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Universidad Industrial de Santander

SIMULATION OF A STEAM CRACKING REACTOR WITH ETHANE-PROPANE MIXTURES USING COMSOL MULTIPHYSICS®

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Introduction

BACKGROUND (2016)

*Availability of propane rich streams in the refinery

*Low price of LPG (Liquified Petroleum Gas)

*Low inventory of ethane in the Colombian market

*Off-line ethane cracking reactor was available

QUESTIONS

*Could an off-line ethane cracking reactor be used to process ethane-propane mixtures?

*Is it necessary to significantly change the operating conditions of the off-line reactor to process the mixtures?

Build-up a reactor model

Metodology

MATLAB

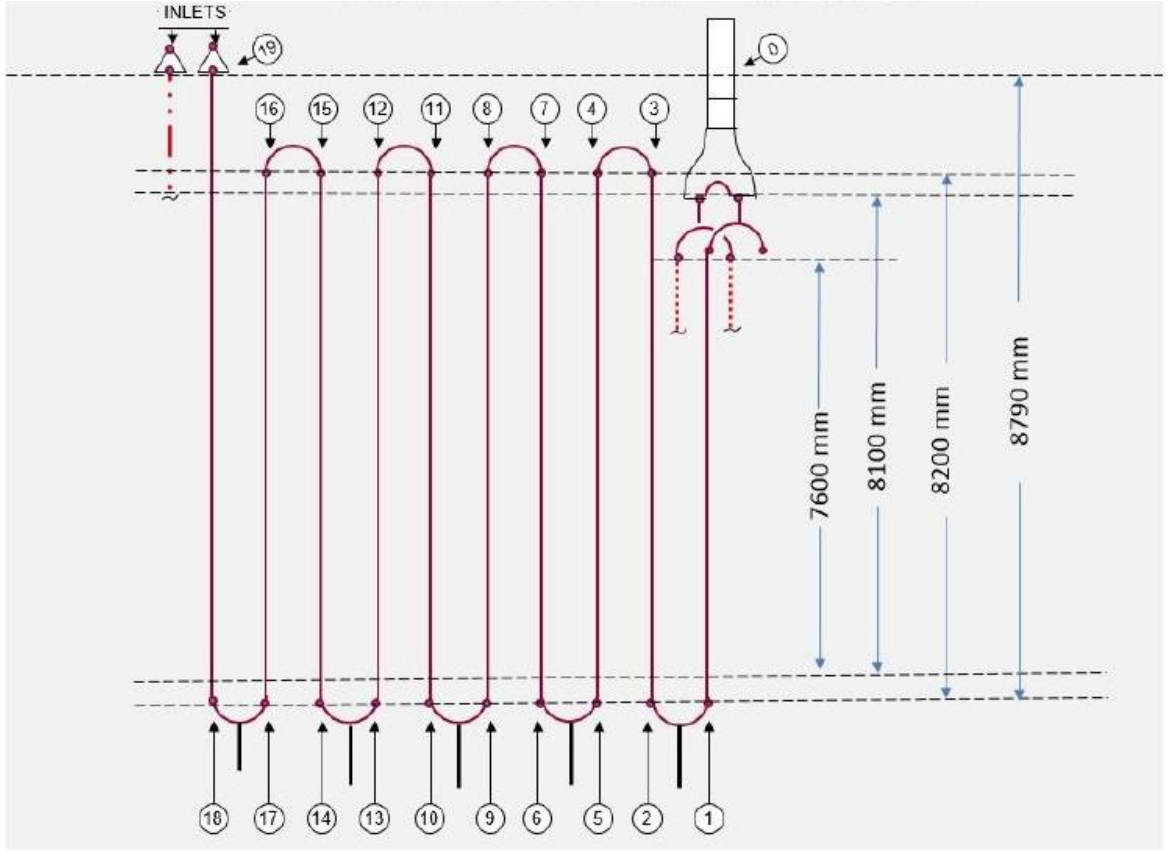
A 1D model for the reactor (only the radiant section) was developed in MATLAB and the model was validated with plant data.

COMSOL

- A 0D model for an offline reactor: no coke deposition, no pressure drop
- A 1D model for the same offline reactor: coke deposition, pressure drop

COMSOL MULTIPHYSICS® ver 5.3
CHEMICAL REACTION ENGINEERING MODULE (Chemical species, reactions, kinetics)
TEA COCO SIMULATOR, ECOPETROL DATABANK (Some thermodynamic and physical properties)
FROMENT et al. (Molecular reaction scheme and kinetics data)
INDUSTRIAL DATA: 931 days in 18 reactor cycles were selected to validate models

Geometry and design parameters of a steam cracking reactor, radiant section



Parameter		Value	Unit
Total Flow		787.65	g/s
Steam/HC		0.4	kg/kg
Temperature in		913.2	K
Temperature out		1118.15	K
Average velocity outlet		206.65	m/s
Tube	Internal diameter	108	mm
	Length straight tube	8.2	m
	Total length	90.4	m
Total length reactor		97.5	m

OD Model: Chemical Reaction Engineering Module

Mass Balance

$$\frac{dF_j}{dV} = \sum_{i=1}^{NR} n_{ij} r_i(V)$$

$$c_j = \frac{P}{RT} \frac{F_j}{\sum_j F_j}$$

Energy Balance

$$\left[\sum_{j=1}^{NC} F_j C_{p,j}\right] \frac{dT}{dV} = Q + Q_{ext}$$

$$Q = -\sum_{i=1}^{NR} \Delta H_i r_i$$

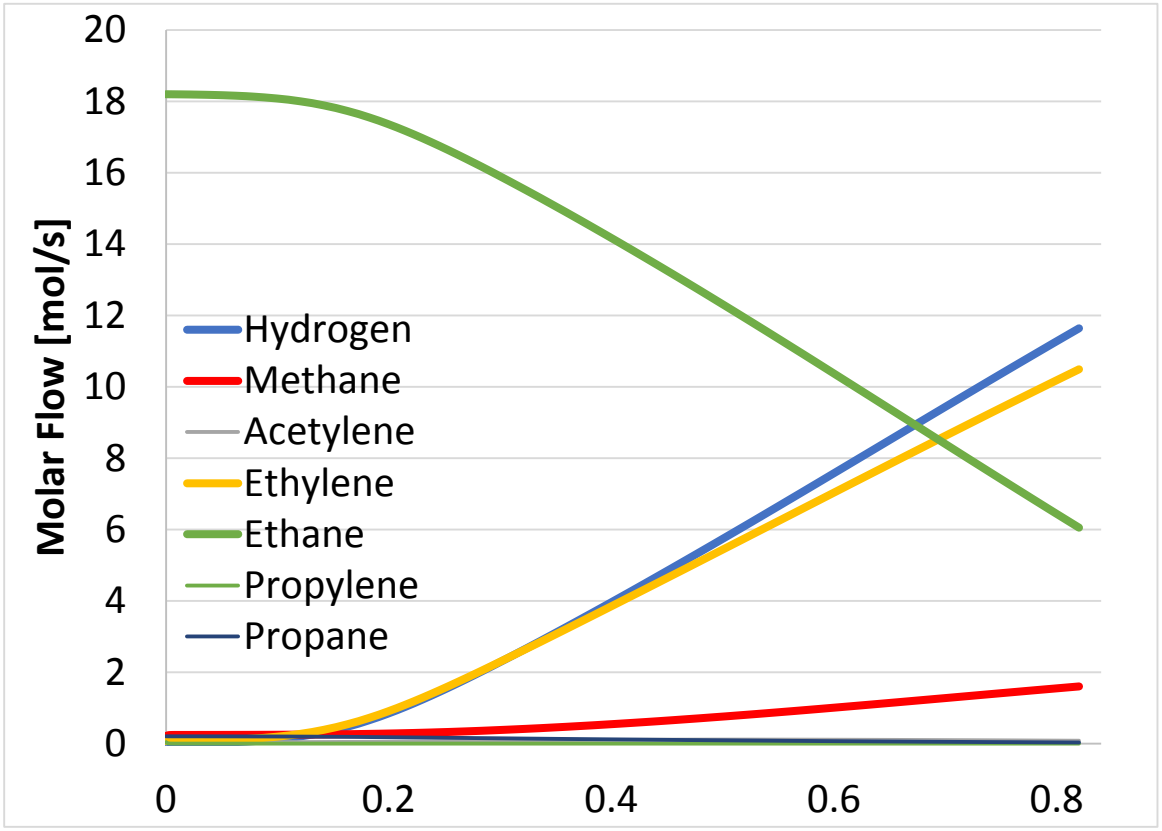
Validation results for clean tubes

Species	%w		
	0D COMSOL	**1D Matlab**	**Datasheet manufacturer***
H_2	2.95	2.69	3.00
CH_4	13.61	13.75	12.00
C_2H_4	43.38	41.55	38.00
C_2H_6	18.42	21.85	26.00
C_3H_6	8.77	8.80	8.00

*Technip, Rome, Italy, 1980.

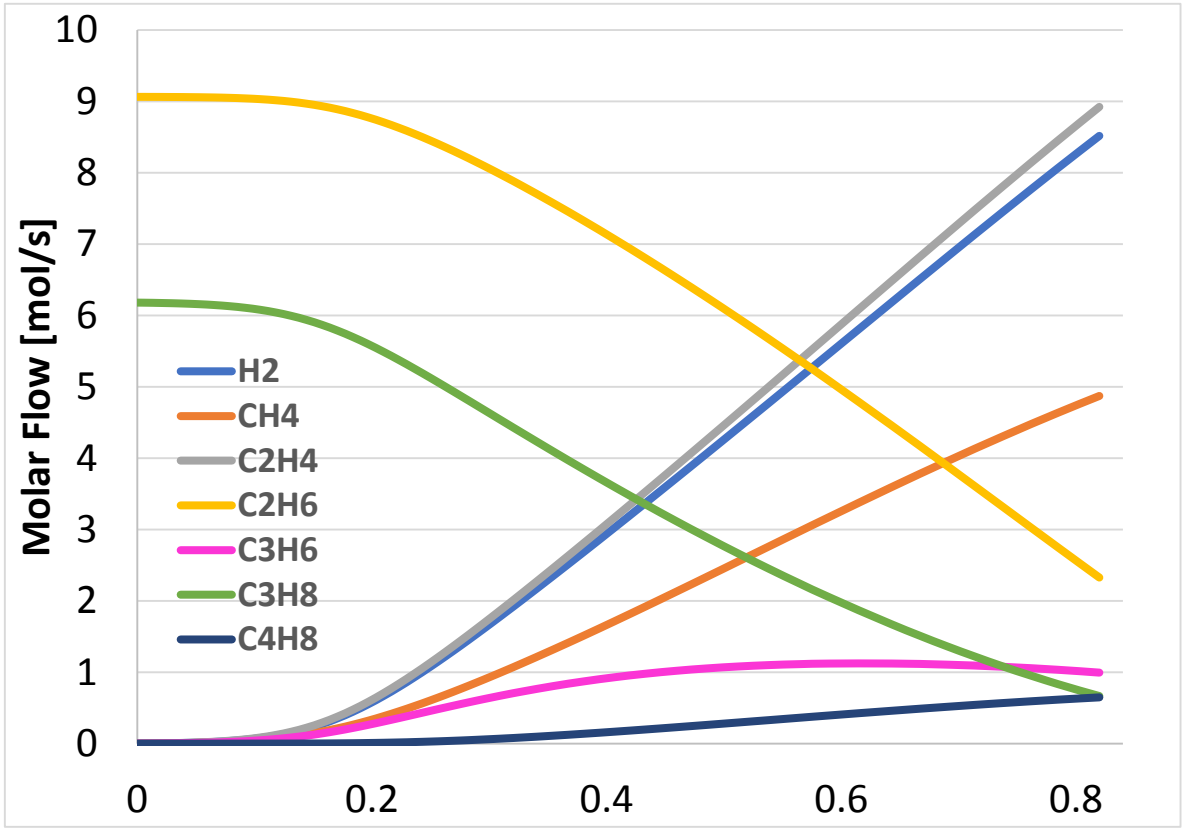
Results COMSOL 0D Model

Feed: Ethane, outlet temperature=1105 K



Reactor Volume, m³

Feed: Ethane-propane 50/50 %wt, outlet temperature=1110 K



Reactor Volume, m³

- **SHORTCOMINGS**
- No coke deposition
- No pressure drop

1D COMSOL Model: Chemical Reaction Engineering Module

Material Balance

$$\frac{dF_i(z)}{dz} = \sum_{j=1}^{NR} n_{i,j} r_j(z) \frac{p\left(D_i - 2\delta(z)\right)}{4}$$

$$r_j(z) = A_j e^{-E_{a_j}/RT(z)} \prod_{i=1}^{NC} C_i^{n_{ij}}(z)$$

$$C_i(z) = \frac{F_i(z)}{N_{steam} + \sum_{i=1}^{NC} F_i(z)} \left(\frac{P(z)}{RT(z)} \right)$$

Coke Deposition

$$\frac{d\delta(z)}{dt} = \frac{r_c(z)}{r_c}$$

$$r_c(z) = A_c e^{-E_c/RT(z)} C_{C_3H_6}(z)$$

Energy Balance

$$\frac{dT(z)}{dz} = \frac{1}{\sum_{j=1}^{NC} F_j C_{pj}} \left[q(z) p\left(D_i - 2\delta(z)\right) + \frac{p\left(D_i - 2\delta(z)\right)^2}{4} \sum_{i=1}^{NR} \left(-\Delta H_{Ri}(z) \right) \right]$$

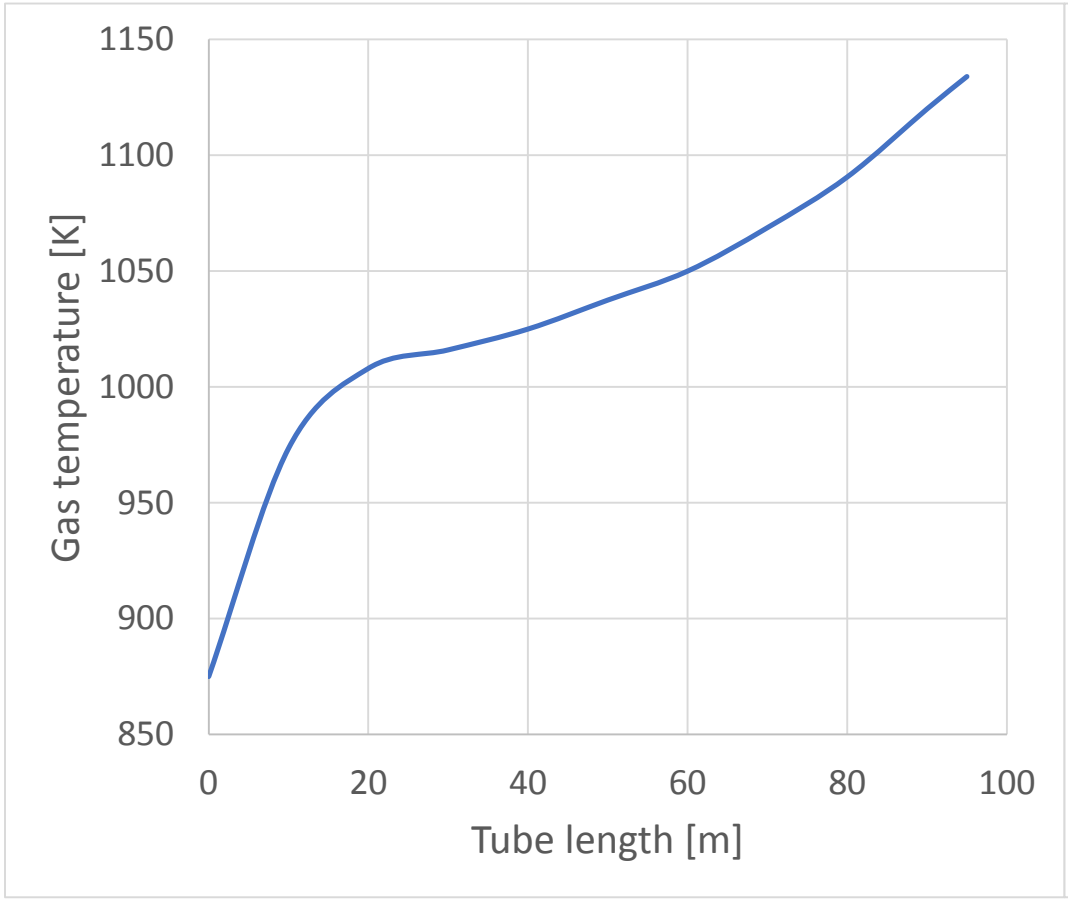
$r_i(z)$

Momentum Balance

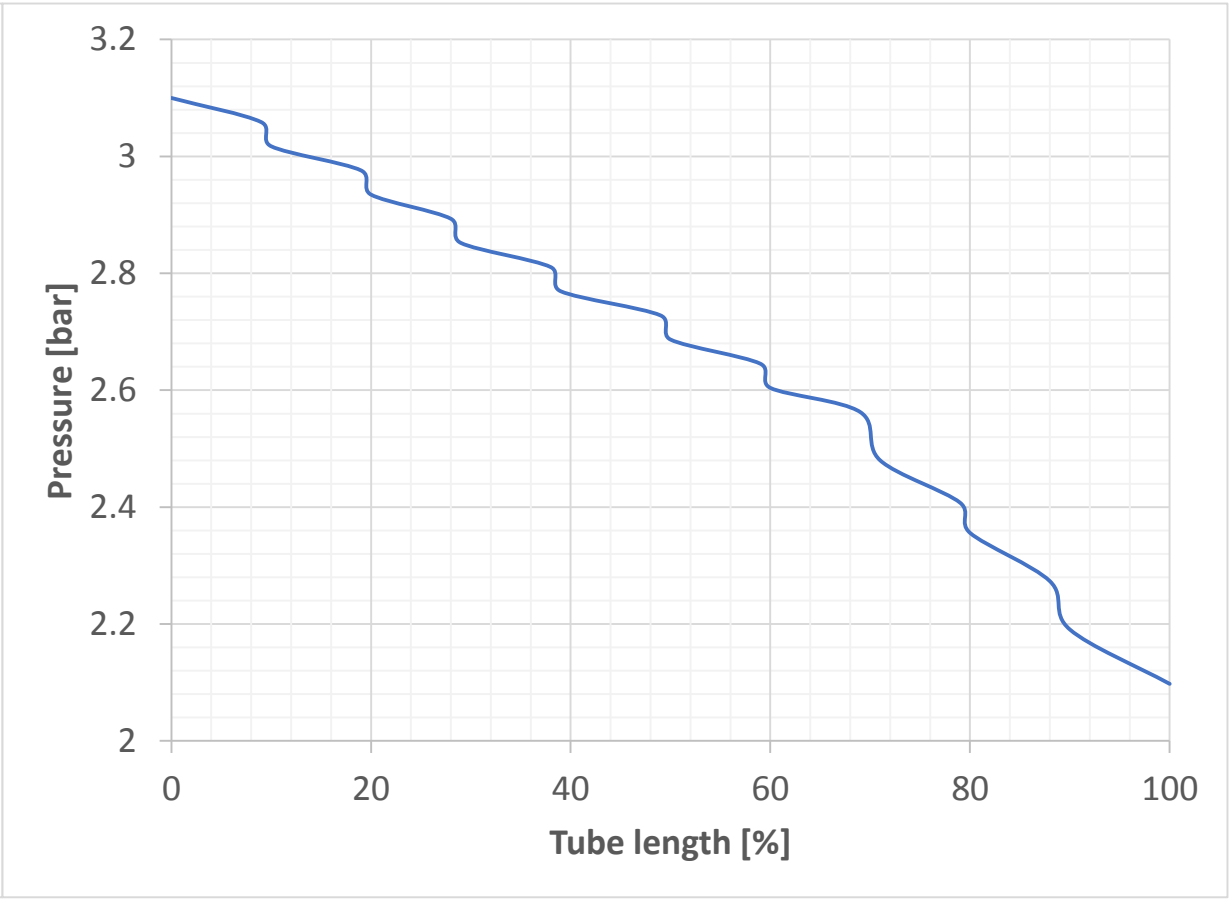
$$\frac{dP_T(z)}{dz} = \frac{\frac{d}{dz}\left[\frac{1}{M_w(z)}\right] + \frac{1}{M_w(z)}\left[\frac{1}{T(z)}\frac{dT(z)}{dz} + \left(\frac{2f(z)}{D_i - 2\delta(z)} + \frac{\rho(z)}{\rho r_b}\right)\right]}{\frac{1}{M_w(z)P_t(z)} - \frac{P_T(z)}{a\left[G(z)\right]^2 RT(z)}}$$

$$\frac{d}{dz}\left(\frac{1}{M_w}\right) = \frac{\sum_j \frac{dF_j}{dz}}{GW}$$

COMSOL 1D Model: Temperature and Pressure Profiles, Tin=875 K, steam/HC ratio =0.4, ethane



Temperature profile



Pressure profile

Comparison actual conditions vs models (Thermal cracking cracking of ethane)

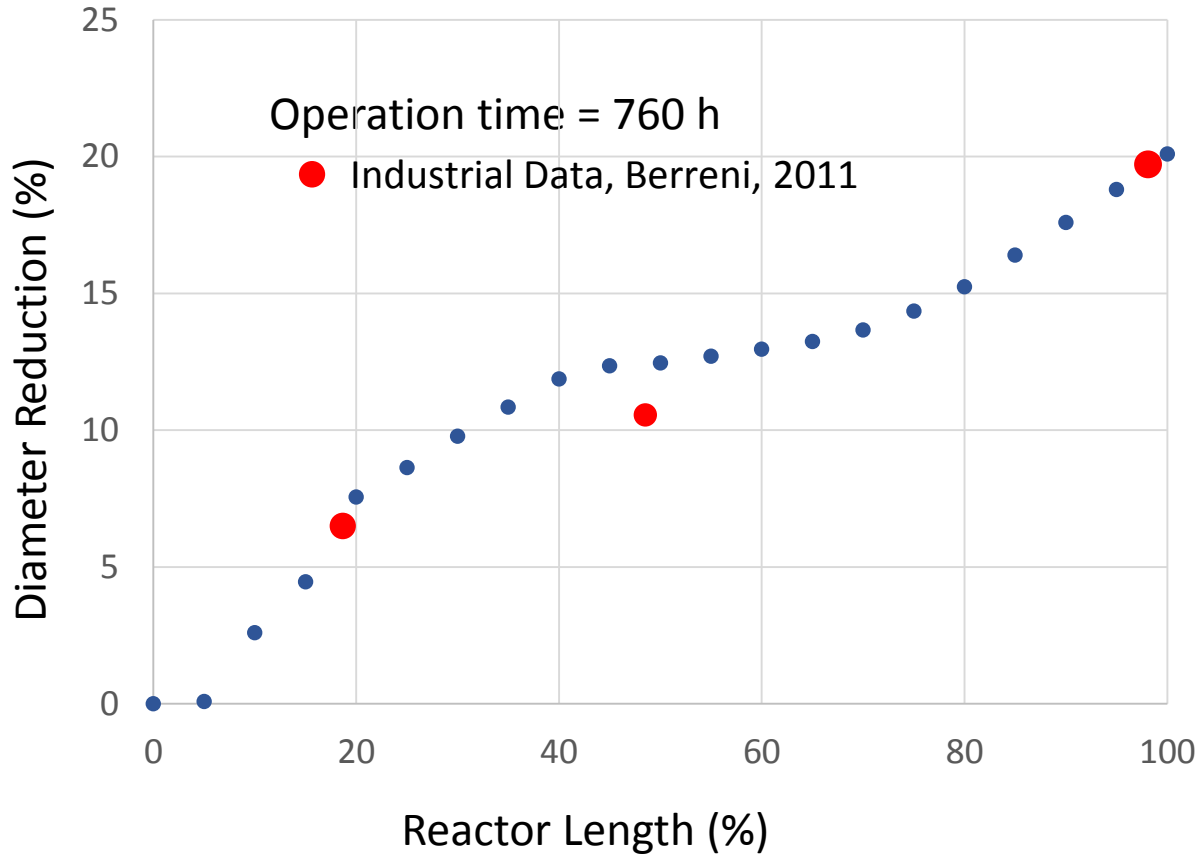
Gas species	Real Conditions GC Analysis %mol	MATLAB 1D Model %mol	COMSOL 1D Model % mol	Absolute difference GC vs MATLAB model	Absolute difference GC vs COMSOL 1D model
H_2	28.42%	30.68%	35.34%	2.26%	6.92%
CH_4	6.61%	6.49%	6.50%	0.12%	0.11%
C_2H_2	0.16%	0.34%	0.33%	0.18%	0.17%
C_2H_4	28.73%	27.06%	27.09%	1.68%	1.64%
C_2H_6	34.59%	32.67%	32.75%	1.92%	1.84%
C_3H_6	0.69%	0.36%	0.38%	0.33%	0.31%
C_3H_8	0.46%	0.49%	0.49%	0.04%	0.03%
C_4H_6	0.34%	1.91%	1.93%	1.57%	1.59%
Total	100%	100%			

	Real conditions	Matlab 1D Simulation	COMSOL 1D Simulation	Units
Outlet temperature	1097	1097	1097	K
Inlet pressure	273646	273646	273646	Pa
ΔP	54782	56282	50046	Pa
Q(z)	-	61800	58400	W/m^2
Coke thickness @ 72 h Operating time	-	1.405	1.578	mm
Ethane Conversion	59.5	56.3	58.2	%

Results COMSOL 1D model for ethane/propane mixtures

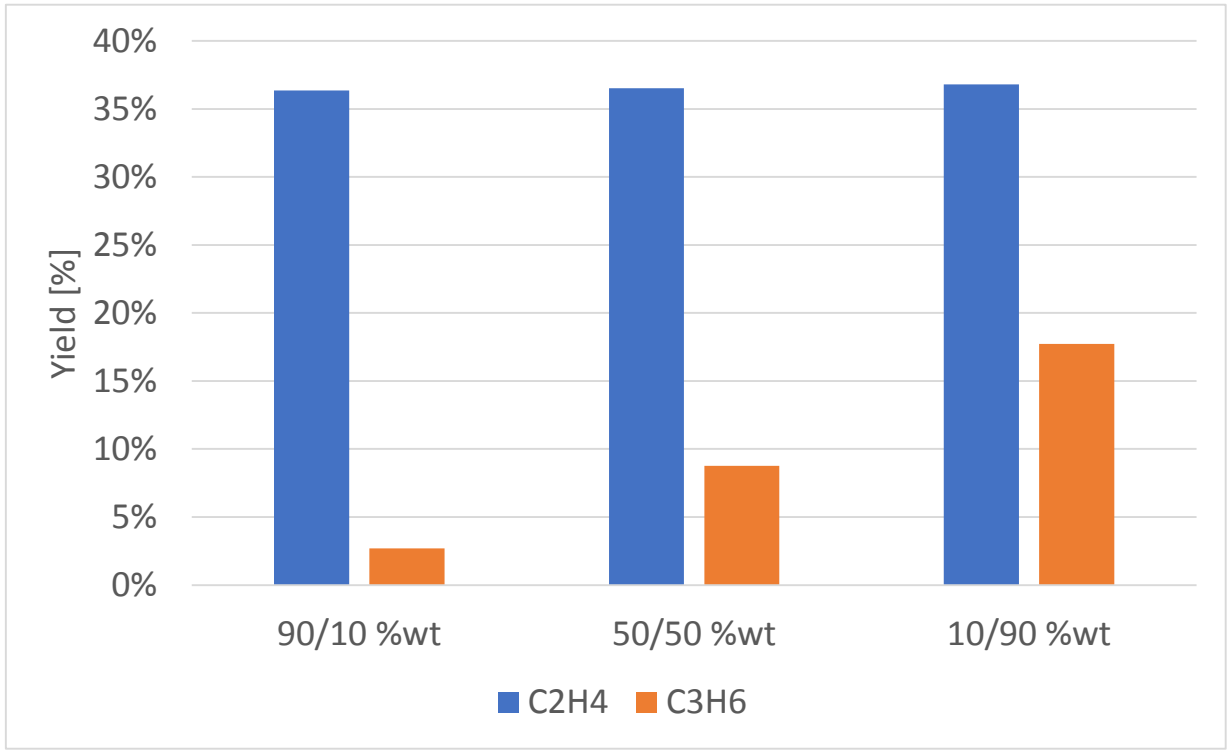
Ethane/Propane mixtures %wt			
Gas species	25/75	50/50	75/25
	Composition product stream %wt		
H_2	2,12%	2,70%	3,29%
CH_4	18,63%	13,70%	8,62%
C_2H_2	0,15%	0,10%	0,06%
C_2H_4	36,83%	41,69%	46,43%
C_2H_6	13,11%	21,51%	29,41%
C_3H_6	12,67%	8,84%	5,71%
C_3H_8	9,48%	5,68%	2,60%
C_4H_6	1,83%	1,37%	0,85%
C_4H_8	1,25%	1,58%	1,32%
C_6	3,93%	2,83%	1,72%
Total	100%	100%	100%

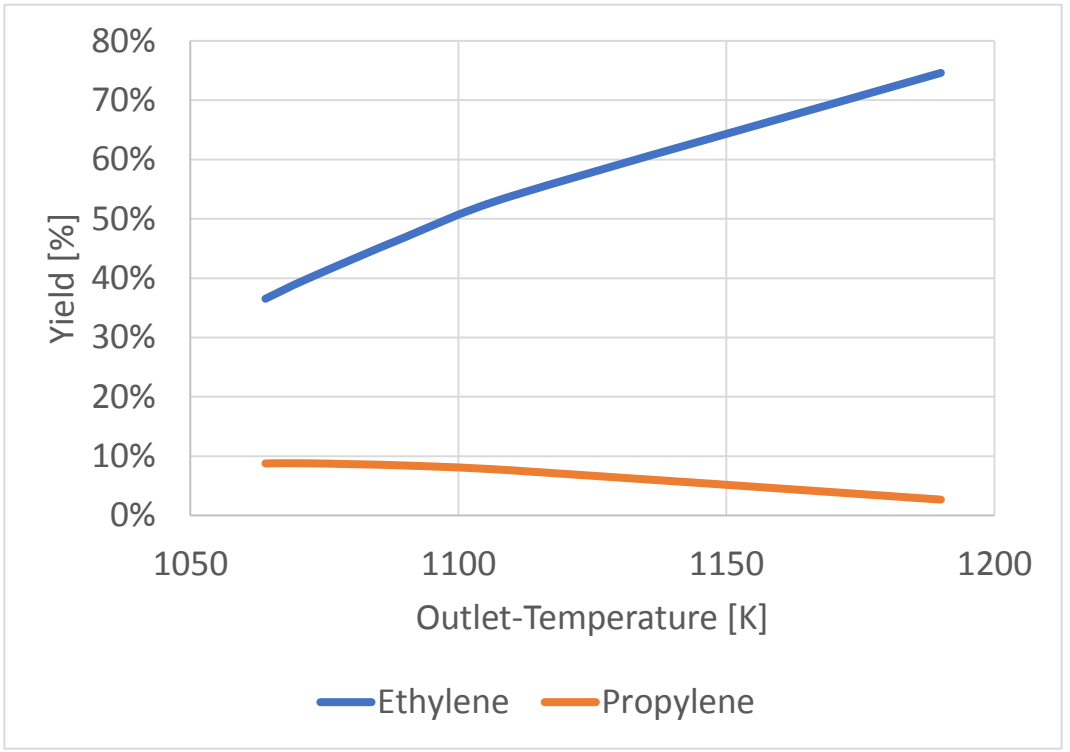
Outlet temp = 1060 K, Steam/ HC = 0.3



Results COMSOL 1D model for ethane/propane mixtures

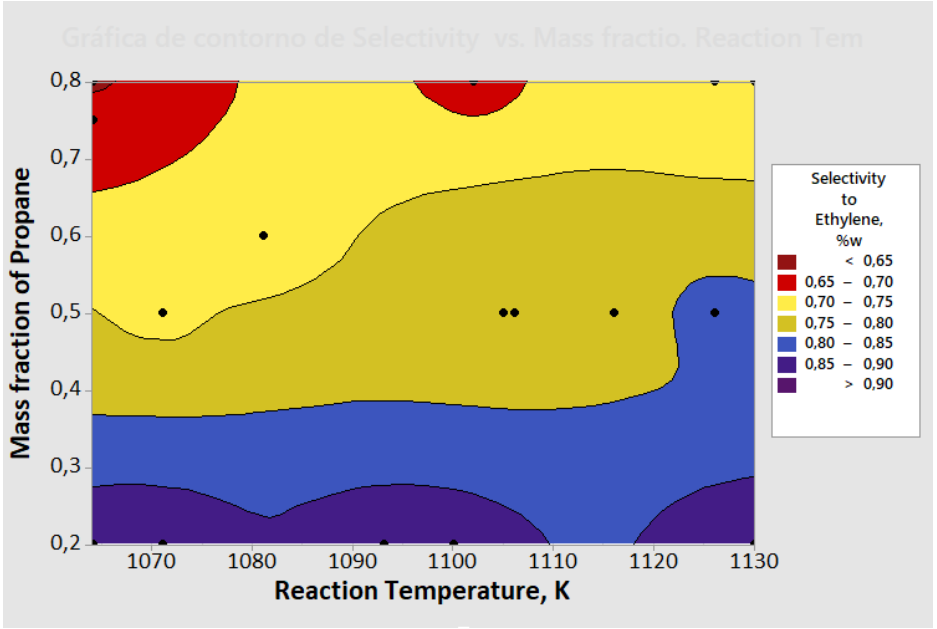
Outlet Temperature =1064 K, Inlet P = 303 kPa, steam/HC =0.3





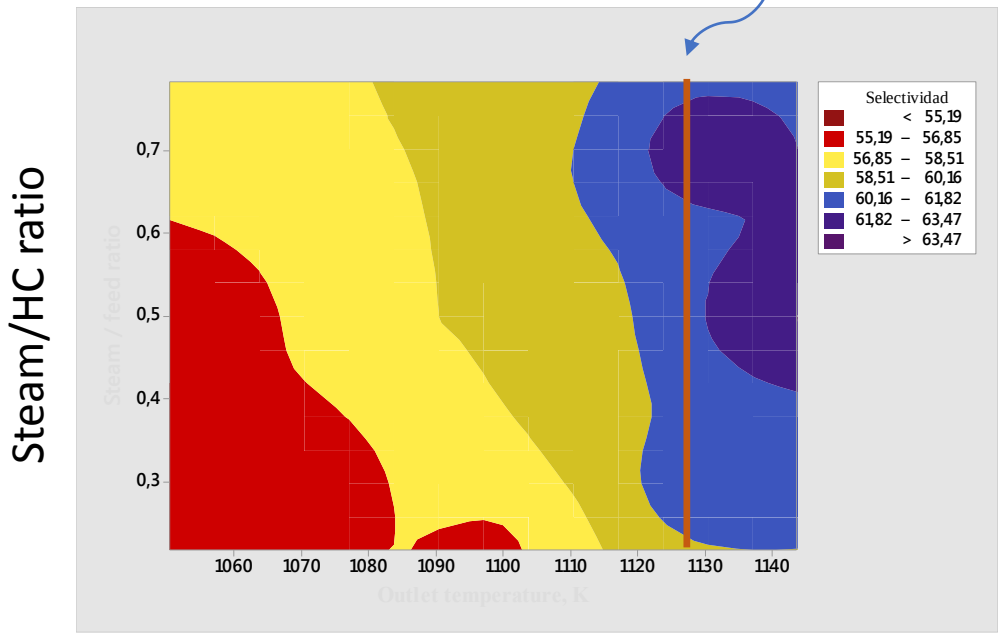
Inlet P = 300 kPa, steam/HC = 0.3, feed = 50/50 w% Ethane/propane

Fractional Factorial Analysis (Minitab)



Ethylene selectivity vs Outlet temperature and mass fraction of propane

Max temp. Allowed
For standard operation



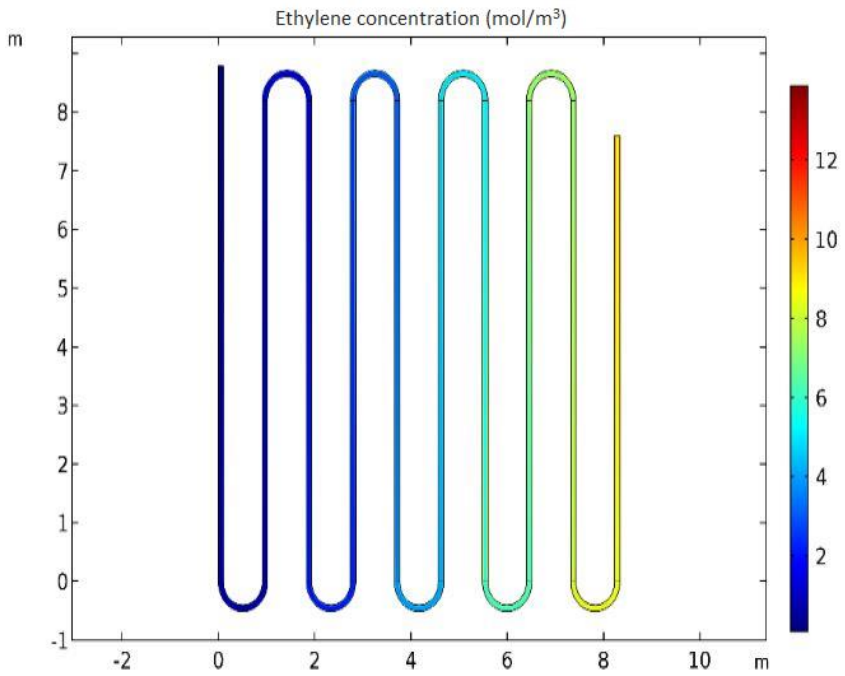
Ethylene selectivity vs outlet temperature and steam/HC ratio

Summary of profit margin for diferent simulation runs

Run	Outlet Temp	Steam/HC ratio	Propane amount	Coke thickness @ 760h operation	Run time	Cycles/year	Profit margin	Ethylene production	Propylene production
	K		%	mm	days		10^6 US$/year	Ton/year	Ton/year
1	1064	0,3	20%	13,37	47,37	7,39	30,552	22029,2	3655,8
3	1064	0,7	20%	9,87	64,73	5,47	24,896	18350,5	3020,7
5	1064	0,3	80%	11,18	56,65	6,22	25,702	17643,3	10862,1
7	1064	0,7	80%	7,53	84,15	4,24	20,467	14551,0	10159,9
9	1071	0,5	20%	12,51	50,63	6,94	31,165	22641,5	3447,7
10	1081	0,5	60%	12,43	50,95	6,89	30,754	21594,9	8276,6
11	1102	0,4	80%	15,19	41,69	8,35	33,724	23060,0	9965,8
12	1071	0,3	50%	13,09	48,38	7,24	29,981	21123,4	7072,0
13	1093	0,5	20%	15,77	40,16	8,66	39,939	28663,5	3619,8
15	1105	0,3	50%	17,57	36,05	9,59	39,345	27533,4	6197,5
16	1106	0,5	50%	15,52	40,81	8,53	39,127	27571,7	6579,9
18	1064	0,4	75%	10,42	60,78	5,81	25,373	17615,8	10203,7
19	1116	0,4	50%	17,85	35,48	9,74	42,182	29580,9	5941,0
20	1100	0,3	20%	18,19	34,82	9,91	42,793	30437,8	3722,7
23	1107	0,4	20%	18,22	34,76	9,93	45,056	32085,0	3609,9

Present Work

- Development of a 2D in COMSOL
- Inclusion of an external time dependent temperature profile
- Coupled simulation of furnace and cracking reactor in 3D
- Simulation of butane cracking



Ethylene concentration profile in a 2D model

Conclusions

Simulations of the COMSOL 1D model for thermal cracking of ethane at plant conditions show absolute deviations less than 5% when you compare them with actual GC analysis.

According to the fractional factorial analysis and simulation results the recommended intervals are:

- Concentration of propane in the feed: between 35 and 70 % w
- Outlet temperature: Between 1064 and 1118 K
- Steam/HC ratio: Between 0.3 and 0.7
- The coke thickness a 760 h of continuous operation produces a diameter reduction between 17% and 40%. Therefore the reactor cycle is limited to 40 - 80 days depending of outlet temperature and steam/HC ratio.

These limited conditions are framed also by the burner capacities, tube metallurgy and steam/HC ratio.

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Thanks for your Attendance

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Mathematical Equations for a 1D pseudo-dynamic model

Assumptions

- No radial gradient
- All cracking reactions take place in the reactor
- No hydrodynamic entrance effects
- No thermal entrance effects
- Ideal gas behavior
- Coke buildup is considered dynamically
- Froment molecular reaction scheme is used