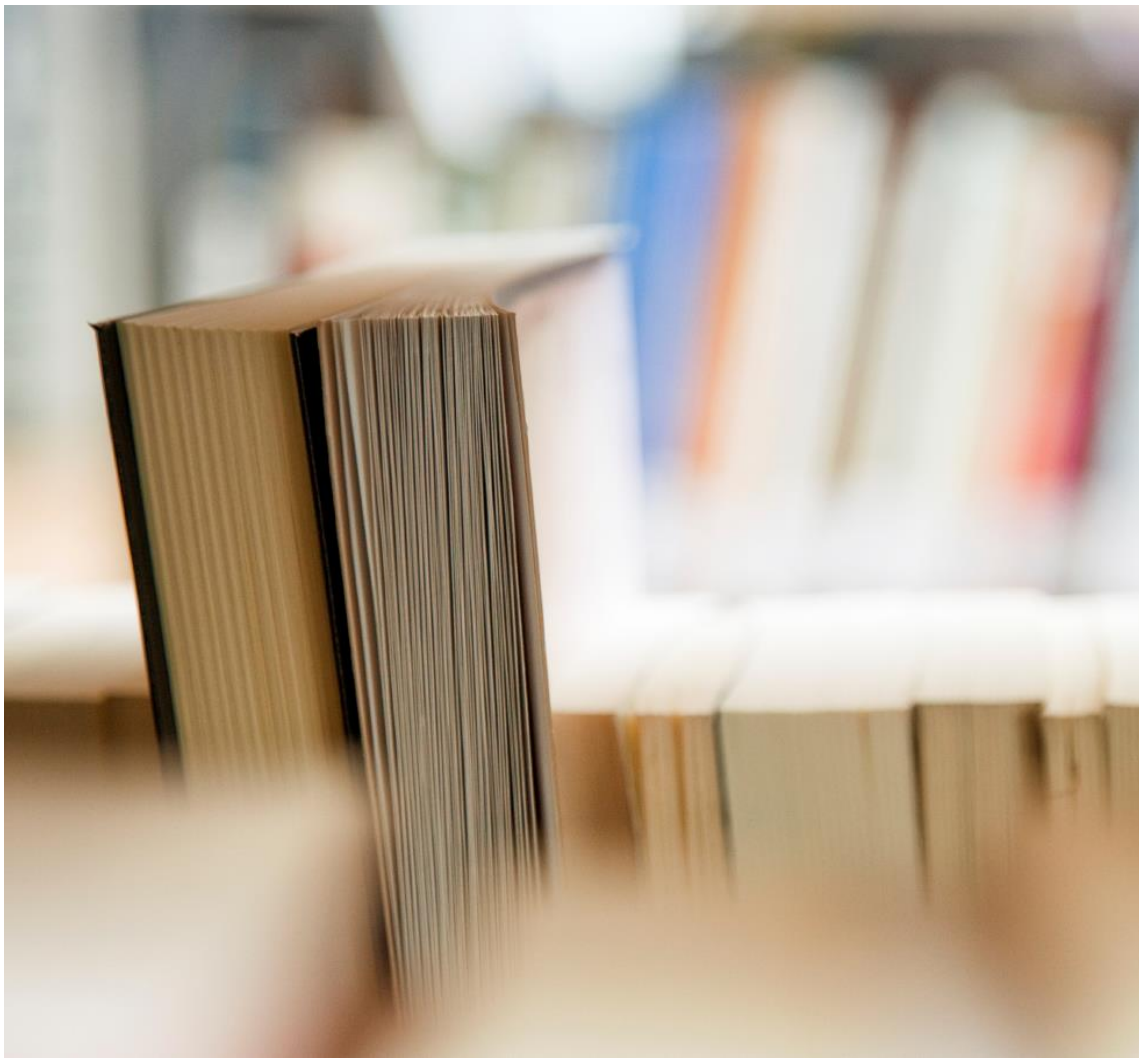

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School of Chemical Engineering, University of Tehran

2022 - 2023 Academic year

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Prologue

Zahra Mansoorpour
Vice Chancellor for Education
School of Chemical Engineering, University of Tehran

Chemical Engineering is the bridge between chemistry and the real world outside the laboratory. Chemical engineers design and optimize chemical reactions in industrial scales in order to manufacture various products in a safe, sustainable and economically viable manner.

Chemical Engineering at the University of Tehran is the oldest program in the nation, established in 1941. The School of Chemical Engineering at the University of Tehran enjoys a reputation for excellence in education and research, regularly topping national charts.

In undergraduate level, in addition to a traditional chemical engineering program, students may choose polymer engineering and petroleum engineering. The school of chemical engineering offers several Master's and PhD level degrees including process design, environmental engineering, gas process and transportation, biotechnology, nanotechnology, pharmaceutical engineering, polymer engineering, drilling engineering, production engineering, and hydrocarbon reservoirs.

The faculty and students of the school of chemical engineering engage in an integrated research and educational environment in more than 40 well-equipped laboratories. The school is also home to the fully open access, semiannual Journal of Chemical and petroleum Engineering. The UNESCO Chair on Water Reuse was established in the school of chemical engineering in 2013 to promote domestic and international cooperation in this subject.

Data-Driven Diagnosis based on Returning Patterns in Chemical Reactions

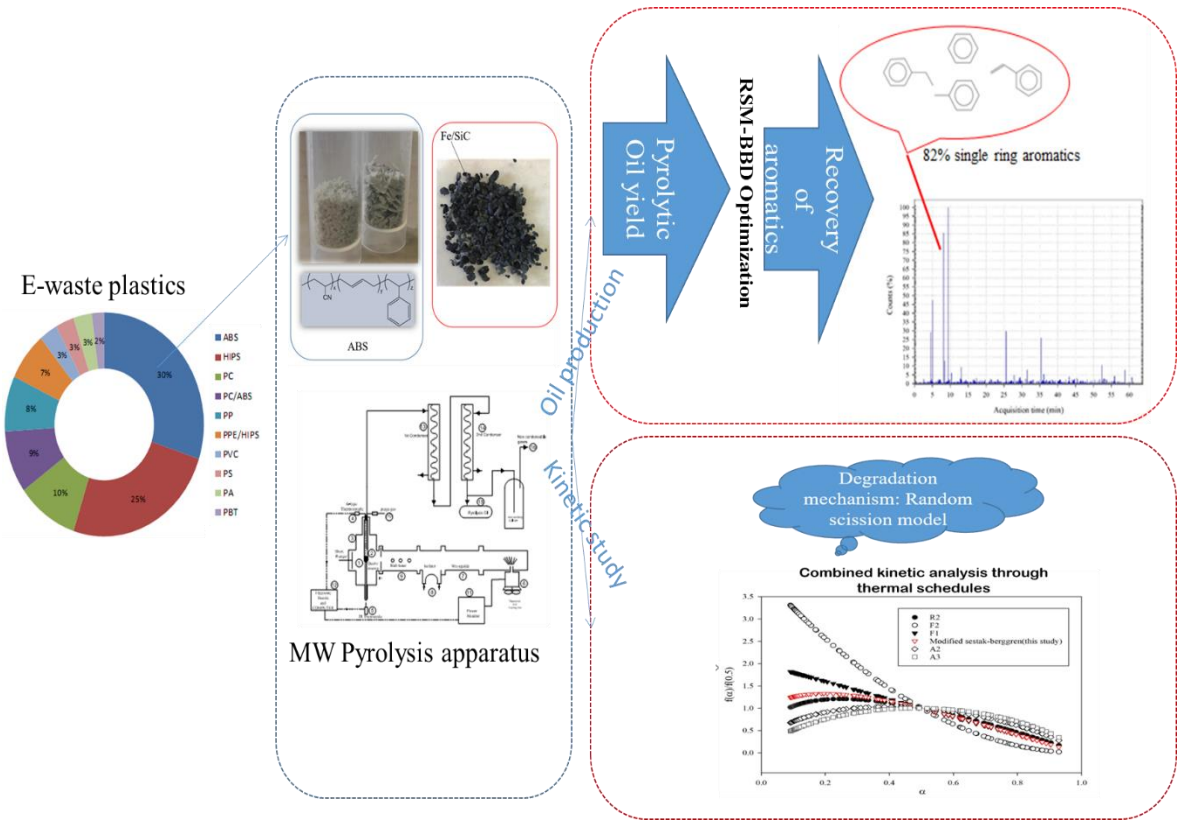
Vahid Mortezaeikia

Fall 2016/ Spring 2022
Supervisor: Omid Tavakoli

Plastic waste from electronic and electrical equipment causes environmental problems. Almost 30% of these plastic wastes contain Acrylonitrile-Butadiene-Styrene (ABS). In this work, Microwave-assisted pyrolysis (MAP) of waste ABS-Br was performed using SiC, Fe/SiC, GAC, Fe/GAC, and Fe-C as wave receptor and also catalyst to investigate the pyrolytic oil yield and aromatics recovery. Response surface methodology coupled with Box–Behnken design (RSM-BBD) was applied to optimization of the process. Four parameters (microwave power, final temperature, carrier gas flow rate, and receptor/plastic ratio) were tested and reduced-quadratic model was best fitted to the experimental data. The optimal conditions found to be at a temperature of 471°C, a microwave power of 1.54 amps, carrier gas flow rate of 215 mL/min and catalyst/plastic weight ratio of 0.05. Under such conditions, 56.97% of ABS was recovered as oil. The liquid fractions were characterized using quantitative GC–MS analysis showed high concentration of single ring aromatics (61.5% when SiC used as catalyst). The impregnation of Fe to SiC showed higher catalytic activity in conversion of PAHs to single ring aromatics (82% wt. of oil) and also higher fixation of bromine compounds (over 99% adsorbs).

Also, pyrolysis kinetic of Acrylonitrile-Butadiene-styrene (ABS) based electronic waste plastic under microwave irradiation condition was studied. Microwave assisted Thermogravimetric analyzer was developed and different heating schedule, including constant heating rate (27.5, 42.2 and 65 K min^{-1}) and a sample controlled reaction rate (0.01 min^{-1}) was carried out to obtain TG curves. Modified Sestak-Berggren equation was used to model the TG data by the Pearson's linear correlation and related parameters of n=1.129 and m=0.27 was achieved. Since the model solely does not have any physical meaning, the normalized form of the obtained conversion function (f (α)/f (0.5)) was compared with most frequents models for solid-state reactions. Random scission model (L2) was the best to physically justify the experimental data. Also, the kinetic parameters obtained from the model has been rationalized on the basis of the dependence of the effective activation energy (E_α) upon conversion (α) determined via the isoconversional kinetic analysis, and was observed that variation of E_α with α was approximately constant. E_α obtained from combined kinetic analysis was 140.5 and 63.7 kJ/mol for without and with Fe impregnated SiC, respectively.

Keywords: Acrylonitrile butadiene styrene, ABS, Microwave, Pyrolysis, Kinetics, Aromatic


E-waste plastics
ABS
HIPS
PC
PC/ABS
PP
PPE/HIPS
PVC
PS
PA
PBT
30%
25%
10%
9%
8%
7%
3%
3%
3%
2%
Fe/SiC
ABS
MW Pyrolysis apparatus
Oil production
Kinetic study
Pyrolytic Oil yield
RSM-BBD Optimization
Recovery of aromatics
82% single ring aromatics
Acquisition time (min)
Degradation mechanism: Random scission model
Combined kinetic analysis through thermal schedules
R2
F2
F1
Modified sestak-berggren(this study)
A2
A3
α

Total Site Heat Integration Considering Streams Pressure Drops

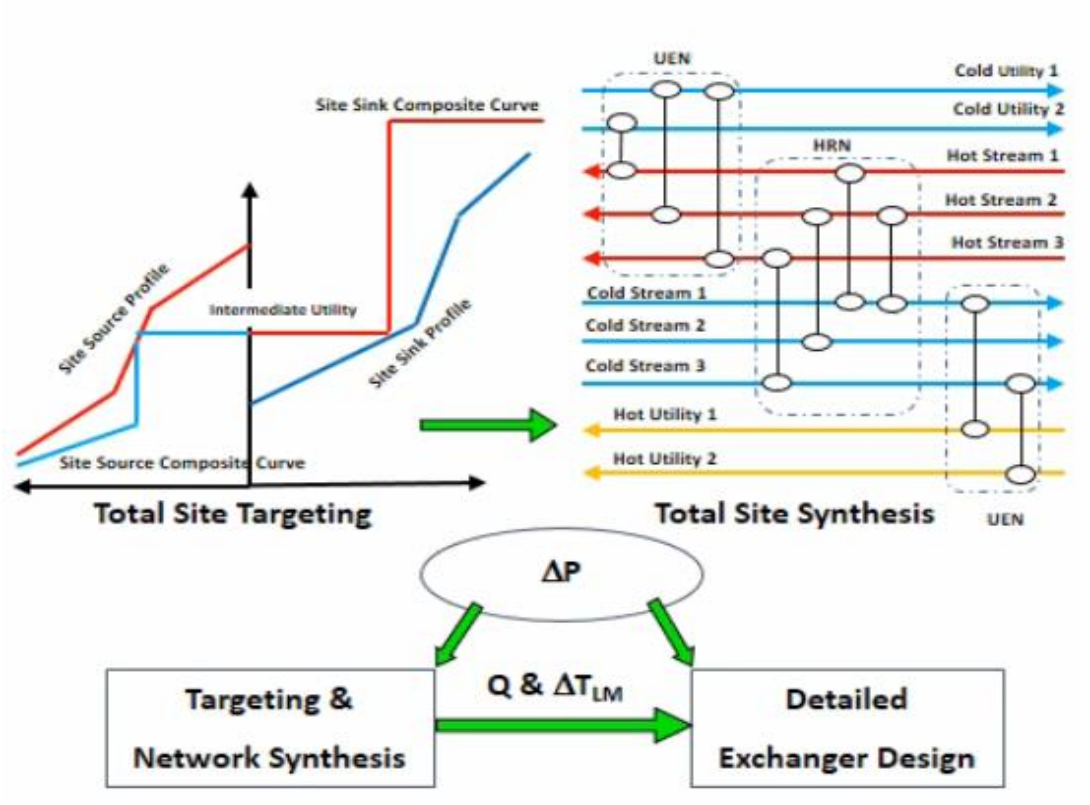
Simin Faramarzi

Fall 2014/ Summer 2022
Supervisor: Nasim Tahouni
Advisor: Mohammad Hassan Panjeshahi

Heat integration can be categorized into individual processes and Total Site. Process streams assumed heat transfer coefficients are employed in targeting and synthesis steps of conventional methods for Heat Exchanger Networks (HENs) heat integration. On the other hand, streams' pressured drops are often the most critical factors in heat exchangers' detailed design step. Therefore, there can be huge differences between heat exchangers' sizes and costs predicted by the network designer and those realized by the exchanger designer. Hence, considering streams' pressure drops is necessary for different steps of individual processes' heat integration. Total Site heat integration is implemented through different processes using a central utility system. Various Total Site targeting methods presented by different researchers are compared through the first part of the methodology. Then, a novel Total Site energy and area targeting method is suggested by considering streams pressure drops. Three case studies are analyzed to verify the novel method, interfacing streams' pressure drops, and Total Site targeting results. There are grass-root problems in case studies analysis, and the outcome of employing the suggested method is compared to the results of applying a conventional Total Site targeting technique. Process streams assumed heat transfer coefficients are used in individual processes and Total Site targeting of the conventional method. A three-way trade-off between energy requirement, area demand, and pressure drop is developed for each individual process in the new approach, assessing the replacement of new pumps/compressors within the context of HENs. Process streams' pressure drops are also optimized in individual processes targeting step. In the next step, the optimized results of individual processes are applied in Total Site targeting to achieve the Total Site optimum point. Then, in the final step, the design of heat exchanger networks is carried out to assess the possibility of achieving targeting results. In the first case study, the Total Annualized Cost of the Total Site optimum point increased by 14% in the new method results compared with the conventional method outcome; however, this parameter decreased by 34% and 3.2% in the second and third case studies, respectively. The results imply that the effect of the three-way trade-off of individual processes in the Total Site level does not have a similar trend. In some cases, pressure drop optimization causes total cost improvement. One of the main reasons for this unspecified trend is the optimization of streams' heat transfer coefficients because of streams' pressure drop optimization that has a significant effect in central utility system area and Total Site cost. In the synthesis step, the energy requirement for three case studies in both methods equal targeted energy values; however, Total Site Central Utility System area results differ from the targeting outcome at the optimum point in both methods. In the first case study, the area of designed TS CUS at the optimum point of conventional and suggested methods are 9% and 6% higher than the targeted values. This parameter in the second case study is 18.5% and 9.6% higher than the targeted value at the optimum point for conventional and suggested methods, respectively. Moreover, the mentioned parameter in the third case study is 9% and 2.4% higher than the targeted values at the optimum point of conventional and suggested methods, correspondingly.

The main reason for the mentioned differences is that in the targeting step, area calculation is carried out by vertical heat transfer in enthalpy blocks of the Total Site profile, while in the synthesis step, there is non-verticality in area calculation. The outcome emphasizes the necessity of performing the suggested modified technique for the Total Site targeting and synthesis stages to have more practical results in the following Total Site Heat Integration stages.

Keywords: Total site integration, Streams optimized pressure drops, Energy and area trading, Total site profile



Study of atomic layer deposition (ALD) method in synthesis of Cr and Ga-based nanocatalysts for dehydrogenation of propane with CO_2

Fatemeh Gashoul

Fall 2016/ Summer 2022
Supervisors: Abbas Ali Khodadadi and Yadollah Mortazavi

Chromium oxide (CrO_x) and gallium oxide (Ga_2O_3) catalysts were deposited with the gas phase sequential and self-limited atomic layer deposition (ALD) method on silica and alumina supports respectively and were used in the propane dehydrogenation reaction to propylene in presence of CO_2 (CO_2-ODHP) at various reaction conditions. The performance of these catalysts was compared with equivalent catalysts synthesized with the conventional impregnation method.

For the synthesis of catalysts with the ALD method, the acetylacetonate of chromium and gallium were used as precursors. In the first step of ALD, Cr and Ga precursors were sublimed using inert gas at a suitable temperature and deposited on silica and alumina support within the appropriate ALD temperature range. This temperature range was achieved to be 200 to 230 and 160 to 240 °C for the ALD of $Cr(acac)_3$ and $Ga(acac)_3$, respectively.

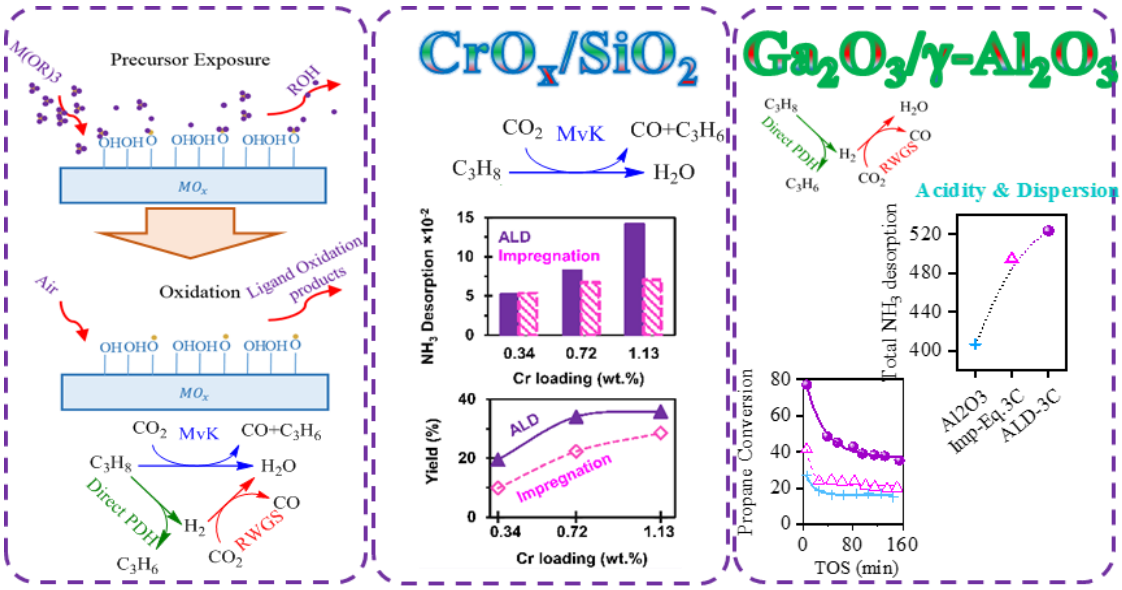
For the structural, chemical and surface characterization of catalysts, Raman spectroscopy, UV-Vis diffuse reflectance (UV-Vis DRS), X-ray diffraction (XRD), inductively coupled plasma-optical emission spectroscopy (ICP-OES), Fourier transform infrared spectroscopy, photoelectron X-ray spectroscopy, X-ray absorption near edge structure (XANES), temperature programmed reduction (TPR), NH_3-temperature programmed desorption, temperature programmed oxidation (TPO), surface area measurement and pore size distribution using BET-BJH method and high resolution transmission electron microscopy imaging equipped with EDS-Mapping were used.

For the silica supported chromium oxide catalysts (CrO_x/SiO_2), Cr weight loading of 0.34, 0.72 and 1.13% were obtained by changing the $Cr(acac)_3$ chemisorption time in the first ALD step. The CO_2-ODHP reaction performance results at TOS of 100 min and temperature of 600 ºC, showed 18% and 15% improvement in propane conversion and propylene selectivity for the best ALD sample with 0.72 wt.% of Cr in comparison to the equivalent impregnation sample. The conversion and yield for this ALD catalyst were 39 and 34%. Based on characterization analyses, it was concluded that the increase in the chromium oxide dispersion, higher NH_3 chemisorption up to 2 times, the higher content of polychromate species and higher reducibility of ALD catalysts in comparison to the impregnation ones were the main reasons for the enhancement of propylene yield.

For the γ-Al_2O_3 supported gallium oxide catalysts (Ga_2O_3/γ-Al_2O_3), Ga weight loading of 1, 2.1 and 2.9 were achieved by changing the ALD cycles from 1 to 3. The reaction performance results showed the improvement of conversion and selectivity of ALD catalysts. When the catalysts came close to stability at 600 ºC, the propane conversion of 32% and the propylene yield of 26% were acquired for the ALD sample with 2.9 wt.% of

Ga. These values were 1.7 and 1.8 times higher than those of attained for the equivalent impregnation catalyst. From the XPS results, the larger shift of Al 2p toward lower binding energies was observed for the ALD catalyst as compared with its equivalent impregnation sample originating from the higher density of Ga-O-Al bonds on the surface structure of ALD catalysts. In all, from the results of characterization experiments, the higher dispersion of Ga_2O_3 and the higher number and the stronger Ga-O-Al surface bonding in ALD catalysts were explicated.

Keywords: Atomic layer deposition, Gallium oxide, Chromium oxide, Propane, Carbon dioxide, Dehydrogenation



Characterizations: XPS, XANES, Raman, UV-Vis DRS, HR-TEM/STEM Mapping, FTIR, Pore Size Distribution, BET, NH_3-TPD, TPO, TPR, XRD

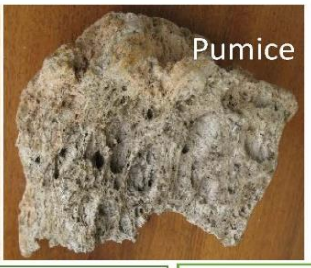
Development of Sustainable Self-healing Cementitious Materials via Microbially Induced Calcium Carbonate Precipitation

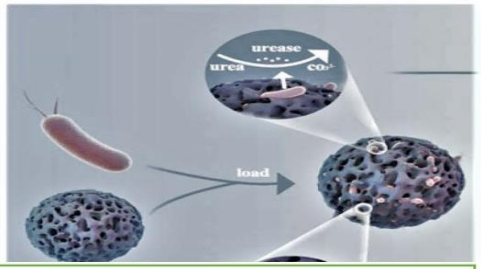
Farshad Farmani

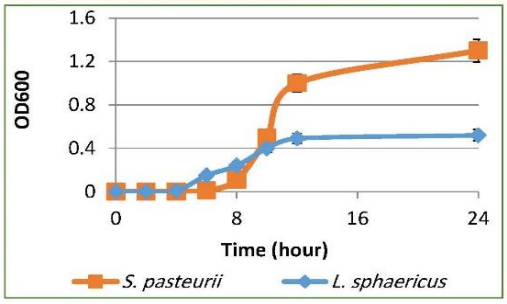
Fall 2014/ Summer 2022
Supervisors: Parissa khadiv-Parsi and Ali Akbar Ramezanianpour
Advisor: Fatemeh Yazdian

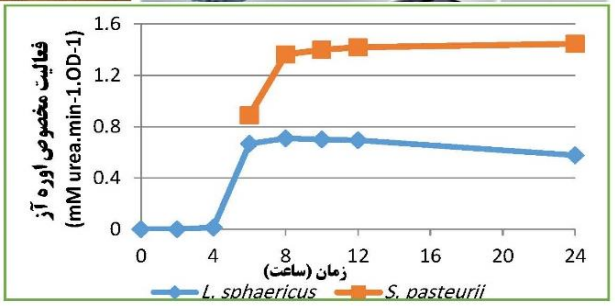
Concrete is the most widely utilized construction material worldwide. Its durability, however, is negatively impacted by its susceptibility to cracking and the penetration of corrosive substances. Additionally, the production of cementitious materials, which is accompanied by the exploitation of natural resources, the enormous consumption of energy reserves, and the emission of greenhouse gases, has very detrimental effects on the environment. Therefore, increasing the durability of these materials will be an effective step toward sustainable development. The partial replacement of cement or natural aggregates with industrial wastes and using microbially-induced carbonate precipitation to heal cracks are two developing methods to make more sustainable concrete. The harsh and highly alkaline environment of cementitious materials is the main challenge for the use of microorganisms as healing agents. In this research, both of the aforementioned methods were used for the development of sustainable self-healing cementitious materials: the partial replacement of natural aggregates with porous aggregates as a new protector for bacterial spores and the use of silica fume, as a relative substitute for cement and a novel idea to create more favorable pH. *Sporosarcina pasteurii* and *Lysinibacillus sphaericus* were selected and compared in terms of growth, enzyme activity, and high pH tolerance. Mortar samples were made with each of the two bacteria, with different cell concentrations, carrier types, and calcium acetate concentrations. *S. pasteurii* with a concentration of $5x10^8$ cells/ml and using scoria as a carrier created optimal conditions with a 25% increase in compressive strength. With the use of healing agents, the results indicated the improvement of flexural and compressive strength by about 13% and 10% in samples without silica fume and 18% and 15% in samples amended with silica fume. The absorption coefficient decreased to 49% for normal samples and 63% for samples with silica fume. This study shows that the use of silica fume and porous aggregates in concrete would improve self-healing mechanisms, lower manufacturing costs, reduce the extraction of energy and natural resources and greenhouse gas emissions, and ultimately result in more sustainable construction.

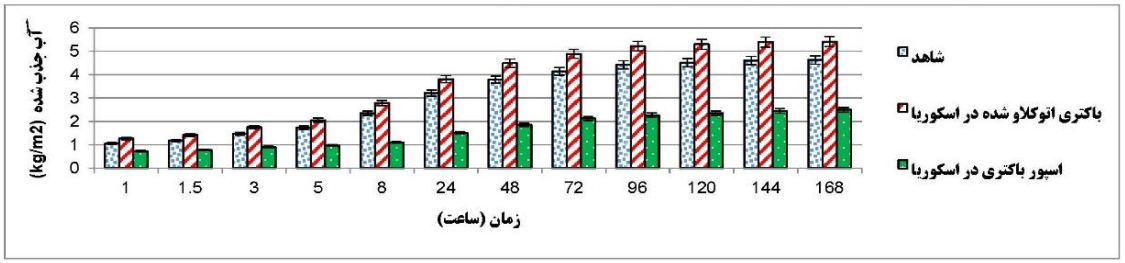
Keywords: Self-healing cementitious materials, Microbially-induced carbonate precipitation, Bio-cement, Concrete durability, Sustainable construction, Microbial concrete

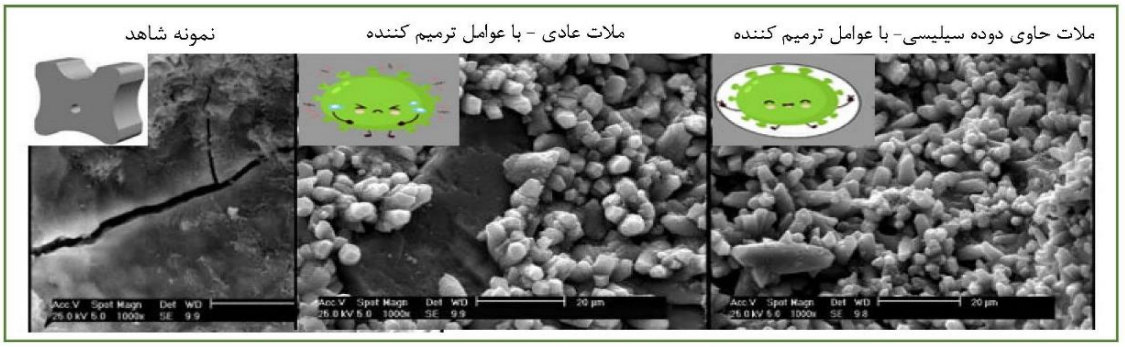




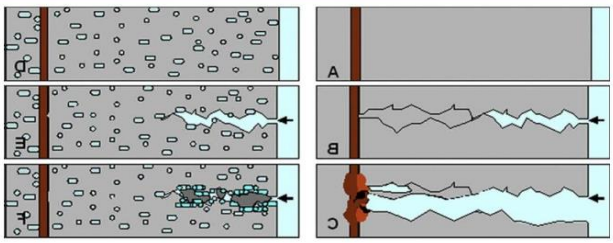








عامل	سطح بهینه
غلظت سلولی (cells/ml)	۵×۱۰^۸
غلظت کلسیم استات (٪)	۵
نوع باکتری	*S. Pasteurii*
سنگ حامل	اسکوریا
مقاومت فشاری (Mpa)	۵۷



Mechanistic Study of Miscible and Near-Miscible Gas Injection in a Matrix Block Under Gravity Drainage

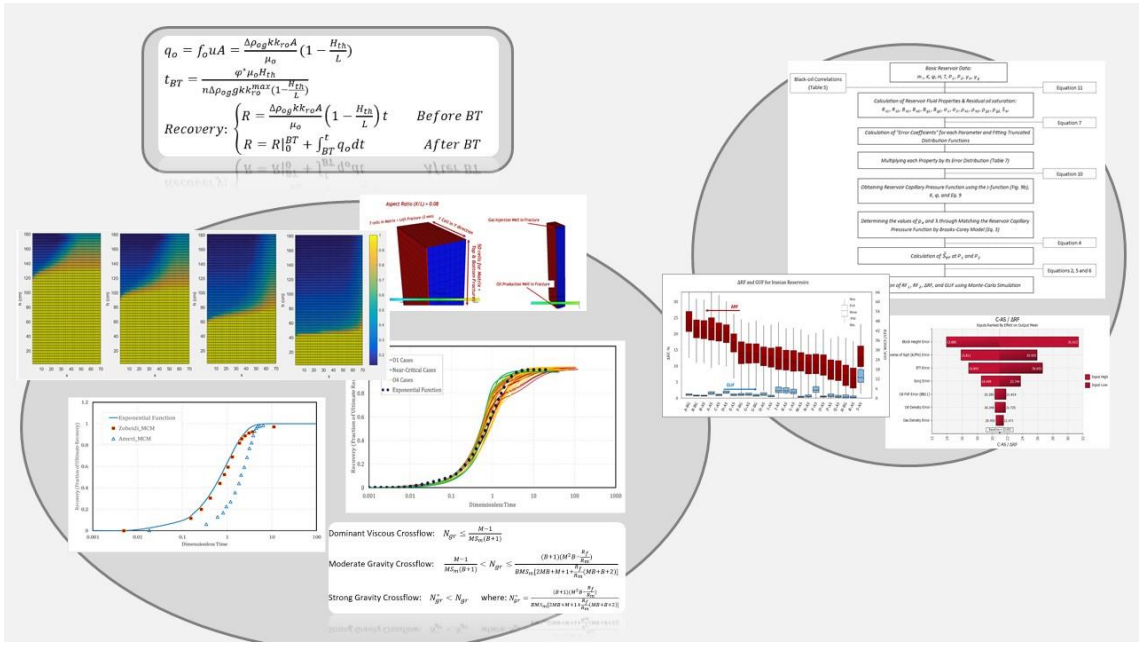
Naeimeh Alimohammadi

Fall 2016/ Summer 2022
Supervisors: Behzad Rostami and Mehran Pooladi-Darvish
Advisor: Maryam Khosravi

Giant Iranian Naturally Fractured Carbonate Reservoirs with low-permeable oil-wet matrix rocks, have low natural depletion recoveries. Producing their remaining oil is one of the crucial challenges in the management of such reservoirs, showing the importance of implementation of enhanced oil recovery techniques, especially gas-based ones in these reservoirs. Despite of the desire to implement gas injection projects to enhance the recovery of gravity drainage in these reservoirs, the availability of gas and the costs associated with these projects are other considerations that require cost-benefit analysis. In this thesis, we have focused on two methods of i) pressurization by immiscible gas injection in reservoir gas cap and ii) rich gas injection. While the latter is known as a method to increase the recovery from the oil column of the reservoir, the former as laboratory studies and field projects have also shown, by improving the recovery of gravity drainage is known as a method to enhance the recovery from the gas-invaded zone. Note that available laboratory data in the literature have shown an average increase of 20% in the recovery factors of gravity drainage with pressurization.

Studies carried out in this thesis on pressurization by immiscible gas injection have concluded to the development of simple relationships to estimate the additional oil recovery by pressurization and, for the first time, to propose a method to screen and rank fractured reservoirs candidate to pressurization and gas injection. Using this approach, we identified six reservoirs out of more than 20 fractured reservoirs in Iran that have the potential to improve oil recovery by more than 20%, in order to conduct more detailed laboratory and modeling studies. In addition, by using the presented PVT study workflow, we have also quantified the range of applicability of the screening method for lean gas injection cases. Mechanistic studies of miscible/near-miscible injection of rich non-equilibrium gas in fractured reservoirs using the numerical simulation carried out in this thesis also led us to a more accurate and comprehensive understanding of the mechanism of gravity drainage of oil from the matrix block in the presence of enriched gas, which finally concluded to an analytical model to estimate the recovery of non-equilibrium condensing-drive gravity drainage. Before this study, primary estimation of gravity drainage recovery in the presence of rich non-equilibrium gas should be done using detailed and time-consuming simulation studies, while the model proposed in this research, which its accuracy has been confirmed using both simulation results and laboratory data from the literature, can be used for preliminary calculations of oil recovery and time-scale in order to screen and identify candidate fractured reservoirs with potential to improve oil recovery by rich gas injection for more comprehensive laboratory and modeling studies. Among other results obtained in this research is the modification to one of the analytical models for gravity drainage available in the literature, resulting to its more accurate results.

Keywords: Naturally Fractured Reservoirs, Gravity Drainage, Pressurization, Miscible Gas Injection, Screening


$q_o = f_o uA = \frac{\Delta\rho_{og} k k_{ro} A}{\mu_o}(1 - \frac{H_{th}}{L})$
$t_{BT} = \frac{\varphi^* \mu_o H_{th}}{n\Delta\rho_{og} g k k_{ro}^{max}(1-\frac{H_{th}}{L})}$
$Recovery: \begin{cases} R = \frac{\Delta\rho_{og} k k_{ro} A}{\mu_o}\left(1 - \frac{H_{th}}{L}\right) t & Before\ BT \\ R = R|_0^{BT} + \int_{BT}^{t} q_o dt & After\ BT \end{cases}$
Aspect Ratio (AR) = 0.08
Gas Injector Well in Fracture
Oil Production Well in Fracture
Basic Reservoir Data:
Black-oil Correlations (Table 3)
Calculation of Reservoir Fluid Properties & Residual oil saturation:
Equation 11
Calculation of "Error Coefficients" for each Parameter and Fitting Truncated Distribution Functions
Equation 7
Multiplying each Property by its Error Distribution (Table 7)
Obtaining Reservoir Capillary Pressure Function using the J-function (Fig. 9b), K, φ, and Eq. 9
Equation 10
Determining the values of p_d and λ through Matching the Reservoir Capillary Pressure Function by Brooks-Corey Model (Eq. 1)
Equation 4
Calculation of $\bar{S}_{wi}$ at P_d and P_b
Equations 2, 5 and 6
ΔRF and GIIP for Iranian Reservoirs
ΔRF
GIIP
C-AS / ΔRF
Equity Human By Effect on Output Mean
Base High
Base Low
Exponential Function
Zobeidi_MCM
Ameri_MCM
Recovery Fraction of Ultimate Recovery
Dimensionless Time
01 Cases
Near-Critical Cases
04 Cases
Exponential Function
Dominant Viscous Crossflow: $N_{gr} \leq \frac{M-1}{M S_{wi}(B+1)}$
Moderate Gravity Crossflow: $\frac{M-1}{M S_{wi}(B+1)} < N_{gr} \leq \frac{(B+1)(M^2B-\frac{N_{\beta}}{N_{Re}})}{BMS_{wi}[2MB+M+1+\frac{N_{\beta}}{N_{Re}}(MB+B+2)]}$
Strong Gravity Crossflow: $N_{gr} < N_{gr}$ where: $N_{gr} = \frac{(B+1)(M^2B-\frac{N_{\beta}}{N_{Re}})}{BMS_{wi}[2MB+M+1+\frac{N_{\beta}}{N_{Re}}(MB+B+2)]}$

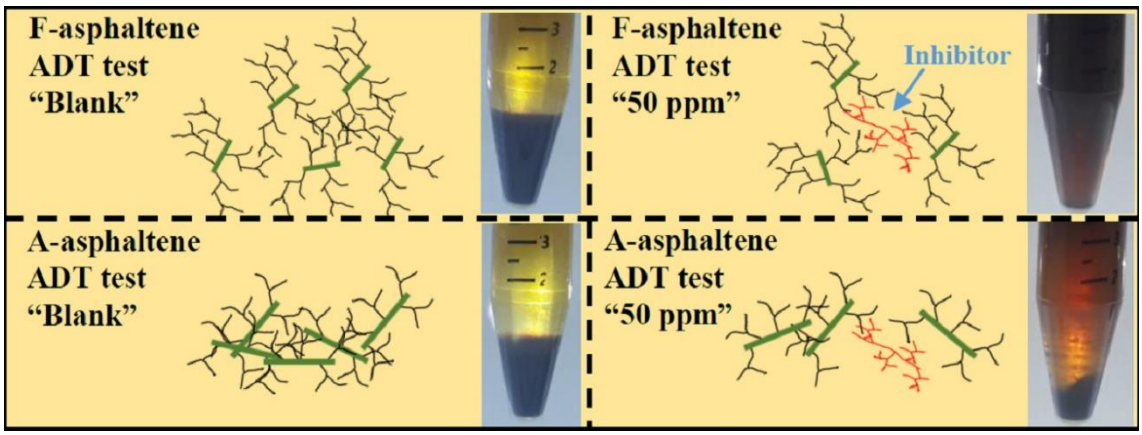
Development, experimental study, and thermodynamic modeling of the performance of carbon-based metal oxide nanostructured asphaltene inhibitors at oil wells conditions

Narges Bahaloo Horeh

Fall 2017/ Winter 2023
Supervisors: Negahdar Hosseinpour and Alireza Bahramian

Asphaltene precipitation and deposition on near wellbore porous media and/or production tubing will lead to serious flow assurance issues during oil production especially from light oil reservoirs. Therefore, design and synthesis of nanostructured materials to inhibit the asphaltene precipitation and deposition are of prime importance. In this work, graphene oxide was synthesized and then undergone simultaneous functionalization, by alkylamine groups, and partial reduction. The reduced graphene oxide (alkylated rGO) becomes dispersed and stabilized in organic phases via the peripheral alkylamine chains. The alkylated-rGO was loaded with nickel/iron oxide/hydroxide to improve their tendency for interaction with asphaltene. Two dead oil samples were received form two Iranian oil reservoirs with severe asphaltene damage in the field. Asphaltene was extracted from the oil samples and characterized well by advanced techniques. Asphaltene dispersant test (ADT), asphaltene deposition in Couette-Taylor flow conditions, and interfacial tests including dynamic interfacial tension (IFT), interfacial elasticity, and standard deviation from the Young-Laplace drop shape (YL-STD) were employed to evaluate the efficiency of the nanomaterials as asphaltene inhibitors. It is found that the alkylated-rGO nanostructures show high efficiencies for asphaltene stabilization and thus precipitation/deposition control. The inhibitors efficiency improves by the loading of the metal oxide/hydroxides. Loading of 10 wt% nickel oxide/hydroxide on the alkylated-rGO results in the efficiency of 94% at the harsh conditions of the ADT test. The efficiency of the inhibitors depends on not only the molecular structure and functional groups of the inhibitor itself but also the functional group, molecular structure, and molecular configuration of the asphaltenes in the asphaltene aggregates. The asphaltene deposition test in Couette-Taylor flow confirms the efficiency of the inhibitors for not only the asphaltene precipitation control but also the asphaltene deposition. The IFT and YL-STD values decreases in the presence of the inhibitors, indicating there is no rigid interfacial asphaltenic film. This may imply that the inhibitors control the asphaltene self-association and networking in the interface. Thermodynamic modeling of the asphaltene precipitation by CPA EoS reveals that the asphaltene with a larger aromatic sheet size and shorter peripheral chains exhibit a lower association energy when compared to those with smaller aromatic polycyclic sheet and longer peripheral chains. The asphaltene association energy increases by the inhibitors, making the asphaltene precipitation conditions more difficult.

Keywords: Asphaltene, Deposition, Flow assurance, Asphaltene inhibitor, alkylated graphene oxide, CPA.


F-asphaltene
ADT test
“Blank”
F-asphaltene
ADT test
“50 ppm”
Inhibitor
A-asphaltene
ADT test
“Blank”
A-asphaltene
ADT test
“50 ppm”