“Natural gas conversion to higher-value products: Challenges and opportunities”

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This presentation:

- Quantifies the impact of the shale revolution on methane as a feedstock
- Outlines the options for methane conversion*
- Describes (briefly) the indirect, syngas-based process
- Describes two examples for *direct* conversion: aromatization and oligomerization using “superacids”

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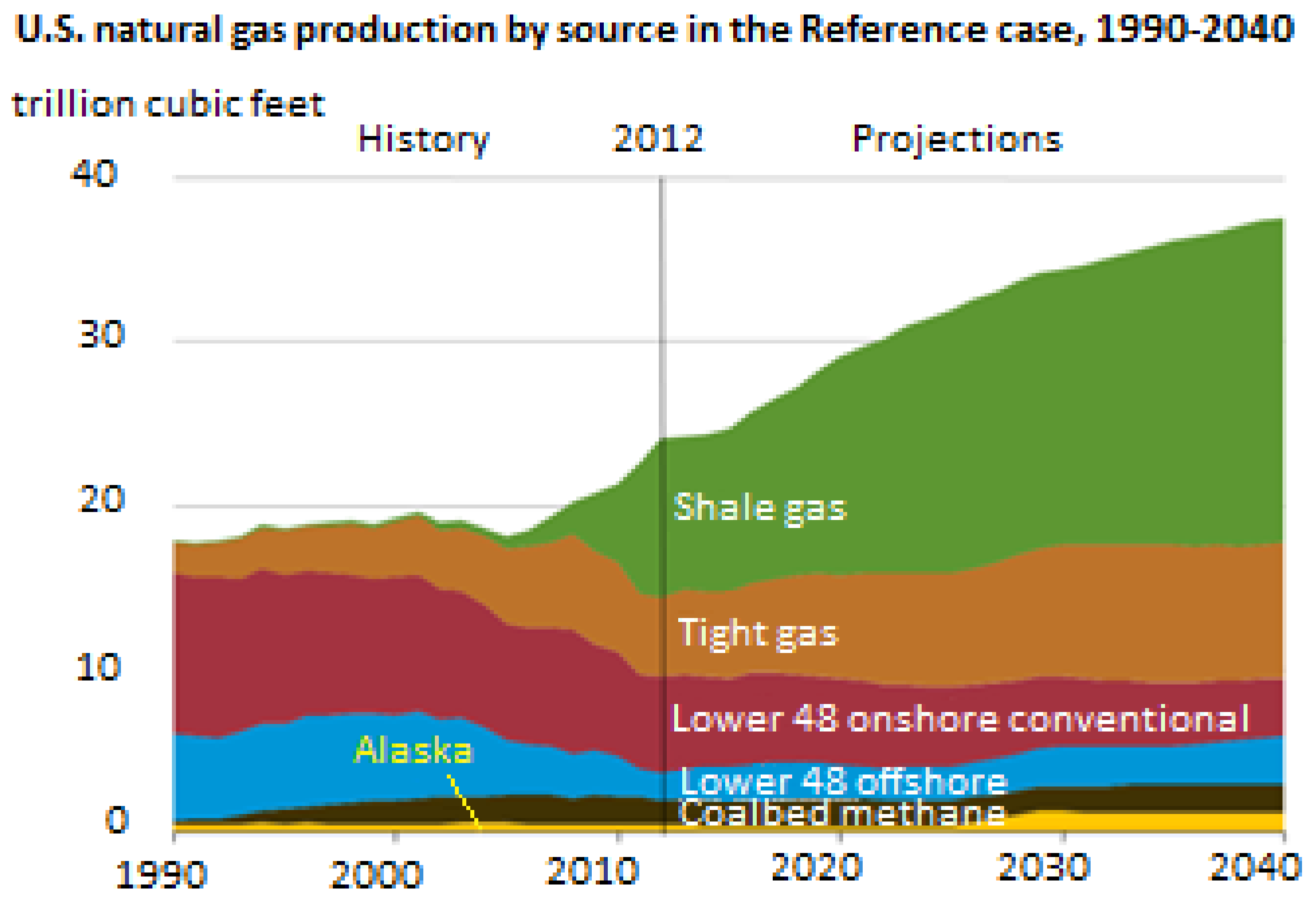
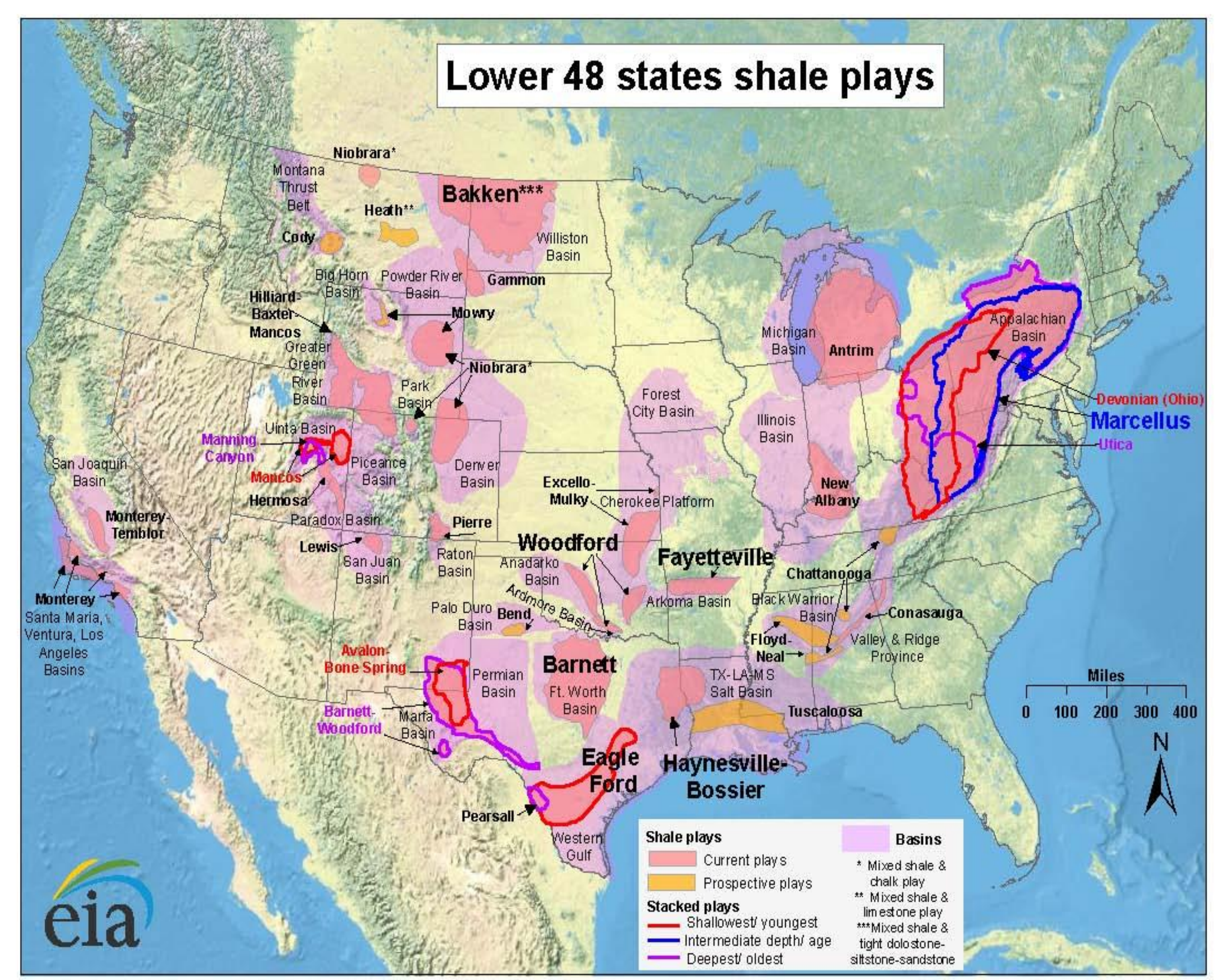
* The focus here is on methane. Natural gas liquids (C_2-C_4) and natural gas condensates (C_5^+) are not discussed here, but are very scientifically and commercial significant.

Significant incentive for methane conversion



Organization for Economic Co-operation and Development (OCED) Environmental Outlook Baseline

Significant natural gas resources on-shore



Just 10 yrs ago………."….. the U.S. chemical industry was in decline. Of the more than 40 chemical manufacturing plants being built worldwide in the mid-2000s with more than $1 billion in capitalization, **none were under construction in the United States"**.

National Academy Press, 2016, "The Changing Landscape of Hydrocarbon Feedstocks for Chemical Production: Implications for Catalysis: Proceedings of a Workshop" ISBN 978-0-309-44479-8 | DOI: 10.17226/23555.

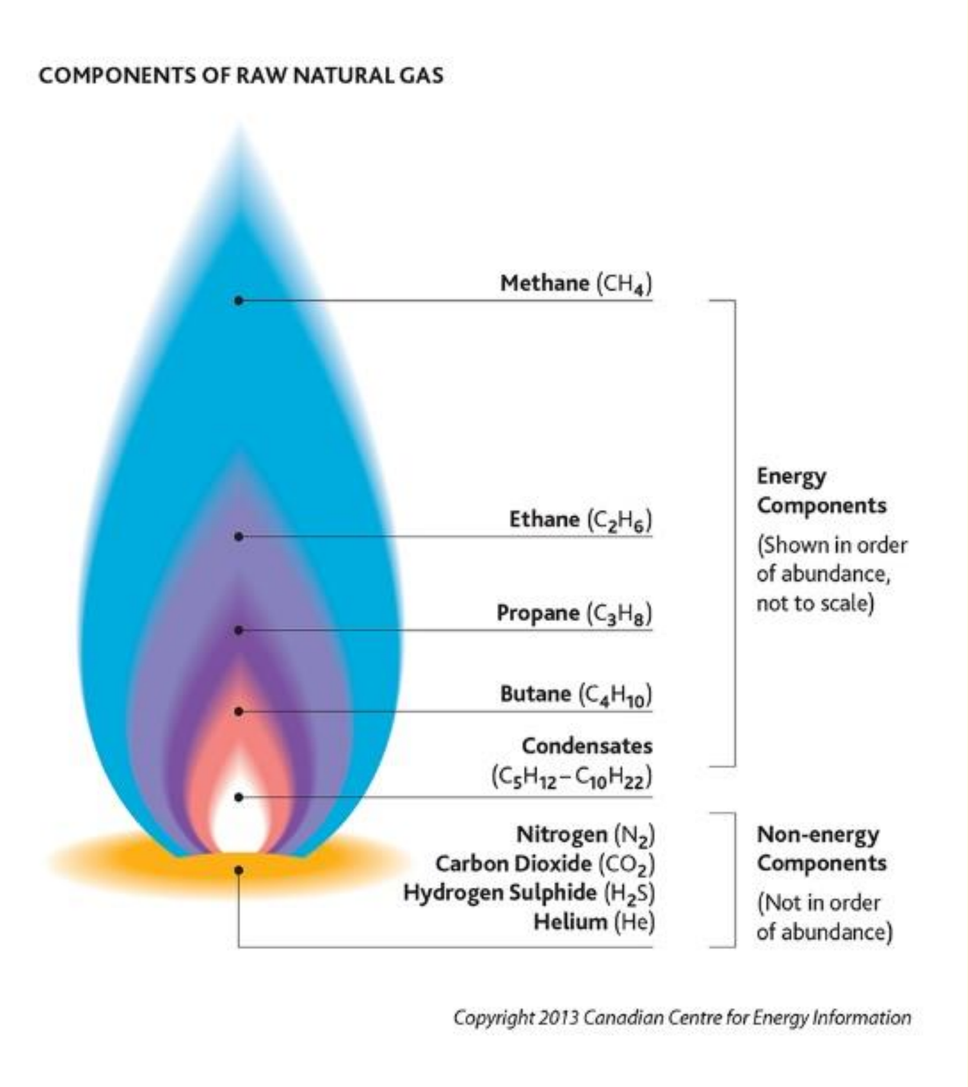
But now………."….. **as a result of abundant natural gas**…as of September 2015 companies from around the world have announced 246 projects and $153 billion in potential capital investments in U.S."

National Academy Press, 2016, "The Changing Landscape of Hydrocarbon Feedstocks for Chemical Production: Implications for Catalysis: Proceedings of a Workshop" ISBN 978-0-309-44479-8 | DOI: 10.17226/23555.

“Natural gas” → CH_4 + higher hydrocarbons

“Natural gas liquids” → C_2-C_4

“Natural gas condensates”→ C_5-C_{10}



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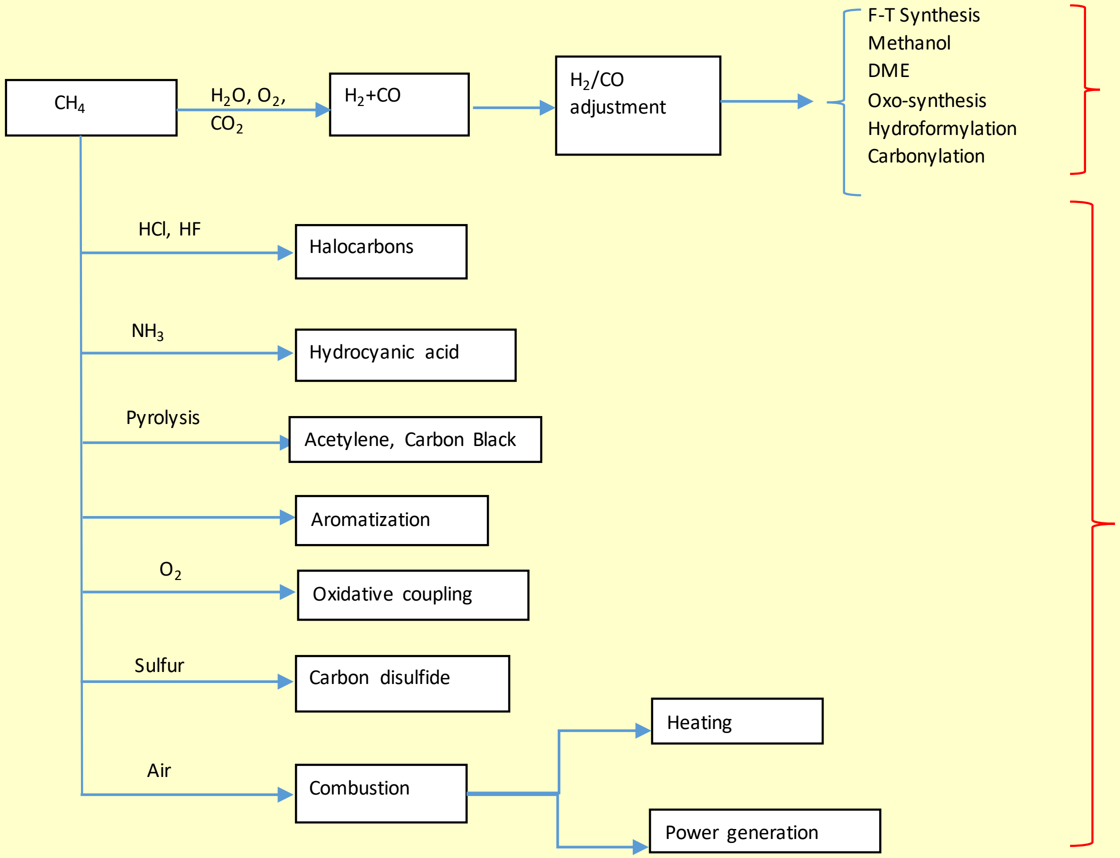
Options for CH_4 conversion



CH_4

H_2O, O_2, CO_2 → H_2+CO → H_2/CO adjustment →
- F-T Synthesis
- Methanol
- DME
- Oxo-synthesis
- Hydroformylation
- Carbonylation

HCl, HF → Halocarbons

NH_3 → Hydrocyanic acid

Pyrolysis → Acetylene, Carbon Black

→ Aromatization

O_2 → Oxidative coupling

Sulfur → Carbon disulfide

Air → Combustion → Heating, Power generation

Indirect Conversion

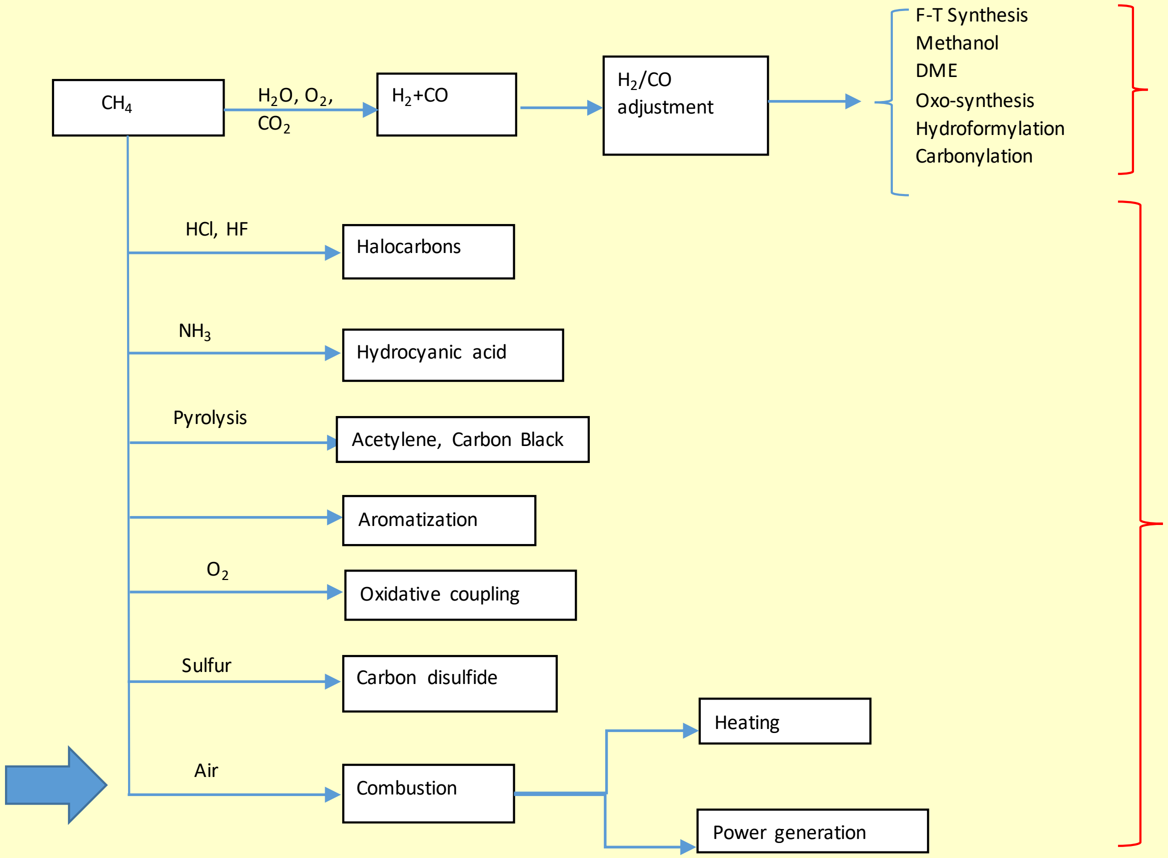
- Industrially practiced

Direct Conversion

- Low yield of products
- Forms undesired CO_2, H_2O
- Further research needed to commercialize the process

Kumar et al., Current Opinion in Chemical Engineering, (2015) 9, pp. 8-15.

Options for CH_4 conversion



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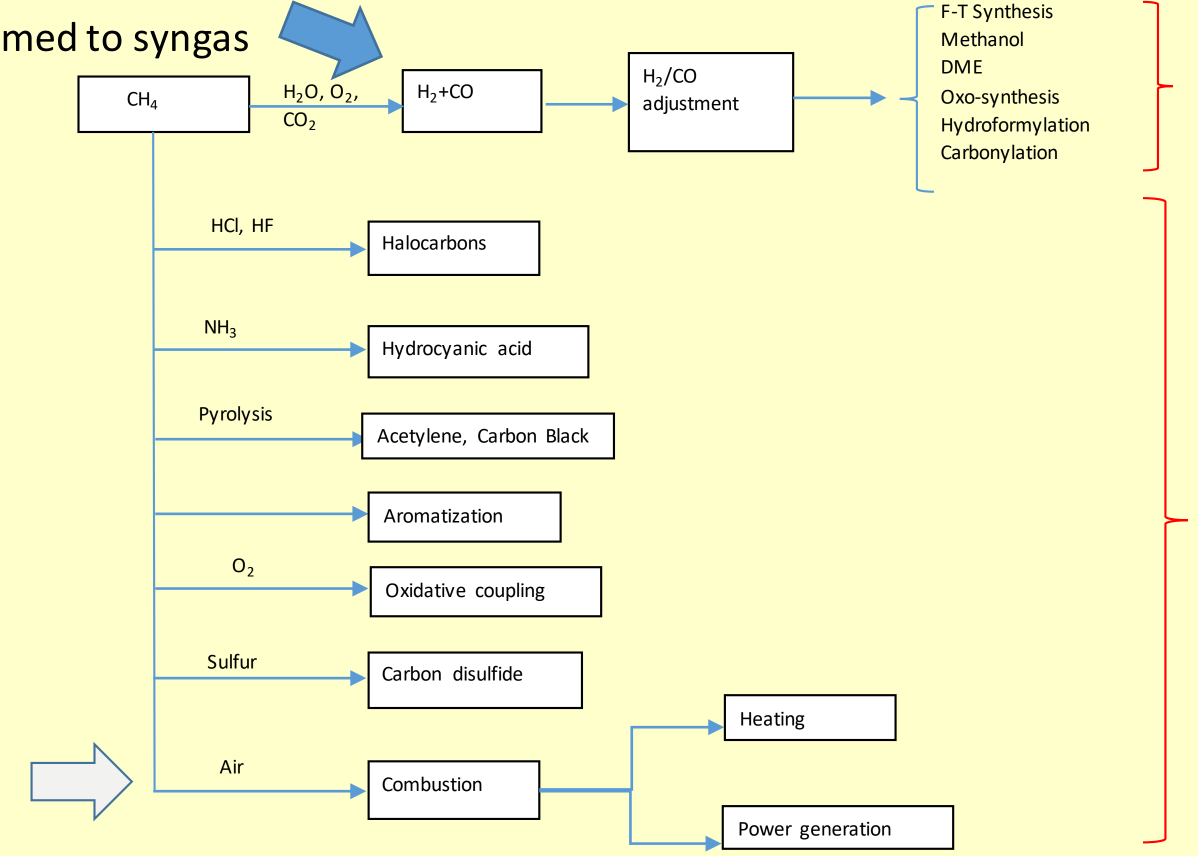
93% of natural gas is combusted to power

Kumar et al., Current Opinion in Chemical Engineering, (2015) 9, pp. 8-15.

Options for CH_4 conversion

Most of the rest is reformed to syngas



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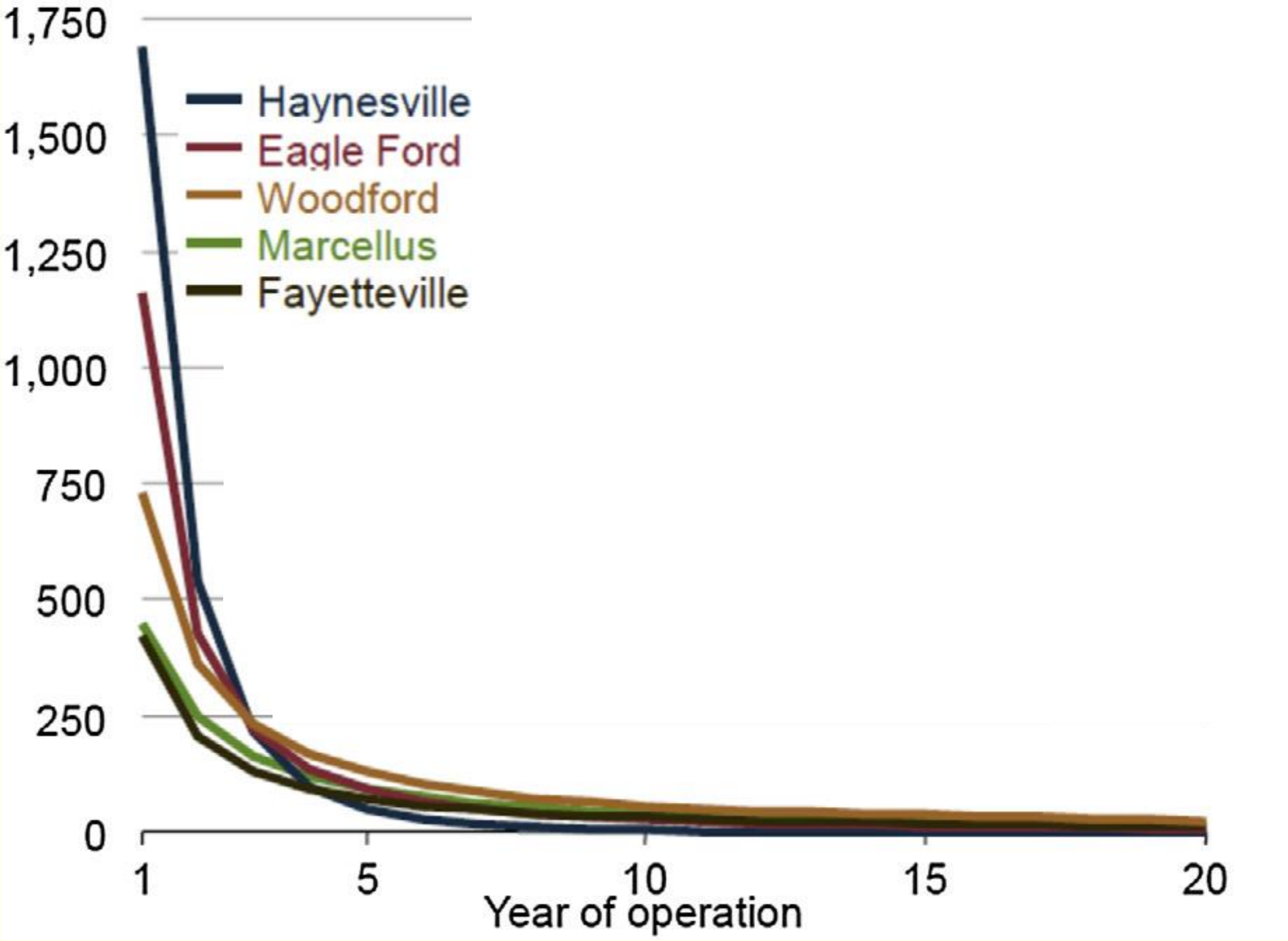
Kumar et al., Current Opinion in Chemical Engineering, (2015) 9, pp. 8-15.

- Wells produce only for a short time

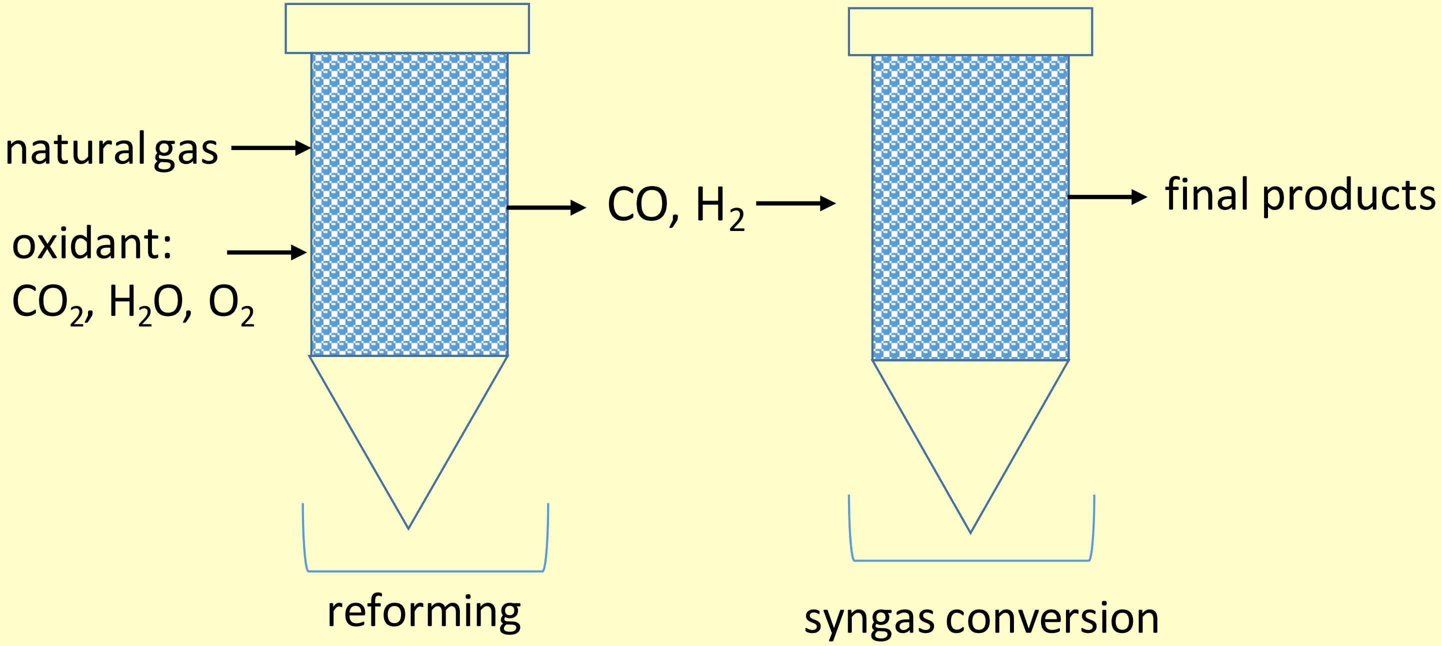
- Many wells are remote

…when there is limited pipeline access, much is flared

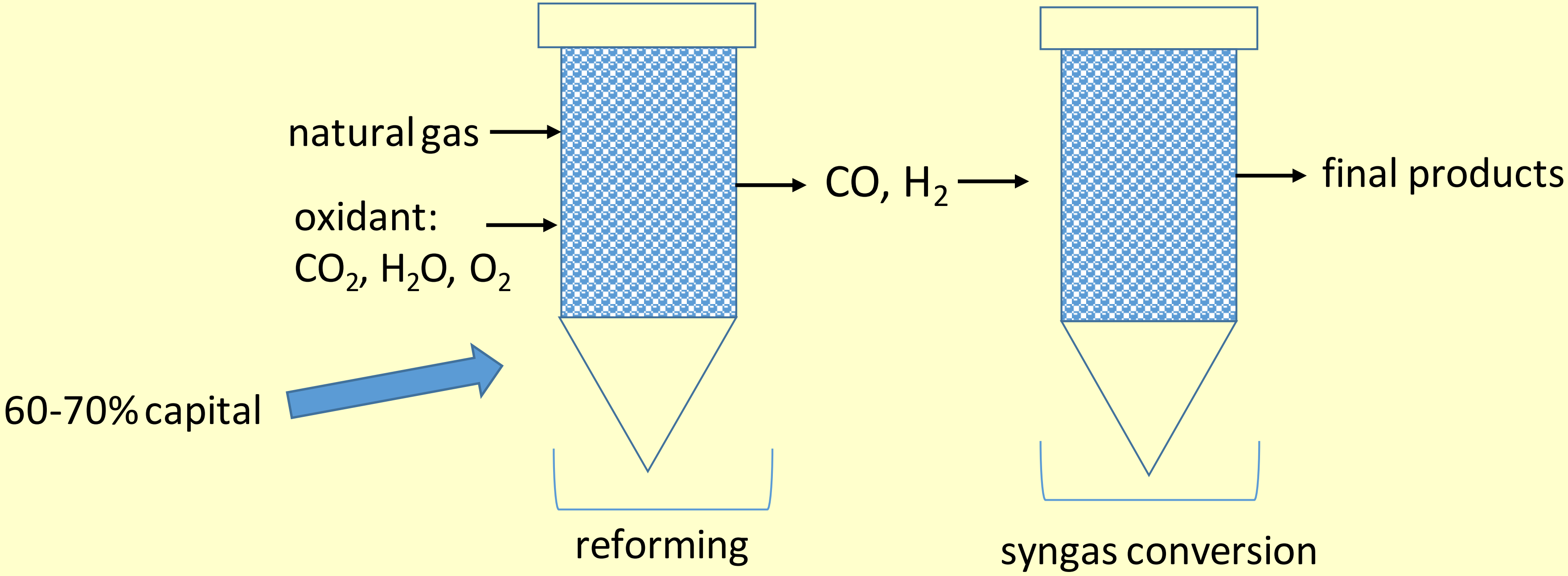


Taifan and Baltrusaitis / Applied Catalysis B: Environmental 198 (2016) 525–547.

Indirect Conversion of Natural Gas



Indirect Conversion of Natural Gas



natural gas

oxidant:
CO_2, H_2O, O_2

CO, H_2

final products

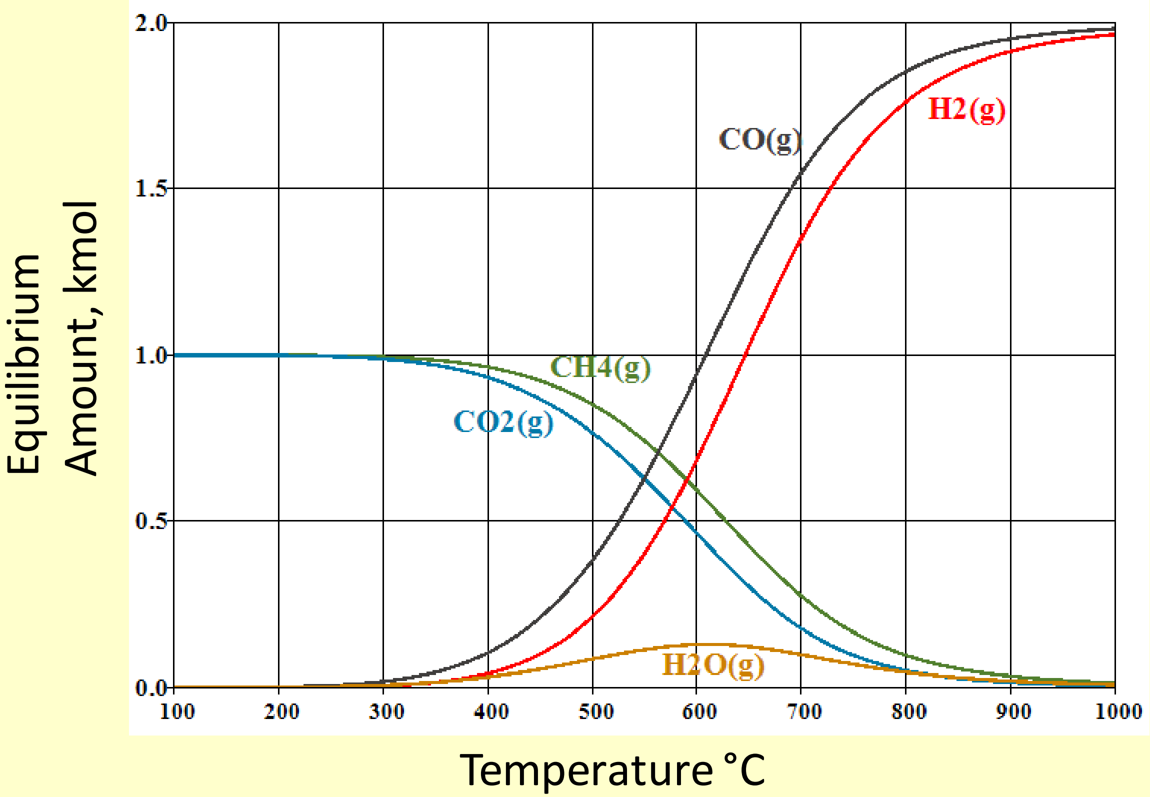
60-70% capital

reforming

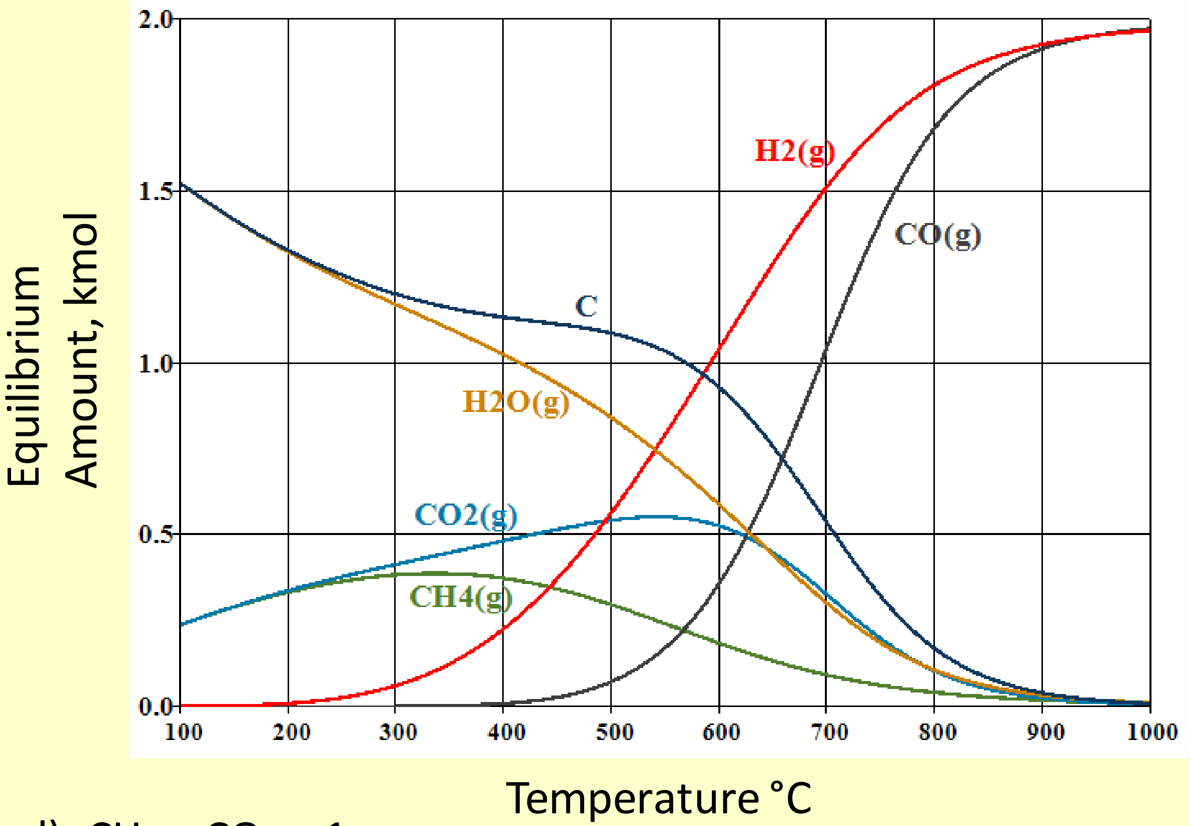
syngas conversion

Thermodynamics[1,2]: $CH_4 + CO_2$

Carbon not allowed



Carbon allowed



Initial amounts (kmol): $CH_4 = CO_2 = 1$

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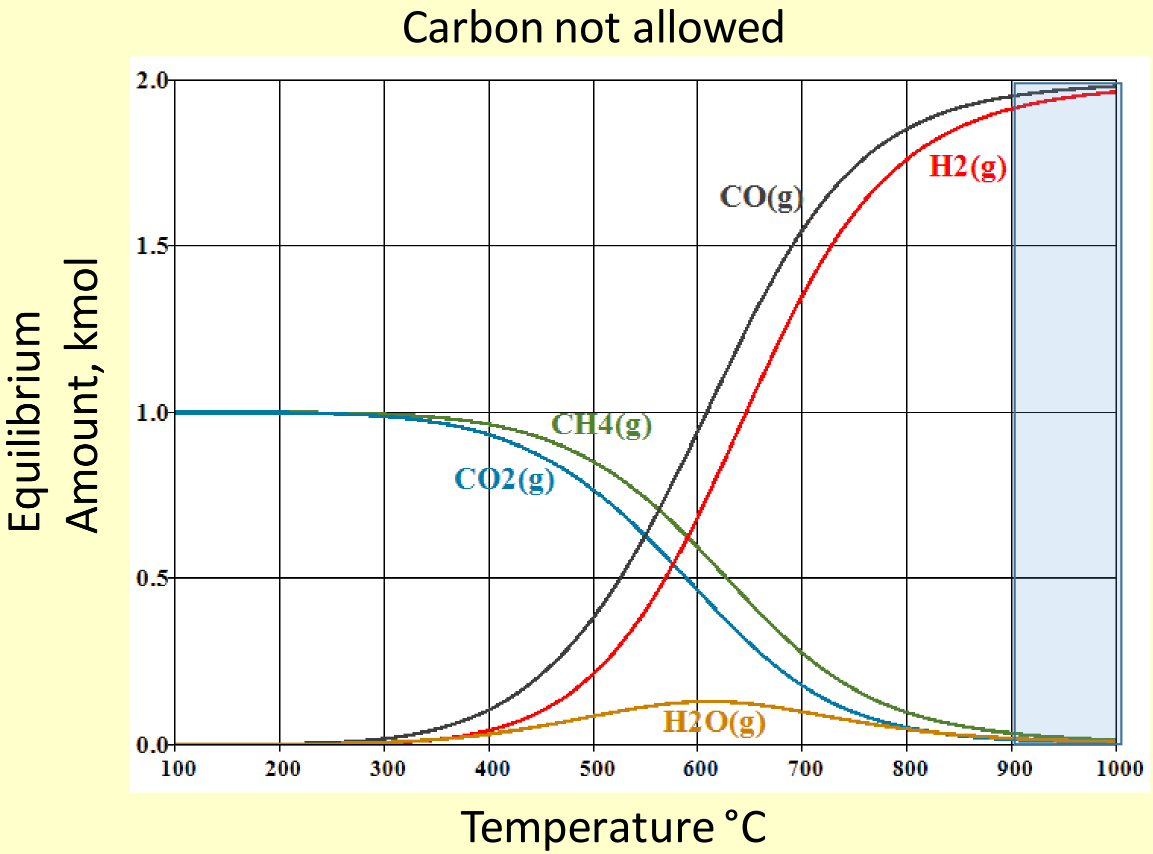
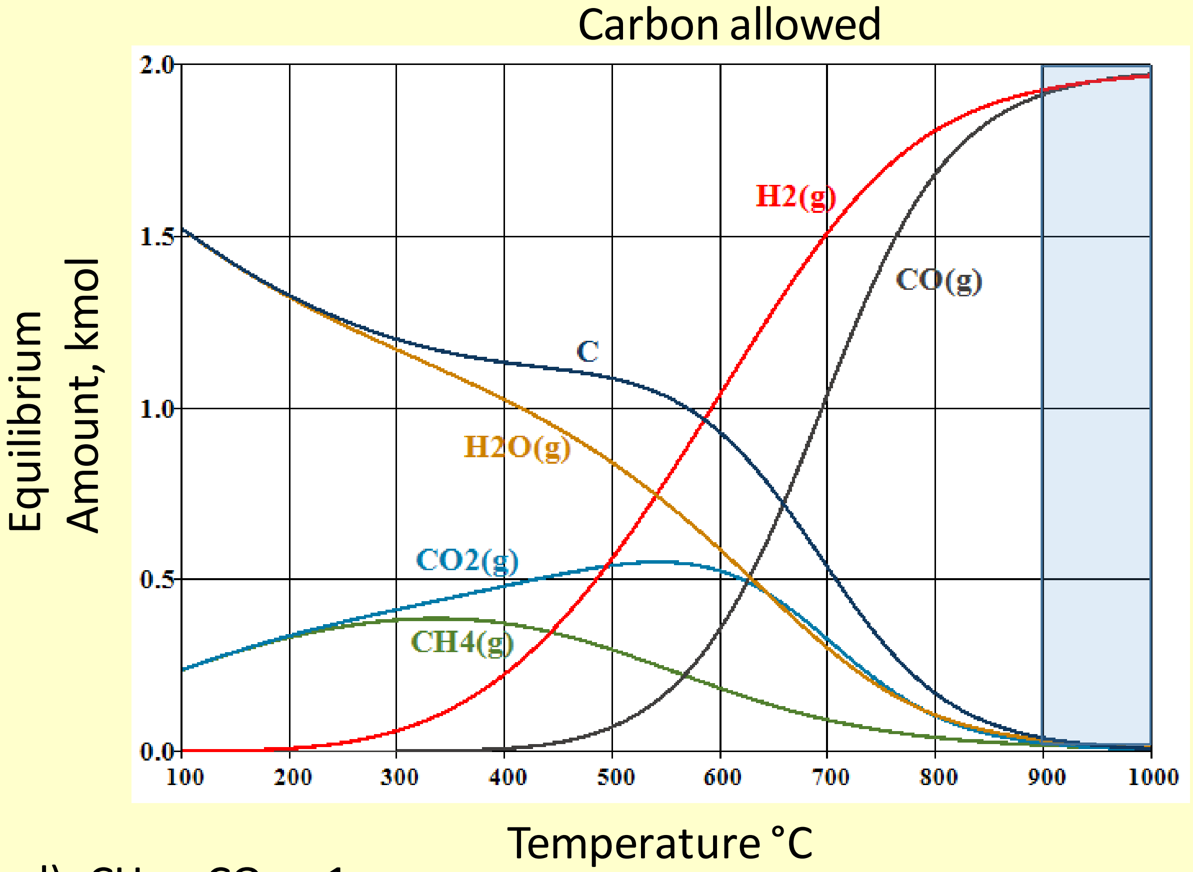
[1] Calculations presented here are carried out using HSC 8, Outepec.

[2] Zhou et al., Energy, 2011, 36, 5450 present similar thermodynamic analysis results.

Thermodynamics[1,2]: $CH_4 + CO_2$





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CH_4 +CO_2 from raw natural gas: reforming?

- CO_2 in raw natural gas can vary from low ppm levels to as high as 90%[1].
- Some fields are not producing because of high CO_2 content.
- Natural gas with CO_2:CH_4 near to 1:1 could be converted to higher value products via reforming.

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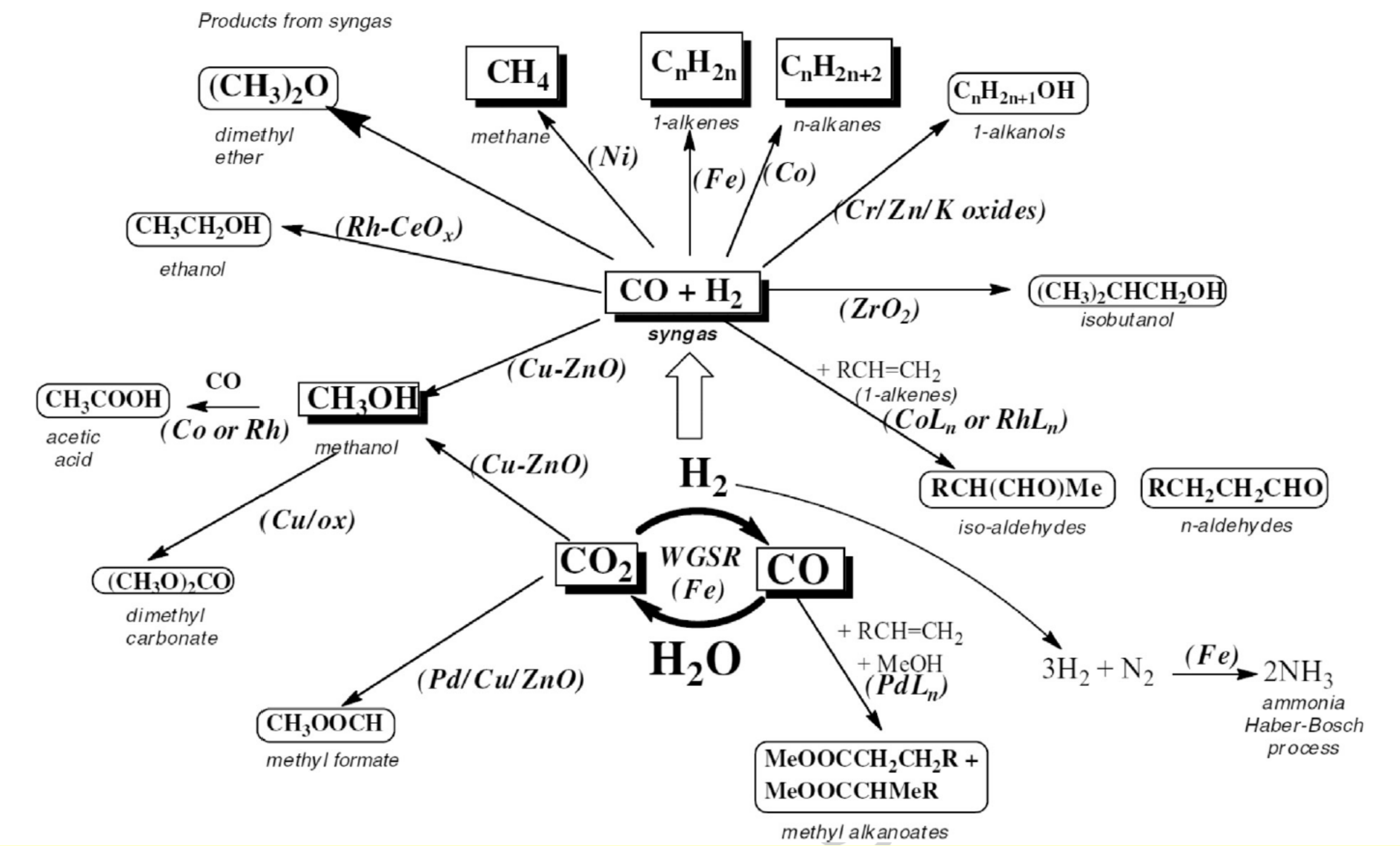
[1] Tan et al., Journal of Natural Gas Chemistry 21(2012), 7–10. Tan et al. point out that fields in Natuna field in the Greater Sarawak Basin in Indonesia is the largest gas field in south Asia, with estimated 46 trillion cubic feet recoverable reserves. Unfortunately, it remains unexplored due to high CO_2 content of 71% [OECD/IEA, 2008]. In Malaysia, CO_2 content in natural gas fields varies from 28%−87%.

Syngas produces both oxygenates and hydrocarbons



Maitlis et al., 2013, *Greener Fischer-Tropsch Processes for Fuels and Feedstocks,* Wiley-VCH Verlag. p. 131-148.

Challenges for indirect conversion:

- Deactivation of reforming catalysts (mostly from carbon deposition)[1]

- The high capital cost of the reforming step

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[1] National Academy Press, 2016, "The Changing Landscape of Hydrocarbon Feedstocks for Chemical Production: Implications for Catalysis: Proceedings of a Workshop" ISBN 978-0-309-44479-8 | DOI: 10.17226/23555, p.13.

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➡ Are there "step change" opportunities, e.g., in Fischer-Tropsch?

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[1] National Academy Press, 2016, "The Changing Landscape of Hydrocarbon Feedstocks for Chemical Production: Implications for Catalysis: Proceedings of a Workshop" ISBN 978-0-309-44479-8 | DOI: 10.17226/23555, p.13.

Direct conversion of methane, examples:

Oxidative coupling $CH_{4(g)} + O_{2(g)} \rightarrow C_nH_{2n} + H_2O_{(g)}$

Metathesis $CH_{4(g)} + C_3H_{8(g)} \rightarrow 2C_2H_{6(g)}$

Aromatization $6CH_{4(g)} \rightarrow C_6H_{6(g)} + 9H_{2(g)}$

Oligomerization with superacids $CH_{4(g)} \rightarrow C_nH_m + H_{2(g)}$

Driving forces

Develop catalysts/processes to convert natural gas and natural gas liquids into:

1. higher-value products, rather than burning them for energy----which is its lowest value.
2. higher energy-density liquids---to valorize natural gas instead of flaring in remote locations.

Driving forces

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➡ For methane, this generally means forming C-C bonds

Oppotunities for Catalysis

National Academy report (2016)[1]:

"The low cost and increased supply of natural gas …provide an opportunity to discover and develop new catalysts and processes to enable the ***direct*** conversion of natural gas …into value-added chemicals …" (emphasis added)

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[1] National Academy Press, 2016, "The Changing Landscape of Hydrocarbon Feedstocks for Chemical Production: Implications for Catalysis: Proceedings of a Workshop" ISBN 978-0-309-44479-8 | DOI: 10.17226/23555, p.2.

Conceptual routes for methane to higher-value products

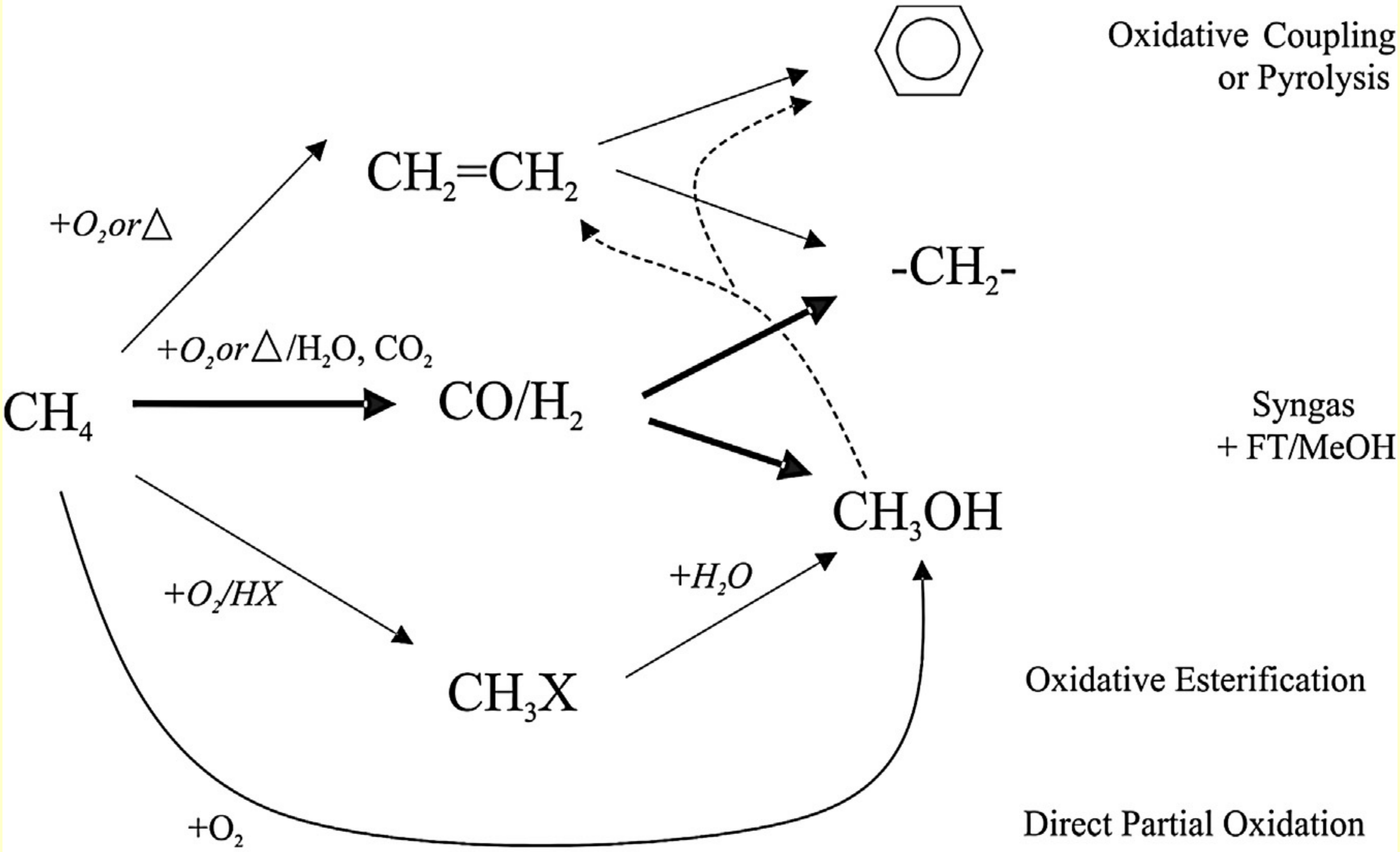
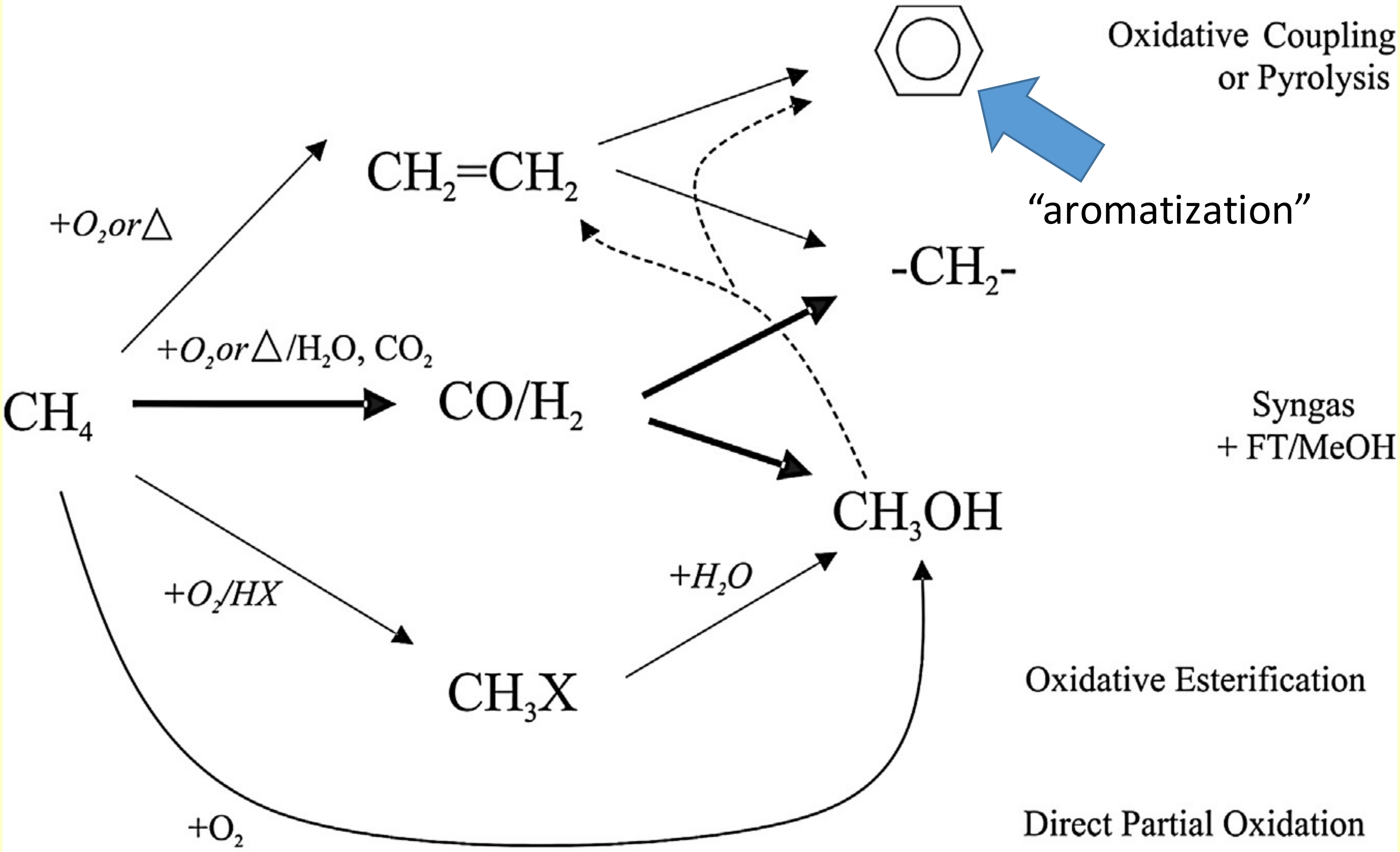


Figure from: Taifan and Baltrusaitis / Applied Catalysis B: Environmental 198 (2016) 525–547.

Opportunity: methane aromatization

Challenge: carbon deposition



“aromatization”

Figure from: Taifan and Baltrusaitis / Applied Catalysis B: Environmental 198 (2016) 525–547.

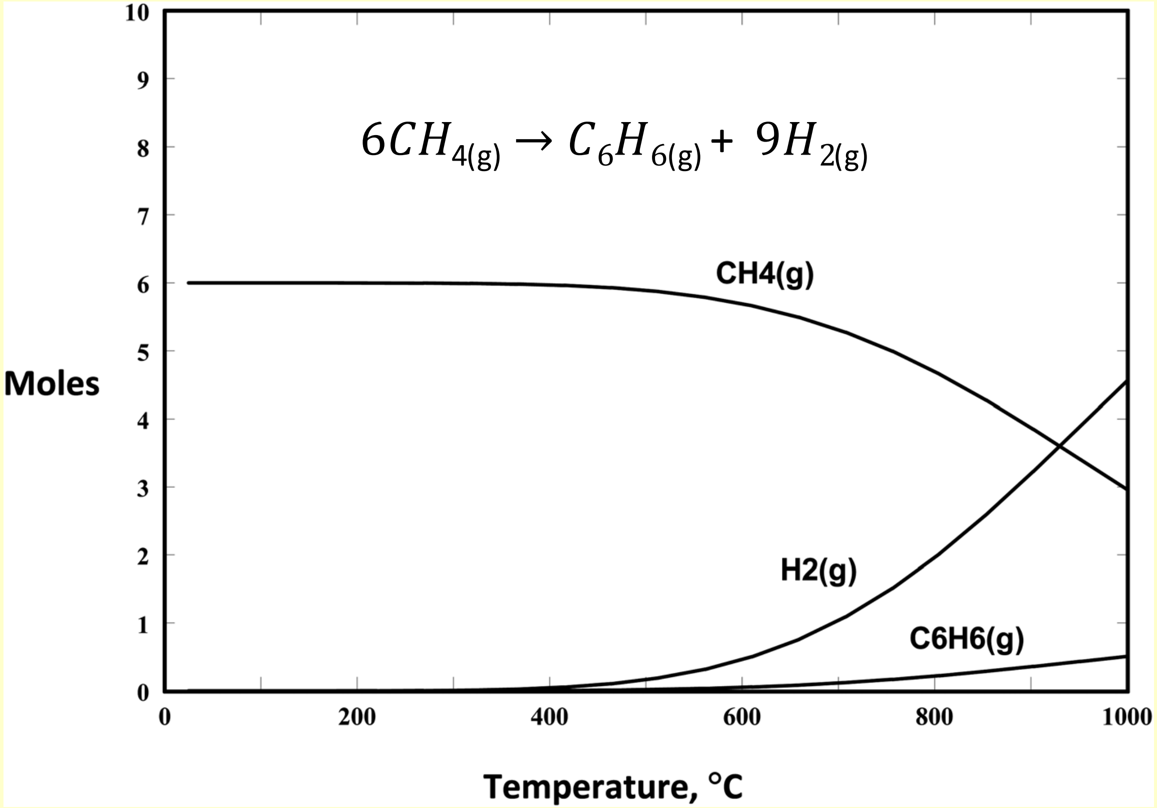
Direct conversion of methane: Aromatization

$$6CH_{4(g)} \rightarrow C_6H_{6(g)} + 9H_{2(g)}$$

$$\Delta G_r^o = +433\ kJ\ mol^{-1} \qquad \Delta H_r^o = +531\ kJ\ mol^{-1}$$

Thermodynamics

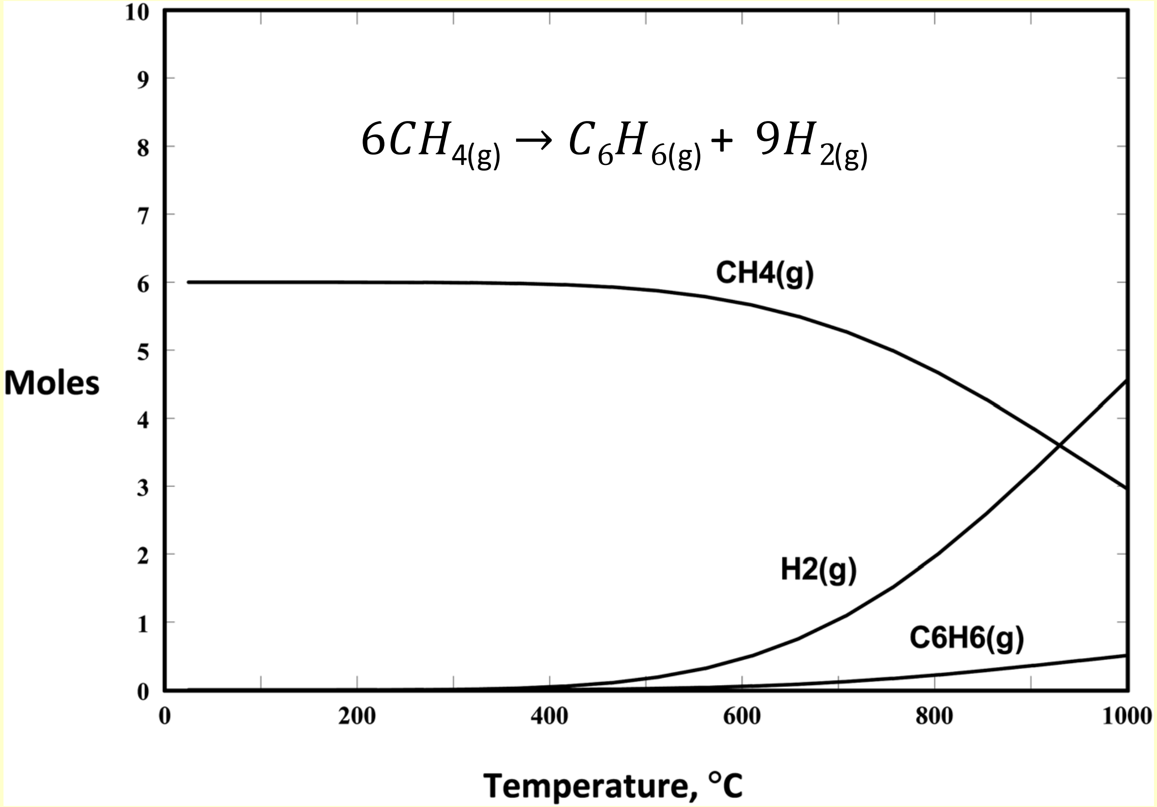
no carbon



Equilibrium amounts (moles), 1 bar, starting with 6 mol CH_4 and allowing only H_2 and benzene as components. Calculated using HSC 7.1 software

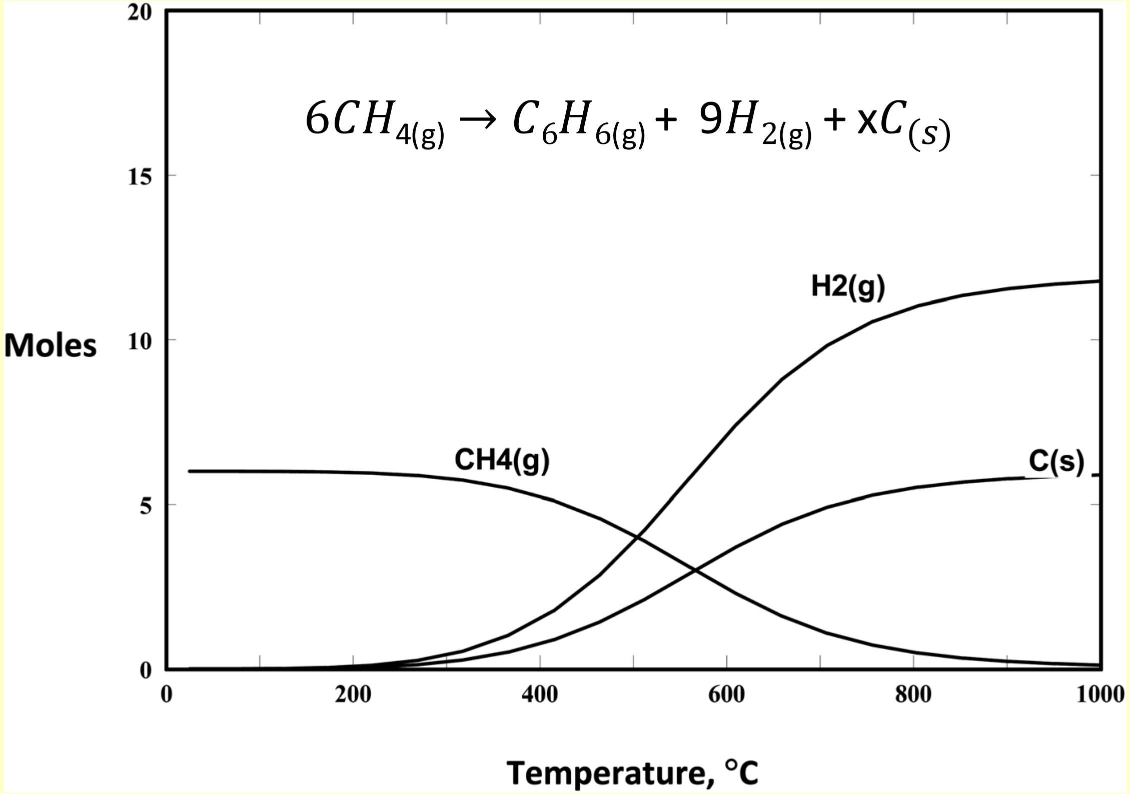
Thermodynamics

no carbon



Equilibrium amounts (moles), 1 bar, starting with 6 mol CH_4 and allowing only H_2 and benzene as components. Calculated using HSC 7.1 software

carbon allowed



Equilibrium amounts (moles), 1 bar, starting with 6 mol CH_4 and allowing C(s), H_2, and benzene as components. Calculated using HSC 7.1 software

Experimental results

$$CH_{4(g)} \rightarrow C_6H_{6(g)} + H_{2(g)}$$

Experimentally, benzene selectivities are 60-80% at methane conversions of ~10%, corresponding to net benzene yields of less than 10%[1].

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[1] J. Spivey and G. Hutchings, Chem. Soc. Rev. 2014, 43, 792-803.

$$6CH_{4(g)} \rightarrow C_6H_{6(g)} + 9H_{2(g)}$$

Mechanism involves Mo-C sites and H-ZSM5 sites, forming byproducts and hydrogen

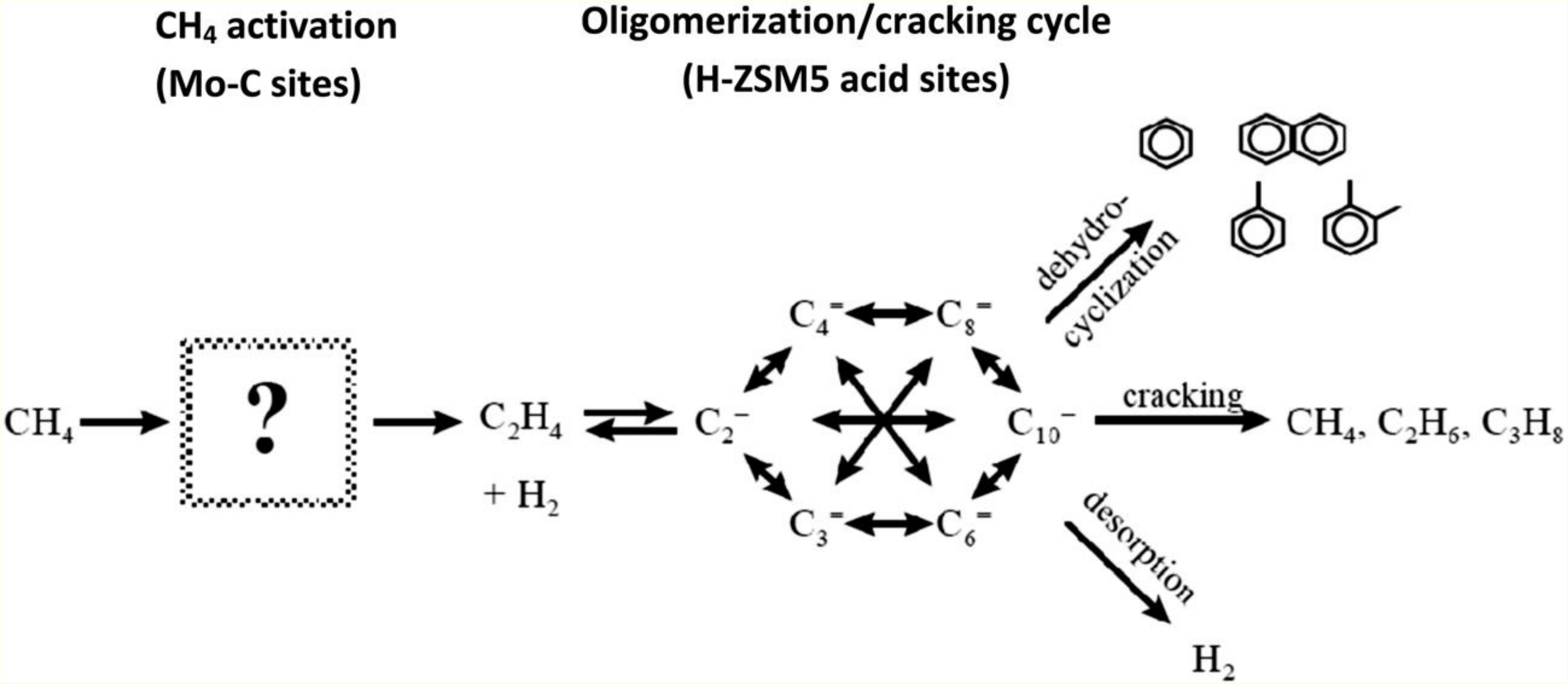

Figure from: R. W. Borry III, E. C. Lu, Y. H. Kim and E. Iglesia, Non-Oxidative Conversion of Methane with Continuous Hydrogen Removal, US Dept. of Energy/NETL, Morgantown,WV, contract DE-AC03-76SF00098.

Carbon deposition

$$CH_{4(g)} \rightarrow C_6H_{6(g)} + H_{2(g)} + C_{(s)}$$

Carbon deposition is the primary limitations to methane deposition

Approaches to minimize carbon deposition:

- Addition of oxidants[1]: NO, O_2, CO, or CO_2
- H_2—added in the feed, and also formed during the reaction[2]
- Reactor design—circulating fluid bed[3], two-zone[4]

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[1] L. Wang, R. Ohnishi and M. Ichikawa, J. Catal., 2000, 190, 276–283; P. L. Tan, Y. L. Leung, S. Y. Lai and C. T. Au, Catal. Lett., 2002, 78, 251–258.

[2] Z. Liu, M. A. Nutt and E. Iglesia, Catal. Lett., 2002, 81, 271–279.

[3] L.L. Iaccino, N. Sangar, E.L. Stavens, 2010, Patent, Production of aromatic hydrocarbons from methane, ExxonMobil Chemical Patents Inc. (Houston, TX) US7683227

[4] M. P. Gimeno, J. Soler, J. Herguido and M. Menendez, Ind. Eng. Chem. Res., 2010, 49, 996–1000.

Challenges to aromatization[1]

- deactivation of the catalyst by coking
- low methane conversion rates that result from the buildup of hydrogen
- cost-effective methods to remove hydrogen from the reactor and to separate benzene from naphthalene.

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[1] National Academy Press, 2016, “The Changing Landscape of Hydrocarbon Feedstocks for Chemical Production: Implications for Catalysis: Proceedings of a Workshop” ISBN 978-0-309-44479-8 | DOI: 10.17226/23555, p.26.

Oligomerization of methane using superacids[1]

$$n\,CH_4 \xrightarrow{[superacid]} C_nH_m + x\,H_2$$

$$\Delta G_r^o = +69\ kJ\ mol^{-1} \qquad \Delta H_r^o = +66\ kJ\ mol^{-1}$$

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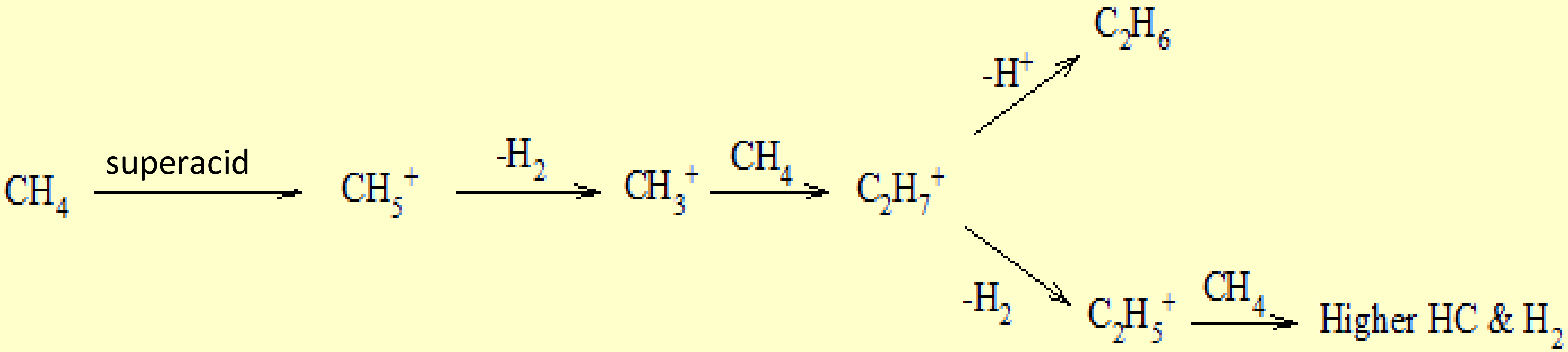
[1] Thermodyamic properties are based on ethane as the sole product, calculated using HSC Chemistry 8, Outotec Technologies

What is a superacid?

- Can be a liquid, gas, or solid
- As a liquid, the Hammett acidity function (H_0) is lower than 100% H_2SO_4 (H_0= -12)
- Can isomerize alkanes at room temperature, which is not possible with pure H_2SO_4

Mechanism[1]



$$CH_4 \xrightarrow{\text{superacid}} CH_5^+ \xrightarrow{-H_2} CH_3^+ \xrightarrow{CH_4} C_2H_7^+$$

$$C_2H_7^+ \xrightarrow{-H^+} C_2H_6$$

$$C_2H_7^+ \xrightarrow{-H_2} C_2H_5^+ \xrightarrow{CH_4} \text{Higher HC \& } H_2$$

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[1] G. A. Olah et al., (a) Superacids,Wiley Interscience Publication, 1985, p. 52; J. Am. Chem. Soc., 1968, 90, 2726; J. Am.Chem. Soc., 1969, 91, 3261.

Status—methane oligomerization using superacid

- The reaction has been demonstrated
- Example superacids:
  - Liquids[1]: $FSO_3H\text{-}SbF_5$
  - Solids[2]: SO_4^{2-}/ZrO_2
  - Gases[3]: $H^+/AlBr_4^-$

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[1] G. A. Olah et al., (a) Superacids,Wiley Interscience Publication, 1985, p. 52; J. Am. Chem. Soc., 1968, 90, 2726; J. Am.Chem. Soc., 1969, 91, 3261.
[2] W. Hua et al., Applied Catalysis A: General, 2001. **219**(1–2): p. 201-207; R.L. Martins, Applied Catalysis A: General, 2006. **308**(0): p. 143-152.
[3] S. Vassireddy et al., Chem. Comm., 2010, DOI: 10.1039/c0cc01886d.

Challenges—methane oligomerization using superacids

For liquids and gases: separation of the catalyst and products

For liquids: H_2 deactivates the catalyst (FSO_3H-SbF_5)[1]

For all[2,3]: poor product selectivity (a mixture of tertiary carbocations and polymeric material)

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[1] G. A. Olah et al., (a) Superacids, Wiley Interscience Publication, 1985, p. 52; J. Am. Chem. Soc., 1968, 90, 2726; J. Am.Chem. Soc., 1969, 91, 3261.

[2] W. Hua et al., Applied Catalysis A: General, 2001. **219**(1–2): p. 201-207; R.L. Martins, Applied Catalysis A: General, 2006. **308**(0): p. 143-152.

[3] S. Vassireddy et al., Chem. Comm., 2010, DOI: 10.1039/c0cc01886d.

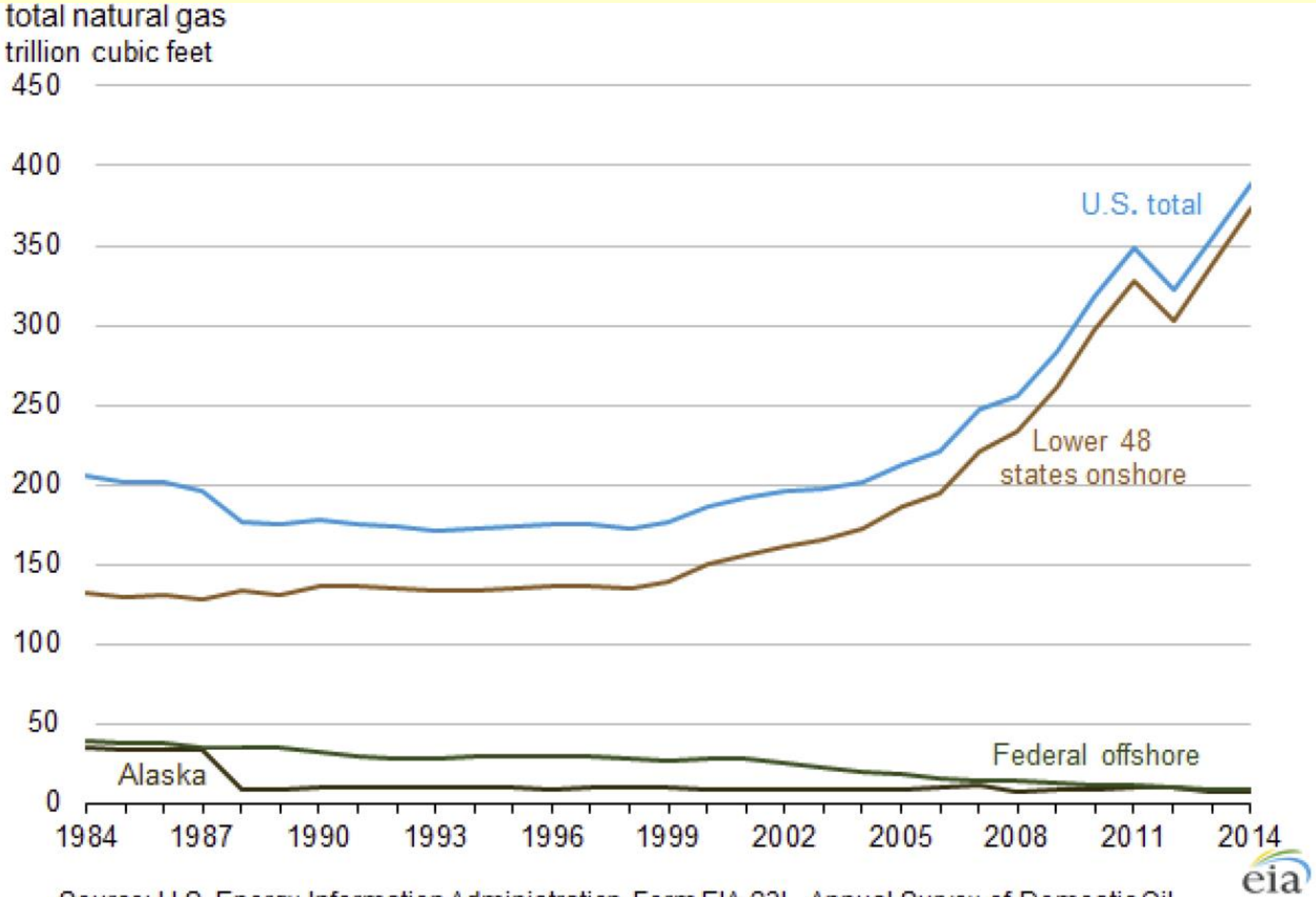
Conclusions

- Low cost natural gas here to stay. The goal—”turn methane into money”
- Industry is making a transition from petroleum-based feedstock to natural gas
- Current processes rely primarily on indirect conversion---via syngas
- Improvements to indirect conversion processes will likely be incremental
- Despite the appeal of direct conversion processes, significant challenges have limited deployment---the primarily due to carbon deposition

Acknowledgements

- US Dept. of Energy/NETL
- LSU Energy Studies (Dave Dismukes)
- Albemarle Company

Thanks



Source: U.S. Energy Information Administration, Form EIA-23L, Annual Survey of Domestic Oil and Gas Reserves

FIGURE 1-2 U.S. proven reserves of natural gas and natural gas liquids, 1984-2014.
SOURCE: U.S. Energy Information Agency, 2015.

National Academy Press, 2016, “The Changing Landscape of Hydrocarbon Feedstocks for Chemical Production: Implications for Catalysis: Proceedings of a Workshop” ISBN 978-0-309-44479-8 | DOI: 10.17226/23555.

“…even with the recent fall in oil prices, natural gas liquids still maintain a significant cost advantage over oil-derived naphtha.”

(and there is plenty of it)

Natural gas liquids contain a significant amount of propane, with the result that propane prices have fallen far enough that it has become economical to produce high-demand propylene directly from propane via catalytic propane dehydrogenation.

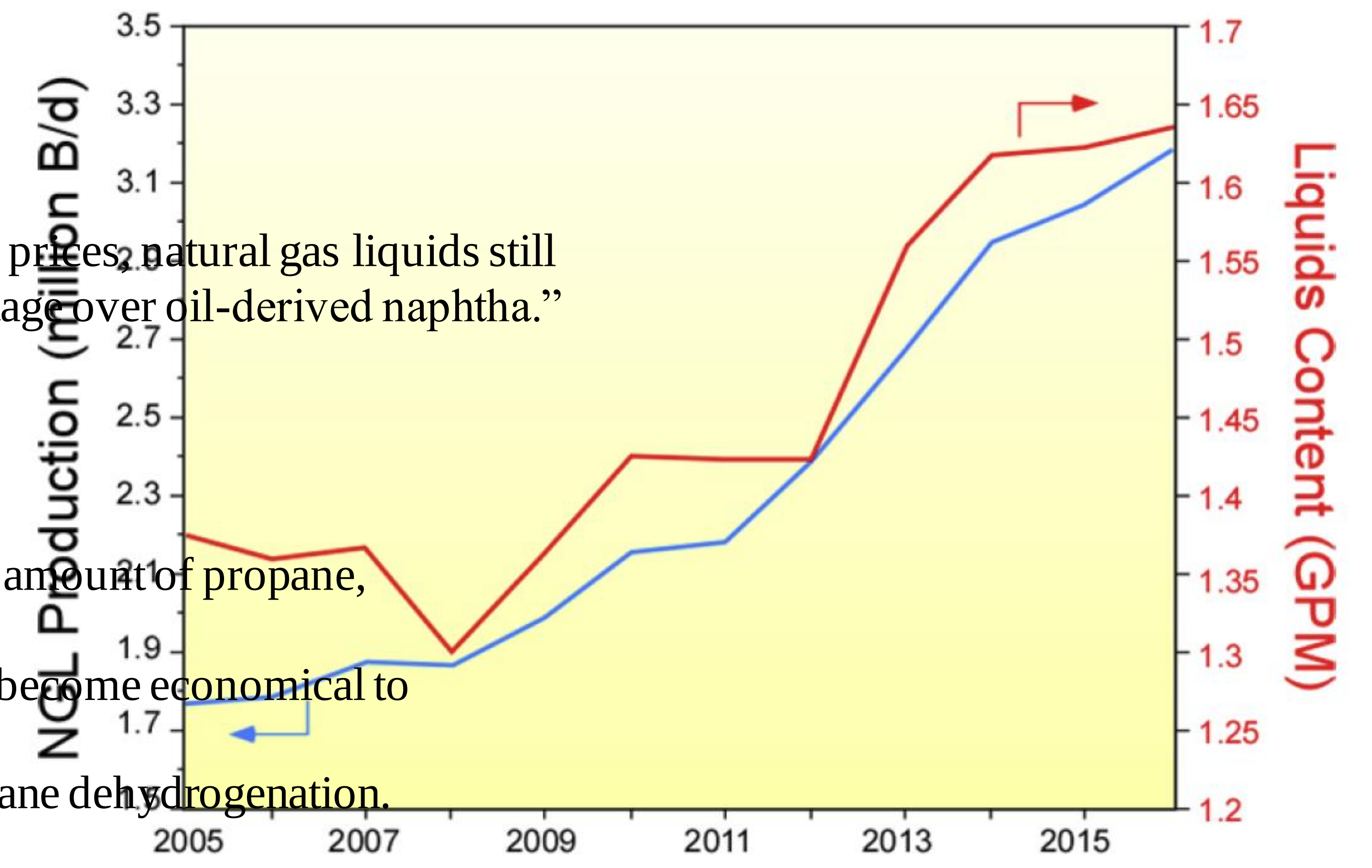


FIGURE 2-2 Growth in production of natural gas liquids.
NOTE: B/d = barrels per day; GPM = gallons per thousand cubic feet; NGL = natural gas liquids.
SOURCE: Jones, 2016.

National Academy Press, 2016, “The Changing Landscape of Hydrocarbon Feedstocks for Chemical Production: Implications for Catalysis: Proceedings of a Workshop” ISBN 978-0-309-44479-8 | DOI: 10.17226/23555.

“…the availability of low-cost methane and natural gas liquids offers a transitional
opportunity to lower the carbon footprint of the chemical industry if new catalytic approaches
can be developed, said Johannes Lercher, professor of chemistry at the
Technical University of Munich and Director of the Institute for Integrated Catalysis at the
Pacific Northwest National Laboratory.

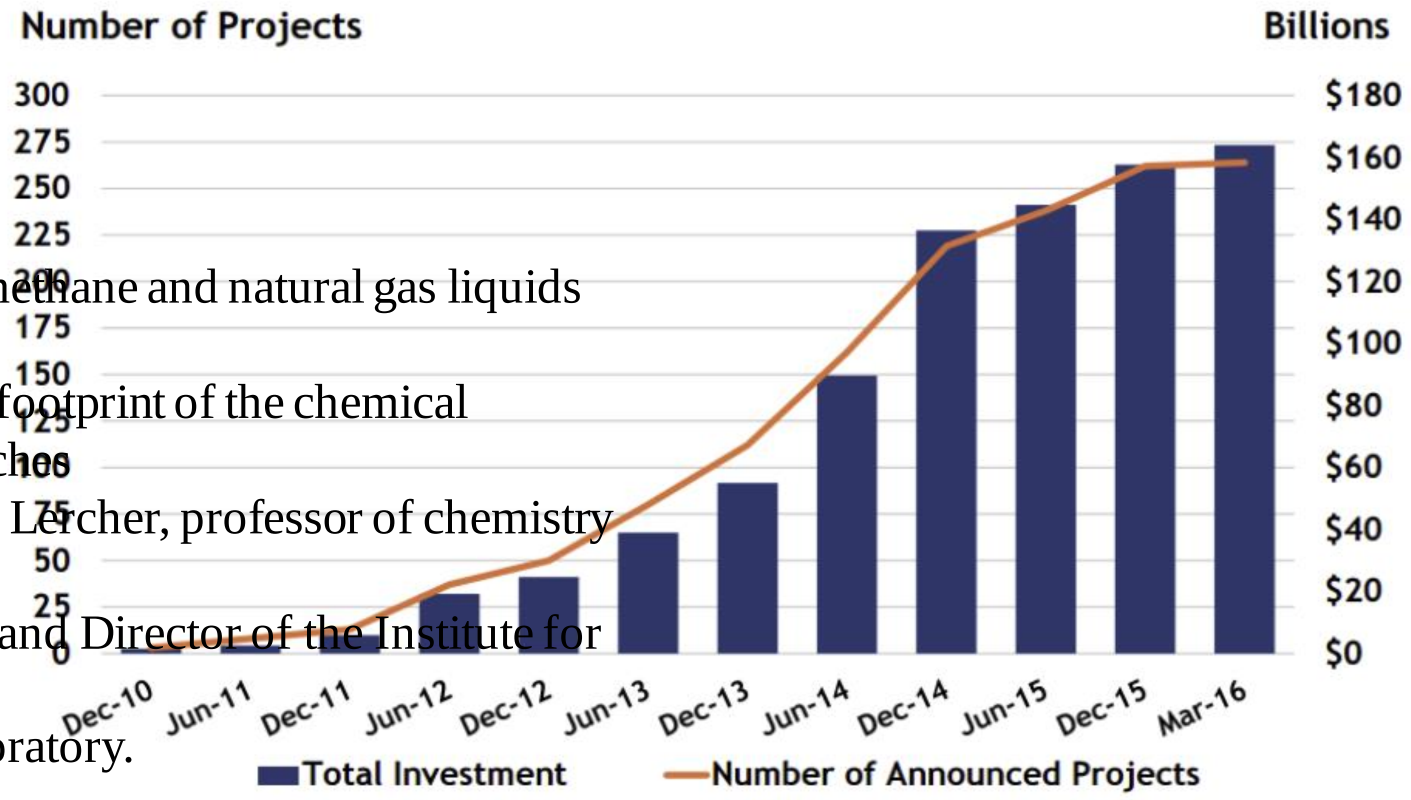
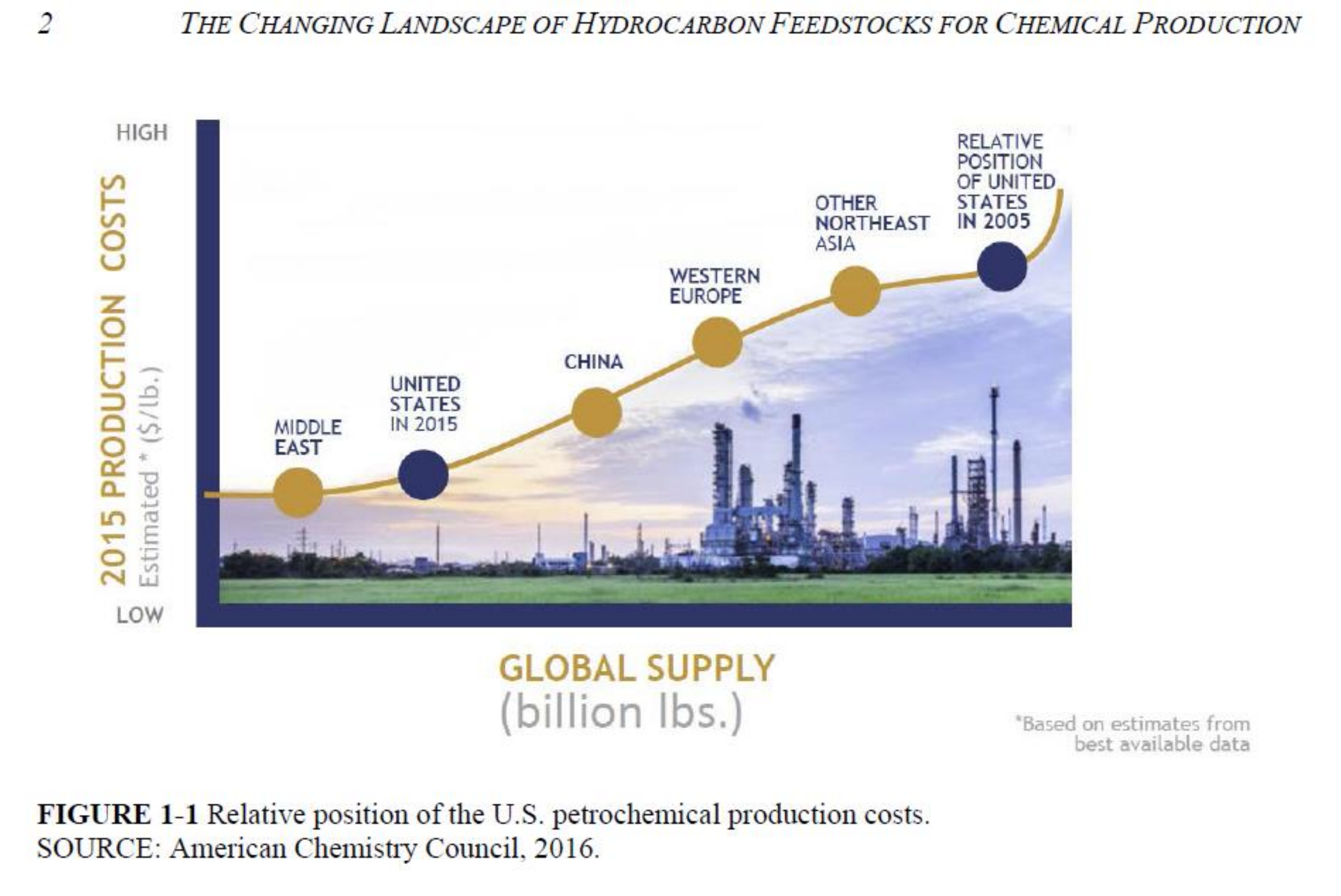


FIGURE 2-5 Cumulative announced chemical industry investments from shale gas from December 2010 to March 2016.
SOURCE: American Chemistry Council, 2016.



2 *THE CHANGING LANDSCAPE OF HYDROCARBON FEEDSTOCKS FOR CHEMICAL PRODUCTION*

FIGURE 1-1 Relative position of the U.S. petrochemical production costs.
SOURCE: American Chemistry Council, 2016.

National Academy Press, 2016, “The Changing Landscape of Hydrocarbon Feedstocks for Chemical Production: Implications for Catalysis: Proceedings of a Workshop” ISBN 978-0-309-44479-8 | DOI: 10.17226/23555.

The change from naphtha to natural gas liquids has caused ethylene prices to drop because NGLs can be used to produce ethylene, but butadiene and aromatic chemicals such as benzene (produced from naphtha) have become “constrained”

the trend is toward lower production of these chemicals as more ethane and natural gas liquids are used to produce olefins.

Catalytic opportunity: commercially developed catalysts for conversion of NGLs to olefins to