1	$-R_{CO} = \frac{KP_{CO}}{(1 + aP_{CO}^{0.5} + bP_{H_2}^{0.5})^2}$
FT-I-2	$-R_{CO} = \frac{KP_{H_2}}{(1 + aP_{CO}^{0.5} + bP_{H_2}^{0.5})^2}$
FT-I-3	$-R_{CO} = \frac{KP_{CO}^{0.5}P_{H_2}^{0.5}}{(1 + aP_{CO}^{0.5} + bP_{H_2}^{0.5})^2}$
FT-I-4	$-R_{CO} = \frac{KP_{CO}^{0.5}P_{H_2}^{0.75}}{(1 + aP_{CO}^{0.5}P_{H_2}^{-0.25} + bP_{H_2}^{0.5})^2}$
FT-II-1	$-R_{CO} = \frac{KP_{CO}}{1 + aP_{CO}^{0.5}}$
FT-II-2	$-R_{CO} = \frac{KP_{H_2}}{(1 + aP_{CO}^{0.5})^2}$
FT-II-3	$-R_{CO} = \frac{KP_{CO}}{(1 + aP_{CO}^{0.5})^2}$
FT-II-4	$-R_{CO} = \frac{KP_{CO}^{0.5}P_{H_2}}{1 + aP_{CO}^{0.5}}$
FT-III-1	$-R_{CO} = \frac{KP_{CO}}{1 + aP_{CO}}$
FT-III-2	$-R_{CO} = \frac{KP_{CO}P_{H_2}}{1 + aP_{CO}}$

FT-III-3	$-R_{CO} = \frac{KP_{CO}P_{H_2}^2}{1+aP_{CO}}$
FT-III-4	$-R_{CO} = \frac{KP_{H_2}}{(1+aP_{CO})^2}$
FT-IV-1	$-R_{CO} = \frac{KP_{CO}}{1+aP_{CO} + bP_{H_2}^{0.5}}$
FT-IV-2	$-R_{CO} = \frac{KP_{H_2}}{(1+aP_{CO} + bP_{H_2}^{0.5})^2}$
FT-IV-3	$-R_{CO} = \frac{KP_{CO}P_{H_2}^{0.5}}{(1+aP_{CO} + bP_{H_2}^{0.5})^2}$
FT-IV-4	$-R_{CO} = \frac{KP_{CO}P_{H_2}}{(1+aP_{CO} + bP_{H_2}^{0.5})^2}$

4. Discussion

For more discuss and research on the experimental data power law model also presented. From important supposes for analysis of data with this model is that gases are ideal. Power law model is written like this:

$$-RCO = KPCO^m \times PH_2^n \tag{8}$$

Where k parameter follows from Arrhenius equation like this:

$$K = K^{\circ} \exp(-E/RT) \quad (9)$$

With replacement of Arrhenius equation in power law model velocity equation became like this:

$$-RCO = K^{\circ} \exp\left(-\frac{E}{RT}\right) PCO^m \times PH_2^n \quad (10)$$

Now experimental values and power law model insert to polymath software and after that will be analyzed. Convergence coefficient is 0.949 and shows that this model has good accordance with data. Activation energy which is obtained from power law model is equal with 23.19 kj. This value has good accordance with data. Analysis of CO consumption shows that FT-III-2 model is only model that produce positive coefficients. Therefore selected kinetic model is for reaction of adsorbed CO and molecular hydrogen reaction stage.

5. Conclusion

The main aim of the model discrimination in this study was investigation about rate expression for FT synthesis and effect of some operation parameter such as temperature, pressure and feed ration H_2 / CO on CO consumption. Analysis of CO consumption and formation of hydrocarbons show that equation FT-III-2 is best model which have good parameters in FT reaction.

For model discrimination estimate of positive parameters with good statistical fit of the data is necessary. For hydrogenation over catalyst Ce 20%, Fe 80% for velocity limiting reaction which is adsorbed CO and molecular hydrogen produce and grow chain.

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