Speciation Study of the Emission Inventory from Flaring

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Texas State Implementation Plan needs refinements

- Air model simulation predictions are often under predict observed peak O_3 with current HRVOC emission inventory.
- Current air emission inventory from flaring is simply a mass throughput with 98% reduction without any considerations of by-product or intermediate formation through combustion.

Experiences working for flare minimization

- Different species for different chemical process (Refinery, Olefin, Polymer, and Exploration fields)
- Different mass flow rate at different operation mode (Emergency, Startup, Shutdown, and Normal)

- Different flare design provides different combustion environment

Project Objectives

- To investigate the flare mass flowrate & chemical species as function of
  - process plant type (Refinery/Olefin/Polymer/Exploration),
  - Feedstock (General Hydrocarbon/Naphtha/ Ethane/Propane, etc.) and
  - operation mode (Emergency/Start up/Shutdown/Normal)

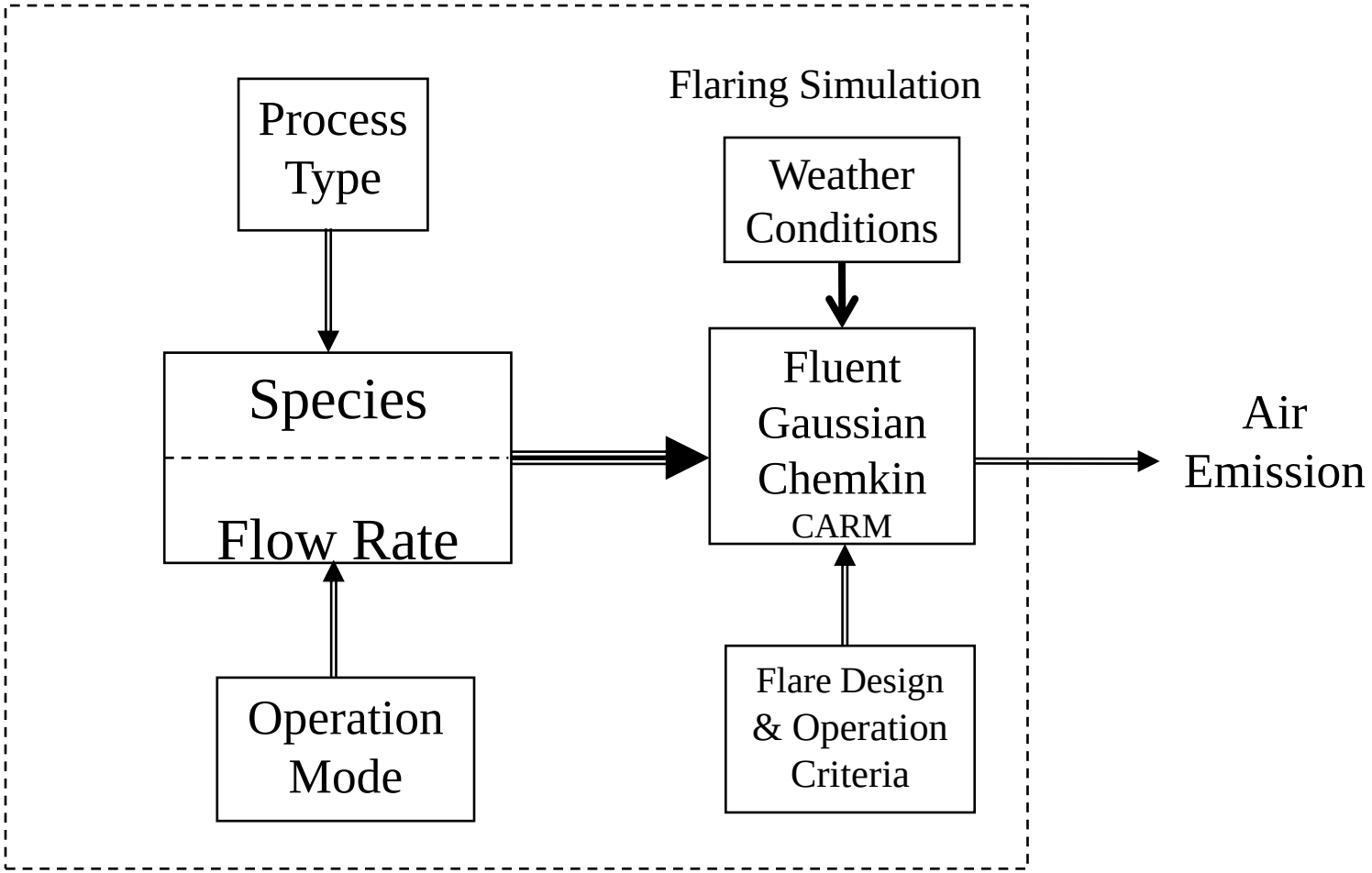
Project Objectives

- To infer the combustion efficiency and emission species by using a computational fluid dynamics (CFD, i.e. Fluent) modeling of industrial flaring system together with a complex combustion kinetic chemistry model (Chemkin) and an *ab initio* molecular calculation (Gaussian) under different process operating/weather conditions.

Project Objectives

To develop new computer code that can be used with SMOKE emissions models to translate chemical species passed through flares into emitted species.

Functional diagram of this study



Analysis of Emission Event Data

Brazoria County : Emission event during 1/1/2006 to 12/31/2006 (Source : TCEQ Online Database)

No	Entity name	Began	Ended	Source	Operation mode	Emission details		
						Contaminant	Limit	Amount Released (est) (lbs)
85518	CHEVRON PHILLIPS CHEMICAL	12/30/2006	12/31/2006	Unit 33 Process Flare, EPN	Emergency shutdown	Acetylene	0	147
	SWEENY COMPLEX	9:15PM	6:00PM	number 56-61-22	(High liquid levels in the suction drums serving the 2nd and 3rd	Benzene	0	371
		Total Time	20.45 hrs		stages of the cracked gas compressor activated the	Butadiene, 1-3	0	322
					compressor's emergency shut-down system. Unit shutdown	Butane	0	235
					following loss of cracked gas compressor resulted in flaring of	Butenes, All Isomers	0	176
					several process strea)	Carbon Monoxide	0	7733
						Ethylene (gaseous)	0	3156
						Isobutane	0	70
						NITRIC OXIDE	0	1017
						Nitrogen dioxide	0	54
						Propane	0	1122
						Propylene (Propene)	0	1086

emission

Flaring

Species & rate for flaring

Species & lb for flaring

Species & lb released

Top Six Plants in Air Emission Houston-Galveston Area 2006 data

Chemical Plant	Lb for flaring	Lb reported
CHEVRON PHILLIPS CHEMICAL SWEENY COMPLEX	2,329,950	46,599
CHANNEL VIEW COMPLEX	1,949,600	38,992
BY PRODUCTS NORTH AMERICA TEXAS CITY	1,267,612	25,352
VALERO REFINING TEXAS CITY REFINERY	1,241,126	24,822
SWEENY REFINERY	1,060,900	21,218
DOW TEXAS OPERATIONS FREE PORT	948,022	18,960

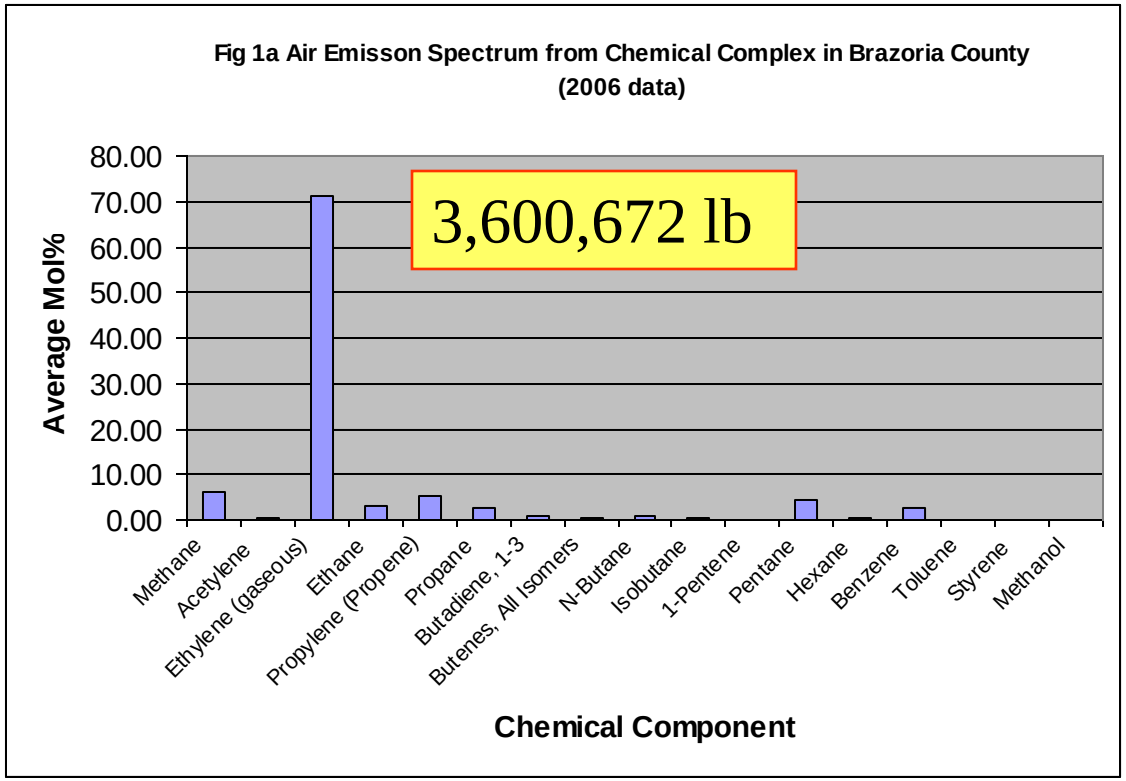
Top 4 Counties in Emission (2006)

COUNTY NAME	ALL EMISSION EVENTS	HRVOC EVENTS	HRVOC for Flaring, lb	HRVOC Reported, lb
BRAZORIA	60	23	4,661,572	93,231
HARRIS	60	36	4,369,200	87,384
GALVESTON	60	37	2,508,738	50,174
CHAMBERS	60	43	1,630,014	32,600

Chemical Plants 3,600,672 lb (77%)

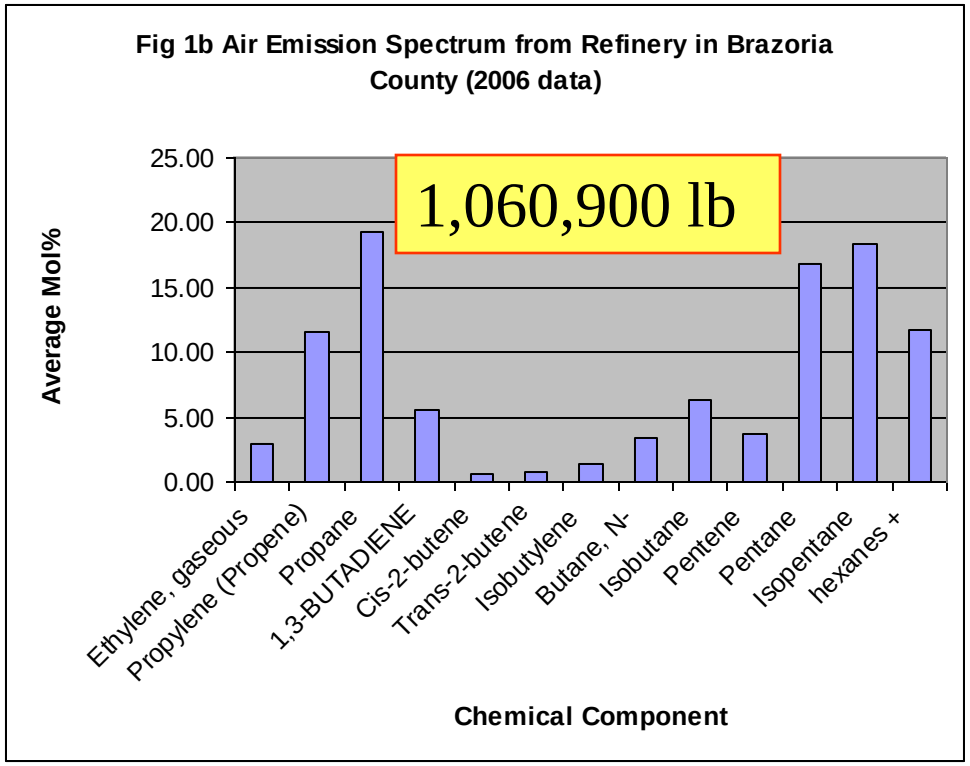
Refinery 1,060,900 lb (23%)

Emission Spectrum from Chemical Complex in Brazoria County



Component	Ave Mol%
Methane	6.37
Acetylene	0.54
Ethylene (gaseous)	71.30
Ethane	3.27
Propylene (Propene)	5.43
Propane	2.51
Butadiene, 1-3	1.00
Butenes, All Isomers	0.26
N-Butane	0.82
Isobutane	0.31
1-Pentene	0.01
Pentane	4.59
Hexane	0.62
Benzene	2.59
Toluene	0.19
Styrene	0.01
Methanol	0.19

Emission Spectrum from Refineries in Brazoria County



Component	Ave Mol%
Ethylene, gaseous	2.99
Propylene (Propene)	11.61
Propane	19.30
1,3-BUTADIENE	5.58
Cis-2-butene	0.66
Trans-2-butene	0.70
Isobutylene	1.43
Butane, N-	3.43
Isobutane	6.39
Pentene	3.67
Pentane	16.81
Isopentane	18.43
hexanes +	11.69

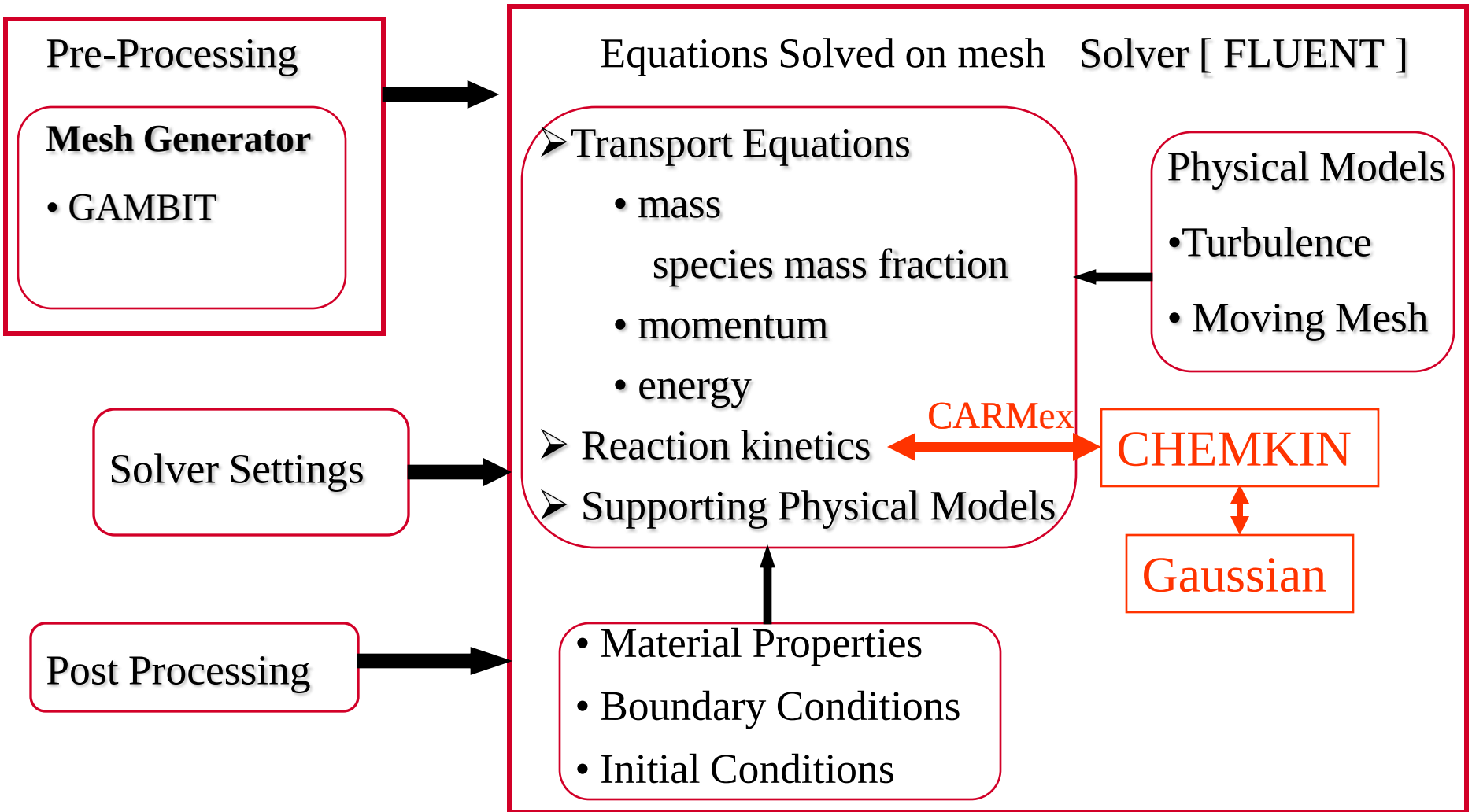
Adiabatic Steam-aided Flaring with 65% Air Supply

	GAS-IN	AIR	STEAM	FL-GAS
Temperature C	**30**	**30**	**194**	**1603.1**
Pressure bar	**1**	**1**	**13.605**	**1**
Vapor Frac	1	1	1	1
Mole Flow kmol/hr	247.922	2563.462	167.112	3281.328
Mass Flow kg/hr	8601.618	73104.628	3010.566	84716.812
Volume Flow cum/hr	6201.001	64567.348	445.651	511954.8
Enthalpy MMkcal/hr	**2.263**	**-4.512**	**-9.451**	**-11.699**
Mole Flow kmol/hr				
ACETYLENE	6.261	0	0	**3.304**
BENZENE	5.267	0	0	0
1,3-BUTADIENE	6.602	0	0	0
N-BUTANE	4.484	0	0	0
1-BUTENE	1.739	0	0	0
CIS-2-BUTENE	1.739	0	0	0
ETHYLENE	124.764	0	0	**17.449**
ISOBUTANE	1.336	0		0
NITRIC-OXIDE	37.588	0	0	0
NITROGEN-DIOXIDE	1.302	0	0	0
PROPANE	28.218	0	0	**0.003**
PROPYLENE	28.621	0	0	**0.038**
ARGON	0	17.941	0	17.941
OXYGEN	0	470.36	0	0
NITROGEN	0	1995.594	0	2015.039
WATER	0	79.567	0	370.705
STEAM	0	0	167.112	**370.705**

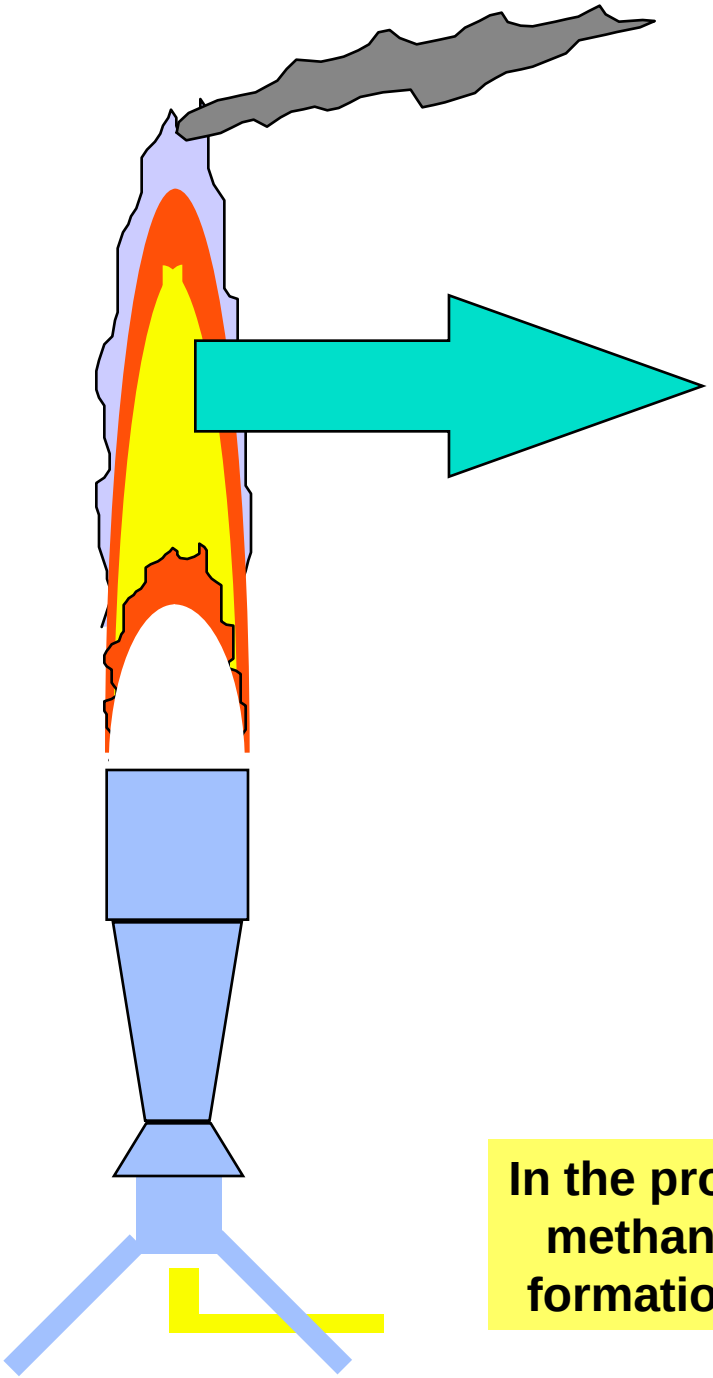
Residures, By-products and Flare Temperature at different Air Supply (RGibbs)

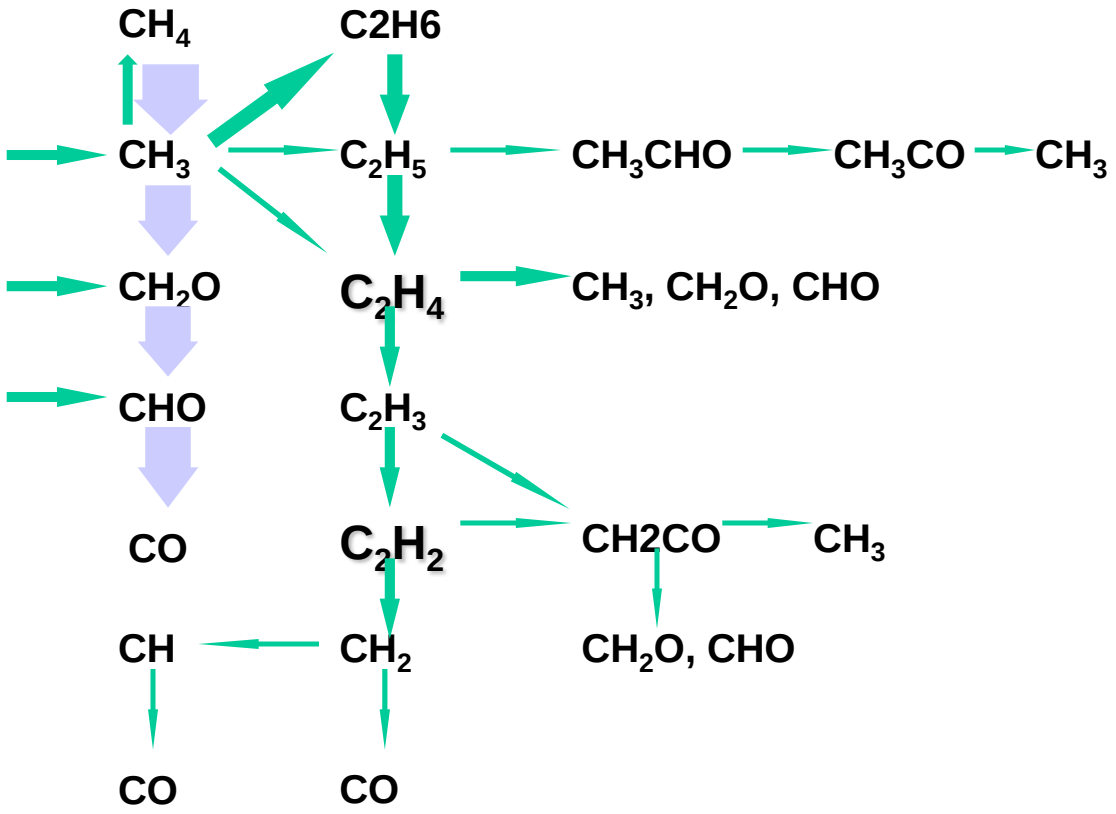
Stichiome-tric Air	Unreacted Reactants (kmol/hr)	Products (kmol/hr)	Adiaba-tic Flare Temp(C)
65% Air Supply	Ethylene (17.449) Acetylene (3.304) Propane (0.003) Propylene (0.038)	Formaldehyde (0.074) Acetaldehyde (0.001) Methanol (0.005)	1603-1606
55% Air Supply	Ethylene (51.819) Acetylene (5.249) Propane (0.032) Propylene (0.234) Butadiene (0.001)	Formaldehyde (0.076) Acetaldehyde (0.001) Methanol (0.008) Cyclopropane (0.001)	1537-1540

CFD Modeling Overview



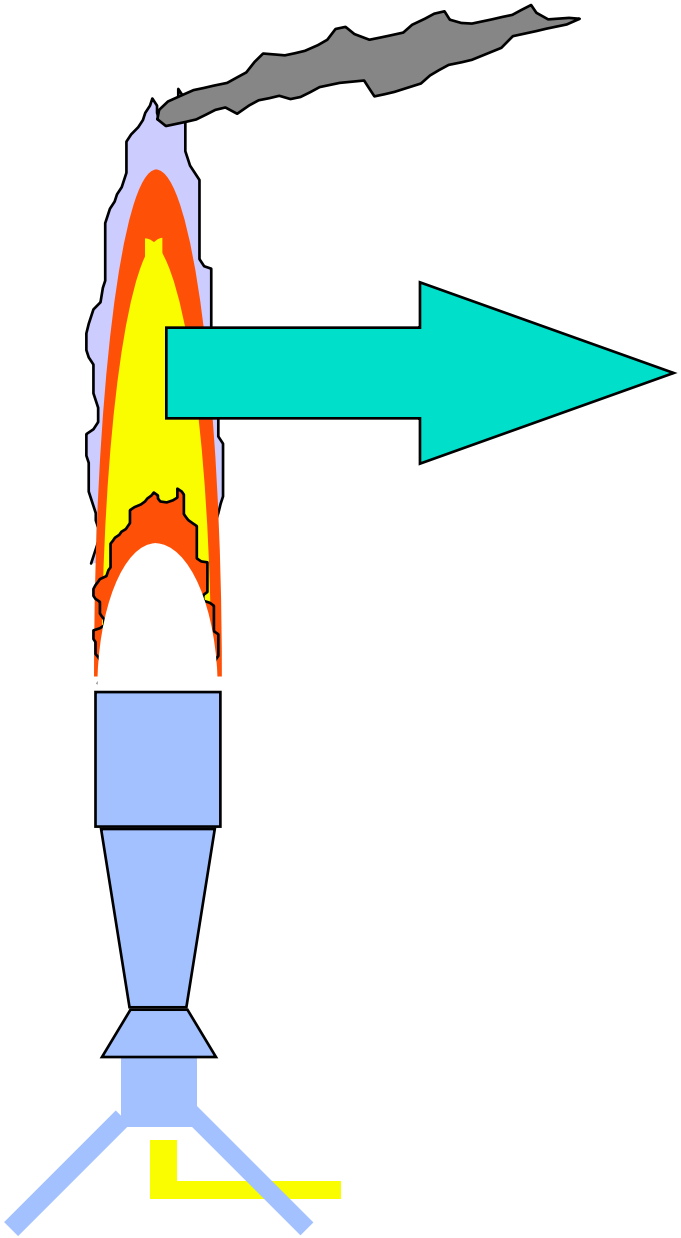
CH_4 ----> CO Reactions

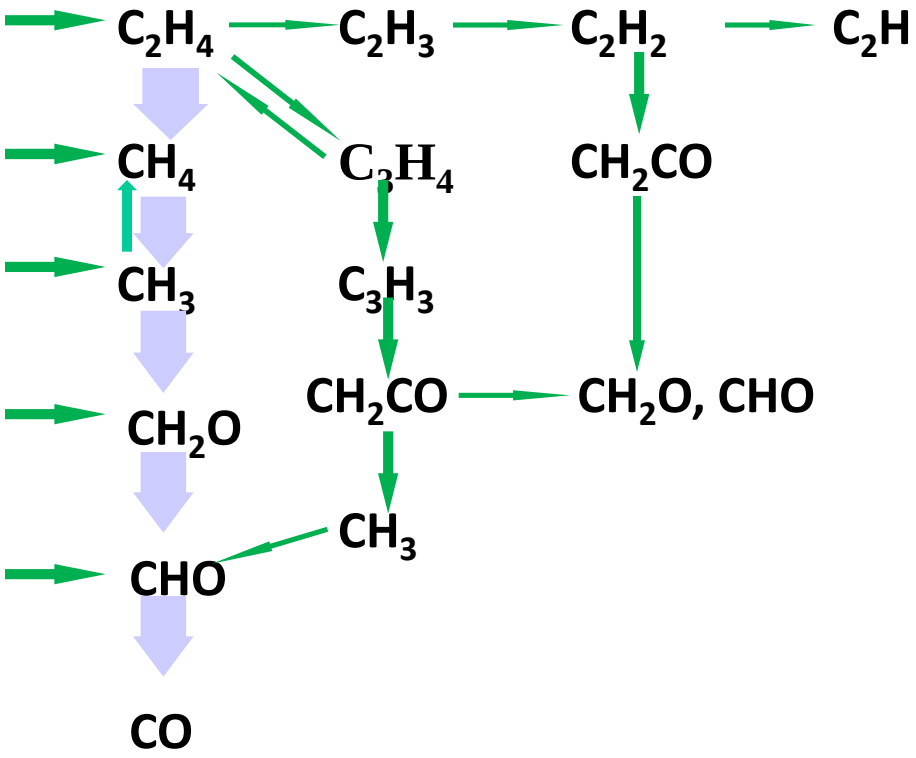




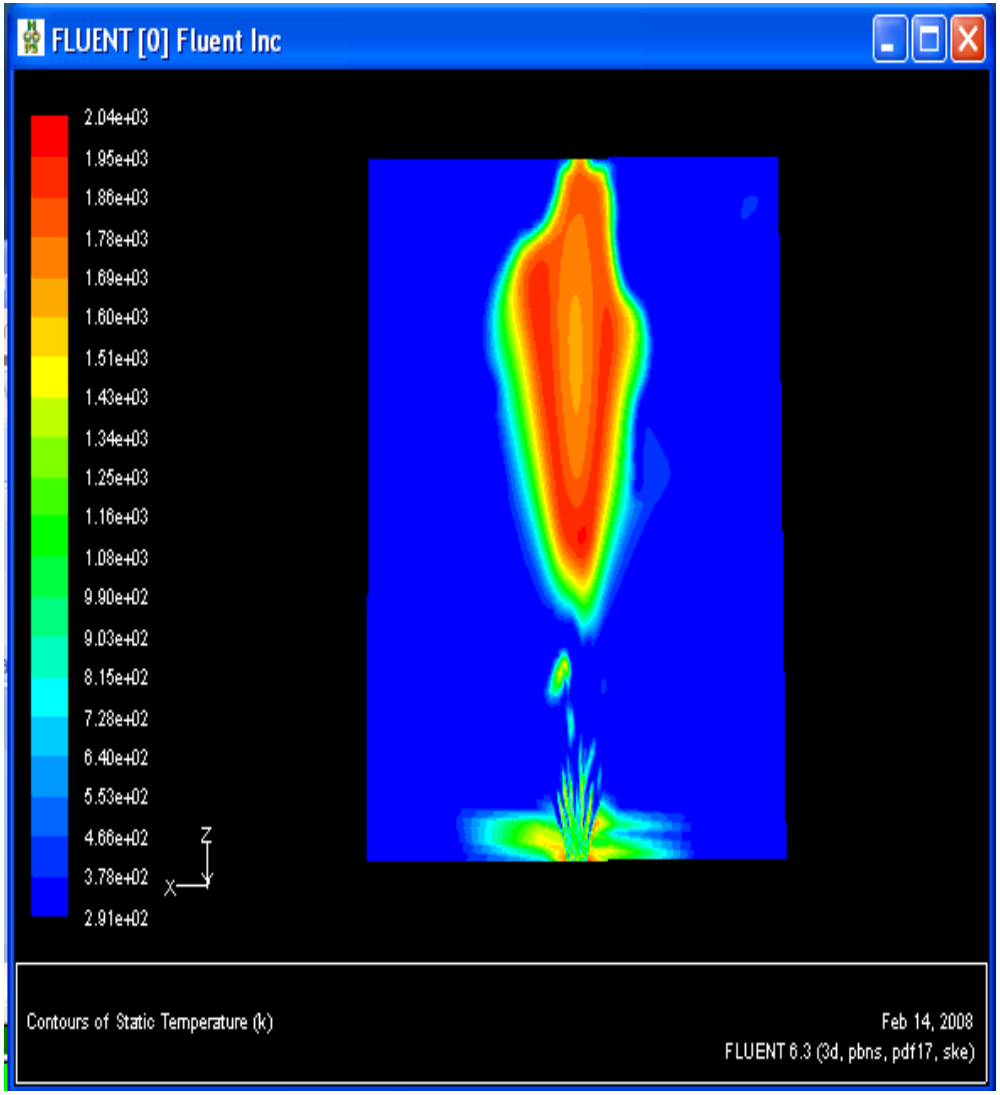
In the process of making CO, even a compound as simple as methane has many intermediate reaction pathways. Note formation of ethylene and acetylene groups in the process.

Ethylene Reaction Pathways





Preliminary Fluent Results



Complement IFC with this Model Study

- This model will provide insights and a cost-effective tool for predicting the yield of new HRVOC species, and
- Predicting easy-to-use ratios such as HCHO to C2H4 or C3H6 ratio from flaring

– International Flare Consortium (IFC)

How the Emissions Inventory be Improved?