

MTP STAGE-II Presentation

Modeling and Simulation of an Isomerization Reactor using OpenModelica

Venkata Sai Pavan Chetan Annam
203020008

under the guidance of
Kannan Moudgalya,
Sanjay M. Mahajani.

Department of Chemical Engineering,
Indian Institute of Technology, Bombay.

June 27, 2022



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- 2 Isomerization Unit
- 3 Vapor Phase Reactor Model
- 4 Modeling Results
- 5 COBYLA
- 6 Interoperability
- 7 Optimization of Vapor Phase Reactor Model
- 8 Liquid phase Reactor Simulation

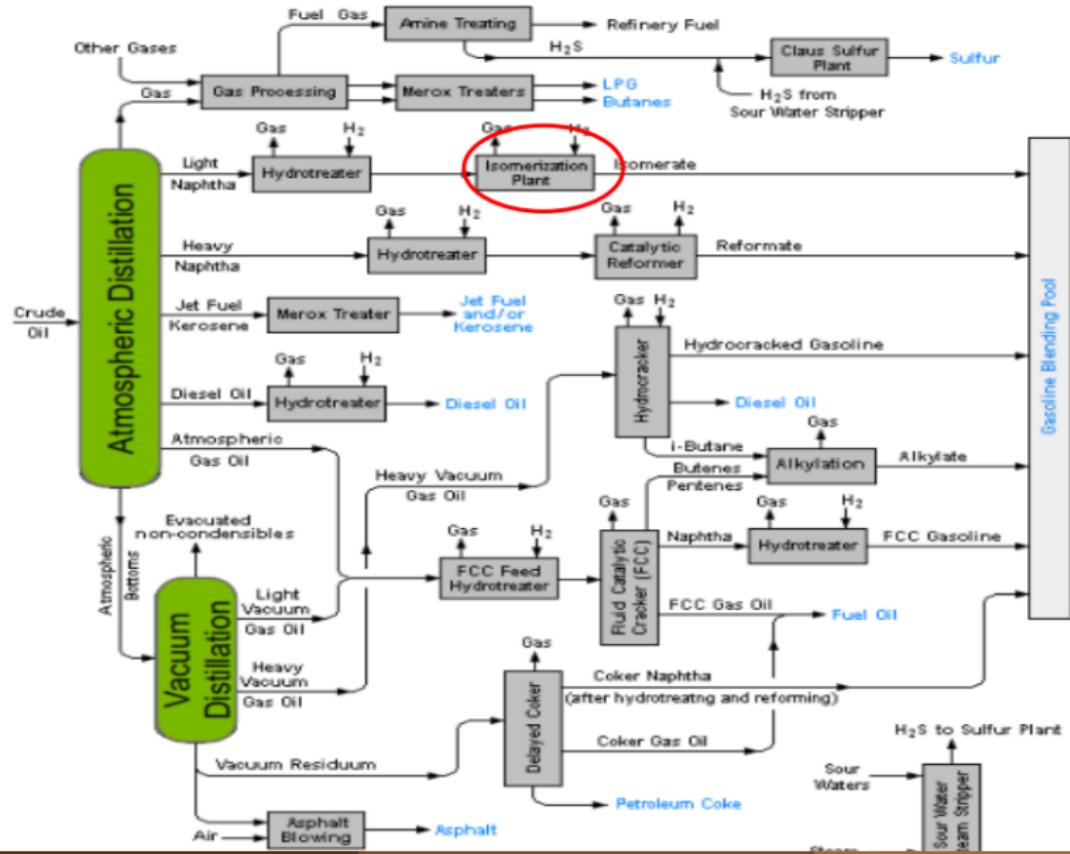


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Background



Background

① What is an Isomerization unit?

- Processing one of the streams of CDU called Light Naphtha.
- To convert LN to high octane numbered fuel.
- Also to remove benzene content.

② Motivation

- PSUs approached Centre of Oil, Gas and Energy, IIT Bombay.
- Commercial packages are expensive.
- Government approvals are required and it takes time

③ Objective

- Build an ISOM model using OpenModelica.
- Integrating the OM model with Optimizer.
- Validating with some plant data.



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- **Feed Characterization**
- **Chemistry**
- **Catalysts**
- **Thermodynamics**
- **Operating conditions**
- **Performance parameters**
- **Flowsheets**



Feed Characterization

Table showing the typical composition of the Light Naphtha stream (Prof. Garg-class notes)

Component	%wt Light Naphtha	%wt Isomerate	Octane number
C4-	0.4	1.8	98
Isopentane	21.6	34.9	92.3
n-pentane	26.5	14.0	61.7
Cyclopentane	1.4	1.4	101.6
2,2DMB	0.9	13.4	91.8
2,3DMB	2.2	4.6	100.5
2-methylpentane	13.1	13.7	73.4
3-methylpentane	10.2	7.8	74.5
n-hexane	18.6	5.1	24.8
Methylcyclopentane	2.8	0.6	81.7
Cyclohexane	0.4	1.4	79.6
Benzene	1.9	0	101
C7+	0	0.3	0



Four types of reactions happen in the ISOM unit:

- Isomerization reaction
- Benzene saturation
- Ring Opening of naphthenes
- Hydro cracking reactions



Reactions

Reactions considered in this work (enikeeva et al.,2021)

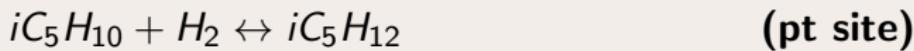
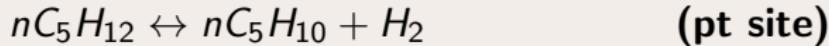
No	Reaction	E, kJ/mol	lg(k ₀)	No	Reaction	E, kJ/mol	lg(k ₀)
1	n-C ₅ H ₁₂ →iso-C ₅ H ₁₂	148.93	15.74	28	MCP+H ₂ →2-MP	129.29	8.31
2	iso-C ₅ H ₁₂ →n-C ₅ H ₁₂	154.28	15.92	29	3-MP→MCP+H ₂	154.54	14.86
3	n-C ₆ H ₁₄ →2-MP	143.17	7.59	30	MCP+H ₂ →3-MP	98.63	10.18
4	2-MP→n-C ₆ H ₁₄	151.41	7.68	31	2,2-DMP→MCP+H ₂	150.29	13.80
5	n-C ₆ H ₁₄ →3-MP	150.98	18.08	32	MCP+H ₂ →2,2-DMB	102.35	6.99
6	3-MP→n-C ₆ H ₁₄	155.92	18.53	33	2,3-DMB→MCP+H ₂	168.13	11.36
7	2-MP→3-MP	152.96	16.19	34	MCP+H ₂ →2,3-DMB	90.70	6.00
8	3-MP→2-MP	149.95	16.19	35	CP+H ₂ →n-C ₅ H ₁₂	177.32	20.89
9	2-MP→2,2- DMB	127.28	11.46	36	n-C ₅ H ₁₂ →CP+H ₂	222.90	10.85
10	2,2- DMB→2-MP	139.07	12.91	37	n-C ₄ H ₁₀ →iso-C ₄ H ₁₀	59.80	12.71
11	2-MP→2,3- DMB	64.50	5.06	38	iso-C ₄ H ₁₀ →n-C ₄ H ₁₀	54.08	11.51
12	2,3-DMB→2-MP	77.06	6.97	39	n-C ₅ H ₁₂ +H ₂ →C ₃ H ₈ +C ₂ H ₆	330.28	10.48
13	3-MP→2,2-DMB	146.14	10.68	40	n-C ₅ H ₁₂ +H ₂ →n-C ₄ H ₁₀ +CH ₄	329.06	25.18
14	2,2-DMB→3-MP	160.28	11.82	41	iso-C ₅ H ₁₂ +H ₂ →iso-C ₄ H ₁₀ +CH ₄	284.97	30.17
15	3-MP→2,3-DMB	98.28	9.65	42	n-C ₆ H ₁₄ +H ₂ →2 C ₃ H ₈	166.32	10.24
16	2,3-DMB→3-MP	105.40	10.65	43	n-C ₆ H ₁₄ +H ₂ →n-C ₅ H ₁₂ +CH ₄	165.82	10.30
17	2,2-DMB→2,3-DMB	3.51	3.40	44	n-C ₆ H ₁₄ +H ₂ →n-C ₄ H ₁₀ +C ₂ H ₆	112.05	9.80
18	2,3-DMB→2,2-DMB	4.79	3.93	45	2-MP+H ₂ →iso-C ₄ H ₁₀ +C ₂ H ₆	265.00	24.85
19	B + 3H ₂ →CH* (cyclohexane)	180.20	30.47	46	2-MP+H ₂ →iso-C ₅ H ₁₂ +CH ₄	264.00	12.85
20	CH* (cyclohexane)→B + 3H ₂	400.43	23.00	47	2-MP+H ₂ →n-C ₅ H ₁₂ +CH ₄	263.50	24.85
21	B + 3H ₂ →MCP	187.05	26.46	48	2-MP+H ₂ →2 C ₃ H ₈	265.00	26.93
22	MCP→B + 3H ₂	300.79	25.00	49	3-MP+H ₂ →iso-C ₅ H ₁₂ +CH ₄	295.62	30.65
23	CH* (cyclohexane)→MCP	51.08	3.164	50	3-MP+H ₂ →n-C ₄ H ₁₀ +C ₂ H ₆	295.00	4.47
24	MCP→CH* (cyclohexane)	341.89	2.80	51	3-MP+H ₂ →n-C ₅ H ₁₂ +CH ₄	295.19	4.90
25	n-C ₆ H ₁₄ →CH (cyclohexane*)+H ₂	129.75	9.87	52	2,2-DMB+H ₂ →iso-C ₅ H ₁₂ +CH ₄	294.00	4.40
26	CH* (cyclohexane)+H ₂ →n-C ₆ H ₁₄	88.64	6.83	53	2,2-DMB+H ₂ →iso-C ₄ H ₁₀ +C ₂ H ₆	274.22	27.83

Chemistry

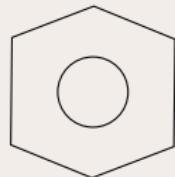
Isomerization Reaction



Mechanism:

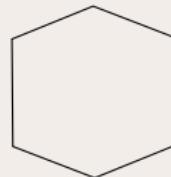


Benzene saturation



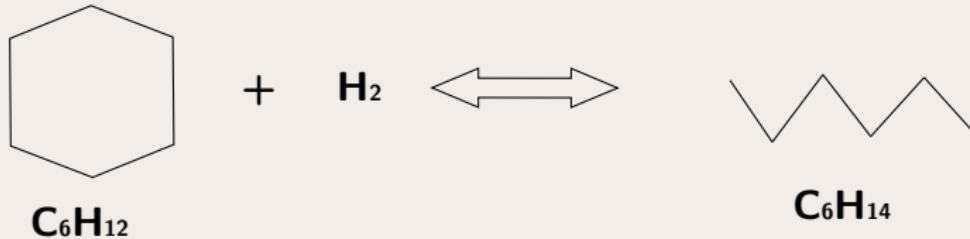
+

$3H_2$

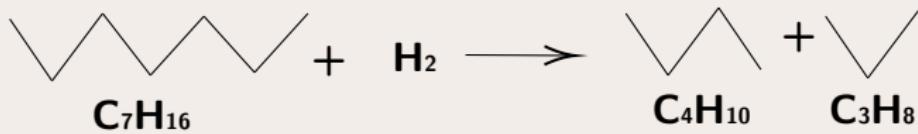


Chemistry

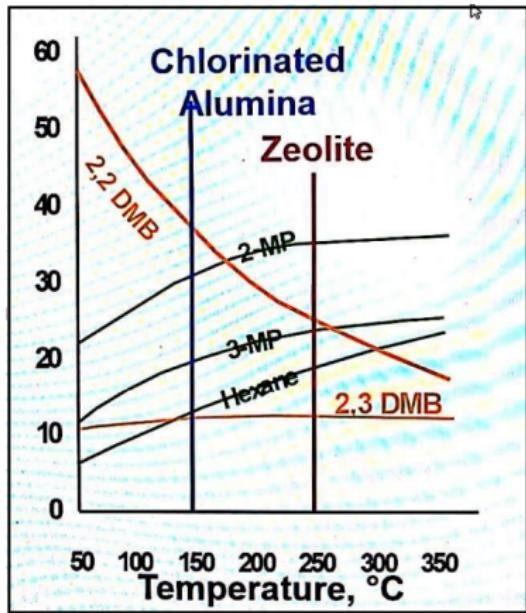
Ring Opening of Naphthenes



Hydrocracking reactions



Thermodynamics



- Effect of Temperature
- Pressure effect
- Low concentration of components

Effect of Temperature upon the yield
(Prof. Garg-class notes)



Catalysts

**Table showing the properties of catalysts used in the ISOM unit
(valvarasu et al., 2013)**

Catalyst	Advantages	Disadvantages
Chloride alumina	Highest RON, Highest Activity, Highest yield.	Continuous Chloride addition is necessary, Sensitive to poisons.
Zeolite type	Regenerable, Highest stability, Can tolerate poisons	Lowest activity
Sulfated Zirconia	Posses intermediate activity, Tolerant to poisons, Regenerable	Requires higher H ₂ /HC ratio.



Operating Conditions

**Table showing the typical operating conditions
(Valvarasu et al., 2013)**

Process Parameter	Chlorinate Alumina	Zeolites	Sulfated Zirconia
Temperature, ($^{\circ}\text{C}$)	130-150	250-280	180-210
Pressure, barg	15-35	15-35	15-35
LHSV, (hr^{-1})	1.0-3.0	1.0-3.0	1.0-3.0
H ₂ /HC (mole)	1.0-2.0	1.0-20	1.0-2.0



Performance Parameters

Product ISO ratios

$$\frac{\frac{\frac{wt\% \ iC5}{wt\% \ iC5 + wt\% \ nC5}}{wt\% \ 22DMB} + \frac{wt\% \ 23DMB}{wt\% \ nC6 + wt\% \ 2MP + wt\% \ 3MP + wt\% \ 22DMB + wt\% \ 33DMB}}{wt\% \ nC6 + wt\% \ 2MP + wt\% \ 3MP + wt\% \ 22DMB + wt\% \ 33DMB}$$

Paraffin Isomerization

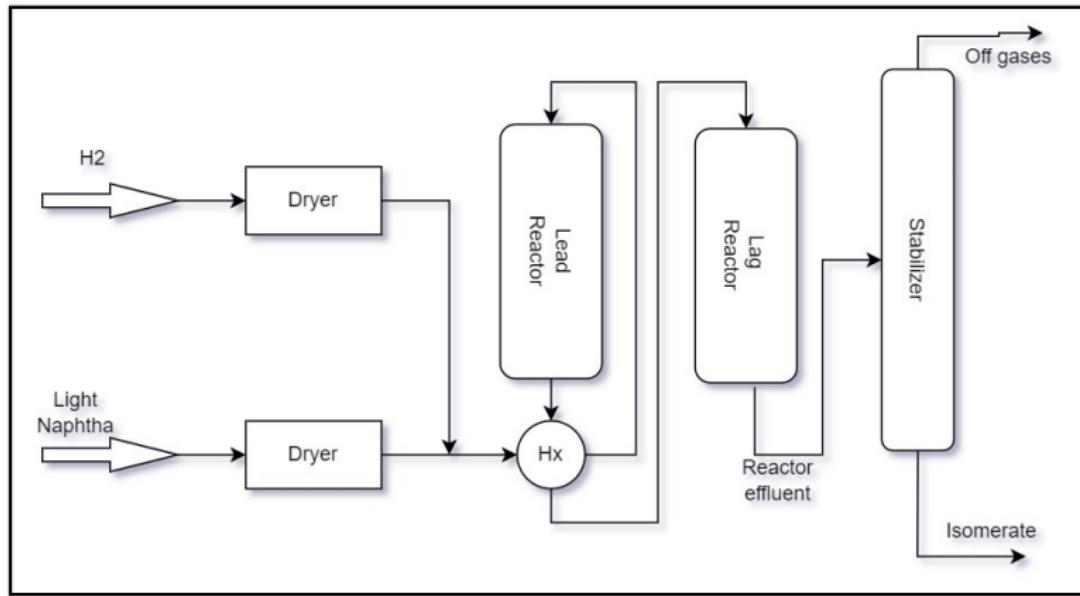
$$PIN = (iC5 + 22DMB + 23DMB) \text{Product ISO ratios}$$

Octane number

$$RON = \sum_i y_i RON_i$$



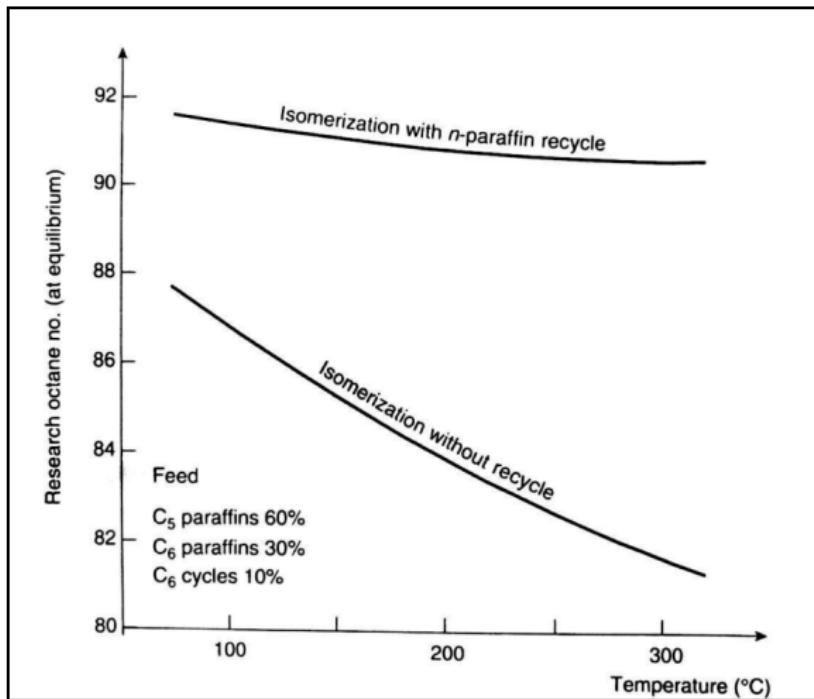
Once Through Process



Flowsheet showing the Once Through process (Prof. Garg-class notes)



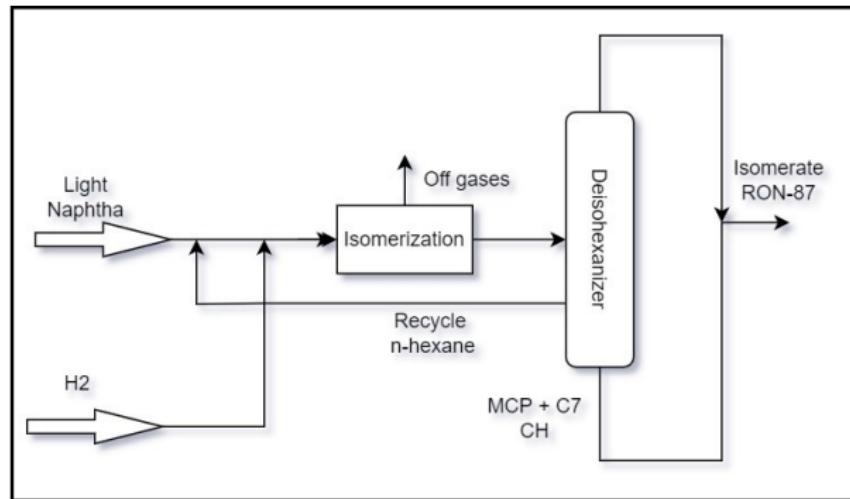
Recycle effect



Effect of recycle upon the Isomerate octane number (Prof. Garg-class notes).



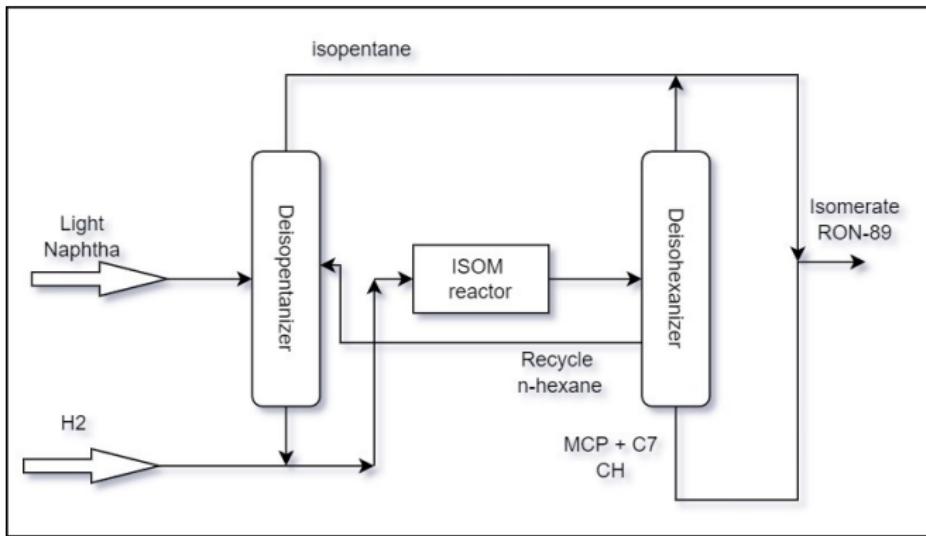
Deisohexanizer



Isomerization unit containing the Deisohexanizer (Prof. Garg- class notes).



Deisopentanizer



Isomerization unit installed with the Deisopentanizer and the Deisohexanizer (Prof. Garg-class notes).



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OM Model

Balances

$$\frac{dC_i}{d\tau} = \sum_{i=1}^{17} \sum_{j=1}^{54} v_{ij} r_j$$

$$\tau = V/S$$

$$\frac{dC_i}{dV} = \frac{1}{S} \sum_{i=1}^{17} \sum_{j=1}^{54} v_{ij} r_j$$

$$\frac{dC_i}{dL} = \frac{ACS}{S} \sum_{i=1}^{17} \sum_{j=1}^{54} v_{ij} r_j$$

$$\frac{dT}{dL} = \frac{ACS}{S} \frac{\sum_{j=1}^{j=54} Q_j r_j}{Ca_m C_{Pm}}$$

$$r_j = K_j C_{HC}^a C_{H2}^b$$

Units

Ca_i - conc. of component i
($kmol/m^3$)

τ - residence time (hr)

r_j - rate of reaction j ($\frac{mol}{m^3 hr}$)

v_{ij} -stoichiometric coefficients

T - temperature (K)

Q_j - heat of j^{th} reaction (kJ/kmol)

S - volumetric flowrate of reaction mixture (m^3/hr)

Ca_m - concentration of the reaction mixture

Cp_m - heat capacity of the reaction mixture (kJ/kmol ${}^\circ K$)

Importance of K_j

Vapor Phase Model

$$r = \eta * k * C_a$$

$$r = K * C_a$$

$$K = K_0 \times \exp\left(-\frac{E_a}{RT}\right)$$

Conversion of Literature
Parameters into the Required
form

$$K' \rightarrow \frac{kmol}{kg - cat.hr}$$

$$K = K' \times \frac{\rho_{cat}}{\phi} \times C_a$$

$$K \rightarrow \frac{kmol}{kg - cat.hr} \times \frac{kg - cat}{m^3} \times \frac{m^3}{kmol}$$

$$K \rightarrow 1/hr$$



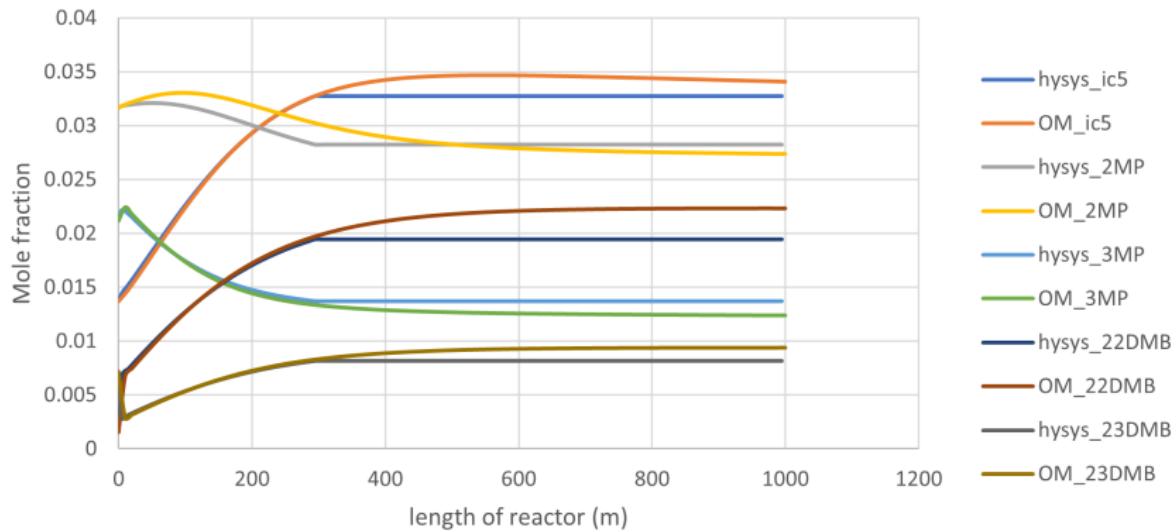
A software based on Modelica language. Some of its features are (Fritzson, 2013):

- **Acasual Modeling**
- **Object Oriented**
- **Multidomain Modeling Capability**
- **Graphical**



Comparison with Aspen-Hysys PFR model

Variation of mole fraction of value added components across reactor length



Performance of OM model in comparison with Aspen-Hysys PFR model



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Block Diagram

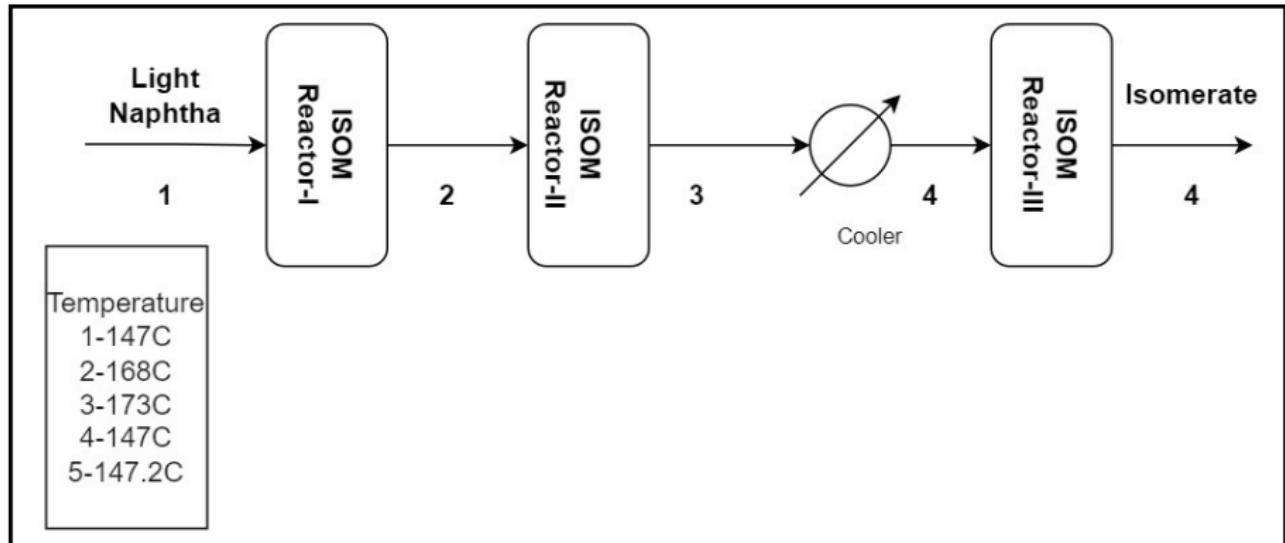


Figure showing the schema of reactors arranged in Enikeeva et al. 2021



Simulation Results using vapor phase model

Table showing the Design parameters

S.No.	Design parameter	value
1	weight of catalyst (kg)	27000
2	density of catalyst (kg/m ³)	2500
3	Area of cross section of reactor (m ²)	4.9
4	length of the reactor (m)	2.19
5	void fraction (ϕ)	0.5

Table showing the operating conditions of the Light Naphta entering the reactor
(enikeeva et al.,2021)

S.No.	Operating parameter	value
1	Temperature (°C)	147
2	Pressure (kPa)	3200
3	Flow rate (kmol/hr)	5653



Simulation Results using vapor phase model

Table showing the kinetic parameters to run the vapor phase model (enikeeva et al., 2021)

rxn	k0 (1/hr)	Ej (kJ/mol)	rxn	k0 (1/hr)	Ej (kJ/mo)
1	2.7477E+19	148.93	28	1.02087E+12	129.29
2	4.15882E+19	154.28	29	3.62218E+18	154.54
3	1.94523E+11	143.17	30	7.56781E+13	98.63
4	2.39315E+11	151.41	31	3.15479E+17	150.29
5	6.01132E+21	150.98	32	48861861048	102.35
6	1.69422E+22	155.92	33	1.14543E+15	168.13
7	7.74408E+19	152.96	34	50000000000	90.7
8	7.74408E+19	149.95	35	3.88124E+24	177.32
9	1.44202E+15	127.28	36	3.53973E+14	222.9
10	4.06415E+16	139.07	37	2.56431E+16	59.8
11	574076810.7	64.5	38	1.61797E+15	54.08
12	46662715040	77.06	39	1.50998E+14	330.28
13	2.39315E+14	146.14	40	7.56781E+28	329.06
14	3.30347E+15	160.28	41	7.39554E+33	284.97
15	2.23342E+13	98.28	42	8.689E+13	166.32
16	2.23342E+14	105.4	43	9.97631E+13	165.82
17	12559432.16	3.51	44	3.15479E+13	112.05
18	42556901.91	4.79	45	3.53973E+28	265
19	1.4756E+34	180.2	46	3.53973E+16	264
20	5E+26	400.43	47	3.53973E+28	263.5
21	1.44202E+30	187.05	48	4.25569E+30	265
22	5E+28	300.79	49	2.23342E+34	295.62
23	7294071.301	51.08	50	147560461.3	295
24	3154786.722	341.89	51	397164117.4	295.19
25	3.70655E+13	129.75	52	125594321.6	294
26	33804148770	88.64	53	3.38041E+31	294.22
27	7.39554E+16	135.45	54	3.45915E+23	278.81



Simulation Results using vapor phase model

Table showing the composition of Light Naphtha entering the stream

S.No.	Component	Mass Fraction	Mole Fraction
1	n-Pentane	0.161843	0.0344
2	i-Pentane	5.54E-02	0.01178
3	n-Hexane	0.168385	0.0299
4	2-Mpentane	0.186026	0.0331
5	3-Mpentane	0.145986	0.0259
6	22-Mbutane	6.94E-03	0.0123
7	23-Mbutane	3.75E-02	0.0067
8	Benzene	1.05E-02	0.00148
9	Cyclohexane	8.13E-03	0.0020
10	Hydrogen	0.105748	0.8048
11	Mcyclopentan	5.17E-02	0.0091
12	Cyclopentane	1.10E-02	0.0024
13	n-Butane	9.91E-04	0.0003
14	i-Butane	3.47E-03	0.001
15	Propane	6.14E-03	0.0021
16	Ethane	1.16E-02	0.0059
17	Methane	2.86E-02	0.0027



Simulation results using vapor phase model

Worksheet			
Worksheet	Stream Name	enikeeva-2	Vapour Phase
Conditions	Vapour / Phase Fraction	1.0000	1.0000
Properties	Temperature [C]	147.0	147.0
Composition	Pressure [kPa]	3200	3200
Oil & Gas Feed	Molar Flow [kgmole/h]	5653	5653
Petroleum Assay	Mass Flow [kg/h]	8.674e+004	8.674e+004
K Value	Std Ideal Liq Vol Flow [m3/h]	254.7	254.7
User Variables	Molar Enthalpy [kJ/kgmole]	-2.187e+004	-2.187e+004
Notes	Molar Entropy [kJ/kgmole-C]	115.0	115.0
Cost Parameters	Heat Flow [kJ/h]	-1.236e+008	-1.236e+008
Normalized Yields	Liq Vol Flow @Std Cond [m3/h]	1.335e+005	1.335e+005
Emissions	Fluid Package	Basis-T	
	Utility Type		

Screenshot from Aspen-Hysys showing the phase of Light Naphtha.



Simulation Results using vapor phase model

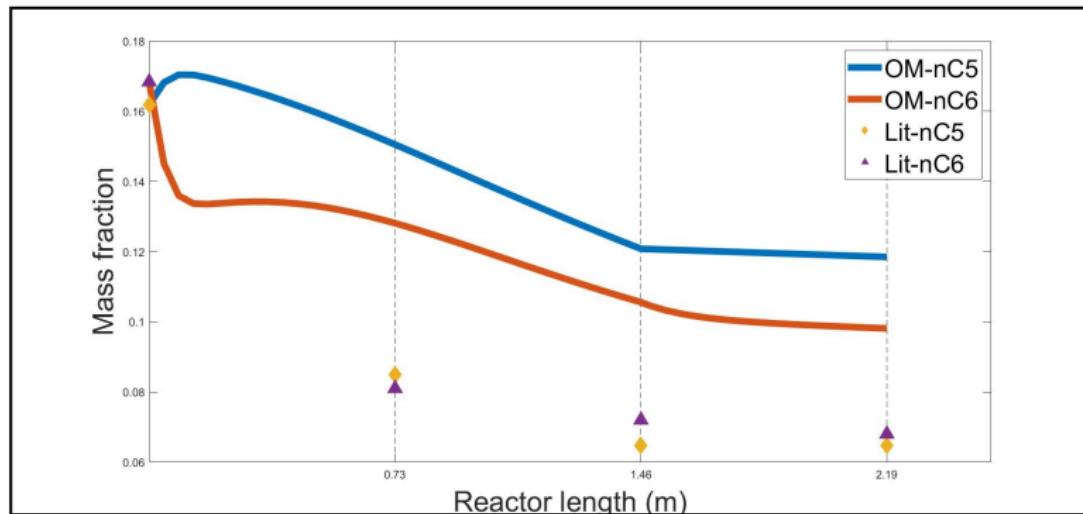


Figure showing the concentration profiles of nC5 and nC6 components along the reactor length.



Simulation Results using vapor phase model

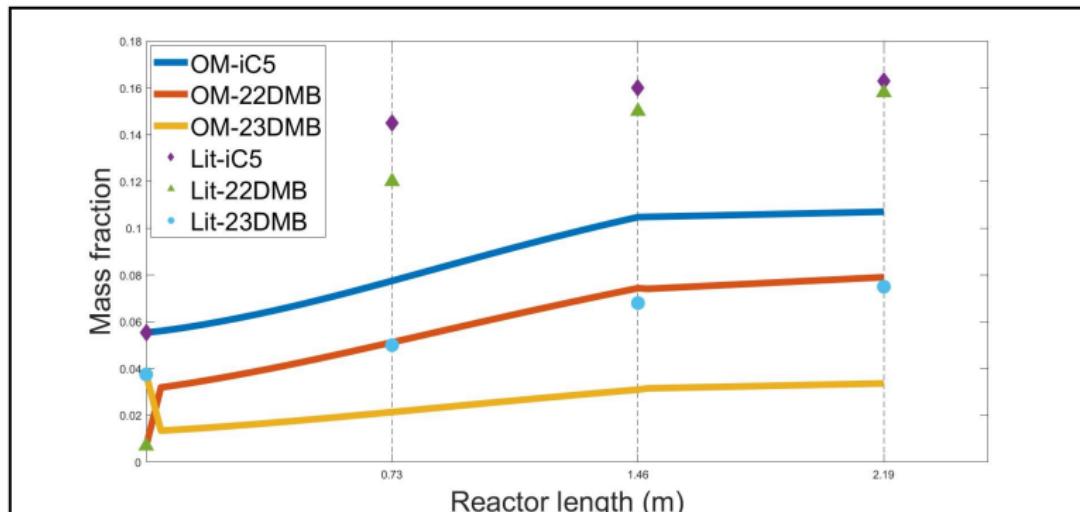


Figure showing the concentration profiles of high octane numbered components along the reactor length



Simulation Results using vapor phase model

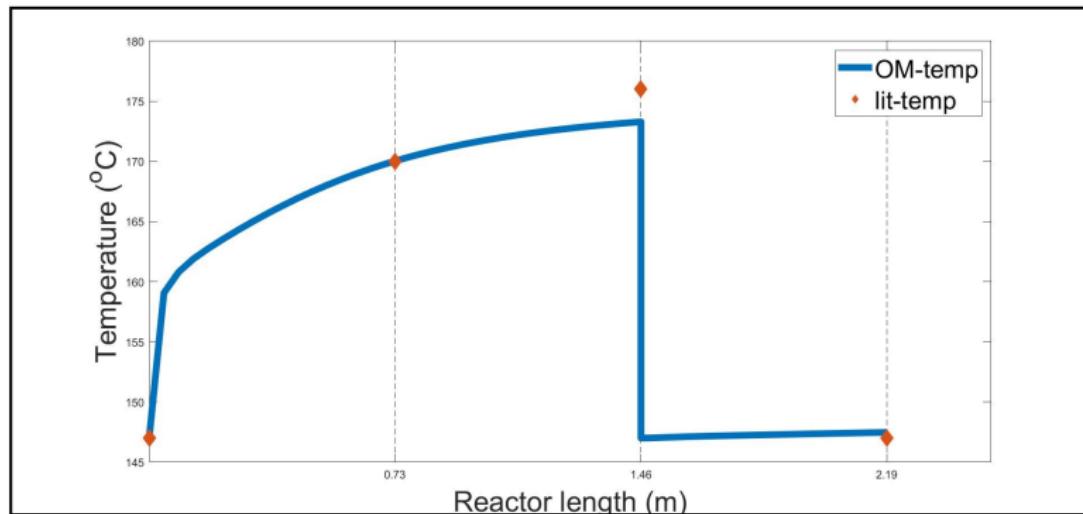


Figure showing the concentration profiles of high octane numbered components along the reactor length



Simulation Results using vapor phase model

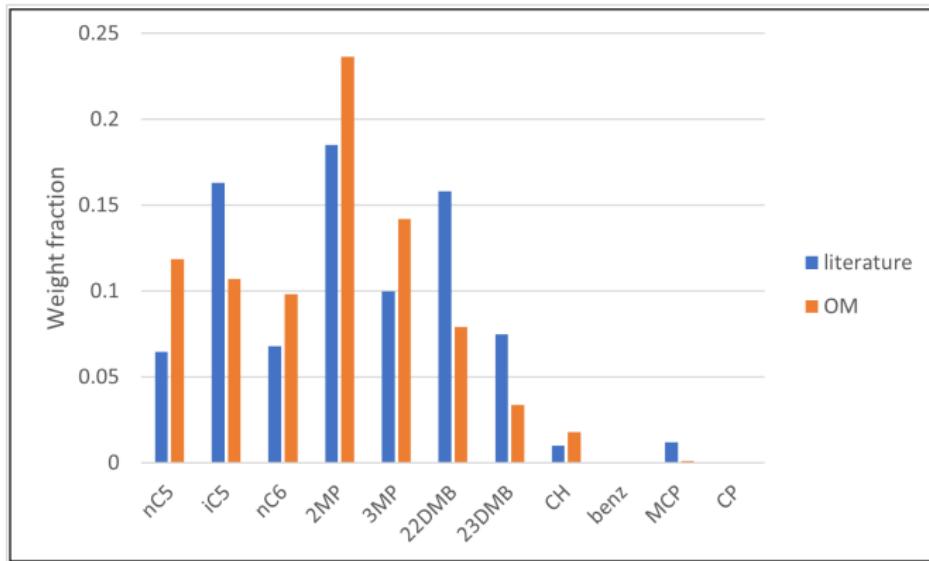


Figure showing the comparison of outlet compositions from (enikeeva et al.,2021) and OM model



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Optimization

- Functional Based optimizer Vs Derivative based optimizer.
- Objective function is not a smooth function.
- No question of gradient.
- COBYLA is chosen in this work which is a functional based optimizer.



Working of Optimization

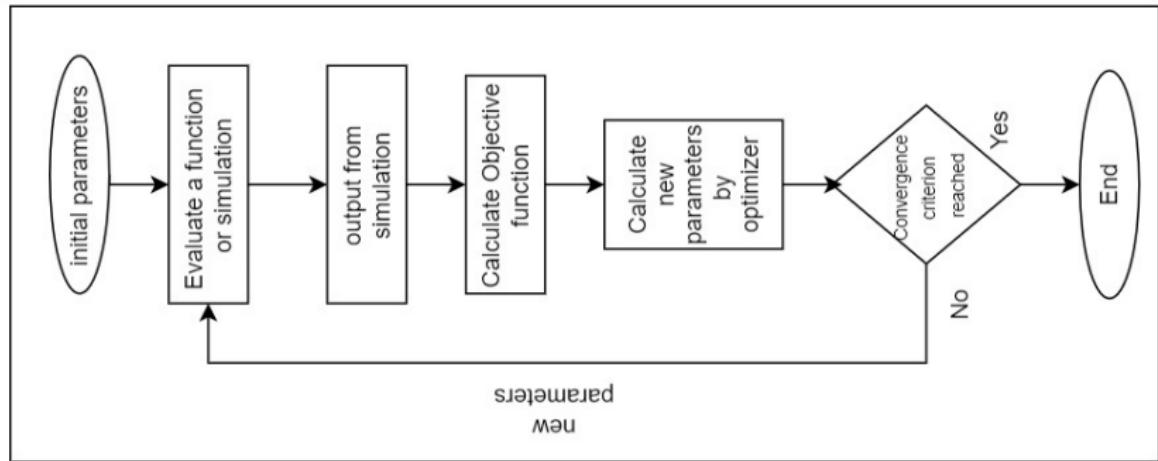


Figure showing the working of a typical optimizer



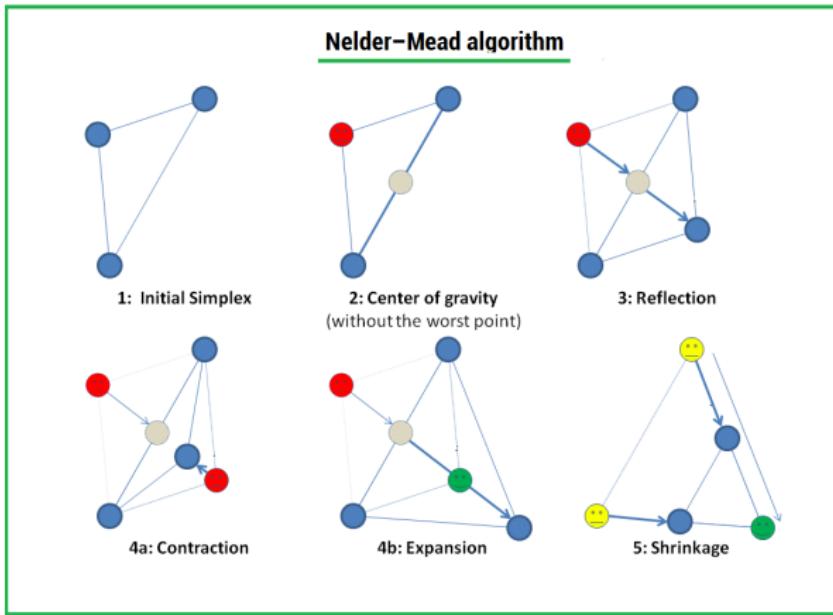


Figure showing the working of Nelder and Mead optimization algorithm¹

¹<https://sudonull.com/post/69185-Nelder-Mead-optimization-method-Python-implementation-example>



COBYLA

- **Objective Function**

$$\text{minimize } F(\bar{x}), \bar{x} \in \mathbb{R}^n$$

subject to $C_i(\bar{x}) \geq 0, i = 1, 2, 3, \dots m$

- **Objective Function of COBYLA**

$$\text{minimize } \hat{F}(\bar{x}), \bar{x} \in \mathbb{R}^n$$

subject to $\hat{C}_i(\bar{x}) \geq 0, i = 1, 2, 3, \dots m$

- A trust region is imposed to have some control over the steps taken by the algorithm. This trust-region remains constant until predicted steps improve the objective function and feasibility conditions fail to occur.
- To compare the goodness of two vectors, a merit function is employed.

$$\phi(\bar{x}) = F(\bar{x}) + \mu [\max \{-C_i(\bar{x}) : i = 1, 2, 3, \dots m\}]_+$$



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OM Script file (External.mos)

```
External.mos  isom101 case14380.atslv  External.mos  ISOM.mo  External.mos
1 loadFile("ISOM.mo"); getErrorString();
2 loadFile("Chemsep_Database.mo");getErrorString();
3 loadFile("Functions.mo");getErrorString();
4 simulate(ISOM.hysys_comparision, numberOfIntervals=100, stopTime=15.92,
5 outputFormat="csv");getErrorString();
```

Figure showing the script file of OpenModelica.



Command Line

```
C:\WINDOWS\system32\cmd.exe
 63 File(s)   43,546,672 bytes
  1 Dir(s)  88,210,638,784 bytes free

C:\Users\pavan\Desktop\ISOM\hysys>omc External.mos
true
"
true
"
true
"
record SimulationResult
    resultFile = "C:/Users/pavan/Desktop/ISOM/hysys_ISOM_hysys_comparision_res.csv",
    simulationOptions = "startTime = 0.0, stopTime = 15.92, numberOfIntervals = 100, tolerance = 1e-06, method = 'dassl', fileNamePrefix = 'ISOM.hysys_comparision', options
= ''", outputFormat = "'csv'", variableFilter = "'.", cFlags = '', simFlags = '',
    messages = "LOG_SUCCESS | info | The initialization finished successfully without homotopy method.
LOG_SUCCESS | info | The simulation finished successfully.
"
    timeFrontend = 0.0779769,
    timeBackend = 0.9256891,
    timeSimCode = 0.2342164,
    timeTemplates = 0.1948585,
    timeCompile = 8.1045172,
    timeSimulation = 2.199585,
    timeTotal = 11.677305
end SimulationResult;
"[C:/OM118/OM64bit/OMCompiler/Compiler/NFFrontEnd/NFUnit.mo:883:7-883:68:writeable] Error: Internal error function lexer failed
"

C:\Users\pavan\Desktop\ISOM\hysys>isom.hysys_comparision.exe
LOG_SUCCESS | info | The initialization finished successfully without homotopy method.
LOG_SUCCESS | info | The simulation finished successfully.

C:\Users\pavan\Desktop\ISOM\hysys>isom.hysys_comparision.exe -override=E[1]=150
LOG_SUCCESS | info | The initialization finished successfully without homotopy method.
LOG_SUCCESS | info | The simulation finished successfully.

C:\Users\pavan\Desktop\ISOM\hysys>
```

Figure showing the basic operations of OM through command line.



Files Generated

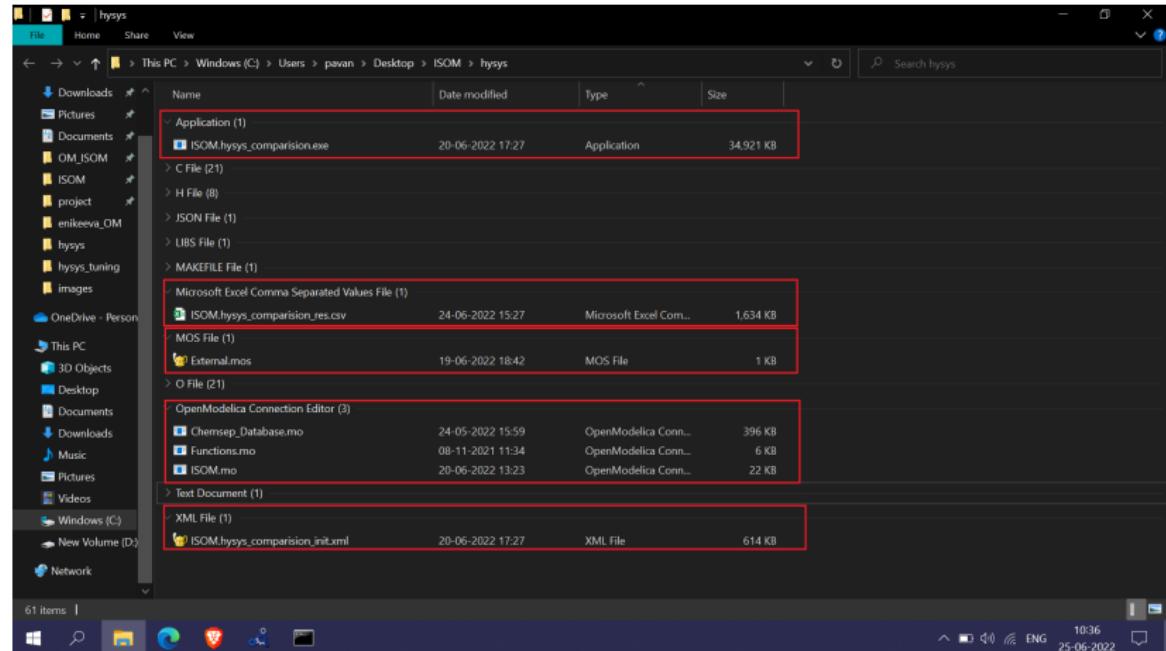


Figure showing the files generated when a script file is executed.



R-language

- **system(paste0("isom.hysys_comparision.exe"))**
- **system(paste0("isom.hysys_comparision.exe
-override=E[1]=",k[1]))**



Interoperability

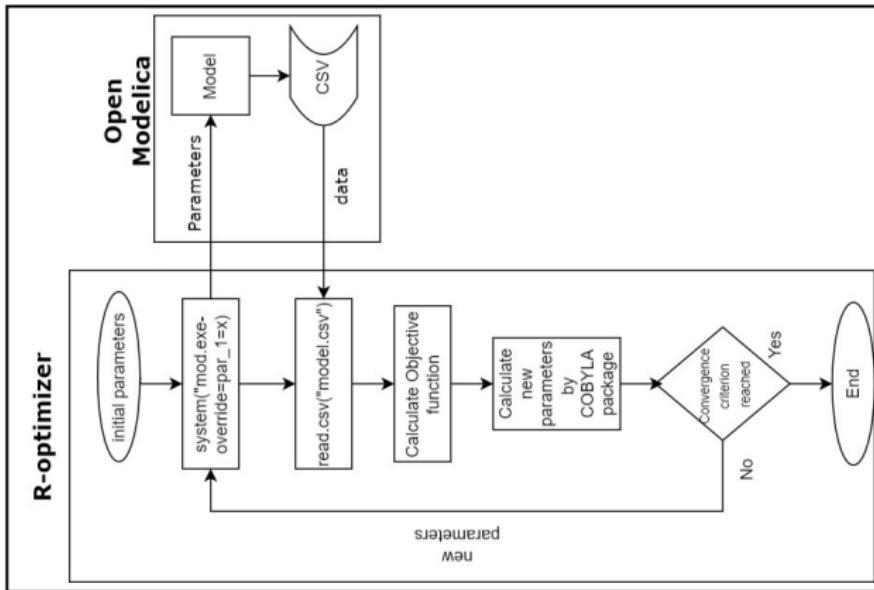


Figure showing how the interoperability works.



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Objective Function

- **Absolute Mean Error**

$$F \rightarrow \frac{1}{n} \frac{\sum_{i=1}^{17} |x_{i,end}^{plant} - x_{i,end}^{model}|}{x_{i,end}^{plant}} \rightarrow \min$$

- **Mean Square Error**

$$F \rightarrow \frac{1}{n} \sqrt{\sum_{i=1}^{17} \left(\frac{x_{i,end}^{plant} - x_{i,end}^{model}}{x_{i,end}^{plant}} \right)^2} \rightarrow \min$$

- **Constraints**

$$\text{subject to } F(E_j, K0_j) = 0$$

$$E_j \geq 0$$

$$-E_j \geq -1000$$

$$K0_j \geq 0$$

$$-K0_j \geq -1e + 50$$



Parameters for the optimizer

Absolute Mean Error (AME)

- **tolerance:** 1e-6
- **number of iterations:** 2000
- **limits:** $\pm 50\%$
- **Converged within 1530 iterations only**

Mean Square Error (MSE)

- **tolerance:** 1e-6
- **number of iterations:** 1530
- **limits:** $\pm 50\%$
- **Not converged**



Results of Vapor phase Model after Optimization

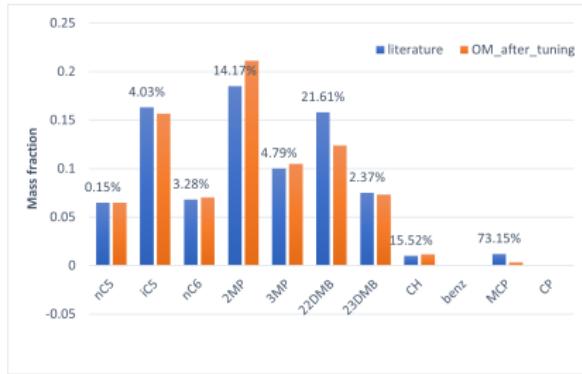


Figure showing the comparison of outlet composition(weight fraction) from both enikeeva et al., 2021 and OM Model after tuning with Absolute Mean Error as objective function. The optimization objective function contains the end point data only.

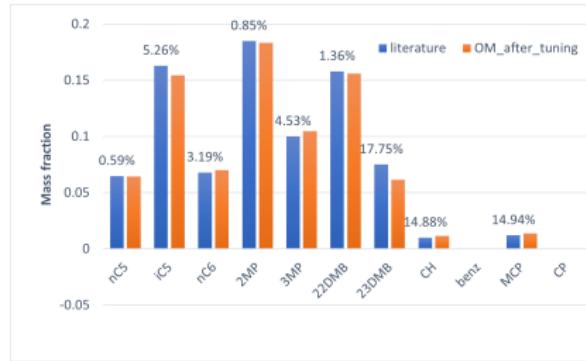


Figure showing the comparison of outlet composition(weight fraction) from both enikeeva et al., 2021 and OM Model after tuning with Mean Square Error as objective function. The optimization objective function contains the end point data only.



Results of Vapor phase Model after Optimization

Table showing the performance parameters for Absolute Mean Error as objective function.

S.No.	Performance Parameter	Model Prediction	Literature enikeeva	%Error
1	iC5/C5P	70.68%	71.55%	1.22%
2	22DMB/C6P	21.23%	26.96%	21.25%
3	23DMB/C6P	12.55%	12.80%	1.92%
4	(2MP+3MP)C6P	54.17%	48.63%	11.39%
5	PIN	1.04	1.11	6.15%
6	RON	77.68087	79.130	0.53%

Table showing the performance parameters for Mean Square Error as objective function.

S.No.	Performance Parameter	Model Prediction	Literature enikeeva	%Error
1	iC5/C5P	70.56%	71.55%	1.384%
2	22DMB/C6P	27.07%	26.96%	0.409%
3	23DMB/C6P	10.72%	12.80%	16.270%
4	(2MP+3MP)/C6P	50.02%	48.63%	2.853%
5	PIN	1.08	1.1135	2.662%
6	RON	78.063	79.130	0.038%



Results of Vapor phase Model after Optimization (MSE)

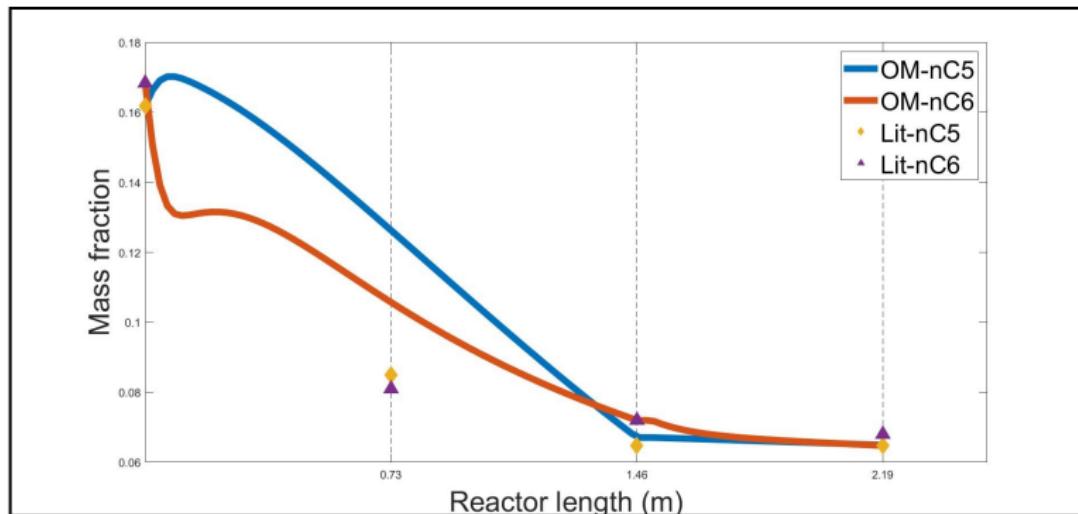


Figure showing the comparison plot of OM model after tuning vs plant data for the n-paraffins.



Results of Vapor phase Model after Optimization (MSE)

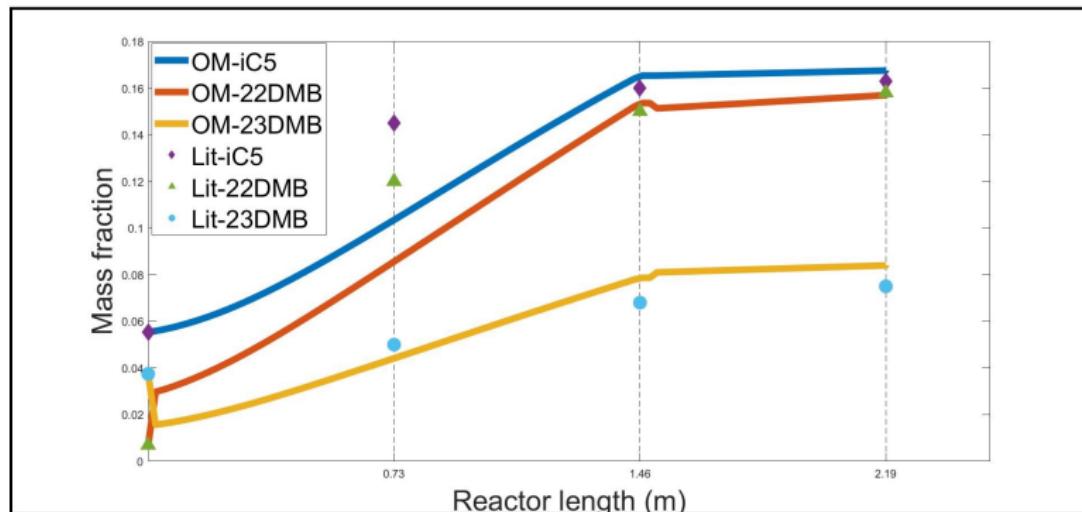


Figure showing the comparison plot of OM model after tuning vs plant data for the value added components.



Results of Vapor phase Model after Optimization (MSE)

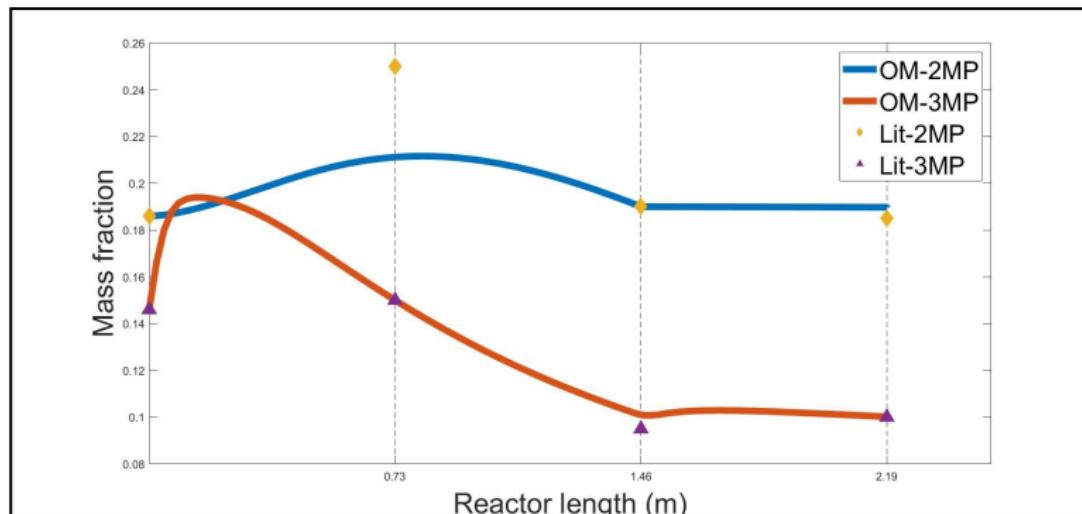


Figure showing the comparison plot of OM model after tuning vs plant data for the 2MP and 3MP.



Results of Vapor phase Model after Optimization (MSE)

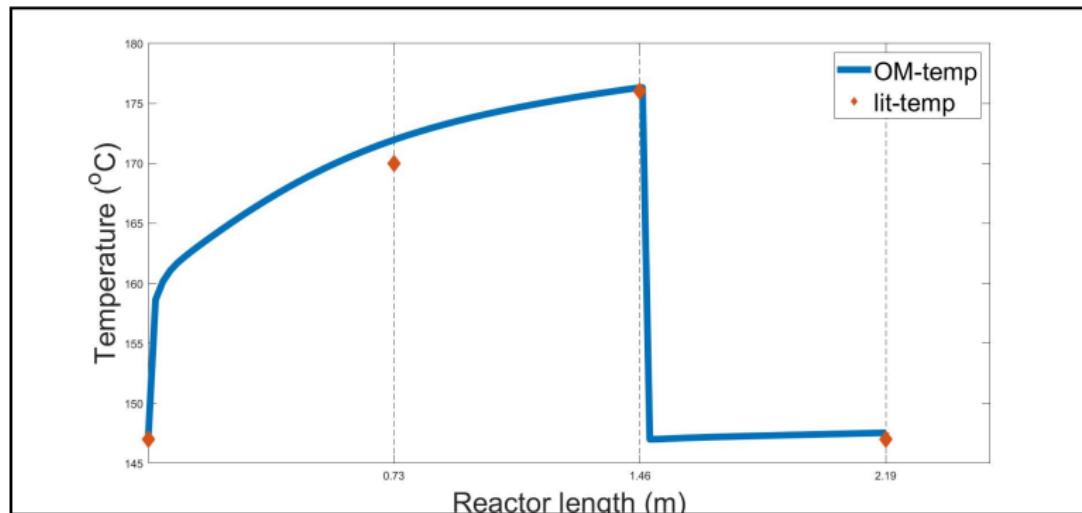


Figure showing the comparison plot of OM model after tuning vs plant data for the temperature.



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Intro

- Previous case was based on vapor phase reactions.
- In this case the reaction happen in liquid phase where it is surrounded by the catalyst.
- Vapor cannot adsorb on to the catalyst surface.
- Aspen-Hysys example of ISOM is being considered.
-

$$r = k * C_{HC}^{liq} * C_{H_2}^{liq}$$

$$r = k * H * C_{HC}^{liq} * C_{H_2}^{vap}$$

$$r = K * C_{HC}^{liq} * C_{H_2}^{vap}$$



Design and Operating Parameters

Table showing the design parameters of the ISOM reactor (Aspen-Hysys)

S.No.	Design Parameter	Value
1	Density of catalyst (kg/m^3)	2500
2	Void fraction (ϕ)	0.5
3	Length of the reactor (m)	7.69*2
4	Diameter of the reactor (m)	2.0

Table showing the operating conditions of the stream entering the reactor (Aspen-Hysys)

S.No.	Design Parameter	Value
1	Flow rate ($kmol/hr$)	550
2	Temperature ($^{\circ}C$)	162
3	Pressure (kPa)	2550



Composition

Table showing the composition of Light Naphtha entering the reactor (Aspen-HYSYS)

S.No.	Component	Molar flow	Mole fraction
1	nC5	108.1266744	0.194615197
2	iC5	59.55329663	0.107188875
3	nC6	82.90315179	0.149215846
4	2MP	39.66378797	0.071390117
5	3MP	26.74985226	0.048146563
6	22DMB	2.539670266	0.004571105
7	23DMB	5.165388492	0.009297087
8	CH	14.15	0.025468323
9	benzene	8.279327144	0.014901807
10	H2	155.1984875	0.27933888
11	MCP	35.9507588	0.064707104
12	CP	11.79028372	0.021221113
13	nC4	1.975246118	0.003555209
14	iC4	0.348156285	0.00062664
15	nC3	0.934851154	0.001682621
16	C2	1.169050036	0.002104151
17	C1	1.094161484	0.001969361



Simulation results

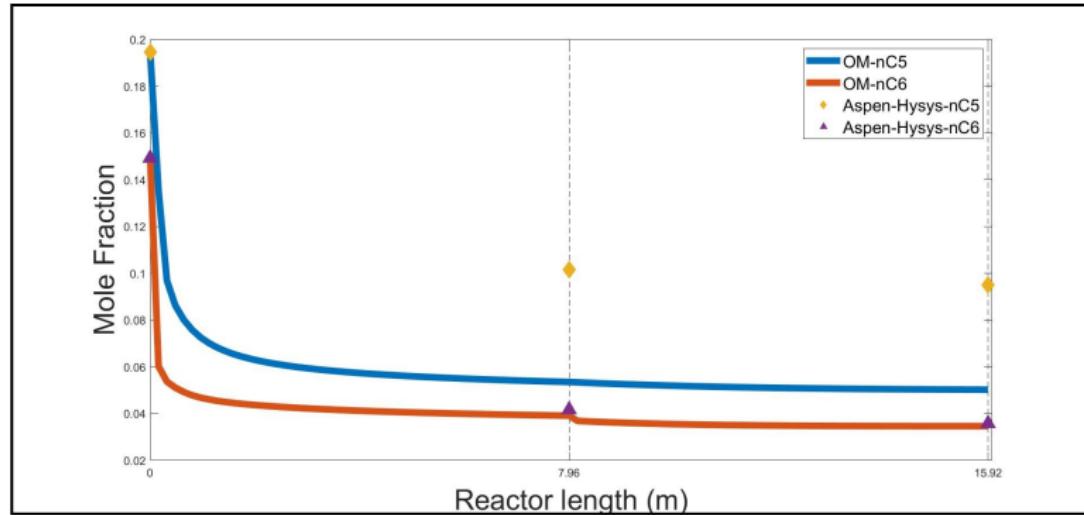


Figure showing the concentration profile of n-paraffins across the reactor length. The solid lines represent the simulation results and the points represent the data from Aspen-Hysys.
Vertical grid lines showing the reactor end.



Aspen-Hysys

Worksheet	Attachments	Dynamics	
Worksheet			
Conditions			
Properties			
Composition			
Oil & Gas Feed			
Petroleum Assay			
K Value			
Use Variables			
Notes			
Cost Parameters			
Normalized Yields			
↳ Emissions			
Stream Name	Hot Feed	Vapour Phase	Liquid Phase
Vapour / Phase Fraction	0.6940	0.6940	0.3060
Temperature [C]	162.9	162.9	162.9
Pressure [kPa]	2550	2550	2550
Molar Flow [kgmole/h]	571.0	396.3	174.7
Mass Flow [kg/h]	3.341e+004	1.953e+004	1.387e+004
Std Ideal Liq Vol Flow [m ³ /h]	54.12	33.38	20.74
Molar Enthalpy [kJ/kgmole]	-9.830e+004	-7.800e+004	-1.443e+005
Molar Entropy [kJ/kgmole-C]	-345.4	-280.5	-492.6
Heat Flow [kJ/h]	-5.613e+007	-3.091e+007	-2.522e+007
Liq Vol Flow @Std Cond [m ³ /h]	59.05	40.58	20.50
Fluid Package	REFSRK		
Utility Type			

OK

Screenshot of Aspen-Hysys showing the phase of Light Naphtha.



Simulation results

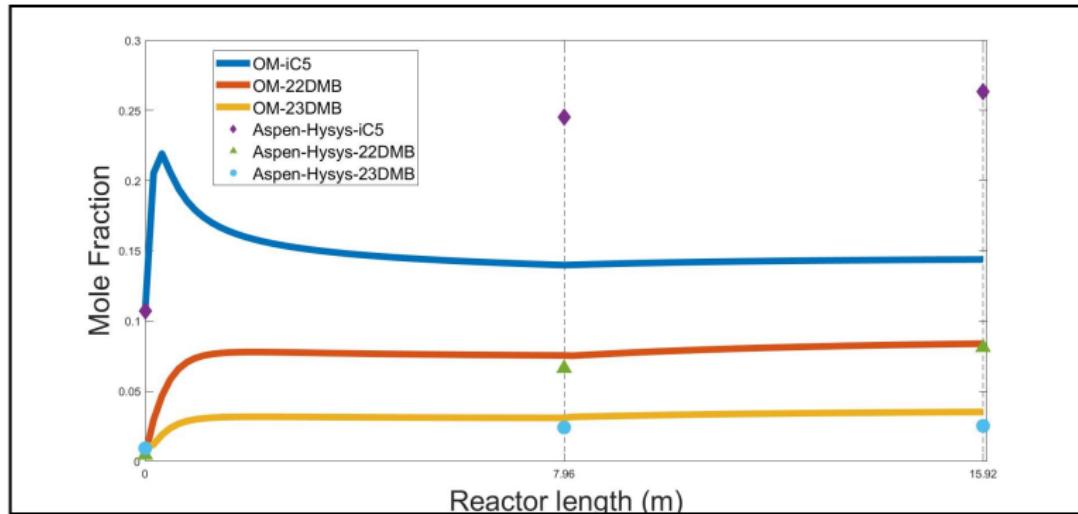


Figure showing the concentration profile of Value added components across the reactor length. The solid lines represent the simulation results and the points represent the data from Aspen-Hysys. Vertical grid lines showing the reactor end.



Simulation results

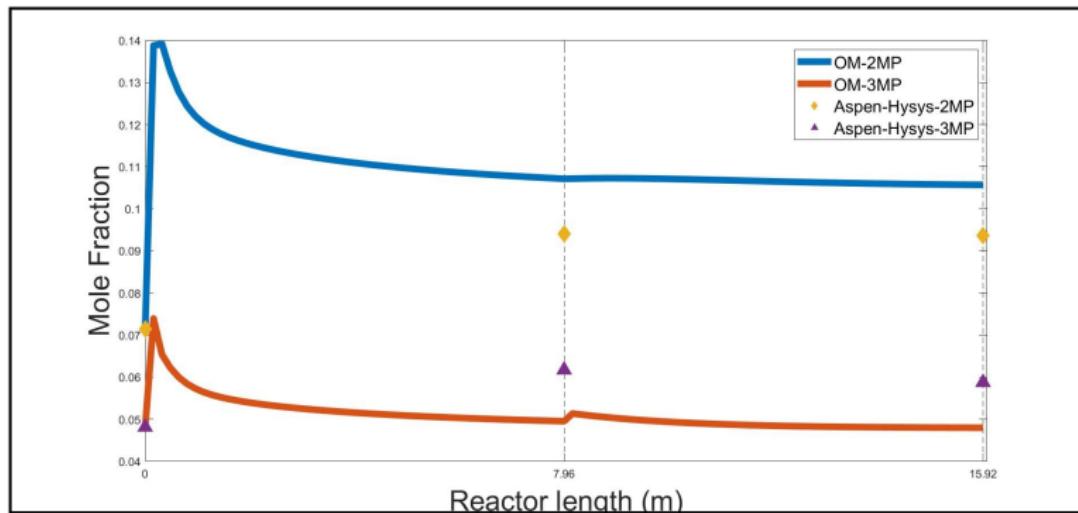


Figure showing the concentration profile of 2MP and 3MP across the reactor length. The solid lines represent the simulation results and the points represent the data from the Aspen-Hysys Simulation. Vertical grid lines showing the reactor end.



Simulation results

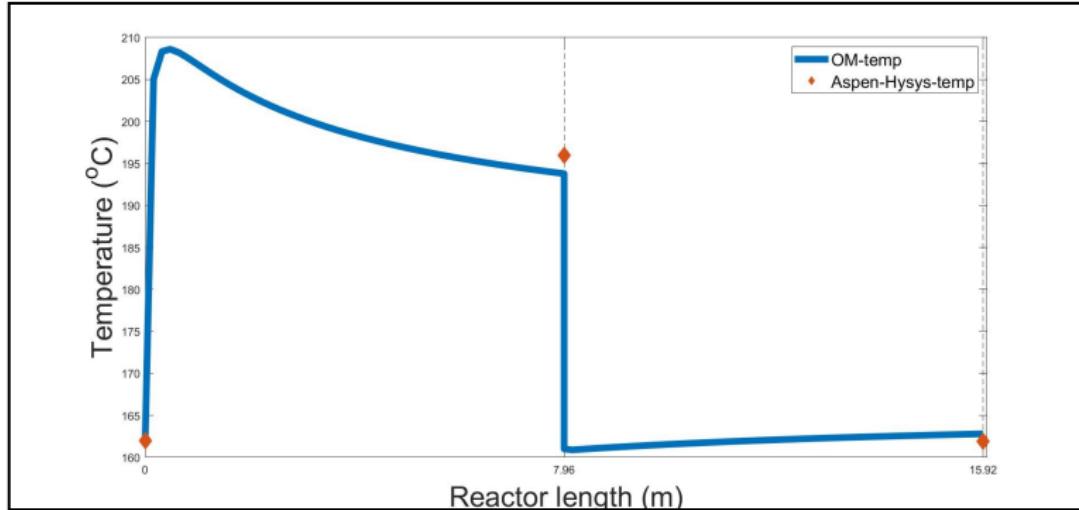


Figure showing temperature profile across the reactor length. The sudden drop in the temperature profile at 1.46m is due to the cooler. The solid lines represent the simulation results and the points represent the data from Aspen-Hysys Simulation. Vertical grid lines showing the reactor end.



Optimization of Liquid phase model

- **Objective Function:** Mean Square Error
- **Initial Parameters:** from Enikeeva et al., 2021
- **Tolerance:** 1e-6
- **Parameter Limit:** $\pm 15\%$
- **Total Number of Iterations:** 2000
- **Sub Iterations:** 1000
- **Solved as 2 sub problems.**



Comparison Plots of the Liquid Phase Model after tuning

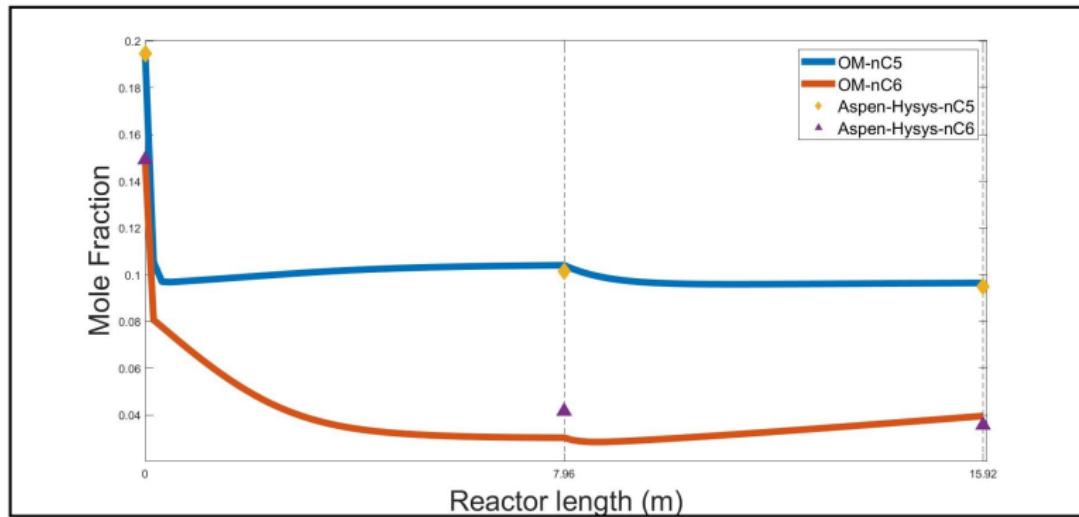


Figure showing the concentration profile of n-paraffins across the reactor length after tuning the OM model . The solid lines represent the simulation results and the points represent the data from Aspen-Hysys. Vertical grid lines showing the reactor end.



Comparison Plots of the Liquid Phase Model after tuning

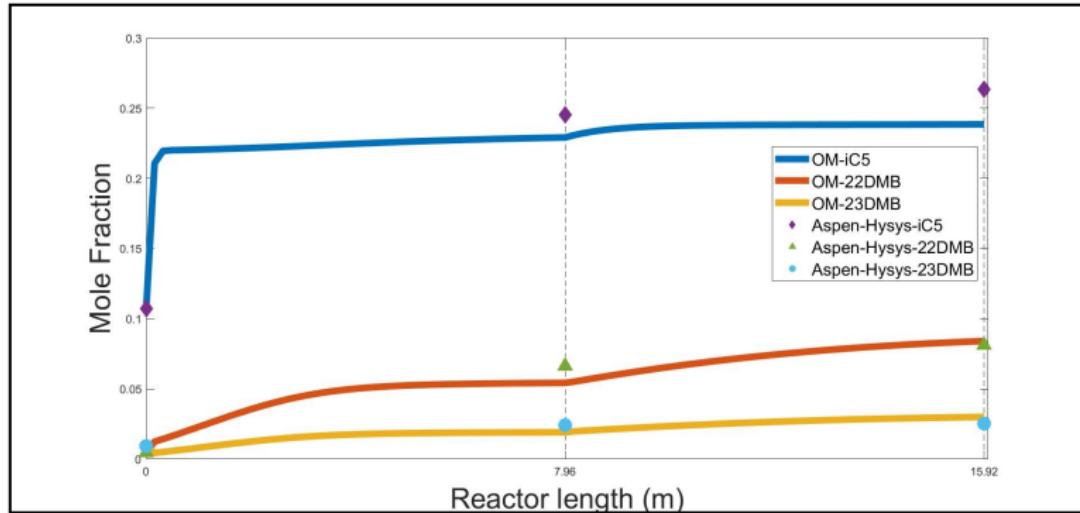


Figure showing the concentration profile of value added components across the reactor length after tuning the OM model . The solid lines represent the simulation results and the points represent the data from the Aspen-Hysys Simulation. Vertical grid lines showing the reactor end.



Comparison Plots of the Liquid Phase Model after tuning

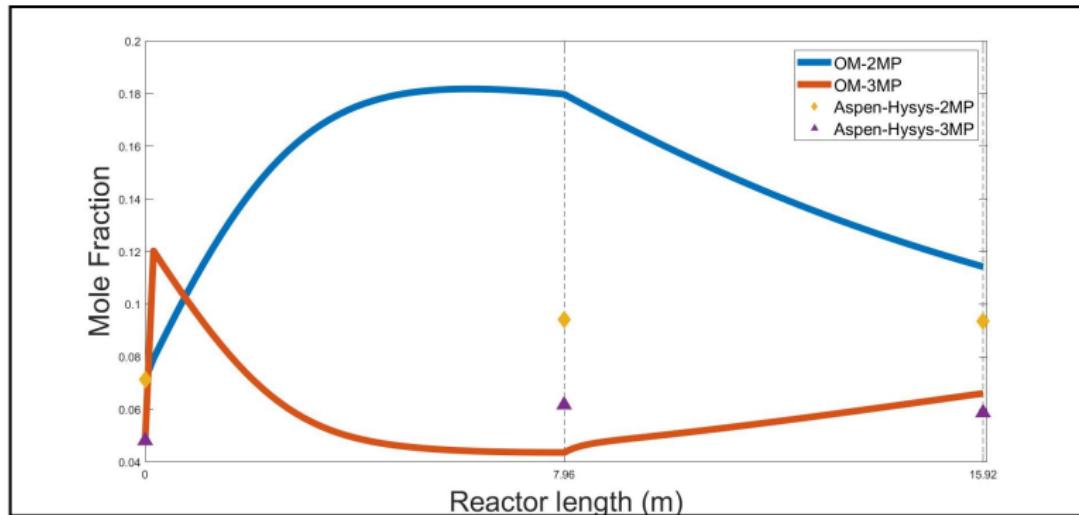


Figure showing the concentration profile of 2MP and 3MP across the reactor length after tuning the OM model . The solid lines represent the simulation results and the points represent the data from the Aspen-Hysys Simulation. Vertical grid lines showing the reactor end.



Comparison Plots of the Liquid Phase Model after tuning

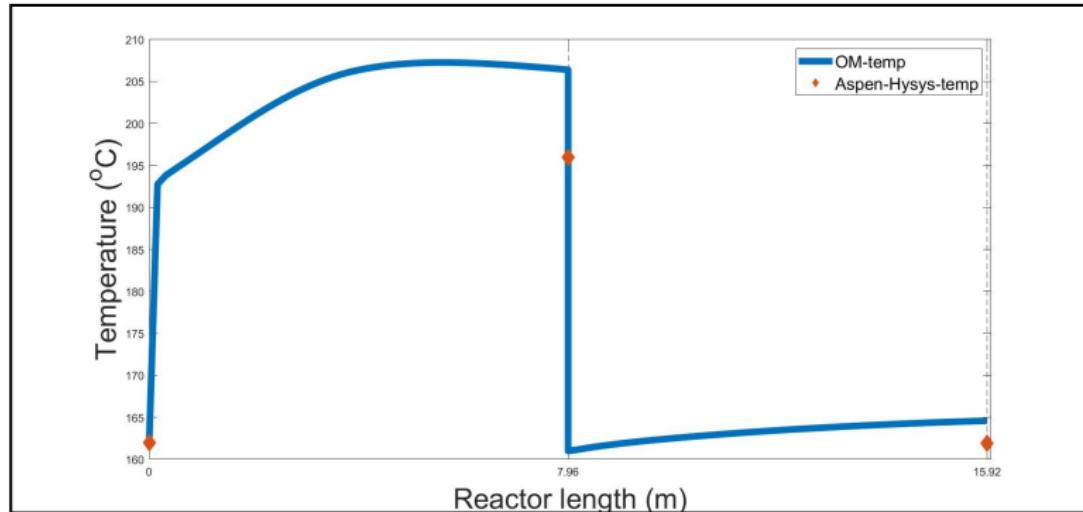


Figure showing temperature profile across the reactor length after tuning the OM model .
The sudden drop in the temperature profile at 7.96m is due to the cooler. The solid lines represent the simulation results and the points represent the data from Aspen-Hysys Simulation. Vertical grid lines showing the reactor end.



Results of the Liquid Phase Model after tuning

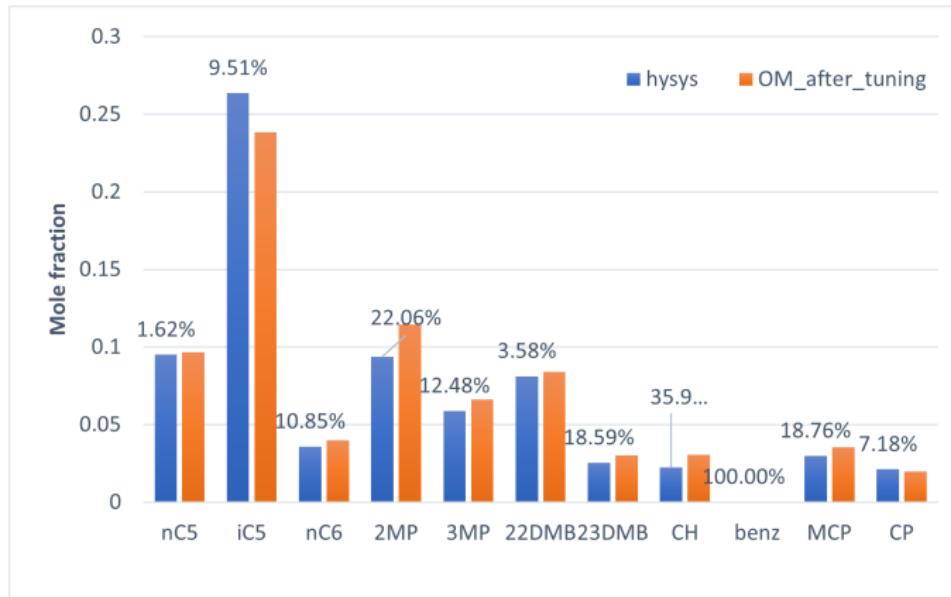


Figure showing the comparison of outlet composition(mole fraction) from both Aspen-Hysys Simulation and OM Model after tuning.



Results

S.No.	Performance Parameter	Aspen Hysys	Model Prediction	%Error
1	iC5/C5P	73.51%	71.19%	3.154%
2	22DMB/C6P	31.36%	28.55%	8.945%
3	23DMB/C6P	9.78%	10.19%	4.257%
4	(2MP+3MP)C6P	58.87%	61.26%	4.0589%
5	PIN	1.15	1.10	4.106%
6	RON	80.76	79.91	1.052%

Table showing the comparison of performance parameters between Aspen-Hysys Simulation and OM Model after tuning.



An attempt to reduce the number of parameters

- Sensitivity analysis
- A perturbation is made in the parameter to know its effect on the Weighted Mean.

$$\frac{1}{n} \sum_{i=1}^{17} \left(\frac{x_{i,end}^{plant} - x_{i,end}^{model}}{x_{i,end}^{plant}} \right)^2$$

- limit: $\pm 10\%$
- We considered the parameters whose errors are larger than 30%.
- 9 parameters were found by doing this study.



Sensitivity analysis

Table showing the sensitivity analysis for activation energy.

param	-10%	10%	param	-10%	10%	param	-10%	10%
1	12%	77%	19	0%	0%	37	4%	7%
2	81%	14%	20	0%	0%	38	6%	4%
3	0%	0%	21	0%	0%	39	0%	0%
4	0%	0%	22	0%	0%	40	0%	0%
5	3%	13%	23	2%	1%	41	84%	90%
6	13%	3%	24	0%	0%	42	0%	0%
7	6%	8%	25	0%	0%	43	0%	0%
8	11%	5%	26	0%	0%	44	23%	2%
9	10%	1%	27	1%	0%	45	41%	0%
10	7%	0%	28	0%	0%	46	0%	0%
11	6%	2%	29	96%	3%	47	10%	0%
12	5%	1%	30	2%	48%	48	94%	15%
13	0%	0%	31	57%	2%	49	38%	3%
14	0%	0%	32	0%	0%	50	0%	0%
15	26%	8%	33	0%	0%	51	0%	0%
16	12%	7%	34	0%	0%	52	0%	0%
17	0%	0%	35	0%	1%	53	29%	0%
18	0%	0%	36	0%	0%	54	0%	0%



Comparison Plots of the Liquid Phase Model after tuning with selective parameters

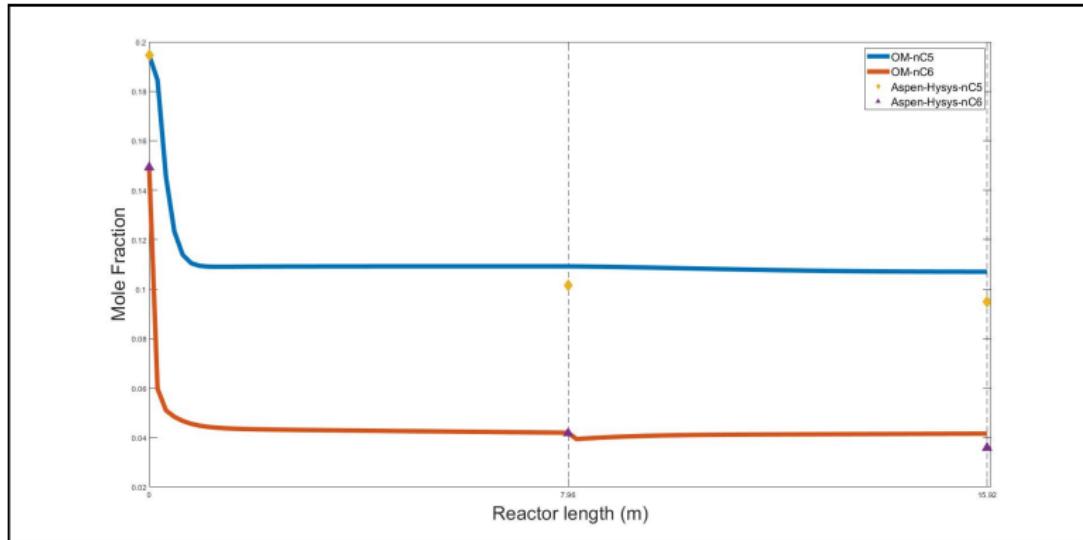


Figure showing the concentration profile of n-paraffins across the reactor length after tuning the OM model with nine parameters. The solid lines represent the simulation results and the points represent the data from Aspen-Hysys. Vertical grid lines showing the reactor end.



Comparison Plots of the Liquid Phase Model after tuning with selective parameters

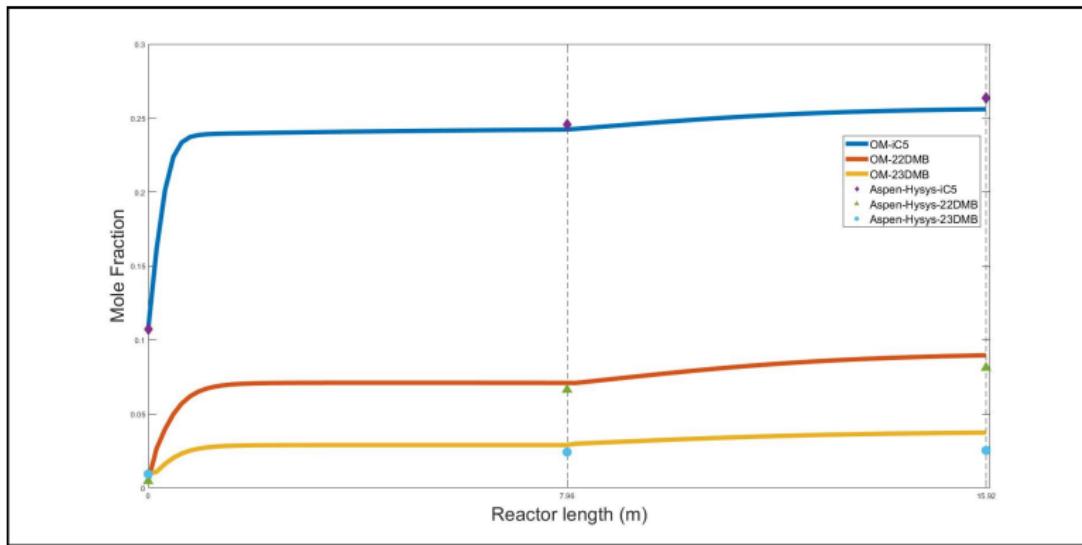


Figure showing the concentration profile of value added components across the reactor length after tuning the OM model with selective parameters. The solid lines represent the simulation results and the points represent the data from the Aspen-Hysys Simulation. Vertical grid lines showing the reactor end.



Comparison Plots of the Liquid Phase Model after tuning with selective parameters

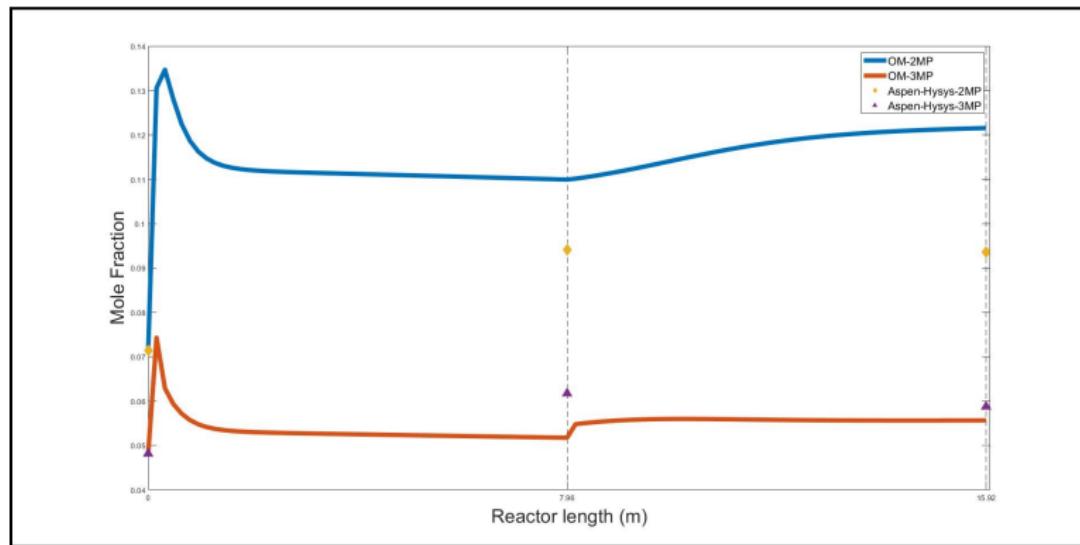


Figure showing the concentration profile of 2MP and 3MP across the reactor length after tuning the OM model with selective parameters. The solid lines represent the simulation results and the points represent the data from the Aspen-Hysys Simulation. Vertical grid lines showing the reactor end.



Comparison Plots of the Liquid Phase Model after tuning with selective parameters

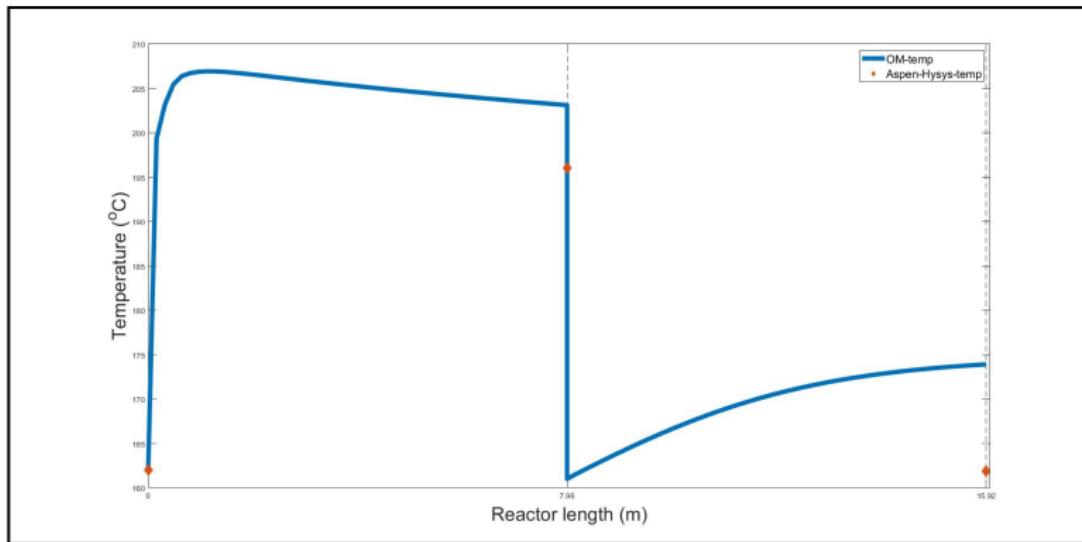


Figure showing temperature profile across the reactor length after tuning the OM model with selective parameters. The sudden drop in the temperature profile at 7.96m is due to the cooler. The solid lines represent the simulation results and the points represent the data from Aspen-Hysys Simulation. Vertical grid lines showing the reactor end.



Results with selective parameters



Figure showing the comparison of outlet composition OM model and Aspen-HYSYS. This is produced by optimizing the OM model with sensitive parameters.



Results with selective parameters

Table showing the comparison of performance parameters between Aspen-Hysys Simulation and OM Model after tuning with selective parameters. Except for 23DMB/C6P ratio everything else is less than 6.5%

S.No.	Performance Parameter	Aspen Hysys	Model Prediction	%Error
1	iC5/C5P	73.51%	70.52%	4.07%
2	22DMB/C6P	31.36%	29.46%	6.042%
3	23DMB/C6P	9.78%	9.78%	25.519%
4	(2MP+3MP)C6P	58.87%	58.87%	1.019%
5	PIN	1.15	1.12	2.086%
6	RON	80.76	79.59	1.455%



Some more study

- A similar kind of study was made upon the pre-exponential factors.
- with the lower limit as 0.5 and upper limit as 2.
- We found the same parameters that we found in Activation energy.
- Increased the parameters to 18 and repeated the tuning process.
- No improvement in the results when compared with the results from 9 parameters. So, 9 parameters are used.
- Enforcing temperature in the objective function is made because

$$F \rightarrow \frac{1}{n} \sqrt{\sum_{i=1}^{17} \left(\frac{x_{i,end}^{plant} - x_{i,end}^{model}}{x_{i,end}^{plant}} \right)^2} + \alpha * \frac{1}{2} \sqrt{\sum_{j=1}^2 \left(\frac{T_{j,end}^{plant} - T_{j,end}^{model}}{T_{j,end}^{plant}} \right)^2} \rightarrow \min$$



Some more study

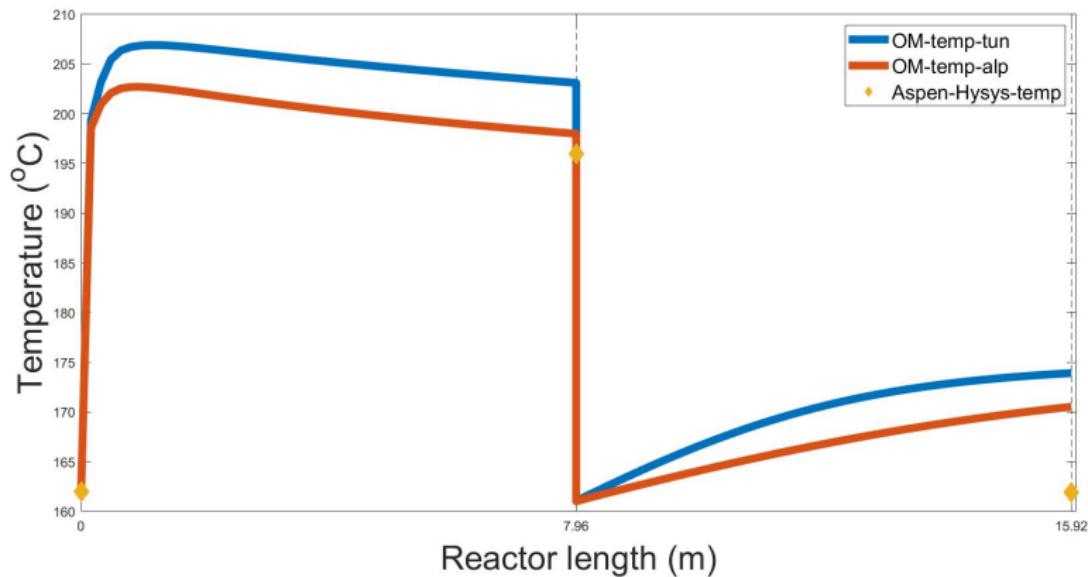
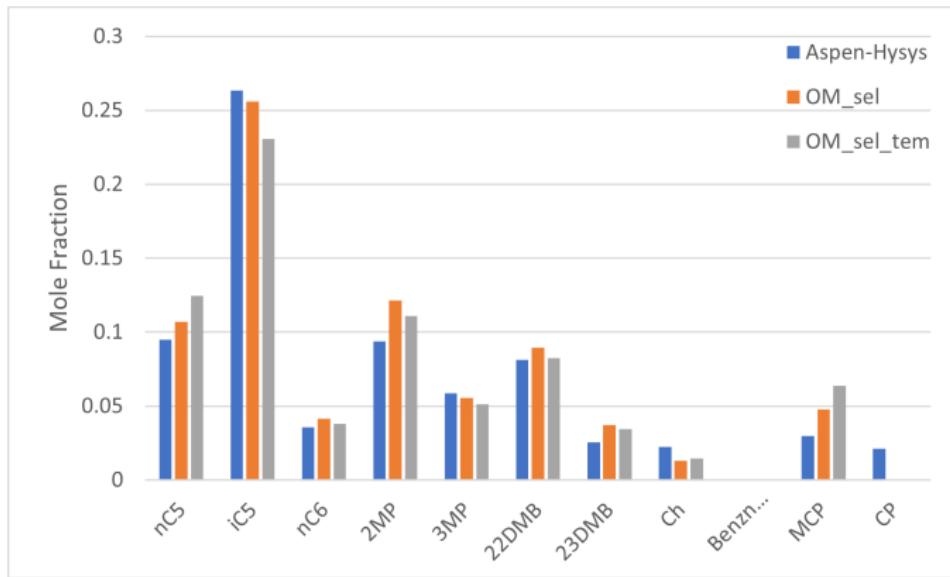


Figure showing comparison of temperature profile across the reactor length after tuning with selective parameters.



Some more study



Bar chart showing the comparison between Aspen-Hysys model, OM model tuned with selective parameters and OM model tuned with selective parameters along with temperature profile with alpha as 0.2.



Conclusion and Future Work

- PFR model is build using OM.
- An optimization method to match with the plant data.
- An Interface has been discovered to communicate R with OM.
- Mean Square Error criterion has been found to be better.
- Validation of model with Vapor phase reactions.
- Validation of model with Liquid phase reactions.
- Integration of this model with CDU.



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Thank You

