The State of Studies of the Fischer-Tropsch Process in Russia

V.I. Anikeev, A. Yermakova, B. L. Moroz

Boreskov Institute of Catalysis, Novosibirsk, Russia

Report supported by Syntroleum Corporation, Tulsa, OK, USA

Russian/Soviet FT Literature

- Literature 1930 to 2003
  - Publications = 450
  - Russian/Soviet Patents = 170
- Fields of Study
  - Reaction Mechanism
  - Catalyst composition
  - Kinetics and Thermodynamics
  - Modeling
  - Commercial Application

Primary Investigators

- The leader of the research of hydrocarbons synthesis from CO and H_2 for long years was Prof. Ya. T. Eidus – Institute of Organic Chemistry of the USSR Academy of Sciences
  - Initial studies and theory of FT catalysis
  - Hydro-condensation of CO with olefins
  - Olefin Hydro-polymerization with CO

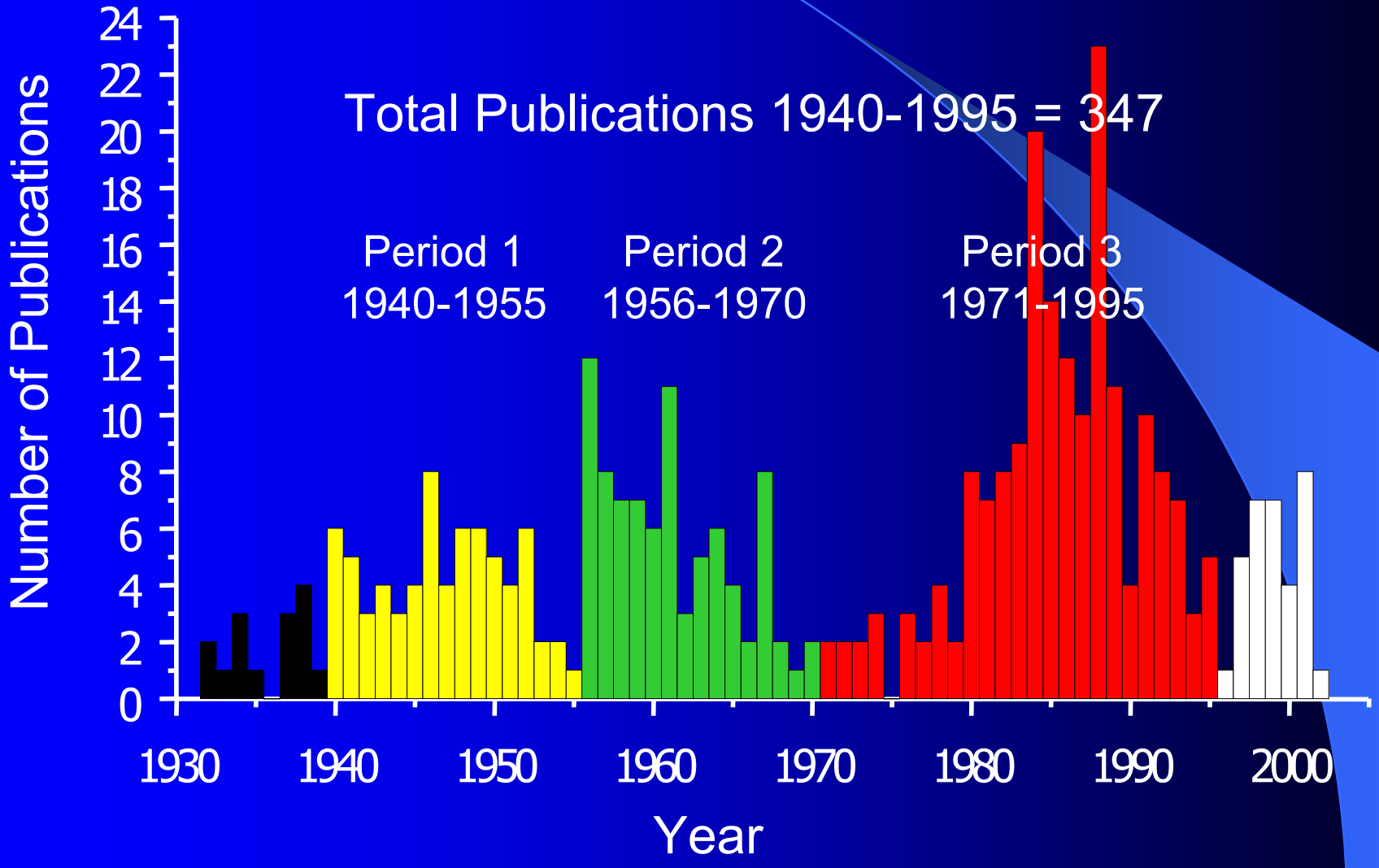
Primary Investigators

- Prof. A. N. Bashkirov – Liquid Fuel Department of the Lomonosov Institute of Fine Chemical Technology
  - Design, preparation, and modification of catalysts
    - Co, Fe, Cu, Mn catalysts
  - Effect of promoters on rate and rxn path
  - Catalyst regeneration
  - Hydrocarbon distribution and fuel production

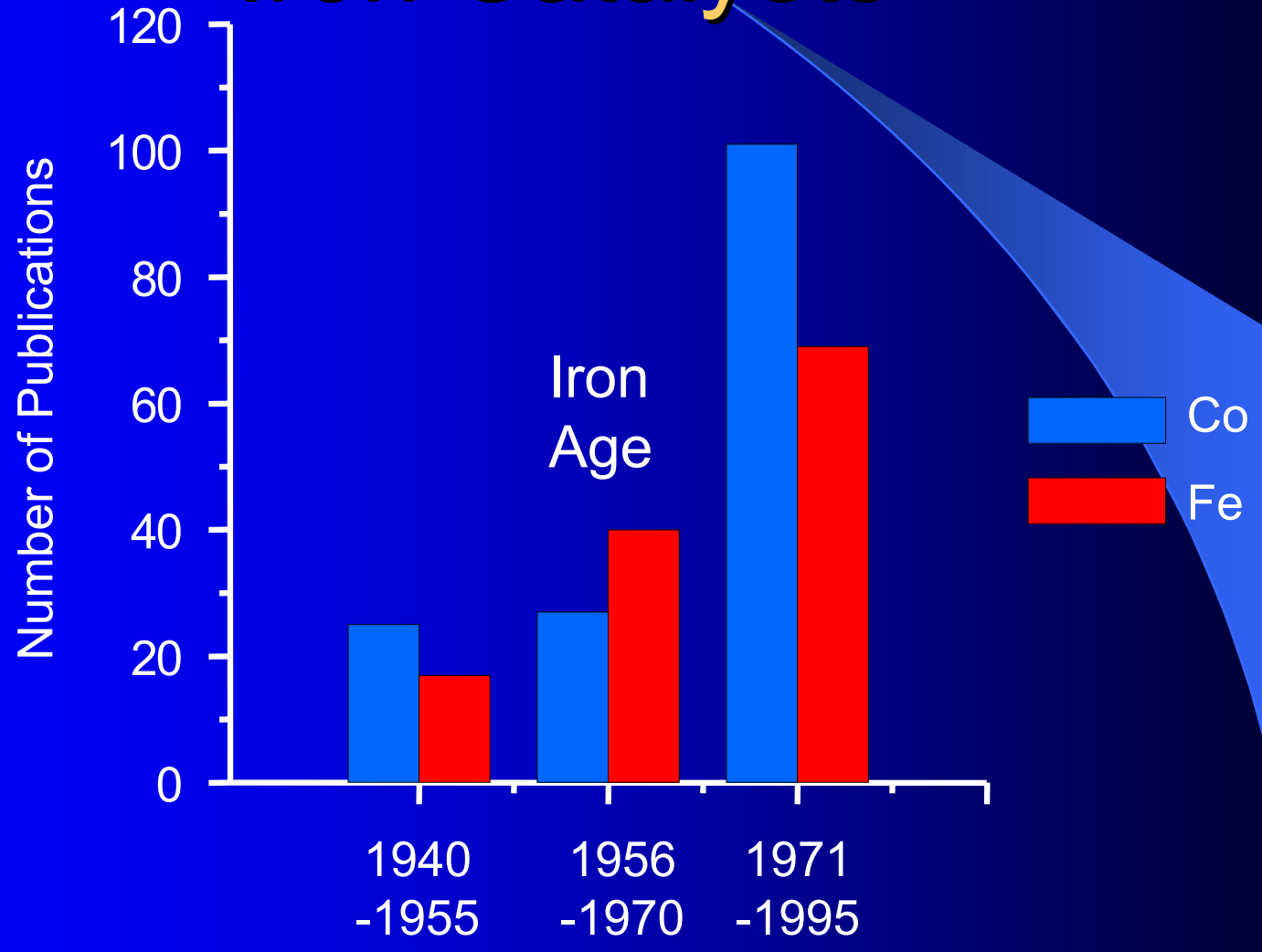
Primary Investigators

- Prof. L. A. Lapidus – Zelinsky Institute of Organic Chemistry Russian Academy of Sciences
  - Cobalt based catalysts
  - Zeolites in FT catalysts
  - Reaction mechanisms

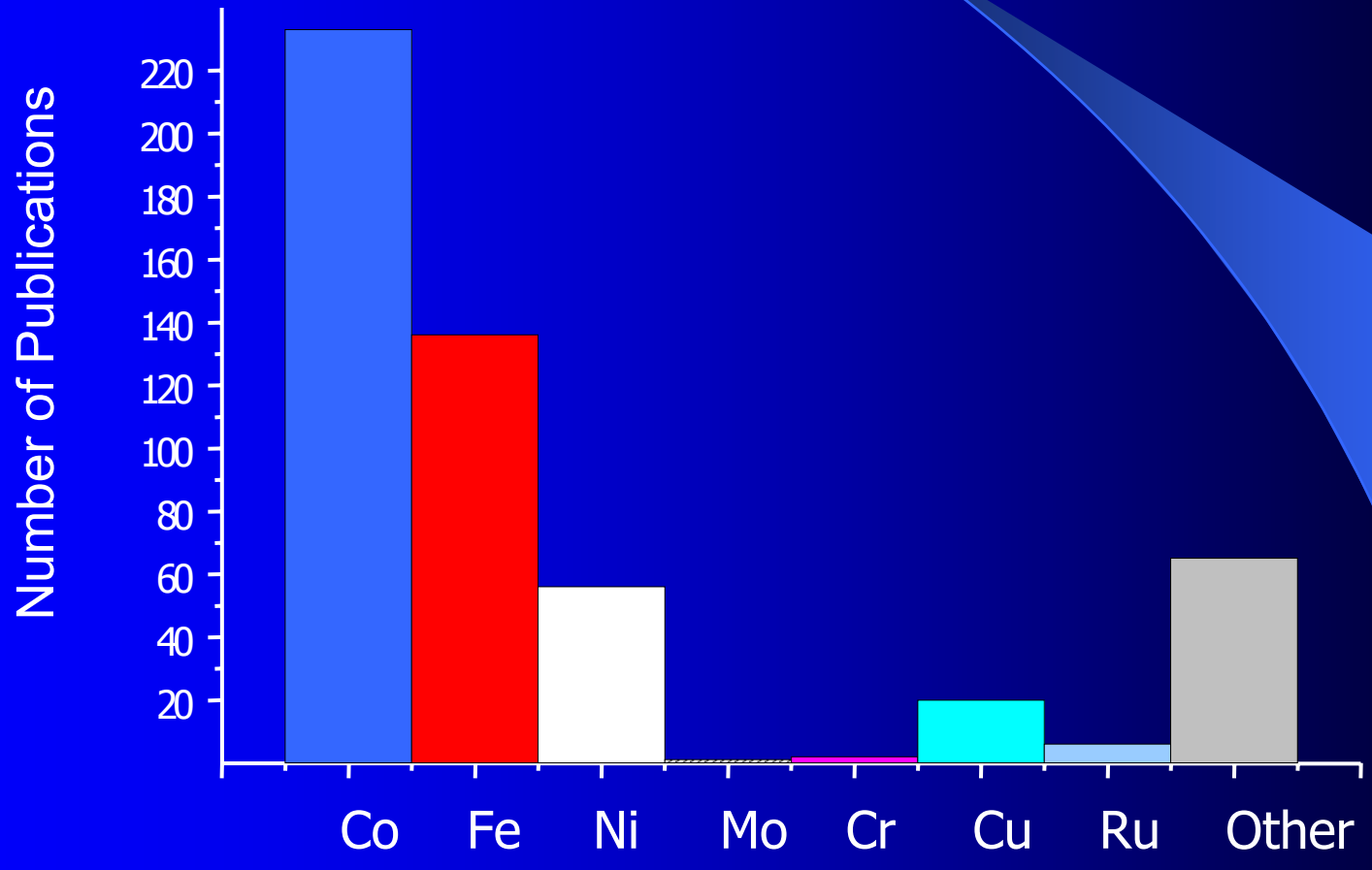
FT Publications By Year



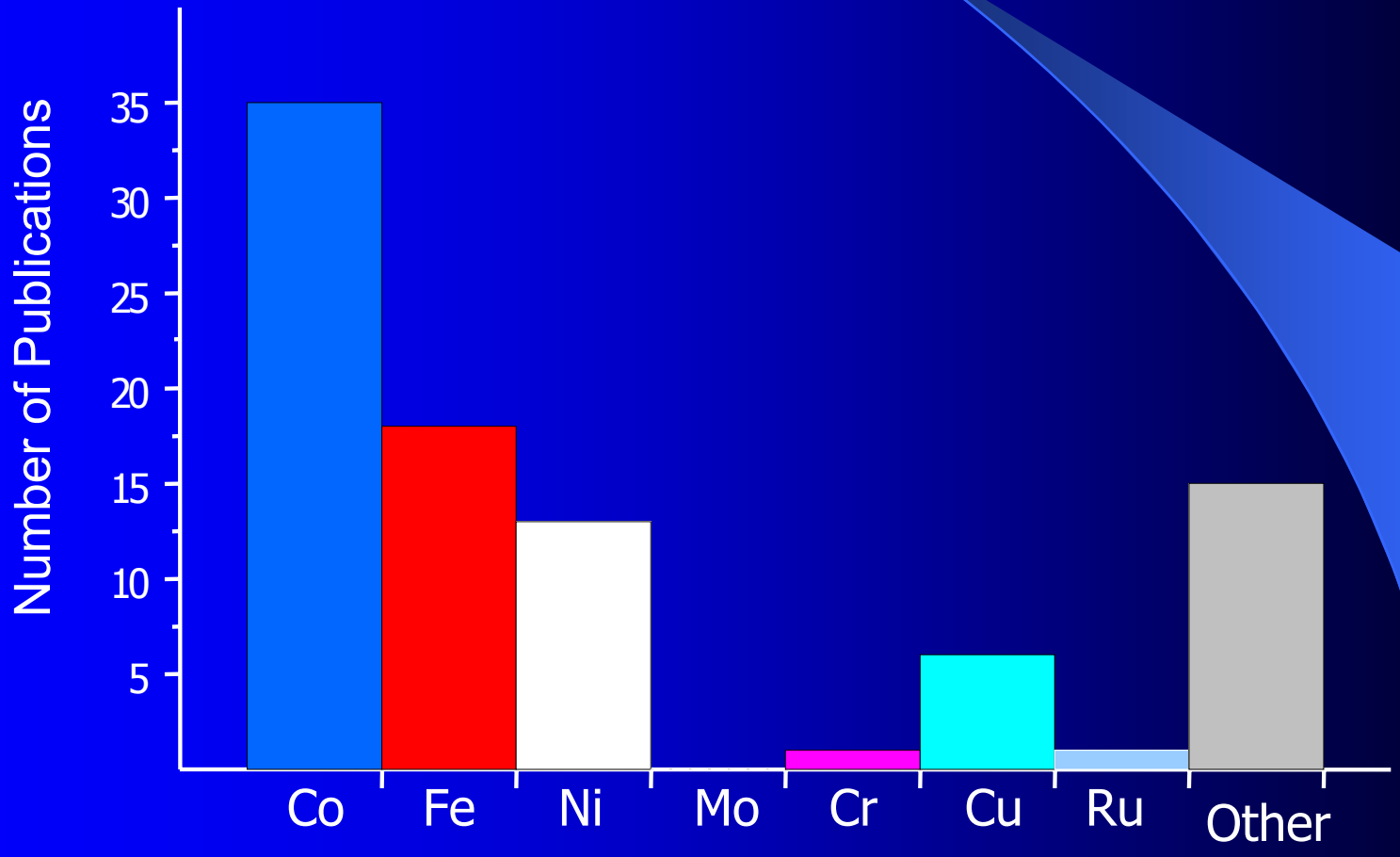
Publications on Cobalt and Iron Catalysts



Publications on Various FT Catalysts



Distribution of Patents on Various FT Catalysts



Mechanisms of hydrocarbon synthesis

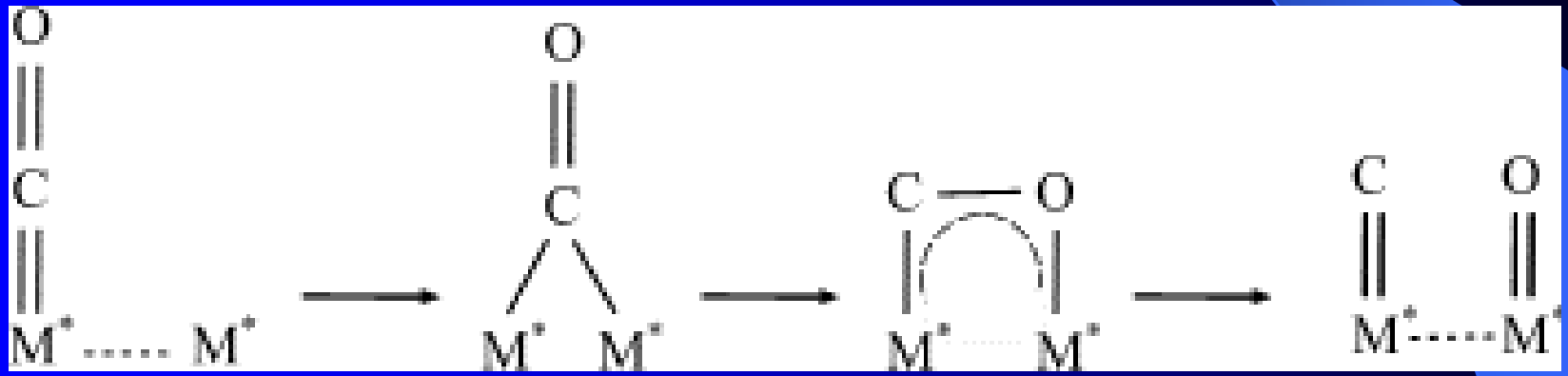
- Research of mechanism of FT synthesis were started by Zelinski and Eidus in 1938 and somewhat later by Roginski; they were aimed at checking of the Fischer's hypothesis concerning the role of bulk and surface metal carbides in catalytic hydrogenation of CO.
- They concluded that cobalt carbide formed on the surface of Co-ThO_2-kieselguhr catalyst could be neither true catalyst nor intermediate for FT synthesis.

Mechanisms of hydrocarbon synthesis

- Russian researches have found that CO adsorbs on Me much stronger than hydrogen. This means that the activity and selectivity of the catalysts for FT synthesis depend on the adsorption characteristics of CO rather than hydrogen.

Mechanisms of hydrocarbon synthesis

Interaction of carbon monoxide with the metal surface can entail dissociation of adsorbed CO molecules by the scheme below



However, the question which adsorbed CO species exactly) takes part in FT synthesis remains unclear

Catalysts and supports

- Studies of Soviet/Russian scientists were focused general on improvement of new generations of FT catalysts in the following principal problems :
- Modification of precipitated Co-catalysts aimed at improvement of the activity and selectivity to formation of certain HC fractions, as well as at substitution of more practicable compounds for individual compounds of the catalysts (ThO_2, kieselguhr)

Catalysts and supports

- Development and characterization of Co, Fe-zeolite catalysts for selective synthesis of high-octane gasolines

Catalysts and supports

- Development of highly efficient impregnated catalysts using cobalt nitrate and carbonyl as precursors of the active component, development of scientific bases for preparation of these catalysts.

- Preparation, characterization and application of skeletal Co-catalysts, studies on the influence of some gaseous additions (NH_3, C_2H_2, N_2 etc.) on the FT synthesis.

Supports

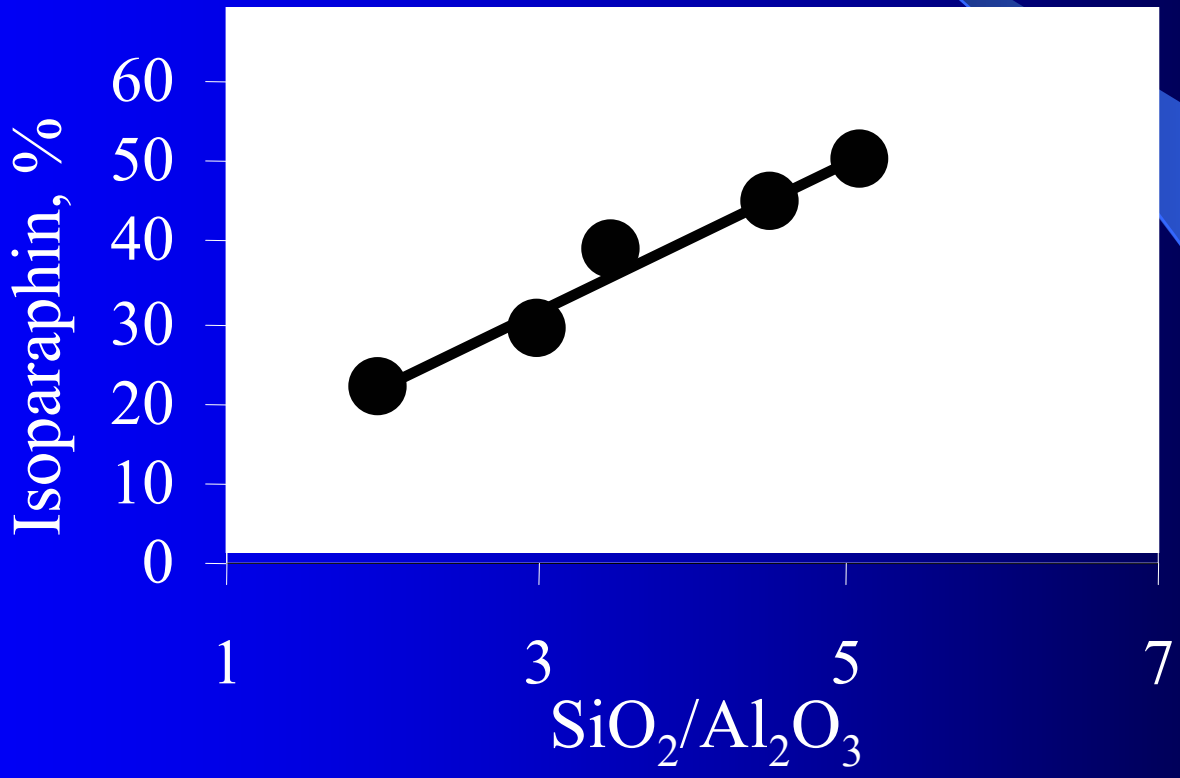
- ***Inert supports*** (graphite and a stronger modification of SiO_2) do not interact with the supported metal, not produce oxide species or oxide phases, and not participate in the catalytic process.
- ***Active supports*** (TiO_2, Al_2O_3, MgO, BeO) are capable of interacting with the metal crystals and, hence, to affect the catalytic properties.
- ***Bi-functional supports*** (Al_2O_3 and polycrystalline aluminosilicate (zeolites), *i.e.* active sites in the forms of both metal and metal oxide are formed on their surface

Characteristics of zeolites

- Effect of zeolite module increasing :

- Does not affect selectivity to paraffins
- Selectivity to *iso*-products increases
- Selectivity to C_{5+} decreases from 60 to 40%

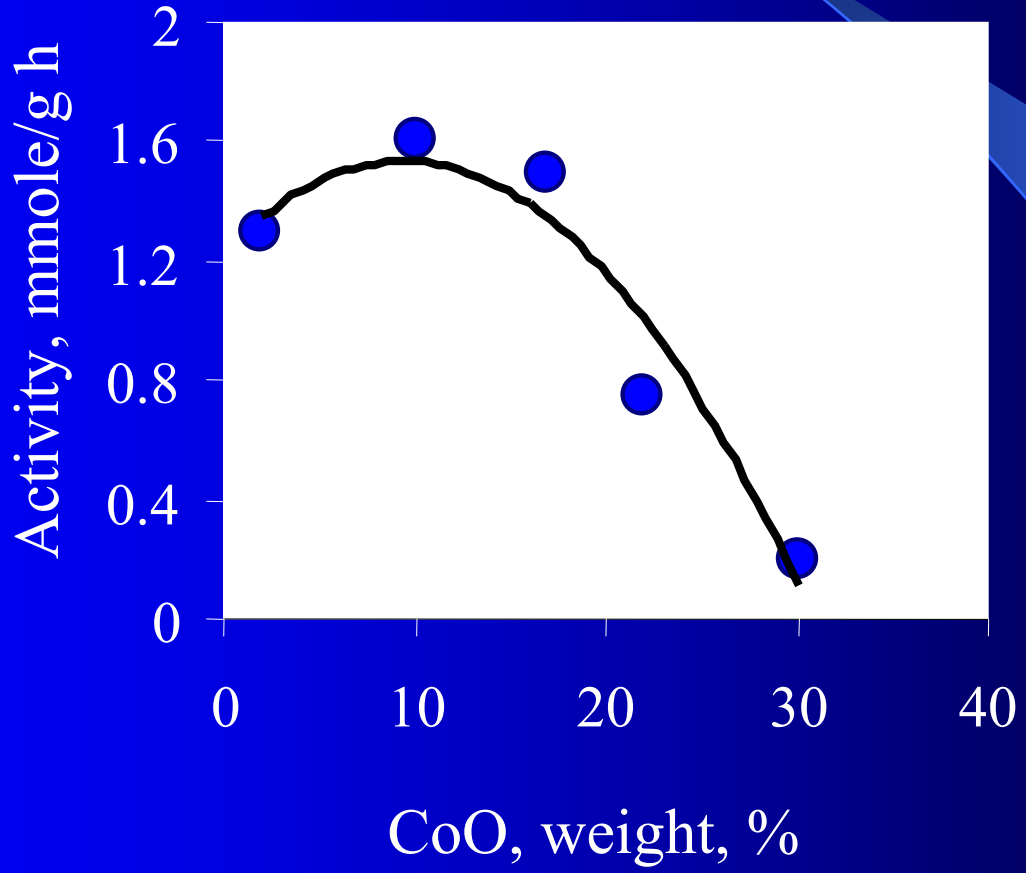
Characteristics of zeolites



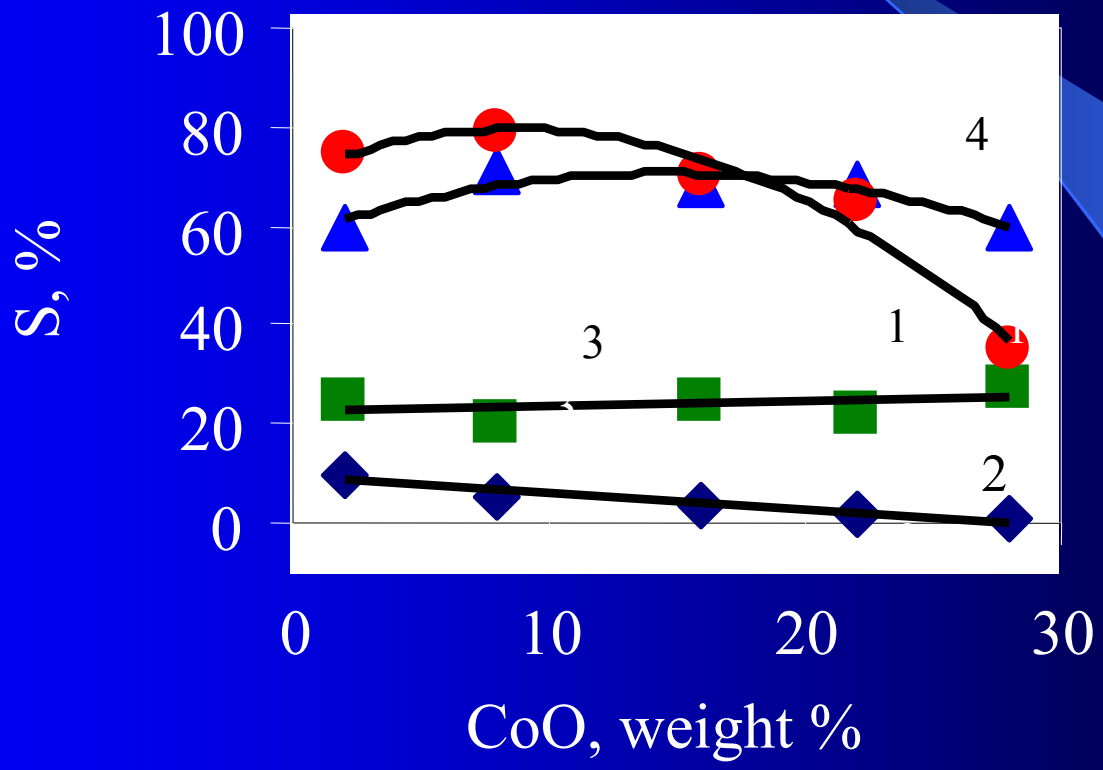
Effect of support in the FT synthesis over precipitated cobalt catalysts at 172-174°C and 0.94 MPa

Catalyst	Yield of liquid hydrocarbons, g/m^3	C_{18}+ content, %
Co-MgO-zeolite CaY	120.0	30.0
Co-MgO-zeolite NaY	95.0	27.6
Co-MgO-AAS	167.8	43.0
Co-MgO-TSEOKAR	142.7	44.3
Co-MgO-ASHNTS-3	153.8	46.0
Co-MgO-ZrO2-AAS	159.0	40.1
Co-MgO-ZrO2-kieselgur	100.0	27.0

Catalyst activity vs the ratio of CoO:Co



Selectivity of FT synthesis products vs CoO:Co ratio



1 - CO conversion, 2 - CO_2 concentration in the reaction products, 3 - methane selectivity, 4 - liquid carbon selectivity

Influence of modifiers on the composition of liquid hydrocarbons produced from CO and H_2 in the presence of catalysts 10%Co-(0-15%M_xO_y)/SiO_2

M_xO_y	$[M_xO_y]$ weight, %	Yield, g/m^3			Composition of paraffins weight, %		
		CH_4	C_{5+}	CO_2	C_5-C_{10}	C_{11}-C_{18}	C_{19+}
-	0	20	67	10	81	18	1
ZrO_2	5	27	85	16	79	19	2
	10	21	92	14	75	22	3
	15	24	78	17	61	33	6
CrO_3	5	10	37	4	49	39	12
	10	7	33	3	46	41	13
	15	4	30	traces	39	43	18
Al_2O_3	5	37	61	14	77	21	2
	10	29	65	10	79	20	1
	15	16	32	traces	78	20	2

Influence of modifiers on the composition of liquid hydrocarbons produced from CO and H_2 in the presence of catalysts 10%Co-(0-15%M_xO_y)/SiO_2

M_xO_y	[M_xO_y] weight, %	Composition C_{5+}, weight, %				α
		Olefins	Paraffins			
			Norm.	Iso-	N/iso	
-	0	13	67	20	3.4	0.69
ZrO_2	5	8	68	24	2.8	0.70
	10	8	69	23	3.0	0.72
	15	6	73	21	3.5	0.79
CrO_3	5	15	59	26	2.3	0.84
	10	18	63	19	3.3	0.85
	15	15	70	15	4.7	0.88
Al_2O_3	5	7	68	26	2.6	0.71
	10	5	75	20	3.8	0.71
	15	5	77	18	4.3	0.71

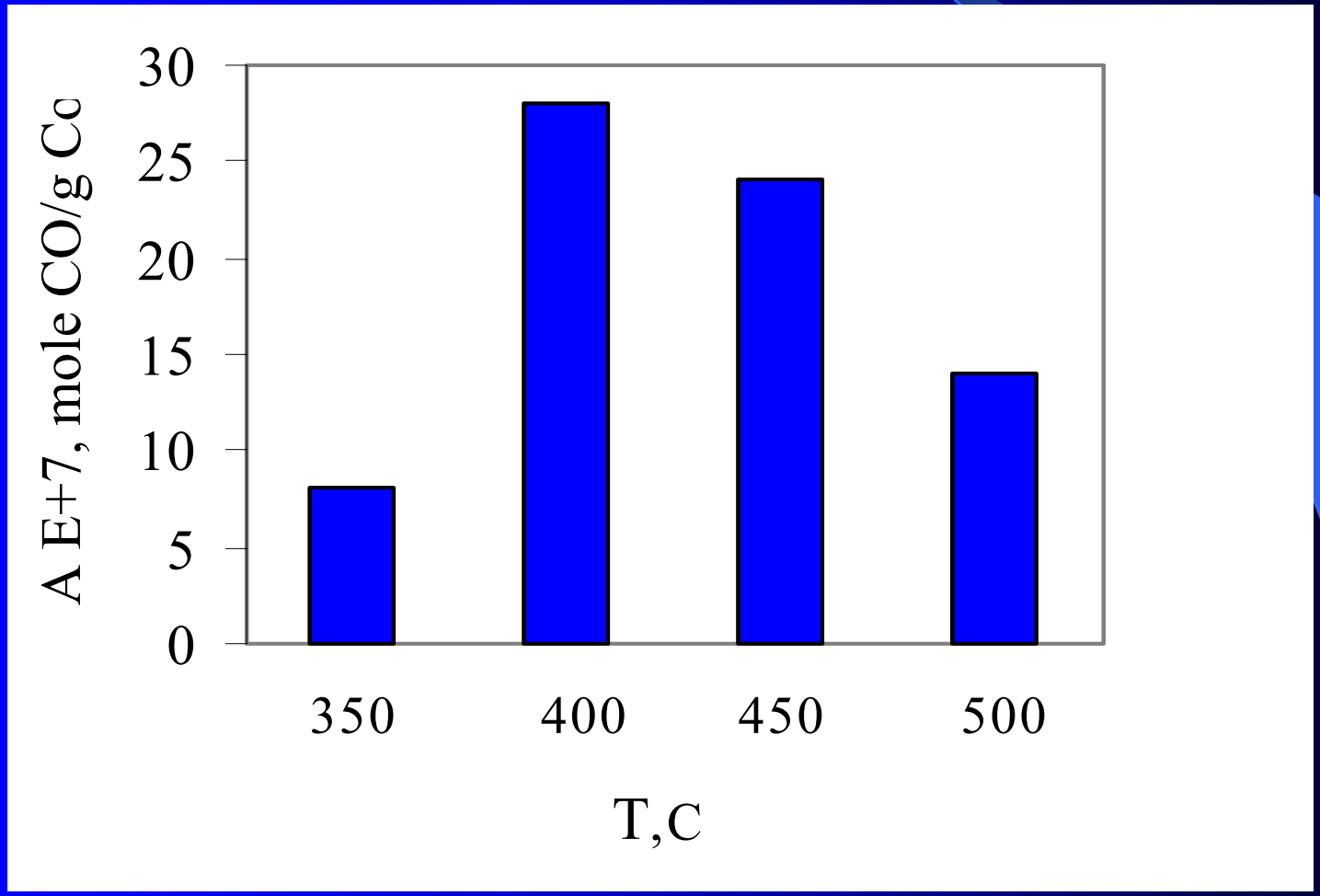
Influence of pretreatment of catalyst 10%Co/SiO_2 on synthesis of hydrocarbons from CO and H_2 (T_{red} = 450°C)

Pretreatment Condition	Conditions		R_{Co}	K_{Co}	Yield, g/m^3				
	W, h^{-1}	τ hour	%	%	CH_4	C_2-C_4	C_{5+}	CO_2	α
Reduction	100	5	68	35	9	13	49	5	0.81
	3000	1	65	50	18	16	68	10	0.78
	3000	0.5	63	47	10	14	61	4	0.78
Reduction-Oxidation-Reduction	100	5	65	44	13	13	70	7	0.81
	3000	1	71	58	15	20	74	10	0.75
	3000	0.5	75	46	10	9	70	5	0.77

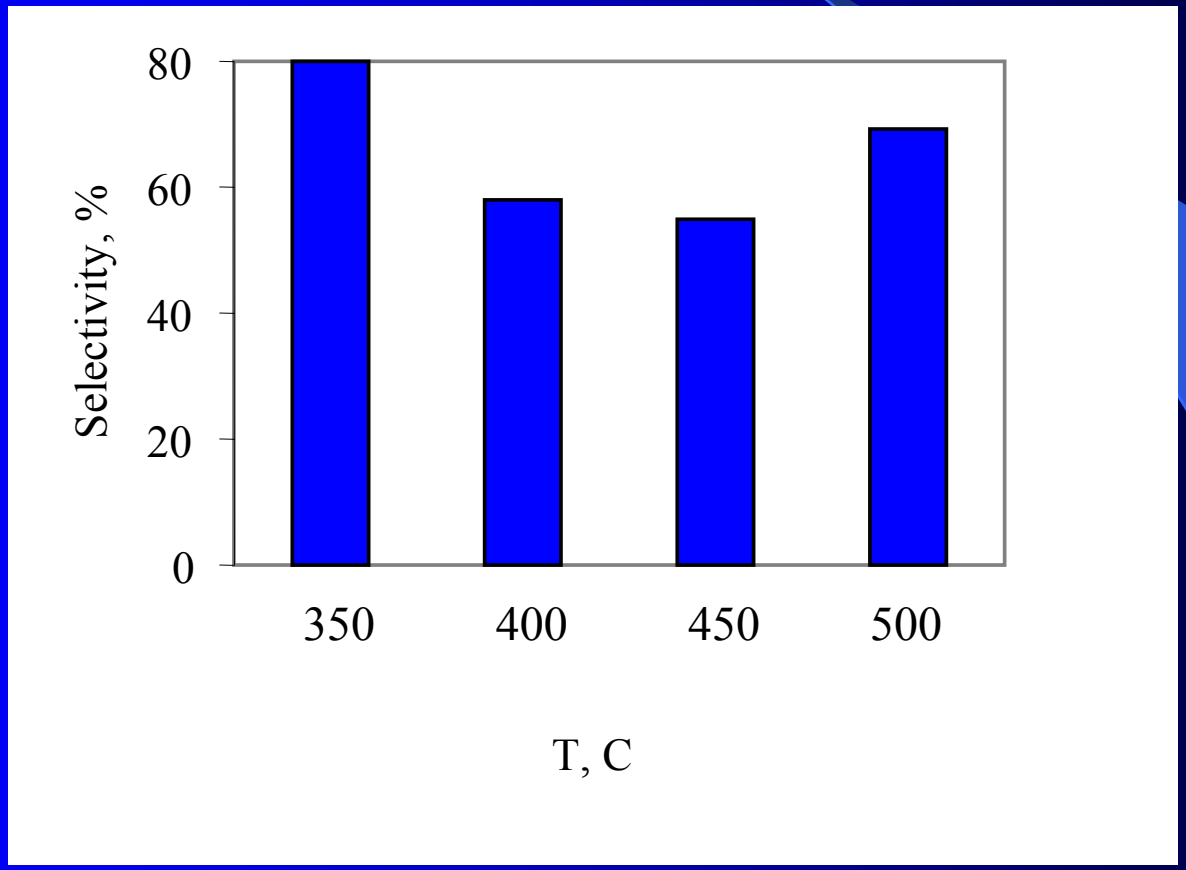
Influence of pretreatment of catalyst 10%Co/SiO_2 on synthesis of hydrocarbons from CO and H_2 (T_{red} = 450°C)

Pretreatment Condition	Conditions		Composition of C_{5+} weight, %			Composition of Paraffins weight, %		
	W, h^{-1}	τ hour	Olefins	n-paraffins	Iso-paraffins	C_5-C_{10}	C_{11}-C_{18}	C_{19+}
Reduction	100	5	10	71	19	56	36	8
	3000	1	6	71	23	64	31	5
	3000	0.5	7	74	19	64	31	5
Reduction-Oxidation-Reduction	100	5	9	71	20	56	36	8
	3000	1	4	72	24	70	27	3
	3000	0.5	7	77	16	66	30	4

Influence of reduction temperature on synthesis of hydrocarbons from CO and H_2 over catalyst 10%Co/SiO_2



Influence of reduction temperature on synthesis of hydrocarbons from CO and H_2 over catalyst 10%Co/SiO_2

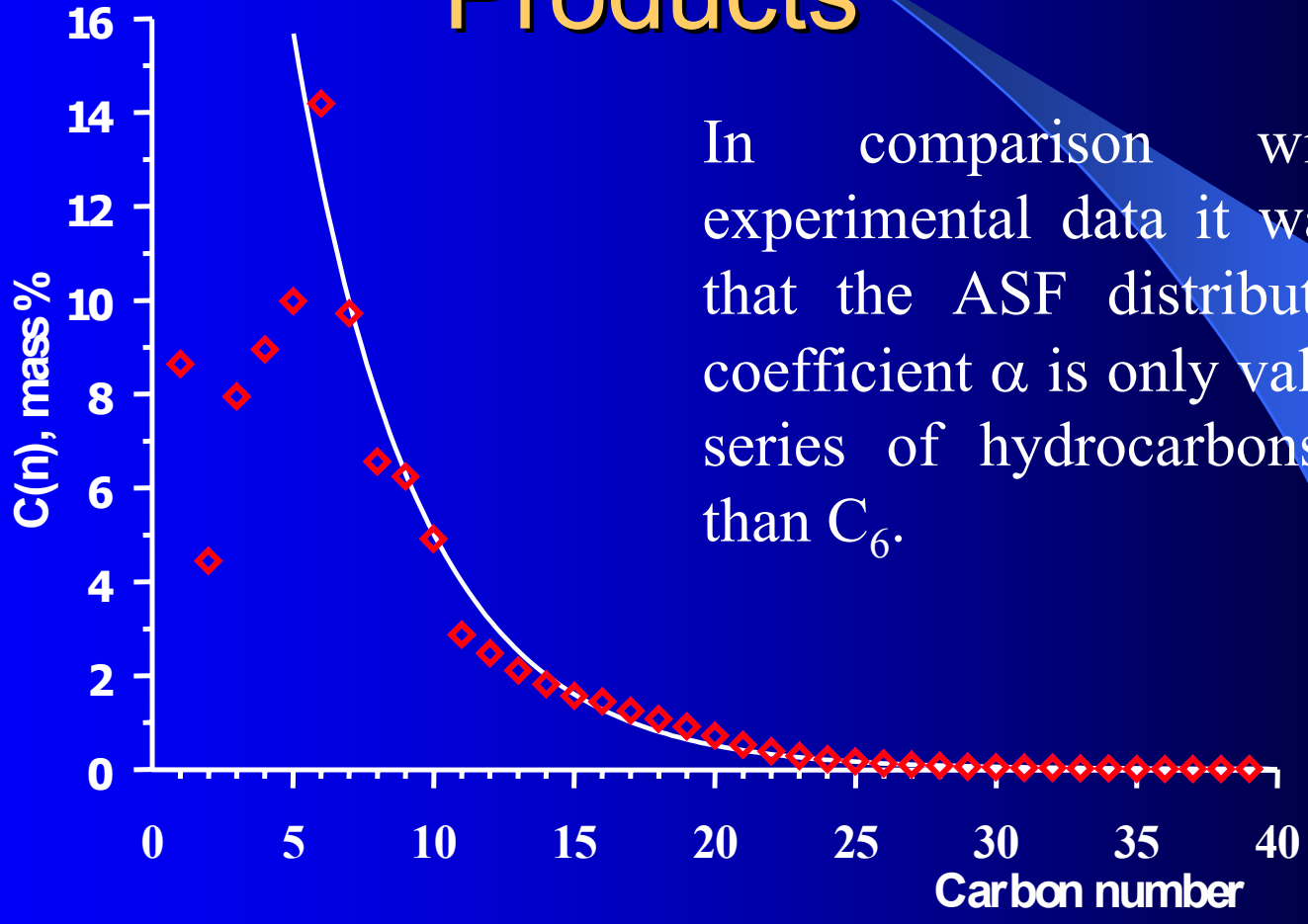


Capacity for liquid hydrocarbons

Kinetics of the Fischer-Tropsch process

- Detailed kinetic model requires for calculations of both total conversion of $CO+H_2$ and individual hydrocarbons formation. Created kinetic models describes the rate of transformation/formation of all the light gases and individual hydrocarbons (including C_{40}).

Carbon Number Distribution of Hydrocarbons in the FT Reaction Products



In comparison with the experimental data it was shown that the ASF distribution with coefficient α is only valid for the series of hydrocarbons heavier than C_6.

Carbon Number Distribution of Hydrocarbons in the FT Reaction Products

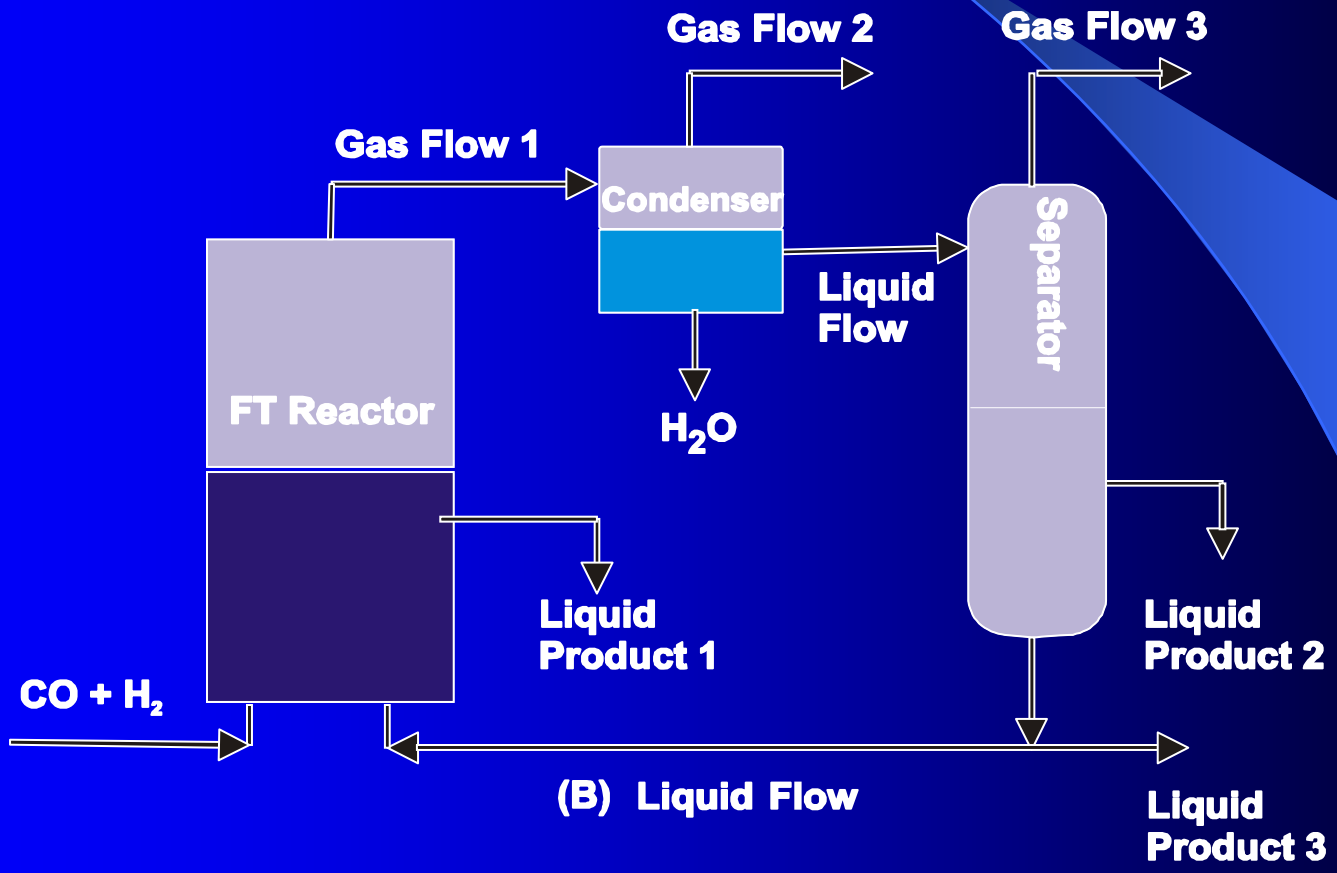
- Coefficient α was not constant for a given catalyst but depended on the concentrations of CO and H_2 in the reaction mixture.
- $$\alpha = \mathrm{A}\frac{y_{CO}}{y_{CO} + y_{H_2}} + B$$
- where A= 0.233+0.074 and B = 0.633+0.042 are constants.

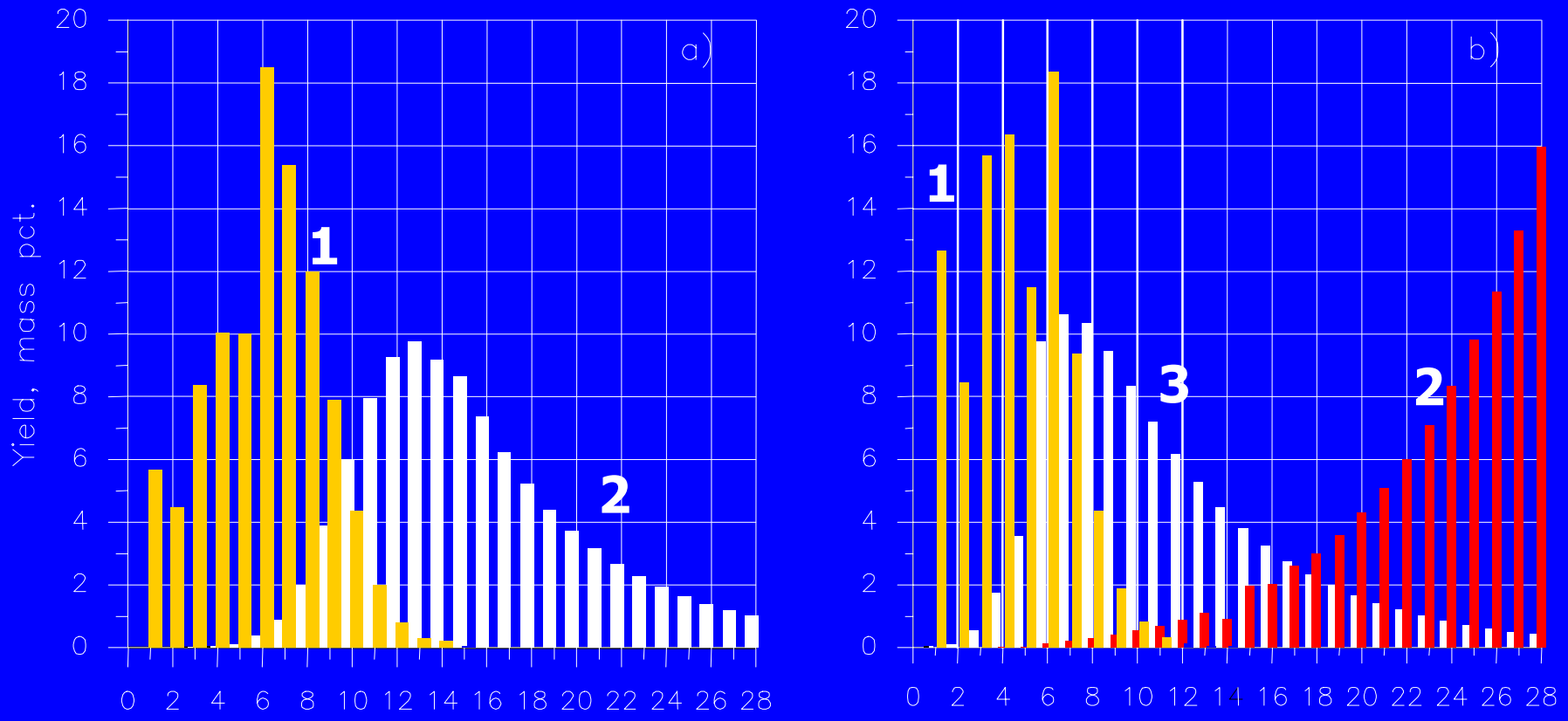
Results for the Identification of Kinetic Model

No.	Reaction	Rate Equation	Rate Constant, mole/(kg_{cat}·h)
1	$CO+3H_2 \Leftrightarrow CH_4+H_2O$	$R_1=K_1 y_{CO} y^3_{H2}$	76.2±1.3
2	$CO+H_2O \Leftrightarrow CO_2+H_2$	$R_2=K_2(y_{CO}y_{H2O}-y_{CO2}y_{H2}/K_{eq})$	5.6±1.5
3	$CO+(5/2)H_2 \rightarrow (1/2)C_2H_6+H_2O$	$R_3=K_3 y^2_{H2}$	4.5±0.75
4	$CO=(7/3)H_2 \rightarrow (1/3)C_3H_8+H_2O$	$R_4=K_4 y^2_{H2}$	6.3±1.5
5	$CO+(9/4)H_2 \rightarrow (1/4)C_4H_{10}+H_2O$	$R_5=K_5 y^2_{H2}$	6.9±1.2
6	$CO+(11/5)H_2 \rightarrow (1/5)C_5H_{12}+H_2O$	$R_6=K_6 y^2_{H2}$	7.52±0.8
7	$CO+(13/6)H_2 \rightarrow (1/6)C_6H_{14}+H_2O$	$R_7=K_7 y_{CO} y^2_{H2}$	49.2±0.6
8	$CO+2H_2 \rightarrow (1/3)C_3H_6+H_2O$	$R_8=K_8 y_{CO} y^2_{H2}$	5.978±1.7
9	$CO+2H_2 \rightarrow (1/4)C_4H_8+H_2O$	$R_9=K_9 y_{CO} y^2_{H2}$	9.153±0.8
10	$CO+2H_2 \rightarrow (1/5)C_5H_{10}+H_2O$	$R_{10}=K_{10} y_{CO} y^2_{H2}$	7.85±1.25

- Mathematical modeling of fragmentary flow sheet of FT process in slurry reactor

Scheme of the FT Reactor Units

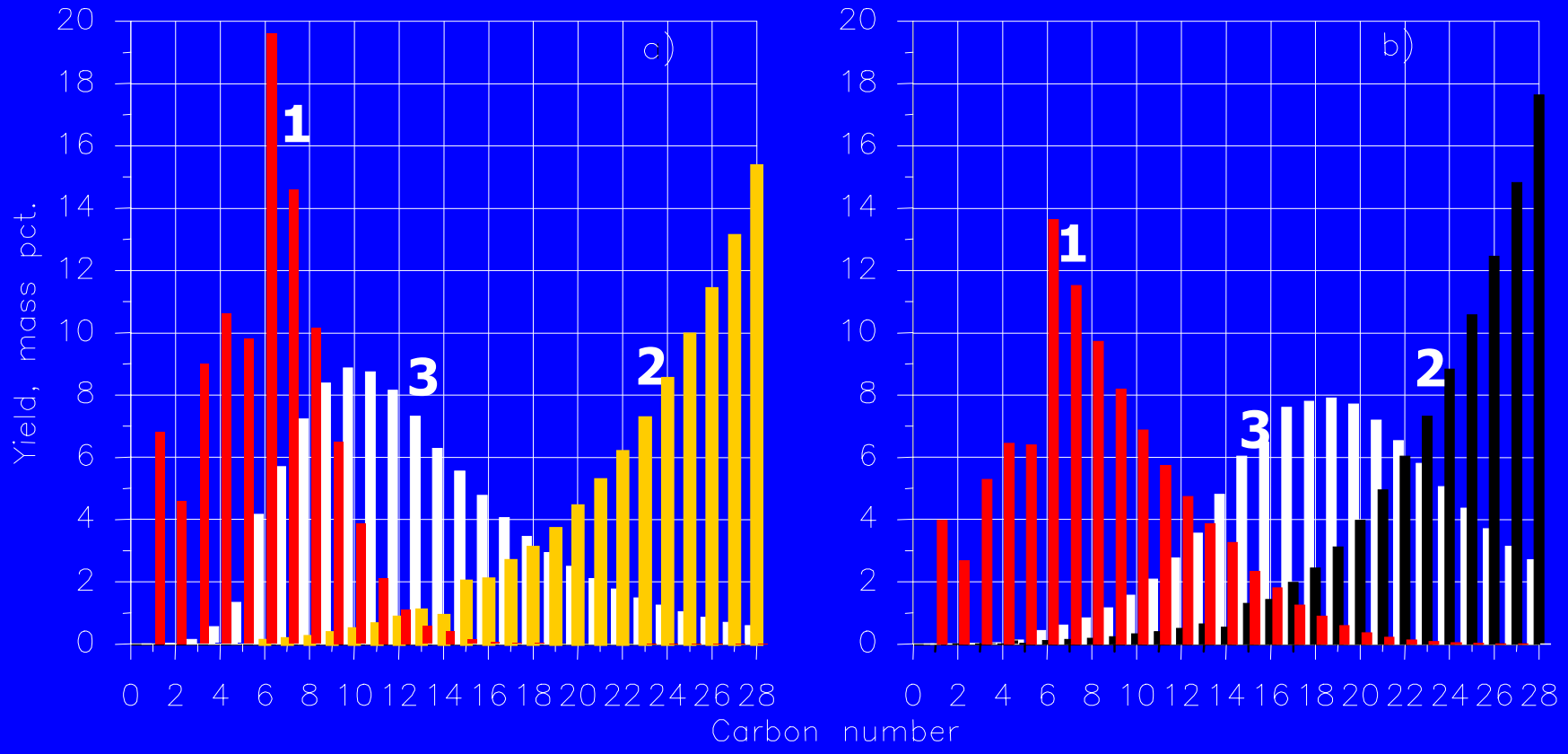




Carbon number

Distribution of hydrocarbons in the product fluxes released from the reactor unit. The temperature of cooler is 373 K. a) β=1, b) β =0.5.

1 - vapor-gas flow after the cooler, 2 - liquid flow after the reactor, 3 - liquid flow after the separator.



Distribution of hydrocarbons in the product fluxes released from the reactor unit. β=0.5. The temperature of cooler is: a) 423 K, b) 473 K.

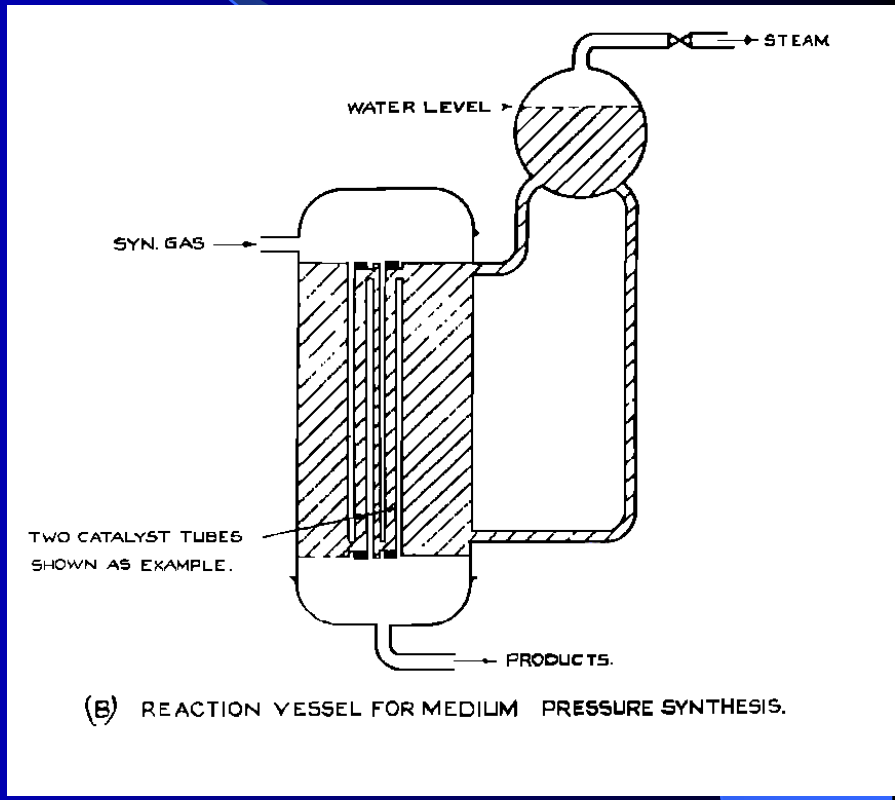
1 - vapor-gas flow after the cooler, 2 - liquid flow after the reactor, 3 - liquid flow after the separator.

NOVOCHERKASSK SYNTHETIC PRODUCTS PLANT 1954-1992

- Design FT Plant
  - Planned capacity 50,000 tpy
  - Primary commercial products
    - *n*-paraffins(C_5-C_{24} reference cetane)
    - solvents (C_5-C_6 and C_6-C_7 paraffin fractions)
    - Oxidation feedstocks (paraffin fractions 179-270, 260-290°C)
    - solid paraffins (ceresin)
- Disadvantages
  - Low process productivity
    - 4 t catalyst reactor load produces 2.5 t/day of C_{2+}
  - Uneconomical production
  - Co catalyst is no more than 9-12 months.

NOVOCHERKASSK SYNTHETIC PRODUCTS PLANT 1954-1992

- Feed
  - 1954 to 1978 anthracite
  - 1978 to 1992 natural gas
- 3-stage multi-tube
  - Temp. 170 to 200° C
  - Pressure 8-10 atm
  - GHSV 100 h^{-1}
  - Productivity 12.8-24 stnd vol CO/vol cat/hr



NOVOCHERKASSK PLANT 1954-1992

- Catalyst History – Catalyst development by Institute of Organic Chemistry of the USSR Academy of Sciences
  - 1954- 1967 German Formulation
    - 100 Co, 8 MgO, 5 ThO_2, 200 kieselgur
  - 1967 – 1977 Thoria Free Catalyst
    - 200 Co, 10 MgO, 260-280 kieselgur
  - 1977 – 1981 Ceresin yield improvement
    - 100 Co, 10 ZrO_2, 200 kieselgur
  - 1981-1992 Ceresin yield improvement
    - 100 Co, 10 MgO, 10 ZrO_2, 200 amorphous synthetic aluminosilicate

ACKNOWLEDGMENT

- Syntroleum Corporation, Tulsa, especially Steve LeViness and Paul Schubert, are gratefully acknowledged for partial support of this work and assistance in preparation of the report