FROM RESIDUAL BIOMASS AND INFERIOR QUALITY COAL TO THE SYNTHESIS OF METHANOL AND THEN TO HYDROCARBONS AND GASOLINE – A ROMANIAN PROJECT OF HIGH SUCCESS

From Residual Biomass and Inferior Quality Coal to the Synthesis of Methanol and then to Hydrocarbons and Gasoline – A Romanian Project of High Success

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Dr. Gheorghe Maria is currently professor in Chemical & Biochemical Reaction Engineering with the UPB - University Politehnica of Bucharest (Romania). He received the PhD in 1987 in chemical engineering at UPB (supervisor Prof. Dr. ing. Raul Mihail). On 1982 he joined ICECHIM (catalysis, and chemical & biochemical energetics Institute, as a senior researcher), and on 1990 he joined UPB as a lecturer. On 1992 he come in Switzerland for working as Assistant Professor with ETH Zürich (with the late Prof. David W.T. Rippin group of Process System Engineering). On 1997 he return to Romania becoming Associate Professor and then full Professor (1999) with UPB. His research interests concern the fields of (bio)chemical reactor and kinetic modelling, biochemical engineering and bioinformatics, risk analysis of chemical plants, modelling of cell metabolic processes, gene expression and regulatory circuits, and drug release kinetics. Over the past 25 years he participated to various national or intl. Projects (more than 15), making short research stages/visitingship at ETH Zürich (3-months on 1997, SNSF fellow on environmental risk analysis), Univ. des Saarlandes (3-months on 1999, DAAD fellow on modelling complex enzymatic kinetics), TU Erlangen (3-months on 2000, catalytic membrane reactors), Texas A&M University (2002-2003, res. scientist on modelling gene expression and gene regulatory networks, synthetic biology), TU Braunschweig (2006) and TU Hamburg (3-months on 2009, DFG and DAAD fellows on simulating bacteria resistance to environmental pollutants), Tianjin Inst. Ind. Biotechnology China (2-months on 2010, in-silico searching for gene knockout strategies for E. coli cell, synthetic biology). He presented more than 31 invited Lectures at various Universities in EU, CAN, USA, China (among them: Princeton Univ. 1994, Texas A&M University 2002, EPFL Lausanne 1997, Queen's Univ. Kingston 1994 Canada, BASF Ludwigshafen 1996). He authored 8 books (with ISBN, from which 3 in USA), 5 teaching books, 6 book chapters (with ISBN), 143 papers in peer reviewed ISI international journals and univ. journals, and 78 in intl. conference proceedings, with more than 1300 citations (h-index 19 and i10 index 41; ResearchGate score > 35). Among them, 38 papers have been published in Chem. Eng. journals with the highest IF≥ 3. According to the Romanian ranking system, he reported high scores signing NP=110 ISI papers as principal author, with a cummultative impact factor of FIC > 160. He is a reviewer for many (bio) chemical engineering journals (25). He co-chaired or was member of the organizing Committees of 16 international conferences Among them: 5th Int. Conference on Computational Bioengineering (ICCB-5), 11-13 September, 2013, Leuven, Belgium; ROMPHYSCHEM-15, 15-th International Conference of Physical Chemistry, 11-13 September, 2013, Bucharest; 13th Edition of Academic Days of Timisoara, June 13-14, 2013, Timişoara (Romania); ELSEDIMA 10-th, 11-th, and 12-th International Conference (Environmental Legislation, Safety Engineering and Disaster Management), 18-19 September 2014 and 26-28 May 2016, and 17-19 May 2018, Cluj-Napoca (RO).

Dedication:

In the memory of Prof.dr.ing. Raul MIHAIL (1920-1985), the founder of the chemical reactor school in Romania.

Contents

Abstract

The MTO-MTG project was a complex scientific and industrial project that involved a significant number of specialists in the chemistry area (scientific researchers, chemists, process analysis engineers, chemical engineers working in math modelling, engineering calculations, model-based plant design, and others) from several institutions including UPB. The project lasted for a decade and a half (1980-1995) and was completed with the design, scale-up, construction, started-up (1985), and optimal semi-automatic operation of an industrial pilot plant (including a complex catalytic fluidized-bed reactor-regenerator system) at the Petrochemical Works Brazi (Ploiesti, Romania). Several other catalytic processes related to the MTO/MTG have also been tested by using the same pilot plant, such as: I) methanol conversion to BTX hydrocarbons (aromatics), ii) benzene/ ethylbenzene (EB) alkylation with ethene to get higher aromatics, iii) ethanol conversion to olefins (EtOH), iv) C4 olefins alkylation with methanol (OA), v) MTG catalyst deactivation kinetics. The present booklet is aiming at reviewing the large number of published scientific contributions by the key-investigators in the area of kinetic modelling of the involved catalytic processes, model-based design of the pilot plant built-up at PWB, and its optimal operation.

Abbreviations: BTX: Benzene, Toluene, Xylene; EB: Ethylbenzene; MTG: Methanol to Gasoline; EtOH: Ethanol Conversion to Olefins; MTO: Methanol to Olefins; FBR: Fluidized-Bed Reactor; OA: C4 Olefins Alkylation with Methanol; IECB: Chemical and Biochemical Institute Bucharest (part of ICECHIM); PWB: Petrochemical Works Brazi (Ploiesti, Romania); IITPIC: Inst. Technological Engineering and Design for Chemical Industry; UPB: University Politehnica of Bucharest; MTH methanol to hydrocarbons

Introduction

The methanol to olefins (MTO) - methanol to gasoline (MTG) project was a complex scientific and industrial project that involved a significant number of specialists in the chemistry area (scientific researchers, chemists, process analysis engineers, chemical engineers working in math modeling, engineering calculations, model-based plant design, and others) from several institutions including UPB. The project lasted for a decade and a half (1980-1995) and was completed with the design, scale-up, construction, put into operation (1985), and optimal semi-automatic operation of an industrial pilot plant (including a complex catalytic fluidized-bed reactor-regenerator system) at the Petrochemical Works Brazi (Ploiesti, Romania) (PWB). Beside the MTO-MTG catalytic processes, several other catalytic processes in the same area of interest have also been tested by using this pilot-scale (see below Chapter), such as: I) methanol conversion to BTX hydrocarbons (aromatics), ii) benzene/ethylbenzene (EB) alkylation with ethene to get higher aromatics, iii) ethanol conversion to olefins (EtOH), iv) C4 olefins alkylation with methanol (OA), v) MTG catalyst deactivation kinetics.

The basic concept of the whole MTO-MTG project was to capitalize on cheap and low-quality(regenerable) natural resources (e.g. residual biomass, wood waste, lower cellulosic material, inferior quality coal) by converting them to methanol (via syngas) and then to hydrocarbons and gasoline.

The present work is aiming to review the large number of published scientific contributions reported by the key-investigators in kinetic modelling of the involved catalytic processes, model-based design of the industrial pilot plant, and optimal operation of the plant. The pilot plant includes a complex catalytic system consisting of two fluidized-bed reactors FBR; that is, one FBR to conduct the MTO-MTG process, and a FBR to regenerate the catalyst of the main reactor; the catalyst has a continuous circulation by pneumatic transport between the two reactors (Figure 1A). Being one of the key investigator/design engineer/math-model developer in this project, it is a duty of honor for me to present some of the remarkable results of this large-scale project.
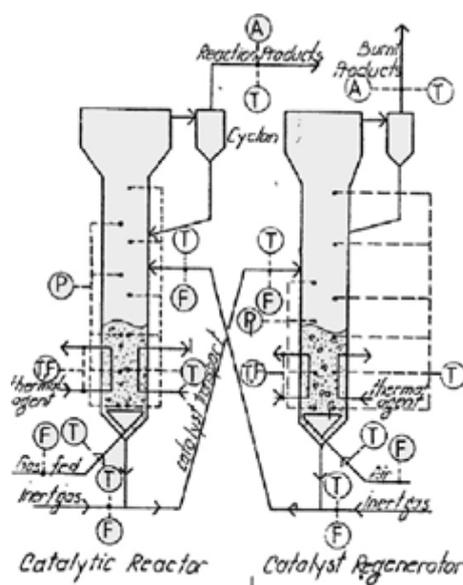
Figure 1A: Scheme of the industrial pilot plant built-up at Ptrochemical Works Brazi PWB (Ploiesti, Romania) [2], including two FBR: one for conducting the desired reaction (MTO, MTG, etc.), and one for catalyst regeneration. The catalyst has a continuous circulation, by pneumatic transport, between the two reactors [1-4].

Participating Teams and Key-Investigators

The project, funded by the Ministry of Chemistry of Romania (1980-1992), has been a major investment and, due to its high complexity, involved a significant number of researchers from academic area (IECB, UPB) and design engineers from IITPIC (Table 1). The project general manager was (now retired) dr. Gavril Musca (IECB), while the scientific part was conducted by the late prof. Dr. ing. Raul Mihail (UPB). This extremely complex and extended project, involved several partner institutions presented together with the involved key-investigators in the Table 1, together with their roles. This large project required an important investment cost (tens of millions US$), justified by the large number of research and design activities, that is: catalyst screening and synthesis (IECB), process check at a lab-/ bench-scale, math (kinetic) modelling of the tested catalytic process (MTO, MTH, MTG, BTX, EB, EtOH, OA) (IECB,UPB), FBR reactor-regenerator system modelling, and model-based reactor design (IECB,UPB), plant technological design, construction, commissioning (1985)(IITPIC), optimization, semi-automatic control (IECB,UPB,IITPIC). The industrial pilot plant was built-up at the Petrochemical Works Brazi PWB (Ploiesti, Romania), taking advantage of the facilities and utilities offered by the petrochemical platform. Due to the pilot plant high operating flexibility, not only the basic MTO, MTH, MTG, BTX processes have been tested, but also several others catalytic processes aiming at producing hydrcarbons of high added value, that is EB, EtOH, OA (see below Chapter).

Table 1: Key-investigators of the involved institutions and their role in the MTO-MTG project.

Institution	Key-Investigator	Role
IECB Chemical and Biochemical Institute Bucharest (part of ICECHIM, central research institute for chemistry)	Senior res. eng. Dr. Gheorghe MARIA (currently prof. dr.ing. UPB)	- Kinetic modelling of catalytic processes; statistical treatment of experimental data; - Math modelling of the two FBR to be used in design; - FBR design; catalytic process scale-up; - Catalytic plant technological design, commissioning, and optimization
	Senior res. eng. Dr. Straja SORIN (currently living in USA)	- Ibidem; - Kinetic modelling of the catalyst deactivation
	Senior res. eng. Dr. Gavril MUSCA (currently retired);	Management
	Senior res. eng. Dr. Grigore POP (currently retired)	
	(late) Senior res. eng. Dr. Ecaterina POP; Senior res. eng. Dr. Tomi PAVEL (currently retired);	- Catalyst synthesis and characterization; - Check catalyst efficiency (process conversion, selectivity, yield), and for stability
	Dr. chim. Doina IVANESCU (currently retired); and many others	
	Junior res. eng dr. Cristian TSAKIRIS (currently lecturer Univ. Ecologica Bucharest).	- Development of empirical statistic models of the investigated catalytic processes.
UPB, University Politehnica of Bucharest, Dept. Chemical Engineering	(late) Prof.dr.ing. Raul MIHAIL	Management
IITPIC Institute of Technological Engineering and Design for Chemical Industry	Senior design engineer Dr. Traian STAN (retired),	Mechanical and technological design, utility routes, electro-installation, etc
	Senior design engineer Dr. Lucica CRETOIU (retired),	
	Senior design engineer Dr. Gigi DAMIAN (retired), and others	

Due to its high complexity, the project has been carried out in several stages, over more than a decade, as follows:

i.   Catalyst synthesis and screening, catalytic process check at a lab-/bench-scale (See the below chapter);

ii.   Math (kinetic) modelling of the tested catalytic process (MTO, MTH, MTG, BTX, EB, EtOH, FT, OA) (See the below chapter);

iii.   FBR (reactor-regenerator system) modelling, and model-based industrial reactor design and optimization (See the below chapter). The industrial pilot plant from PWB was built-up mainly for producing synthetic gasoline (MTG). It was a major industrial achievement at both national and international level. At that time (1985), there was a single similar industrial pilot of Mobil Oil (USA) operated in New Zealand, but of a simpler construction (without continuous recirculation and regeneration of the catalyst).

Catalytic Processes Tested by Iecb at a Lab-Scale and using the Industrial Pilot Plant of Petrochemical Works Brazi (Ploiesti, Romania). Kinetic modelling.

Being of interest in the novel paradigm of this project, not only the basic catalytic MTO, MTH, MTG, BTX processes have been studied and scaled-up, but also some other catalytic processes also developed on zeolite catalysts, as follows [1-21].

i.   Methanol conversion to olefins (MTO)[5-13].

ii.   Methanol conversion to BTX and aromatic hydrocarbons (BTX,MTH)[15].

iii.   Methanol conversion to gasoline (MTG)[14].

iv.   Benzene or Ethylbenzene Alkylation in Vapour-Phase with ethene on a zeolite catalyst (EB)[17,18].

v.   Ethanol conversion to olefins (EtOH)[16].

vi.   C4 olefins alkylation with Methanol (OA)[19].

vii.   Kinetic models for zeolitic catalysts deactivation due to their coking [20].

viii.   Analysis of the Fischer-Tropsch synthesis (FT) (at a bench-scale only)[21].

To get the most suitable/effective catalyst, an extended experimental program was conducted for every above mentioned process. After selection of the most suitable catalyst, every vapor phase mentioned process (MTO, MTG, BTX, EB, EtOH, OA) was tested at the lab-scale, but also with using the industrial pilot (1985-1992) over long times-on-stream (excepting FT). As a result of the tests carried out with using the industrial pilot plant of PWB, important results were obtained. Thus, kinetic studies and mathematical models developed for the studied catalytic processes were published in top journals [1-20]. Also, the kinetic models have constituted the basis for the scale-

up of the main catalytic processes (MTO, MTG, BTX). Below, some information is provided for the main studied catalytic processes, together with the modelling results obtained with using the lab-experiments and checks with the pilot plant of PWB.

Methanol to olefins MTO process

For the MTO process, SAPO-34 has been found to be the best catalyst. The process characteristics are given in the Table 2. As remarked by Sherwin [22], the MTO / SAPO-34 process is more economic than the process of hydrocarbons pyrolysis to produce ethylene. The process is moderately exothermic (ca. 20kcal/mol methanol). Consequently, it is likely to be thermally integrated [23]. A large number of lab-scale checks lead to elaborate and test an extended kinetic model of the MTO process [5-13]. Such a kinetic model is presented in the Table 3A. Basically, the reaction pathway assumes formation of ethylene, and of carbene first (via dimethyl ether), followed by a succession of radicalic/ionic reactions which grow the hydrocarbon chain, followed by their cyclization. Because such an extended kinetic model [6,7] will be further used for engineering calcultations to design the MTO fluidized-bed reactor and, eventually, to optimize the industrial FBR, several reduced forms of the kinetic model have been derived by Maria [7,8,10-13]. Some of them are presented in the Table 3A-B. As proved by Maria [7,8,10-13], the size of the developed kinetic model depends, in fact, on the available experimental information, and on the utilization scope. For design purposes, a reduced kinetic model [1-4] has been used.

Table 2: Performances of the tested MTO process at both lab- and pilot-scales [5-9]. Obs. The MTO / SAPO-34 process is more economic than the process of hydrocarbons pyrolysis to produce ethylene [22].

Raw Material	Commercial Liquid Methanol			
Catalyst and optimal running conditions	SAPO-34 zeolite at 435°C, 1.95 h-1; mordenite-zeolite MZ at 370°C, 1.12 h-1;			
Temperature	360-440°C (normal pressure; reaction is moderately exothermic, ca. 20 kcal/mole methanol)			
LHSV	0.6-2.4 1/h			

Typical product distribution (%wt.) [9]

More than 98% methanol conversion; 90% total olefins selectivity; 61% ethene selectivity. 36-41 g olefins / 100 g fed methanol; 19-27 g ethene / 100 g fed methanol

Compound	Catalyst		Compound	Catalyst	
	SAPO	MZ		SAPO	MZ
H_2	0.43	0.18	C_5H_{12}	0.3	0.22
CH_4	1.35	5	C_5H_{10} and C_6^+	1.06	0.28
C_2H_6	0.17	0.45	CO	_	4.28
C_2H_4	26.65	7.96	CO_2	_	0.13
C_3H_8	0.44	3.43	CH_3OH	1.47	2.97
C_3H_6	10.63	10.23	Dimethyl-Ether	0.91	0.21
C_4H_{10}	0.54	2.82	H_2O	54.66	55.12
C_4H_8	1.39	6.65			

Remark: The MTO/SAPO-34 process is more economic than the hydrocarbon pyrolysis process for producing ethene [22].

Table 3A: The reduced kinetic models for the MTO process proposed by Mihail & Maria et al. [6,7].

Table 3B: Various proposed reduced kinetic models for the MTO process, as followings: (up) Maria and Muntean [8]; (down) Maria [7,10-13]. Notations: A= oxygenates without water, B= carbene, C= olefins, P= paraffins plus aromatics and other products.

Reaction	Kinetic Parameters	
	Model 1	Model 2
$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O$	105	14.47
$CH_3OCH_3 \rightarrow 2\ddot{C}H_2 + H_2O$	7.09	14.05
$\ddot{C}H_2 + CH_3OH \rightarrow C_2H_4 + H_2O$	—	—
$\ddot{C}H_2 + CH_3OCH_3 \rightarrow C_2H_4 + CH_3OH$	2.71	7.56
$\ddot{C}H_2 + CH_3OCH_3 \rightarrow C_3H_6 + H_2O$	0.83	4.04
$\ddot{C}H_2 + C_2H_4 \rightarrow C_3H_6$	1.02	0.59
$\ddot{C}H_2 + C_3H_6 \rightarrow C_4H_8$	1.6	0.93
$\ddot{C}H_2 + C_4H_8 \rightarrow C_5H_{10}$	0.47	0.52
$\ddot{C}H_2 + H_2 \rightarrow CH_4$	4.62	3.14
$C_2H_4 + C_4H_8 \rightarrow C_2H_6 + C_4H_6$	2.05	5.85
$C_2H_4 + C_5H_{10} \rightarrow C_2H_6 + C_5H_8$	50.03	—
$C_3H_6 + C_4H_8 \rightarrow C_3H_8 + C_4H_6$	32.18	26.51
$C_3H_6 + C_5H_{10} \rightarrow C_3H_8 + C_5H_8$	—	—
$C_4H_8 + C_4H_8 \rightarrow C_4H_{10} + C_4H_6$	60.24	92.95
$C_4H_8 + C_5H_{10} \rightarrow C_4H_{10} + C_5H_8$	—	—
$C_4H_{10} + C_5H_{10} \rightarrow C_5H_{12} + C_5H_8$	5.46	259.9
$C_3H_8 \rightarrow C_2H_4 + CH_4$	—	—
$C_4H_{10} \rightarrow C_3H_6 + CH_4$	—	—
$C_5H_{12} \rightarrow C_4H_8 + CH_4$	4.27	—
$CH_3OH \rightarrow CO + 2H_2$	0.51	0.44
$C_2H_4 \rightarrow CH_4 + C$	0.16	0.01

Reaction	Linear Model Clasical Zeolite 370°C [6]	Nonlinear Model Classical Zeolite 370°C [6]	Nonlinear Model SAPO Zeolite 400°C [22]
(1) A → R	2.69	5.24	6.65
(2) A + B → C	—		
(3) C + B → P	$k_3B = 1.51$	$k_2/k_1 = 1.28$	$k_2/k_1 = 6.06$
(4) A → C	3.02	—	—
(5) A → P	—	—	—
(6) A + B → P	—	—	—

Methanol to BTX (aromatic hydrocarbons), and MTH process

The MTH/BTX process has been successfully developed on a zeolite catalyst, with satisfactory performances displayed in the Table 4. The process was also tested at an industrial scale by using the pilot built-up at PWB. The process is more exothermic than the MTO. The reaction pathway is similar to the MTO in the in the preliminary stages. But, once high olefins are formated, they suffer successive cyclizations and dehydrogenations leading to BTX and higher eromatics Ar10+. An extended kinetic model was proposed by Mihail et al.[14,15] including 53 elementary/lumped reactions.

Table 4: Performances of the tested methanol conversion to MTH (including BTX and aromatics) process at both lab- and pilot-scales [15]. Obs. Methanol conversion over 95%; yields of 12 g ethylene / 100 g of fed methanol, 6 g propylene / 100 g fed methanol, 10 g BTX / 100 g fed methanol.

Raw Material	Commercial Liquid Methanol
Catalyst and optimal running conditions	Zeolite
Temperature	380-400°C (normal pressure; moderate exothermic reaction)
LHSV	0.7-1.3 1/h (100% fed methanol; sometimes mixed with water)
Typical product distribution (%wt.) [15]. For 390°C, 1 h-1, 100% fed methanol.	
Catalyst performances: [15] More than 95% methanol conversion; Maximum yields of: 12 g ethylene / 100 g fed methanol; 6 g propylene / 100 g fed methanol; 10 g BTX / 100 g fed methanol	

Compound	%wt	Compound	%wt	Compound	%wt
CH_4	0.41	cis C_4H_8	0.33	Toluene	0.43
C_2H_6	0.15	H_2	0.02	Ethyl-Benzene	1.13
C_2H_4	7.84	CO	0.09	p-Xylene	6.37
C_3H_8	3.88	CO_2	0.60	m-Xylene	0.76
C_3H_6	3.09	DimethylEther	1.19	o-Xylene	0.28
i-C_4H_{10}	3.77	CH_3OH	7.17	Ethyl-Toluene	2.02
n-C_4H_{10}	0.86	H_2O	51.54	Trimethyl-Benzene	1.00
1+i-C_4H_8	0.89	Alif C_5-C_7	2.45	Durene	0.33
i-C_5H_{12}	2.15	Benzene	0.19	Ar 10+	1.14

Methanol to gasoline MTG

The MTG process characteristics are presented in the Table 5 [14]. The process was also tested at the industrial scale by using the pilot plant built-up at PWB. Various zeolitic catalysts have been tested to get the most stable one. One of them, has been proved to be very effective, that is a bifunctional synthetic modified mordenite zeolite containing divalent ions, and having a SiO2/Al2O3 ratio higher than 20 (see details in [14]). An extended kinetic model of the process was proposed by Mihail et al. [14], and used (in a reduced form) to design the industrial fluidized bed reactor at PWB.

Table 5: Performances of the methanol conversion to gasoline MTG [14].

Raw Material	Commercial Liquid Methanol
Catalyst and optimal running conditions	Zeolit
Temperature	345-425°C (normal pressure; moderate exothermic reaction)
LHSV	0.5-2 1/h (50%-100% fed methanol; the used inert is water)

Typical product distribution: (%wt.) [14] for 405°C, 1.75 h-1, 100% fed methanol, sometimes mixed with water.

More than 98% methanol conversion; maximum yields of: 15-20 g aromatics / 100 g fed methanol; 30 g paraffins / 100 g fed methanol; 5 g olefins / 100 g fed methanol

Compound	%wt	Compound	%wt	Compound	%wt
H_2	0.10	C_4H_{10}	10.98	C_6H_6	0.21
H_2O	55.31	C_2H_4	0.98	Toluene	3.77
CH_4	0.89	C_3H_6	1.01	Xylene	9.82
C_2H_6	0.35	C_4H_8	0.97	Tri-methyl-benzene+	3.30
C_3H_8	9.31	C_5^+	3.00	Durene under 2.00	

Benzene or Ethylbenzene (EB) alkylation with ethene to get higher aromatics

The EB process characteristics are presented in the Table 6 [17-18]. The process was also tested at the industrial scale by using the pilot built-up at PWB. The used zeolitic catalyst has been proved as being very stable (for several hours' time-on-stream). The lumped kinetic model proposed by Maria [17-18] even if of very simple form (3 reactions, from which 2 reversible) has been proved to accurately fit the experimental data recorded at 400oC, and for the 1/1.5 benzene/ethylene initial molar ratio (normal pressure).

Table 6: Performances of the tested ethylbenzene EB alkylation with ethene [17-18]. (DEB= di-ethylbenzene).

Raw Material	Commercial Ethyl-benzene from Oil Refinery and Commercial Ethylene
Catalyst and optimal running conditions	Zeolite
Temperature	350°C (normal pressure, low exothermic reaction)
LHSV	1-1.5 1/h (0.6-0.8 moles fed ethylene / mole de EB)

Typical product distribution (%wt.) [14] for 350°C, 1 h⁻¹, 0.73 moles fed ethylene / mole de EB

15-20% EB conversion; 20-30% ethylene conversion; 60% selectivity in EB and p-DEB; 45% selectivity of ethylene in p-DEB.

Compound	%wt	Compound	%wt	Compound	%wt
Alif. C_5-C_7	0.91	Pseudocumene	0.03	n C_4H_{10}	0.13
Benzene	1.89	p DEB	7.25	1 C_4H_8	0.02
Toluene	0.64	m DEB	3.71	i C_4H_8	0.11
Ethyl Benzene	70.88	o DEB	0.05	i C_5H_{12}	0.08
p-Xylene	0.56	C_2H_4	11.12	cis C_4H_8	0.02
m-Xylene	0.10	C_3H_8	0.71	n C_5H_{12}	0.03
o-Xylene	0.07	C_3H_6	0.33	H_2	0.01
Ethyl-toluene	1.03	i C_4H_{10}	0.32		

C4 olefins alkylation with methanol (OA)

The OA process is aiming at converting the C4 fraction of olefins to iso-C5 olefins by alkylation with methanol on a zeolite catalyst [19]. The iso-C5 olefinic fraction is knew as being of high importance as a raw-material for the petrochemical processing industry, and a valuable component of the gasoline. Its non-conventional production by using the olefinic C4 fraction and methanol is attractive from two reasons:

i.   The C4 fraction is thus used in a more efficient way.

ii.   The process involves the methanol, i.e. a non-petrochemical raw-material, possible to be obtained from cheap and possibly renewable raw materials (residual biomass/wood waste, lower cellulosic material, inferior quality coal). The OA process characteristics are presented in the Table 7. The process was also tested at the industrial scale by using the pilot built-up at PWB. The used zeolitic modified ZSM-12 and ZSM-5 catalysts have been proved to be very stable and effective.

Table 7: Performances of the tested C4 olefins alkylation with Methanol, OA [19].

Raw Material	C4 fraction from Catalytic Cracking, and Commercial Liquid Methanol		
Catalyst and optimal running conditions	ZSM-12 zeolite, and modified ZSM-5		
Temperature	300-375°C (normal pressure, low exothermic reaction)		
LHSV	1-4 1/h (0.5-2.5 moles methanol / mole fed butene)		
Typical product distribution (%wt.) [19] for 340°C, 2 h⁻¹, 1 mole methanol / mole butene fed ratio;			
More than 80% methanol conversion; selectivity of 16-24 g isoamylenes / 100 g reacted butene; yield of 5 g isoamylenes / 100 g fed butene, and fed CH_2 from methanol.			

Compound	%wt	Compound	%wt	Compound	%wt
CH_3OH	6.84	n C_4H_{10}	37.03	C_5H_8	0.56
H_2O	11.64	1 C_4H_8	5.73	n C_6H_{14}	0.11
DimethylEther	0.16	i C_4H_8	2.88	C_7H_{16}	0.45
H_2	0.01	Trans-C_4H_8	11.99	Toluene	0.05
CH_4	0.02	Cis-C_4H_8	7.68	p-Xylene	0.46
C_2H_4	0.52	n-C_5H_{12}	2.58	m-Xylene	0.05
C_3H_8	0.37	2MethylButene1	0.34	o-Xylene	0.01
C_3H_6	1.78	2MethylButene2	0.87	Aromatics C_9^+	0.27
i C_4H_{10}	7.53	1 C_5H_{10}	0.07		

Kinetic Model for the Mto, Mtg catalysts deactivation by coking, and its regeneration by burning with air

The zeolitic catalysts used in the MTO/MTG processes suffer an inherent coking due to formation of high hydrocarbons in the catalyst pores at larget contact times and for lower amounts of water vapors to inhibit this undesirable process that diminishes the catalyst activity [2,4,20]. Based on lab-scale experimental studies carried-out by IECB, simple kinetic models for the MTO, MTG catalysts deactivation by coking, and for their regeneration (by burning the coke in the regenerator) have been proposed [2,4,20]. The kinetic models were tested also at the pilot plant scale [4, 20]. For the catalyst coking the integral empirical model is of the form [4]:

$$C_{coke} = C_{coke,0} + a + b{\cdot}t + c{\cdot}t^2$$

where t: contact time in the reactor; [a,b,c]: empirical correlation coefficients depending on the recirculation rate.

The coke balance in the regenerator is [4] (where C_{oxy} is the oxygen molar fraction in the regenerator):

$$D_{cat}\left(C_{coke,inlet} - C_{coke,out}\right) = n_{burn}\, m_{cat} \qquad k = 0.19{\cdot}10^9 \exp(-18989/T_{reg}) \text{ ,s}^{-1}$$
$$n_{burn} = k\, C_{coke,out}\, C_{oxy}$$

Kinetic model for the Fischer-Tropsch synthesis (FT)

With the same aim of evaluating alternative ways to produce gasoline, and hydrocarbons, the classical FT sythesis was investigated at a lab-scale, by using a silica-iron catalyst. Based on own experiments, and on the experiments of Bub et al. [24] conducted at 10-30 atm., and 220-230°C, a complex kinetic model of power-law type was derived. Some ot their features are presented in the Table 8. The process was tested at a bench-scale only [21], because the PWB pilot plant can not support pressures higher than 2 atm.

Table 8: Kinetic model for the Fischer-Tropsch synthesis (FT) (tested at a bench-scale only)[21].

$$\text{cat.} + CO \longrightarrow \text{cat.} - CO \qquad (1)$$
$$\text{cat.} - CO + \text{cat.} \longrightarrow \text{cat.} - C + \text{cat.} - O \qquad (2)$$
$$2\,\text{cat.} + H_2 \longrightarrow 2\,\text{cat.} - H \qquad (3)$$
$$\text{cat.} - O + 2\,\text{cat.} - H \longrightarrow \text{cat.} + \text{cat.} - H_2O \qquad (4)$$
$$\text{cat.} - H_2O \longrightarrow \text{cat.} + H_2O \qquad (5)$$
$$\text{cat.} - CO + \text{cat.} - O \longrightarrow 2\,\text{cat.} + CO_2 \qquad (6)$$
$$\text{cat.} - C + n\,\text{cat.} - H \longrightarrow n\text{-cat.} + \text{cat.} - CH_n \qquad (7)$$
$$\text{cat.} - CH_3 + \text{cat.} - H \longrightarrow 2\,\text{cat.} + CH_4\,(\text{omologi}) \qquad (8)$$

$$nCO + (2n + 1)H_2 \longrightarrow C_nH_{2n+2} + nH_2O$$

$$nCO + 2nH_2 \longrightarrow C_nH_{2n} + nH_2O$$

$$CO + H_2O \longrightarrow CO_2 + H_2$$

$$nCO + (2n + 1/2)H_2 \rightarrow [C_nH_{2n+1}] + nH_2O$$
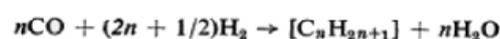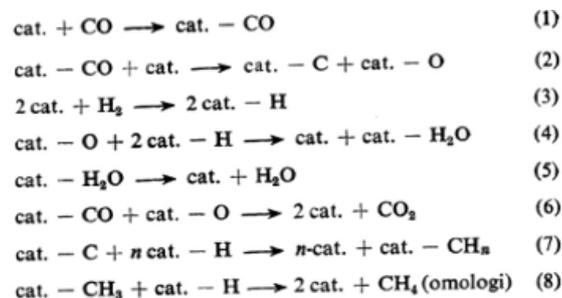
$$r_1 = 3{,}79 \times 10^2 \exp(-60{,}2/RT)\, p_{H_2}^{0{,}38}\, p_{CO}^{-0{,}57}$$

$$r_2 = 2{,}41 \exp(-54/RT)\, p_{H_2}^{0{,}66}\, p_{CO}^{-0{,}46}$$

$$r_2' = 5{,}90 \times 10^4 \exp(-90/RT)\, p_{H_2}^{-0{,}02}\, p_{CO}^{1{,}46}$$

$$r_3 = 1{,}57 \times 10^{-1} \exp(-35{,}8/RT)\, p_{H_2}^{0{,}95}\, p_{CO}^{-0{,}81} \qquad r_{CO}^{hid} = -k_0 \exp(-E/RT) p_{H_2}^{m} p_{CO}^{n}$$

$$r_3' = 1{,}23 \times 10^6 \exp(-99{,}1/RT)\, p_{H_2}^{-0{,}13}\, p_{CO}^{0{,}85}$$

$$r_4 = 2{,}42 \exp(-49{,}4/RT)\, p_{H_2}^{0{,}8}\, p_{CO}^{-0{,}43} \qquad r_{H_2} = -k_0 \exp(-E/RT) p_{H_2}^{m} p_{CO}^{n}$$

$$r_4' = 1{,}19 \times 10^4 \exp(-93{,}2/RT)\, p_{H_2}^{-0{,}22}\, p_{CO}^{0{,}91} \qquad r_{H_2O} = k_0 \exp(-E/RT) p_{H_2}^{m} p_{CO}^{n}$$

Statistic model to characterize the Ethanol conversion to olefins (EtOH) process

Conversion of EtOH to ethylene and higher hydrocarbons on a zeolitic catalyst (ZSM, HZSM5, Al_2O_3/silica(Akzo), and others [16]) has experimentally been investigated by IECB [16]. Based on the recorded kinetic data, a simple statistical model was derived, linking the variables of interest, that is:

$\eta1$ = yield in ethylene (g ethylene/g fed ethanol);

$\eta2$ = yield in aromatics (g aromatics A7-A10/g fed ethanol);

$\eta3$ = yield in gasoline (g fraction C5+/g fed ethanol);

with the control variables: temperature (T), LHSV, ethanol concentration in the fed (C%mol.). To inhibit the catalyst deactivation, the fed ethanol vapours are diluted with water vapours. The obtained results are presented in the Table 9 [16].

Table 9: Performances of the tested Ethanol conversion to olefins (EtOH)[16]. See details in [16].

$$\eta = B_0 + B_1 \cdot C + B_2 \cdot T + B_3(LHSV) + B_4 \cdot C^2 + B_5 \cdot T^2 + B_6(LHSV)^2 + B_7 \cdot C \cdot T + B_8 \cdot C \cdot (LHSV) + B_9 \cdot T \cdot (LHSV)$$

	Randament in etilenă (η_1)	Randament in aromate (η_2)	Randament in benzine (η_3)
B_0	4,107	—2,869	—4,183
B_1	—2,964 × 10⁻²	1,419 × 10⁻²	4,052 × 10⁻²
B_2	—1,092 × 10⁻²	1,143 × 10⁻²	1,264 × 10⁻²
B_3	—1,870	1,013	1,658
B_4	3,712 × 10⁻⁵	1,174 × 10⁻⁵	—8,698 × 10⁻⁵
B_5	7,830 × 10⁻⁶	—1,156 × 10⁻⁵	—1,275 × 10⁻⁵
B_6	2,731 × 10⁻¹	—1,824 × 10⁻¹	—3,218 × 10⁻¹
B_7	3,974 × 10⁻⁵	—3,078 × 10⁻⁵	—4,566 × 10⁻⁵
B_8	7,802 × 10⁻³	—2,101 × 10⁻³	—9,391 × 10⁻³
B_9	2,409 × 10⁻³	—1,490 × 10⁻³	—1,054 × 10⁻³

$\eta1$ = yield in ethylene (g ethylene / g fed ethanol)

$\eta3$ = yield in gasoline (g fraction C5+ / g fed ethanol)

$\eta2$ = yield in aromatics (g aromatics A7-A10/ g fed ethanol)

Mathematical Modelling and Optimal Design of the Fluid-Bed Catalytic Reactor-Regenerator System

The developed kinetic models of the above investigated catalytic processes allowed to design the fluid-bed catalytic reactors of the industrial pilot plant of PWB. Also, the elaborated kinetic models for catalyst deactivation (by coking), and its regeneration (by coke burning with air) allowed to design the fluid-bed regenerator. The reactor and the regenerator are connected, thus allowing the continuous circulation of the catalyst (of ca. 0.06-1mm avg. size) between these two main units of the industrial pilot plant of PWB. From a constructive point of view, the industrial pilot plant of PWB (Figure 1A) consists of two catalytic fluid bed reactors (see the main characteristics of the reactor-regenerator system in the Table 10) The catalyst (ZSM5, mordenite or other modified silicates) is introduced as below-millimeter particles into the reactor where it is entrained by the gaseous reactant (methanol/water vapors, etc.) introduced at the bottom of the reactor. Catalyst elutriation is prevented by the cyclone disposed at the top. The heat of reaction is removed through the cooling tubes immersed in the catalytic bed. The regeneration of the coked catalyst is accomplished by its continuous transport to a fluidized bed regenerator (working similarly to the main reactor), where coke is removed being burned with air. The regenerated catalyst is pumped back to the reactor by the same pneumatic transport with inert nitrogen. The reaction-regeneration process continues until the catalyst is exhausted. The stationary operation of the two catalytic reactors is maintained by a sophisticated computer assisted control system using simple statistical math models of the process [1-4].
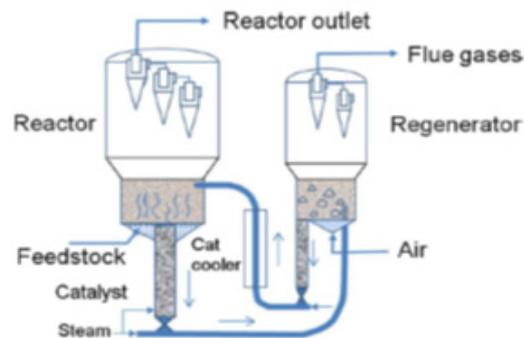
Figure 1B: The industrial pilot plant for the MTO process, including two inter-connected FBR offered by UOP/Hydro comp., Germany (2005), and Chinese Dalian Institute of Chemical Physics (2015) [23].

Table 10: The main characteristics of the industrial pilot plant for the MTO/MTG process from Petrochemical Works Brazi (Ploiesti, Romania, PWB).

Industrial pilot with two catalytic reactors in fluidized-bed (FBR)	A FBR (reactor), and a FBR regenerator (for catalyst regeneration). The continuous circulation of the catalyst between the reactor and the regenerator is accomplished by pneumatic transport with inert nitrogen.
Reactor (fluidized-bed vapour phase catalytic reaction)	0.5m in diameter and 7m in height
Regenerator (fluidized-bed combustion of the coke deposited on the microscopic catalyst)	0.3m in diameter and 7m in height
LHSV; catalyst avg. size	0.4-2 1/h (for the MTG); 0.06-1 mm
temperature range	280-450°C (reactor), and 480-560°C (regenerator)
Pressure	1-2 atm.
Observations	The pilot is equipped with gas-chromatograph analyzers and process computers connected "on-line" and "off-line". Approx. 50 process parameters are continuously recorded through appropriate equipment. A specific software is used for data treatment, with including data acquisition, numerical filtering, statistical calculations, mass and thermal balances, and kinetic evaluations..
Tested catalytic processes	MTO, BTX, MTG, EB, EtOH, OA, catalyst deactivation

The industrial pilot plant, with the characteristics listed in Table 10, was put into operation at PWB on 1985. At that time, only one similar pilot plant of the MOBIL OIL comp. USA, was operated in New Zealand, but of a simpler construction, that is without continuous recirculation and regeneration of the catalyst). For this outstanding achievement at both national and international level, that is

i.   MTO-MTG process investigation, its development/scale-up

ii.   Industrial pilot plant design and building at PWB, and

iii. Testing various catalytic processes at the pilot-plant scale, the MTO-MTG team was awarded the "Nicolae Teclu" Prize of the Romanian Academy on 1985 (Figure 2).

Figure 2: "Nicolae Teclu" Prize of the Romanian Academy awarded on 1985 to the MTO-MTG team for the successfully realization of the industrial pilot plant used to test the MTO-MTG, and other catalytic processes at Petrochemical Works Brazi (Ploiesti, Romania).

Conclusions

The realized industrial pilot plant by the MTO-MTG team was put into operation at PWB on 1985. For this outstanding achievement at both national and international level, the MTO-MTG team was awarded the "Nicolae Teclu" Prize of the Romanian Academy in 1985 (Figure 2). Most important, the realized industrial pilot-plant at PWB was used not only for testing the feasibility of conducting the MTO-MTG process at an industrial scale, but also for testing lot of novel and important catalytic processes at a large-scale. It is to underline that, on 1985, when the industrial pilot plant of PWB was put into operation, in the world, only one similar pilot plant (of the MOBIL OIL comp. USA) was operated in New Zealand but presenting different characteristics (without continuous recirculation of the catalyst). Because the MTO-MTG processes have been proved as being profitable at a large scale, similar industrial plants were later built-up, such as those offered by UOP/Hydro comp. (2005), and by the Chinese Dalian Institute of Chemical Physics [23] (see their constructive scheme in the Figure 1B).

Based on the remarkable results obtained by the Romanian MTO-MTG team, a large number of papers have been published in top scientific journals, being received with a high interest by the international scientific community. Thus, these papers reported more than 500 citations (Googleschoolar). For instance, only the Ref Mihail et al. [14] reported more than 45 citations. Also, some important MTO-MTG project realizations have been included in esteemed reviewing books, as those presented in the Figure 3.
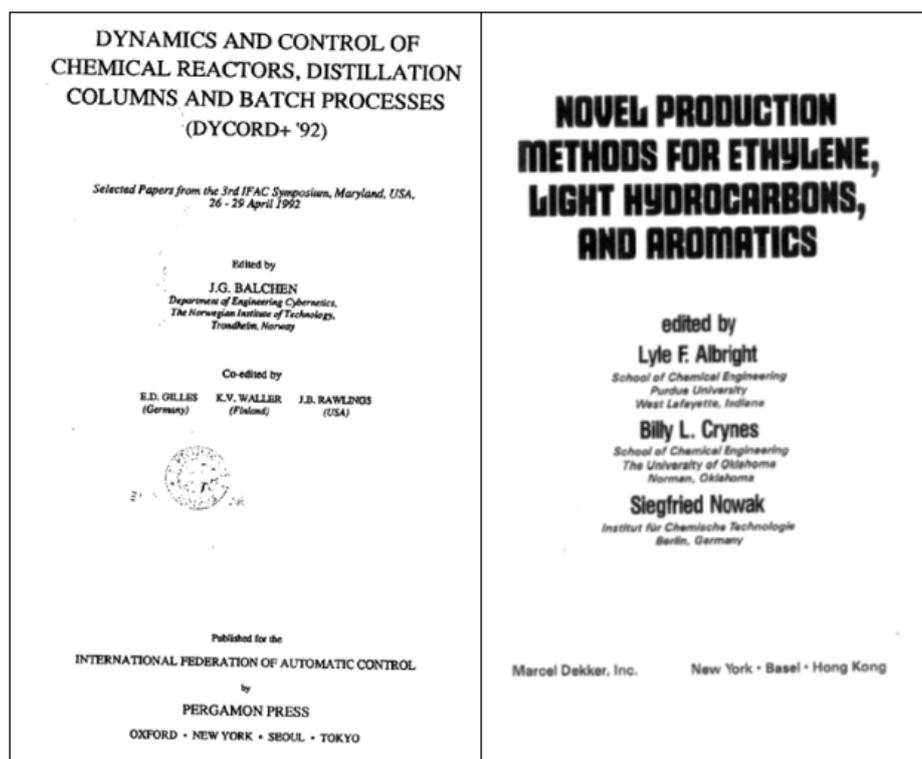
Figure 3: The most important MTO-MTG Romanian project realizations have been included in esteemed publications, such as: (left) realization of the industrial pilot plant used to test the MTO-MTG, and other catalytic processes at PWB (Ploiesti, Romania) [2,4]; (right) some effective catalysts (SAPO-34) for developing the MTO [9] and OA [19] processes.

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