Cracking in the Absence of Steam
Intensifying the Cracking furnace

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Talk Outline

- Motivation for steamless cracking
- Experimental work
- Simulation
- Integration of steamless cracking reactor with the plant

What is Thermal Cracking?

- One of the most important processes in the petrochemical industry.

$$\begin{bmatrix} \text{mixed} \\ \text{hydrocarbons} \end{bmatrix} + \text{steam} \xrightarrow{\text{heat}} \text{ethene} + \text{propene} + \text{co} - \text{products}$$

- Co-products include hydrogen, fuel gas, gasoline, butadiene.
- Endothermic reaction carried out 800-900 C
- Homogeneous gas phase reaction in the absence of catalyst.
- Coke is laid down on the walls of the reaction tubes.

Typical Steam Cracking Furnaces

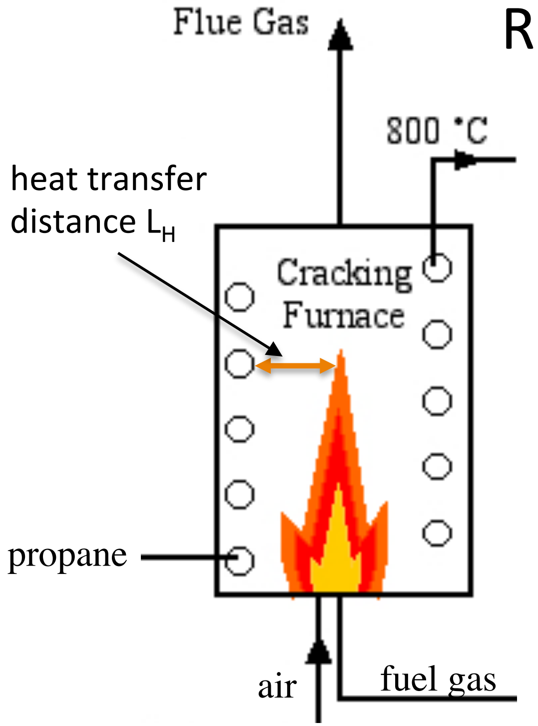
- Total Number of cracking tubes about 600
- Process Volume about 45 m^3. Firebox volume about 4500 m^3
- Total volume : process volume = 100
- Residence Time 0.25 to 0.75 s
- Firebox Efficiency about 65%

The Use of Steam in Thermal Cracking

- Advantages
  - Enhances heat transfer.
  - Reduces coke formation and deposition.
  - Improves selectivity towards olefins by reducing partial pressure.

- Disdavantages
  - Energy is required to generate it.
  - Not entirely inert:
    - Reacts with hydrocarbons and carbon at tube surface to form CO
    - Sulphur in the feed is required to moderate this reaction
    - Forms carboxylic acids, aldehydes, ketones and phenols

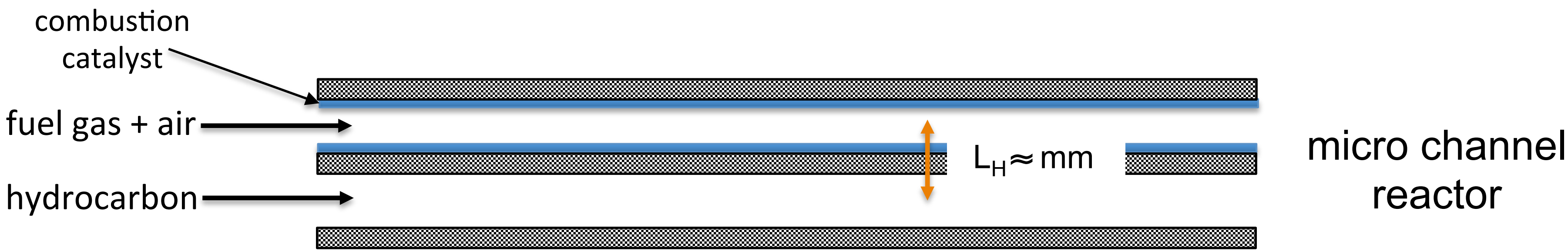
Intensification of the Cracking Process



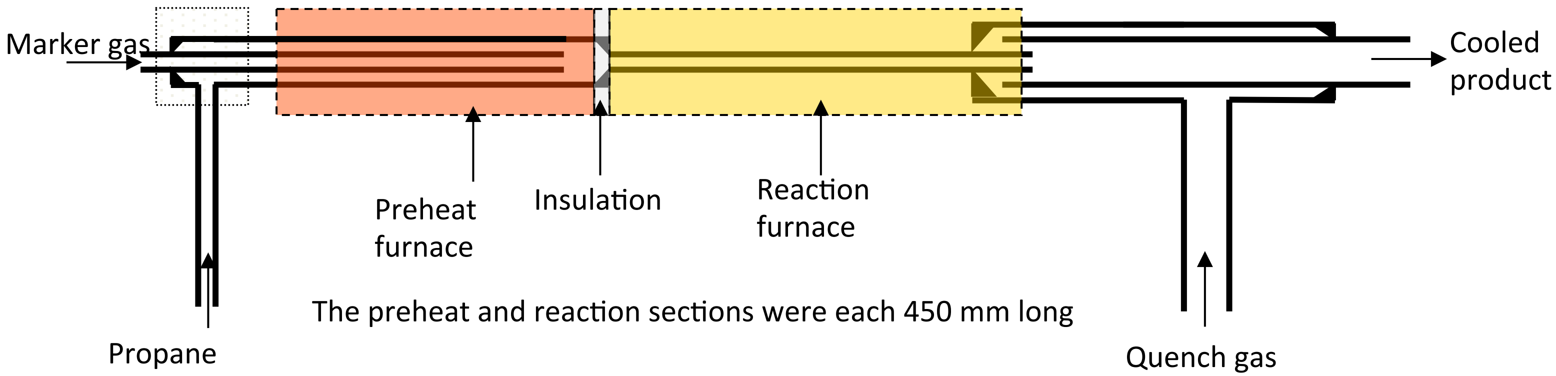
Reducing the size of the Furnace

- In a cracking furnace L_H is of the order of metres.
  - Large ΔT between flame and reaction tubes
  - Coke forms due to:
    - high tube surface temperatures (T_S)
    - catalytic effect of the Ni in the tube walls

- Reduce L_H to reduce the T_S and furnace volume.
- If T_S is lowered maybe we don't need steam.
- Beware! surface area to volume ratio is high in a micro channel – use a non-catalytic material



Laboratory work



- Propane , ethane and n-heptane were cracked.
  - Temperatures 810 - 860°C
  - Pressure 1.1 – 1.7 bar
  - Residence times 0.4 – 1.0 sec.
- Tube inside diameters
  - 2 mm, 3 mm, 4 mm.
- Tube materials
  - Silica, Alumina, Type 316 stainless steel, coated steels.

Analysis of products

- The quenched products were sent to two on-line GCs:
  - Hydrogen, methane, nitrogen and argon on one GC
  - C_2 to C_3 on second GC.

- Yields and conversion determined by ratio to marker gas or quench gas.

- Coke was determined by burning off in nitrogen containing 2% O_2. The gas was passed through heated copper oxide to convert any CO to CO_2 and analysed by an on-line IR analyser.

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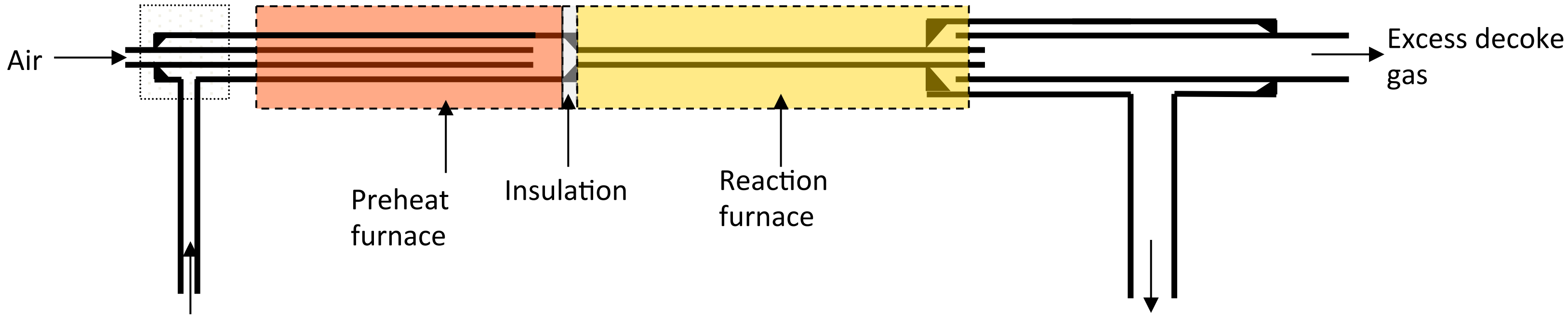
Coke



Decoke flows

- Decokes were normally performed immediately after the run without cooling the furnace.
- Occasionally the tube was removed and decoked using a micro burner moving along the tube.
- Using this method the coke was found to be evenly distributed along the length.

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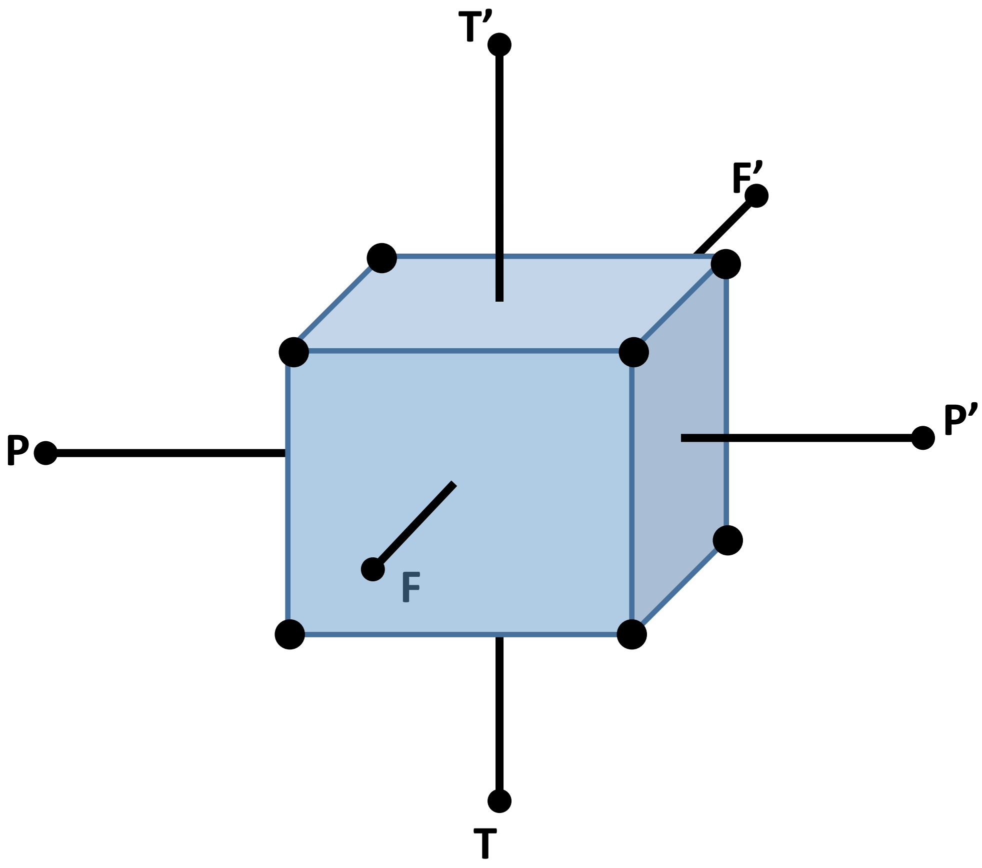
Coke

- Standard runs lasted 2 hours.
- During this time 6-8 product analyses were done. They showed high repeatability and no trend with time.
- A few longer runs up to 8 hours showed that coke deposition increased linearly with time.
- Coke density assumed similar to graphite when calculating reduction in tube diameter.

Design of Experiments



P = pressure
T = temperature
F = flow

Parameters chosen to give highest conversions similar to typical commercial values.

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Effect of pressure on products and coke

4 mm Silica tube:

Flow rate adjusted to maintain 90% conversion at 855 °C

Pressure bar	Propane Flow g/h	Yields %w/w						coke	
		H_2	CH_4	C_2H_4	C_2H_6	C_3H_6	C4+	ppm	mg/h
1.7	32.9	1.31	22.76	35.47	4.23	15.98	7.82	218	7.2
1.4	24.6	1.45	23.00	36.76	3.70	13.86	10.97	187	4.6
1.1	21.1	1.39	21.67	36.39	3.03	14.63	11.17	212	4.5

Yields and Conversion as a function of Temperature
4mm Silica Tube: Propane Flow 15 Nl/h: Pressure 1.6 bar

		Yields %w/w						Coke ppm
Temperature °C	Conversion %	H_2	CH_4	C_2H_4	C_2H_6	C_3H_6	C4+	
810	67.5	1.03	14.57	23.56	2.80	19.07	5.38	31
820	71.5	1.16	16.14	26.35	3.01	19.19	6.25	47
830	75.9	1.27	17.87	29.15	3.25	18.71	7.12	70
840	80.9	1.35	19.80	31.95	3.53	17.63	7.99	105
850	86.6	1.38	21.92	34.75	3.86	15.97	8.86	160
860	93.2	1.38	24.28	37.55	4.27	13.71	9.74	241

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Yields and Conversion for different tube diameters and materials at 850°C and 1.35 bar.

			Yields %w/w						Coke ppm
Tube	Flow Nl/h	Conversion %	H_2	CH_4	C_2H_4	C_2H_6	C_3H_6	C4+	
2 mm Silica	3.7	89.37	1.46	21.92	36.66	3.39	14.03	12.67	407
3mm Silica	7.7	87.8	1.68	23.66	38.98	3.56	15.58	5.24	231
4mm Silica	10.5	88.20	1.46	22.29	36.03	3.57	14.47	10.86	170
Alsint Alumina	10.5	88.5	1.47	22.78	35.75	4.21	13.74	5.67	217
Pythagorus Alumina	10.5	89.5	1.58	24.41	38.54	3.56	3.97	6.70	313

Ethane

4 mm silica tube.

Temp. °C	Pressure bar	Flow N l/h	Conversion %	Coke ppm	Yield (weight %)		
					H_2	CH_4	C_2H_4
850	1.35	16.16	56.71	91	3.54	3.05	46.49
850	1.35	12.06	65.19	137	3.97	4.49	52.32
870	1.35	18.01	65.10	122	3.95	4.11	52.87
900	1.35	30.51	66.07	107	4.20	3.71	50.22
900	2.01	34.53	65.36	125	3.73	4.76	49.19

N-Heptane cracking

4 mm Silica: 1h run length

Temp. ^oC	Pressure bar	Flow g/h	Coke ppm	Pass yield (weight %)					
				H_2	CH_4	C_3H_6	C_2H_4	C_2H_6	C4+
810	1.35	20.2	303	0.76	15.4	14.11	42.61	8.23	18.5
850	1.35	40.7	306	0.81	14.4	14.09	43.71	7.19	19.1

Key Experimental results

- Stainless steel cokes extremely rapidly.
- Coking rates in silica and alumina are similar.
  - Rates extrapolate to on-line time of 15 days between decokes for propane at 90% conversion and 30 days for ethane at 65% conversion.
- Coke lay-down occurs almost evenly along the whole length of the reactor.
- The coated tubes performance deteriorated significantly after only 4 react/decoke cycles.
- Adding steam (in alumina tube) gave coking rate similar to the steam less rate at the same HC partial pressure.

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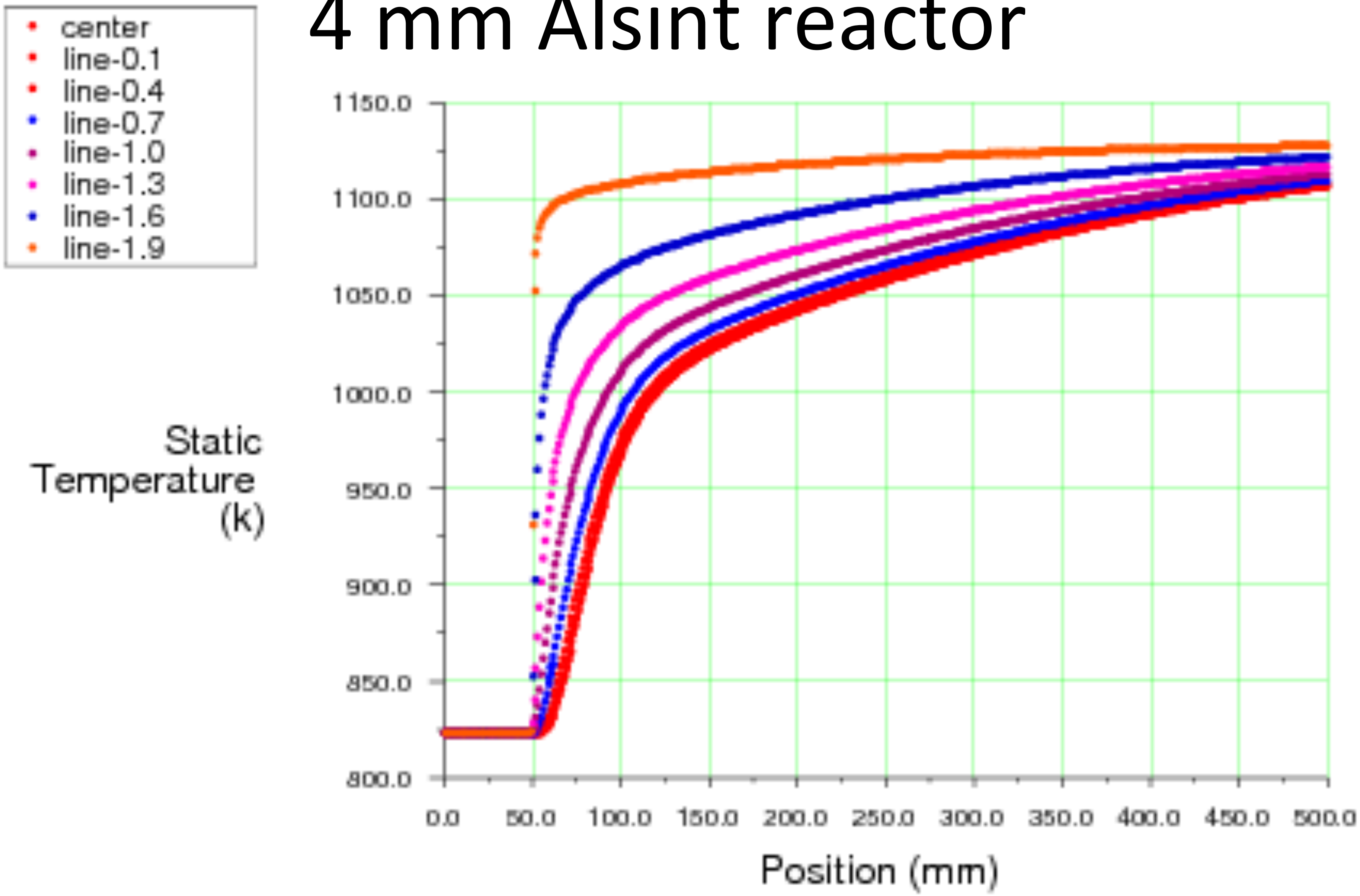
CFD Modelling

- Fluent used
- Model included cracking reactions and combustion
- Simple molecular reaction schemes chosen

Froment - Propane cracking reaction scheme

No.	Reaction	Reaction order	Frequency factor S^{-1}, $l\ mol^{-1}\ s^{-1}$	Activation Energy kJ/ mol
1	$C_3H_8 \rightarrow C_2H_4 + CH_4$	first	4.692×10^{10}	211.71
2	$C_3H_8 \leftrightarrow C_3H_6 + H_2$	first	5.888×10^{10}	214.59
3	$C_3H_8 + C_2H_4 \rightarrow C_2H_6 + C_3H_6$	second	2.536×10^{13}	247.10
4	$2C_3H_6 \rightarrow 3C_2H_4$	first	1.514×10^{11}	233.47
5	$2\ C_3H_6 \rightarrow 0.5\ C_6 + 3CH_4$	first	1.423×10^{9}	190.37
6	$C_3H_6 \leftrightarrow C_2H_2 + CH_4$	first	3.794×10^{11}	248.48
7	$C_3H_6 + C_2H_6 \rightarrow C_4H_8 + CH_4$	second	5.553×10^{14}	251.08
8	$C_2H_6 \leftrightarrow C_2H_4 + H_2$	first	4.652×10^{13}	272.79
9	$C_2H_4 + C_2H_2 \rightarrow C_4H_6$	second	1.026×10^{12}	172.63
10	$C_4H_8 \rightarrow C_6$	first	6.960×10^{7}	143.59

Predicted temperature profiles in the 4 mm Alsint reactor



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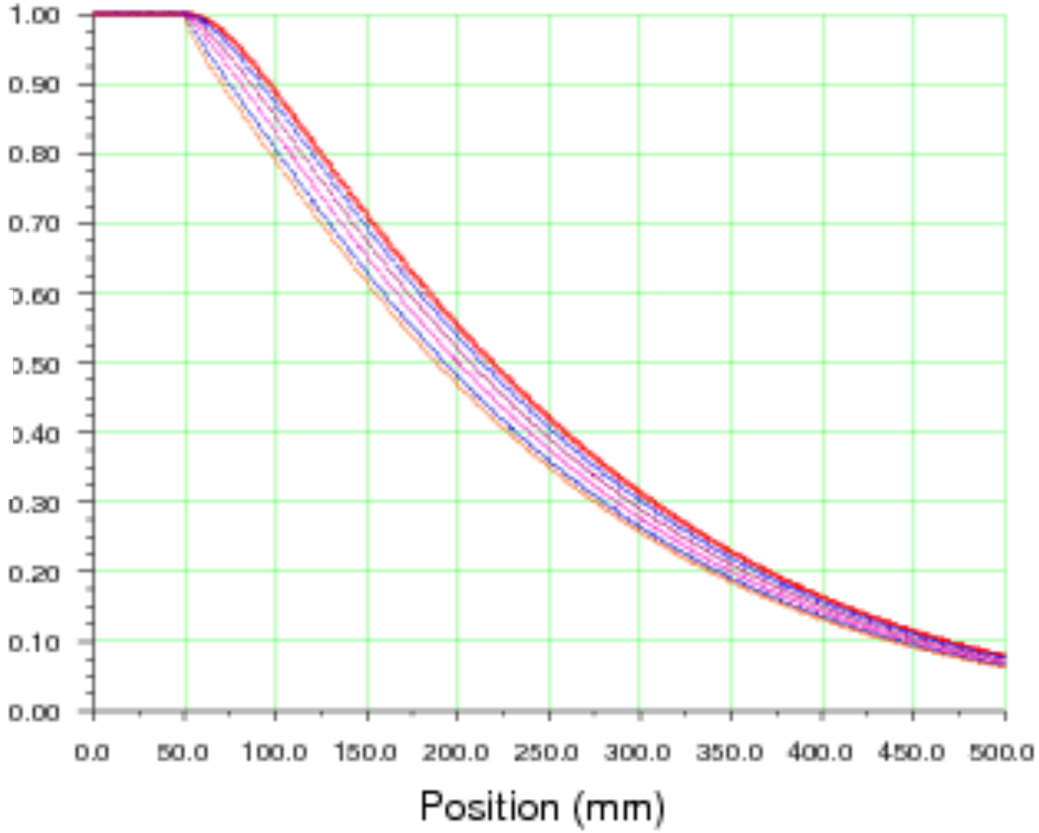
Conversion along 4 mm reactor.

Mass fraction of C_3H_8

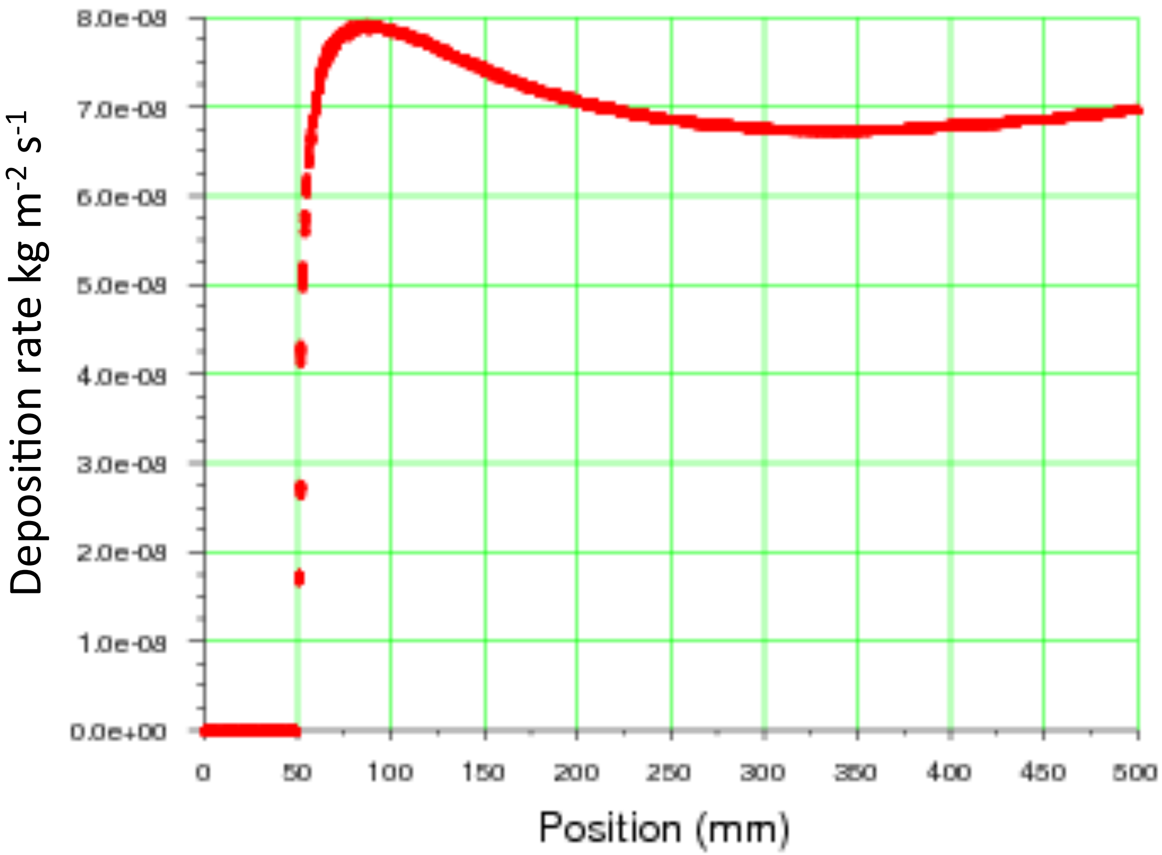


Modelling Coke Deposition

Froment's simple two component model of coke deposition was used.

$C_2H_4 \rightarrow 2C + 2H_2$

$C_3H_8 \rightarrow 3C + 4H_2$



The predicted rate of coke deposition was similar to that observed experimentally

Modelling the effect of coke

- The work did not extend to simulating coke deposition.
- Simulated by a uniform layer of coke 0.4mm thick on the wall of a 4mm tube.
- Comparing this with a clean tube at the same flow rate and furnace temperature:
  - Pressure drop increased from 11 Pa to 25 Pa.
  - Conversion dropped from 92% to 86%.

Integrating Steamless Intensified Reactors into an olefins process.

- Capital savings.
- Environmental savings.
- Energy savings.

Capital savings

- Total volume of 'firebox' reduced to 2-300m^3.
- Dilution steam raising system not required.
- Caustic scrubber to remove CO_2 and H_2S not required.
- Methanator to remove CO not required.
- 'Furnaces' can be factory built and delivered to site.
- Less structural steel and civil work required.

Environmental savings

- No disposal of 'spent caustic' containing Na_2CO_3 , Na_2S and aldehydic polymers.
- No disposal of contaminated process water containing organic acids and phenols.
- Catalytic combustion at lower temperatures reduces the production of NO_x.

Energy savings

- Crackers are energy integrated units.
- Heat input to the furnaces is recovered as high pressure steam and hot water
- These streams provide energy and power for the gas separation section of the plant.
- It is not simple to determine the effect of removing the steam.
- Energy saving calculated by comparing a propane cracker using conventional furnaces with one using steamless intensified reactors.

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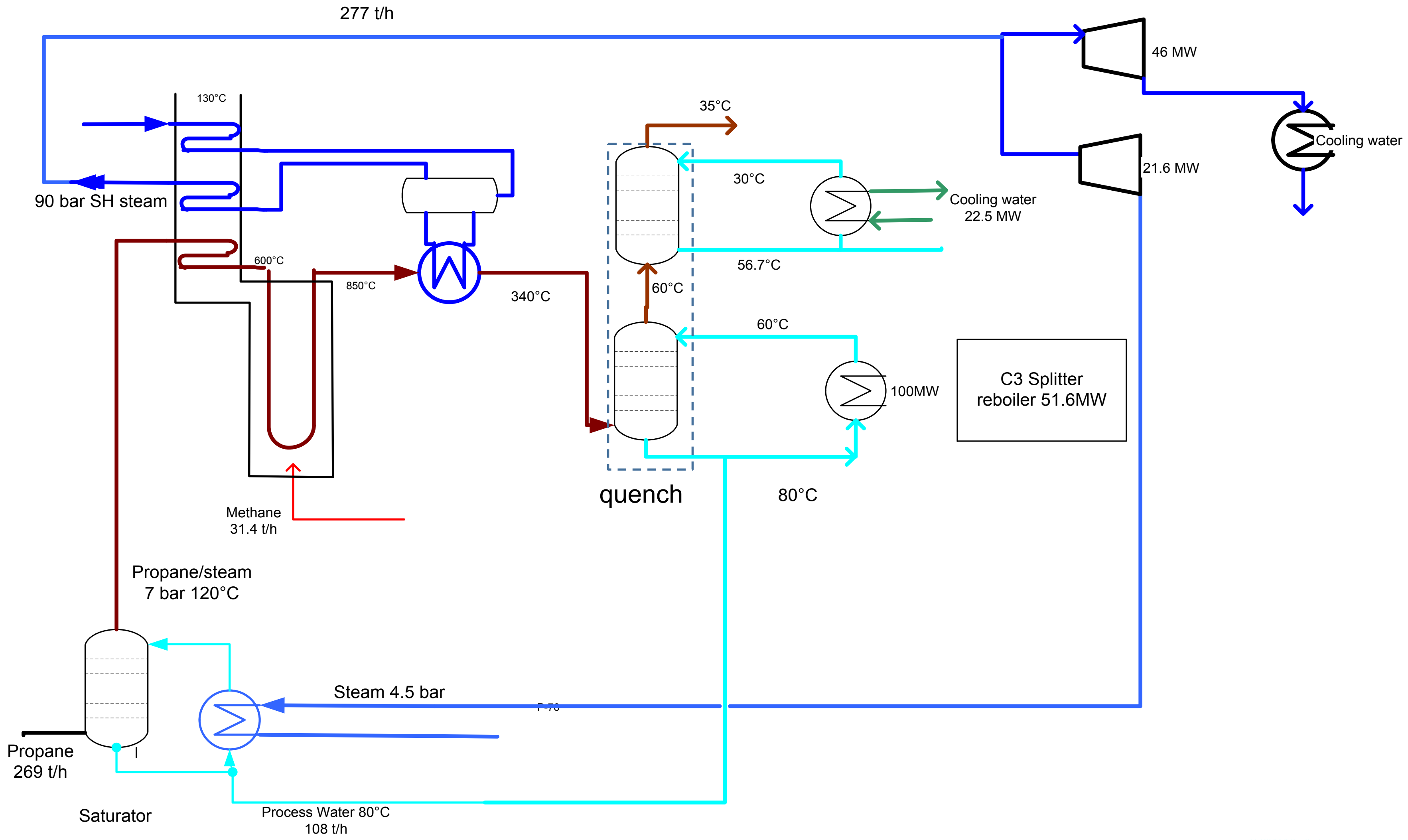
Basis For Comparison
750,000 tpa ethylene unit based on propane

- Plant Feed propane – 269 t/h.
- Steam:propane ratio 0.4
- Ex-furnace yields:

H_2	CH_4	C_3H_8	C_3H_6	C_2H_4	C_2H_6	C_4+
1.5%	24%	9.4%	13.6%	36.8%	3.45%	11.2%

- Coil exit temperature 850°C.
- Temperature after Quench 340°C.
- HP steam pressure 90 bar.

A Conventional Propane Plant ‘Front End’



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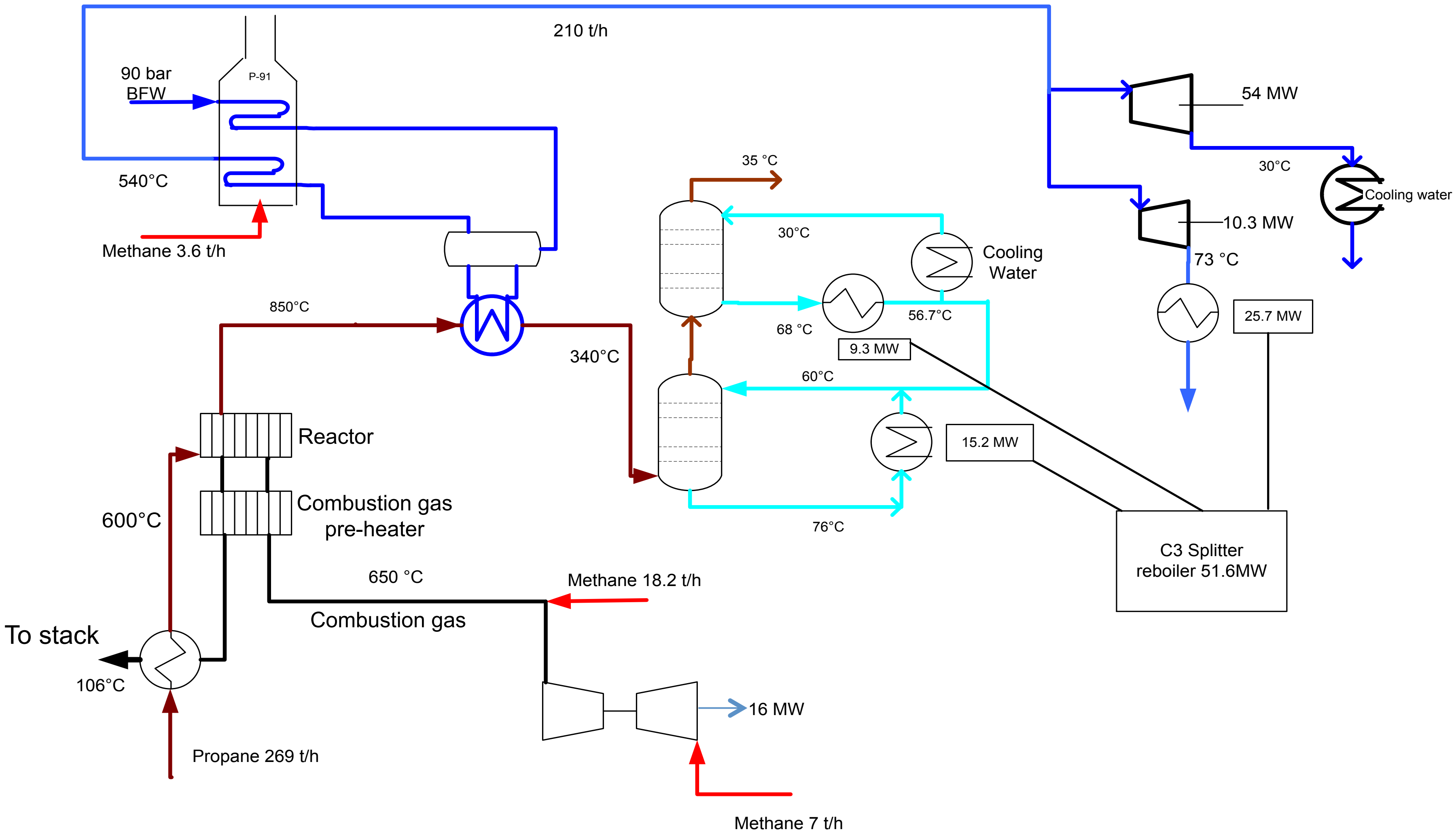
Summary of conventional plant

• Methane consumption	31.4 t/h
• Shaft power	
– Condensing turbine	46 MW
– Pass-out turbine	21.6 MW
– Total	67.6 MW
• Hot Water for propane tower	100 MW
• Propane tower reboil	51.6MW

A Steamless Propane Plant 'Front End'



Summary of Intensified Unit

- Methane consumption:
  - Turbine 7.0 t/h
  - Reactor 18.2 t/h
  - Superheater 3.6 t/h
  - Total 28.8 t/h (31.4 t/h)
- Shaft Power
  - Gas Turbine 16 MW
  - Condensing Turbine 54 MW
  - 73°C condensing Turbine 10.3MW
  - Total 80.3MW (67.6MW)

Crediting the extra Power

1. Credit as electricity generated on a modern power station (60% efficiency): 12.7 MW = 1.4 t/h methane.

2. Extra power is needed on the plant:

   Producing 12.7 MW on conventional boiler/turbine = 2.9 t/h methane.

Therefore saving from omitting steam is

4 to 5.5 t/h methane.

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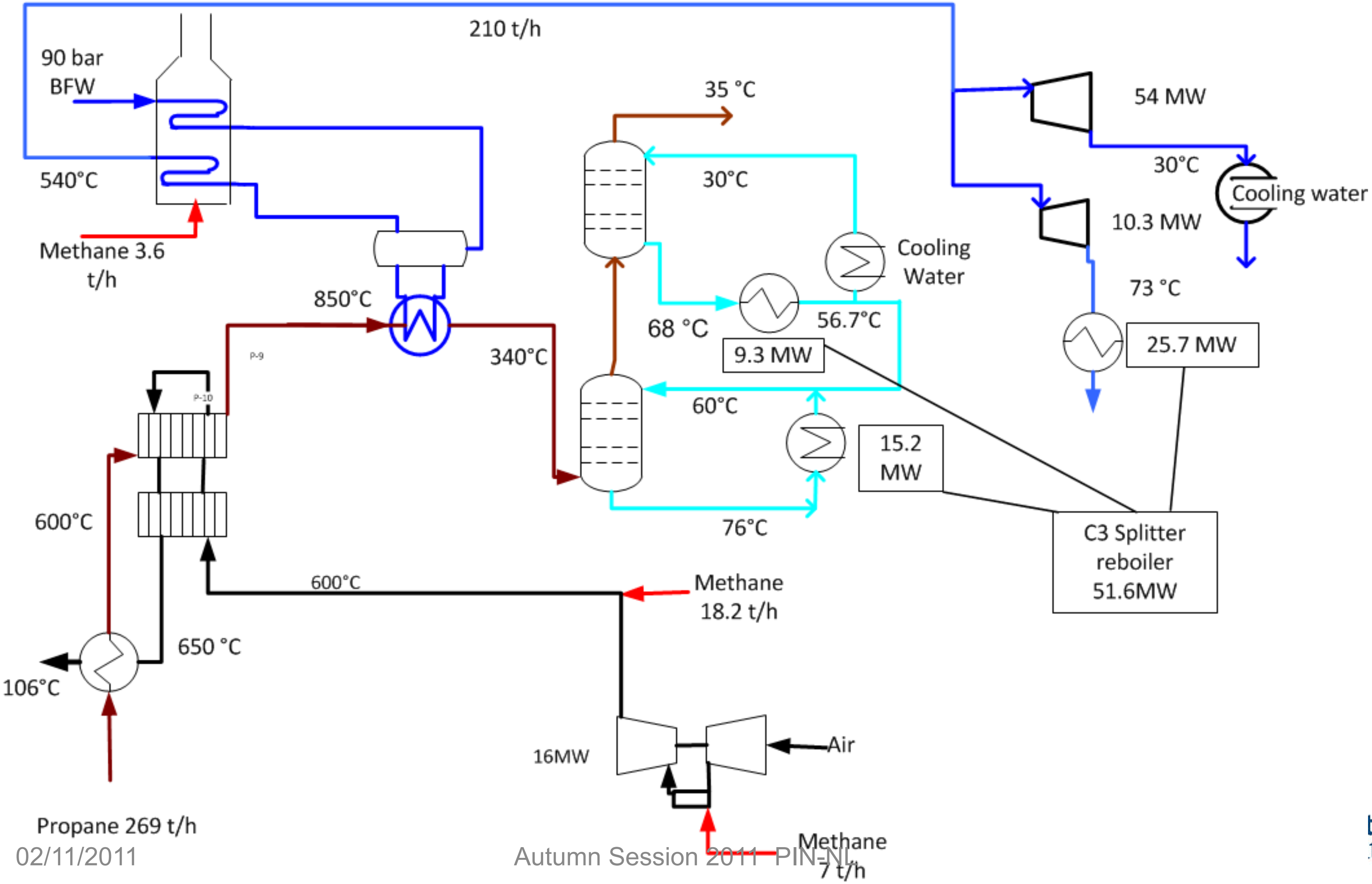
Conclusions

- Demonstrated the feasibility of an intensified steamless cracker.
- Olefins production not affected by removing the steam.
- Rate of coking in silica, alumina and coated stainless steel tubes allow 15 days operation between decoking.
- Lack of steam prevents oxygenated by products from forming.
- Fuel gas savings of 12-18%

Questions?


210 t/h
90 bar
BFW
540°C
Methane 3.6
t/h
850°C
340°C
35 °C
30°C
68 °C
56.7°C
9.3 MW
Cooling
Water
60°C
15.2
MW
76°C
54 MW
30°C
Cooling water
10.3 MW
73 °C
25.7 MW
C3 Splitter
reboiler
51.6MW
600°C
600°C
Methane
18.2 t/h
650 °C
106°C
16MW
Air
Methane
7 t/h
Propane 269 t/h