Process Integration in the Chemical and Petrochemical Industries

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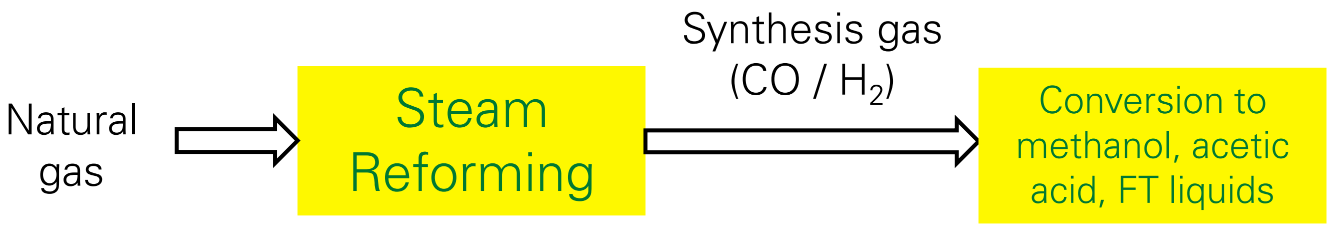
Context

- The chemical and petrochemical industries account for around 30% of industrial energy usage.
  - Hydrocarbons (principally oil and natural gas) are the predominant energy sources, and so these industries contribute a significant proportion of industrial CO_2 emissions.
  - The figures include hydrocarbons used both as feed stocks for the products and as the source of energy for conversion processes.
  - The end products are a wide range of consumer goods, particularly polymers, whose Greenhouse Gas consequences depend on their end use and disposal: these are not discussed here.
- This paper focuses on conversion energy, where process integration methods are applicable.

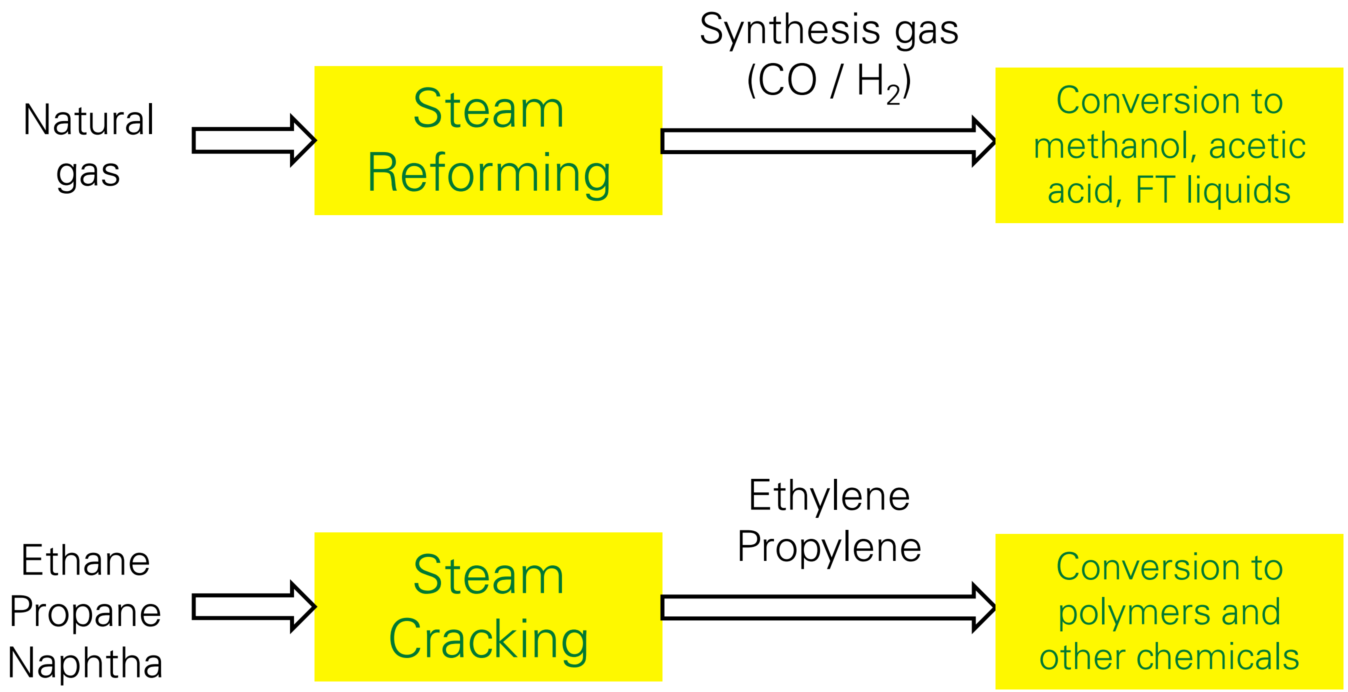
Comparison with Oil Refining

	Oil Refining	Petrochemicals
Definition	Produces hydrocarbon mixtures (typically fuels, *e.g.* gasoline, diesel, bitumen).	Produces single chemical species (often polymers), *e.g.* acetic acid, ethylene, polypropylene.
Process Diversity	A few very commonly used processes.	A few very commonly used "front end" processes, plus a huge array of "derivative" processes.
Scale	Typical refinery 5 to 20 million tonnes/year.	Bulk petrochemicals typically 0.1 to 1 million tonnes/year. Many chemicals at smaller scale.
Variability	Need to adapt to changing crude oil mixtures on frequent basis.	Usually one consistent feed and one consistent product.

Integrated Petrochemical Manufacture



Integrated Petrochemical Manufacture



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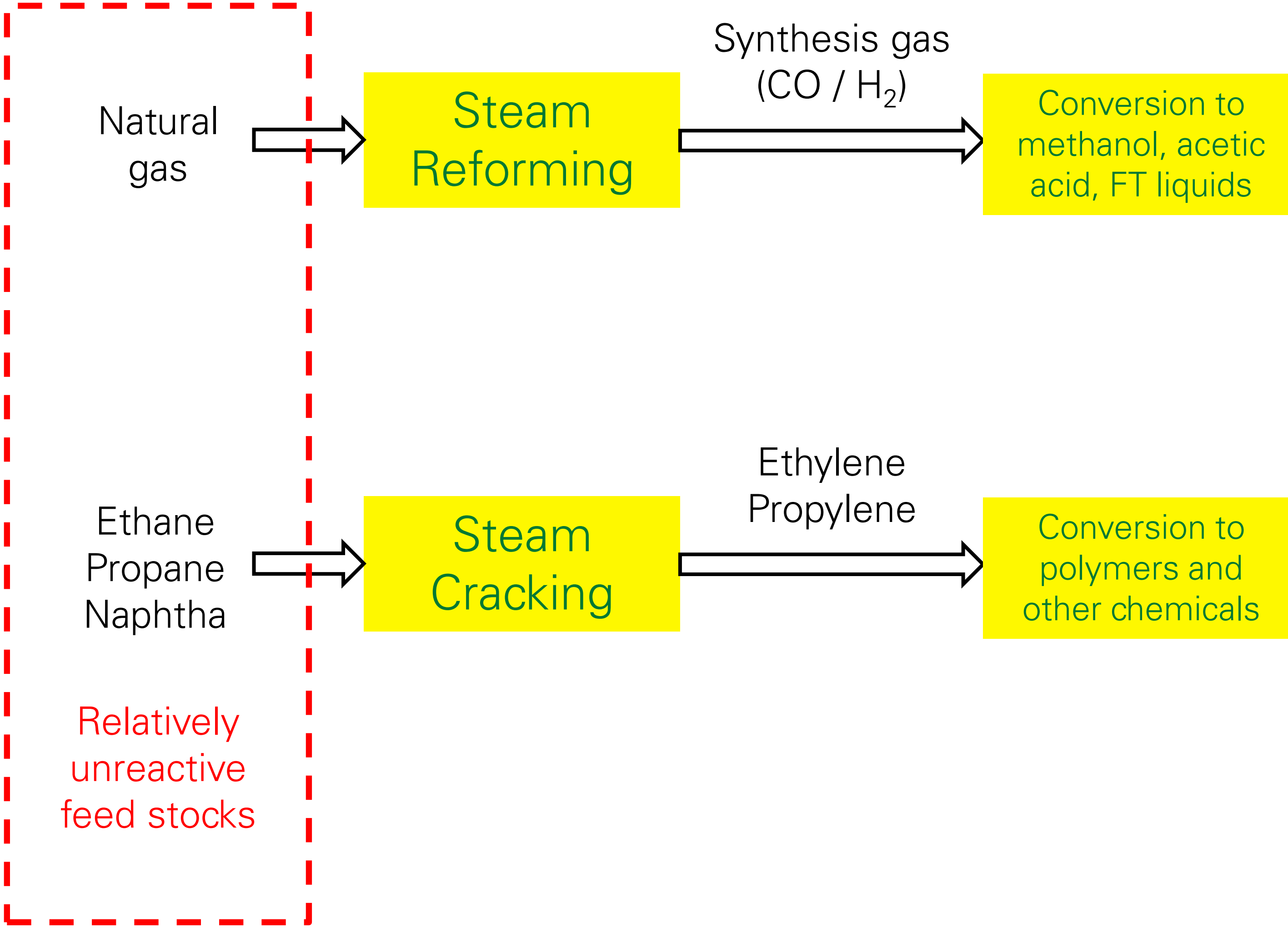

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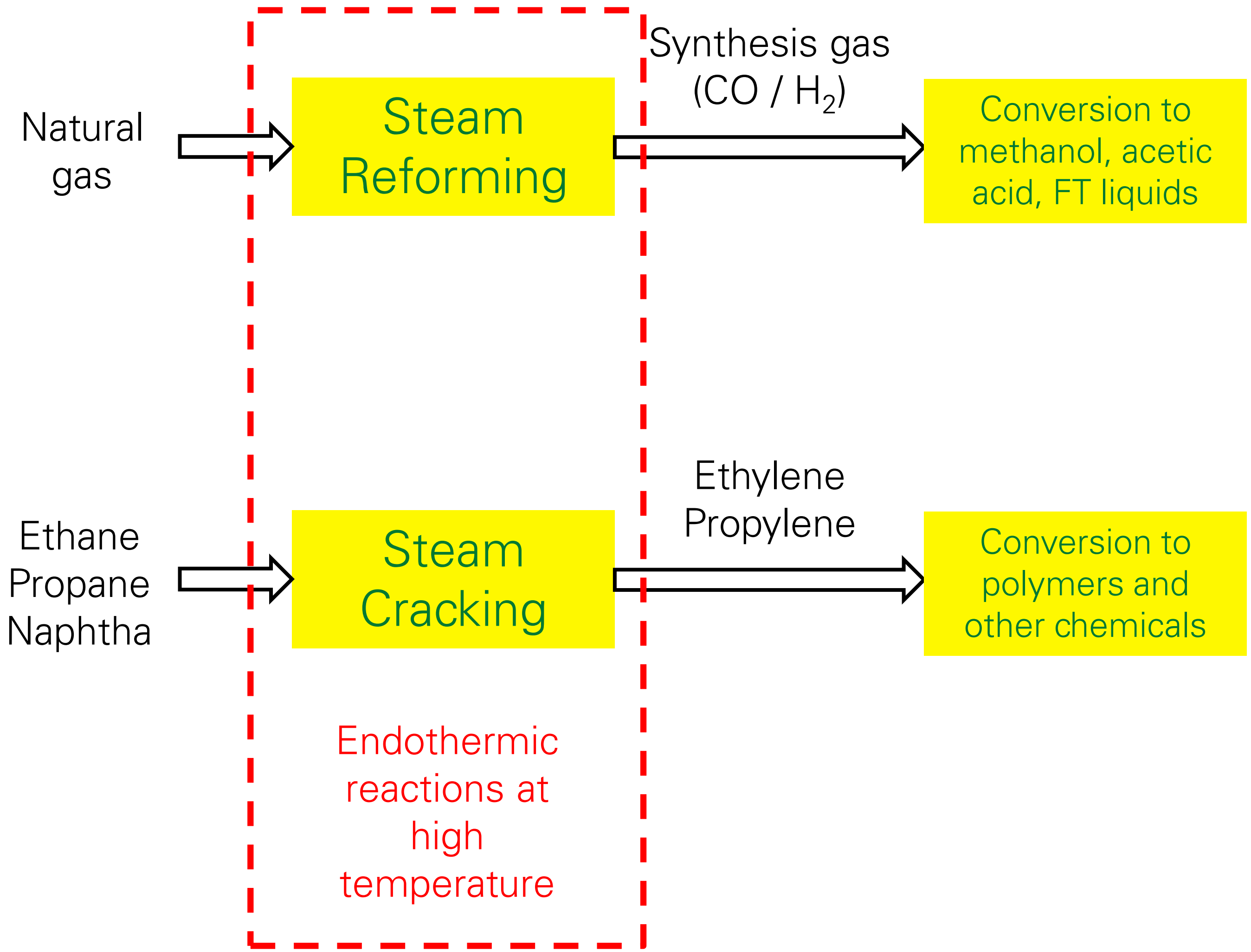

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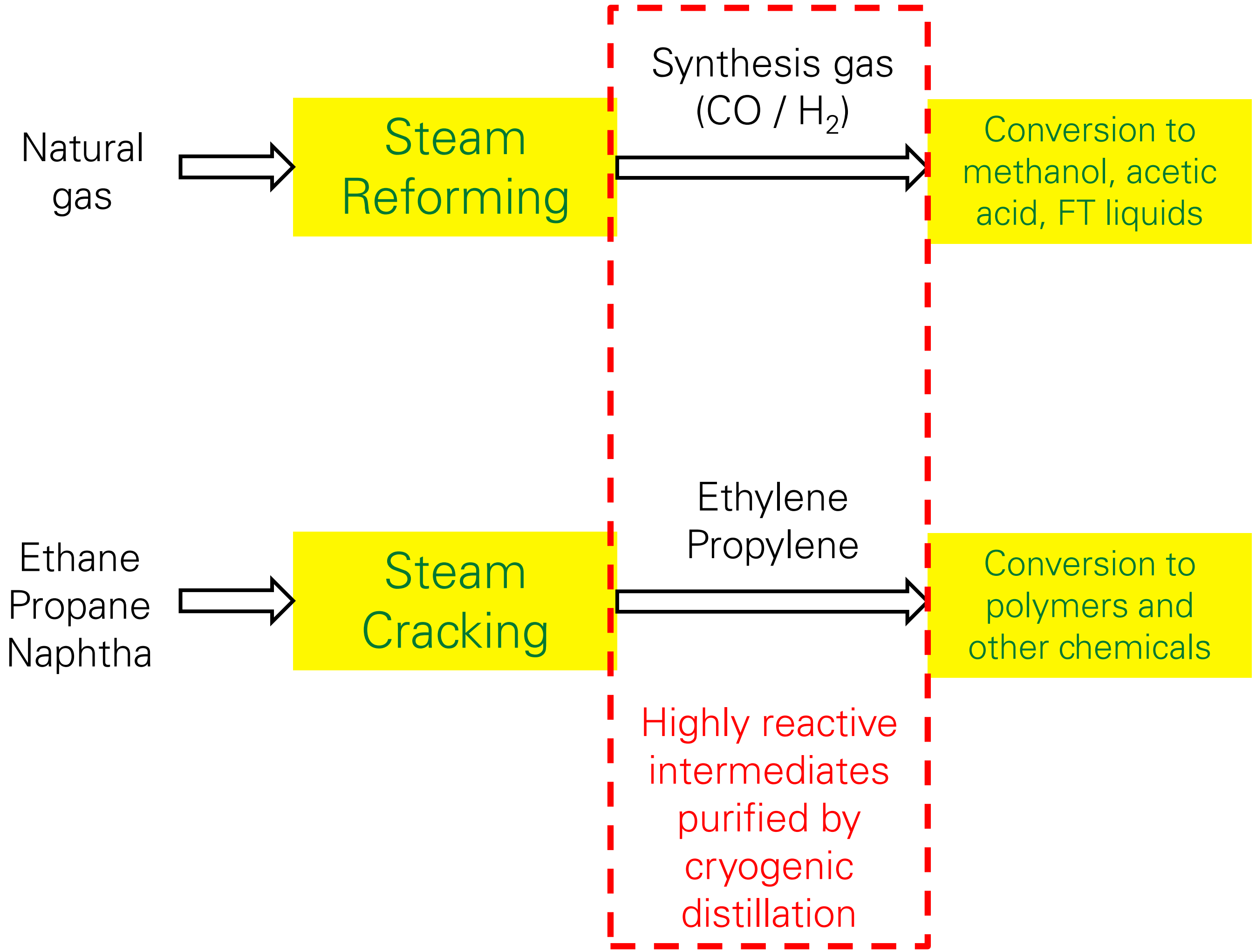

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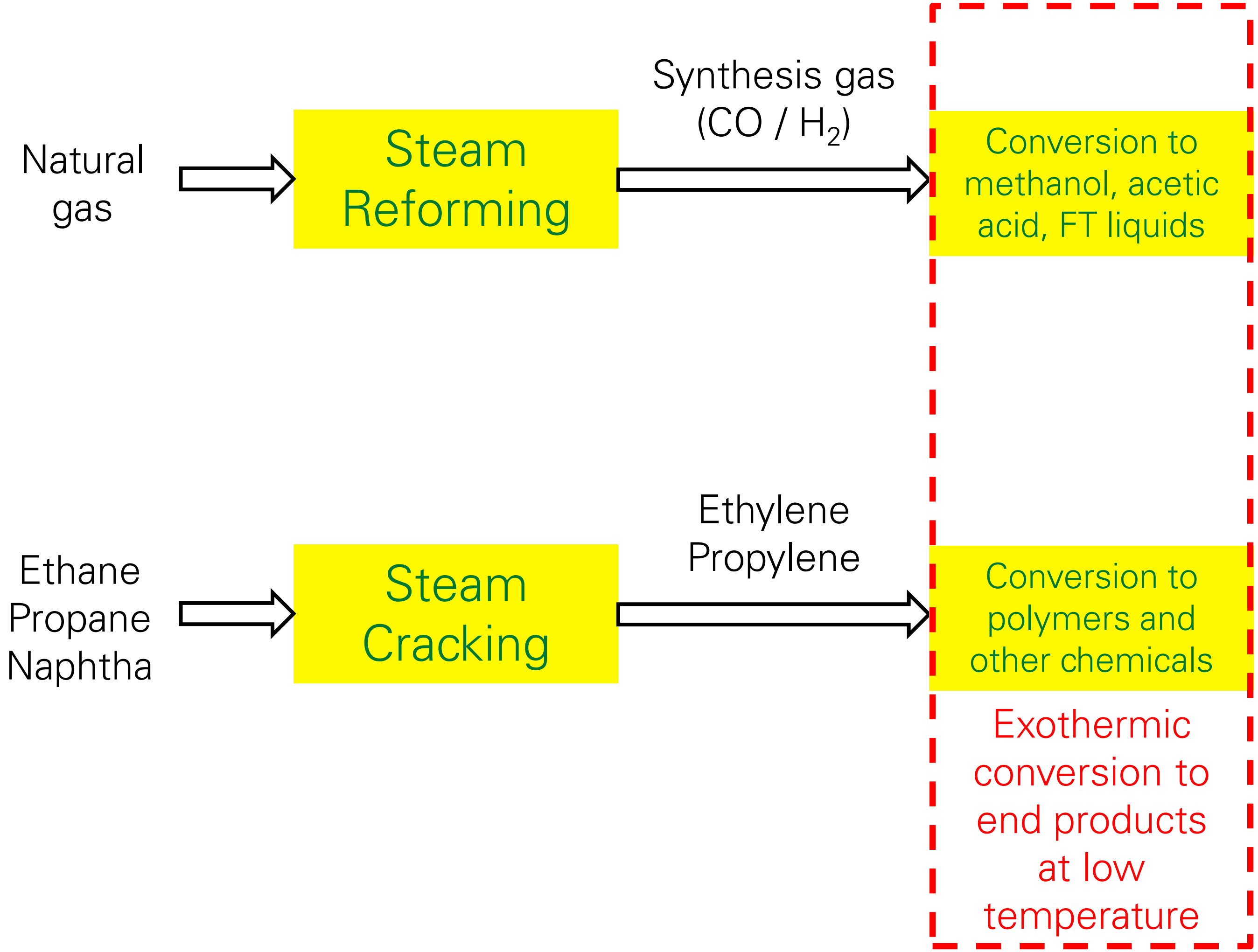

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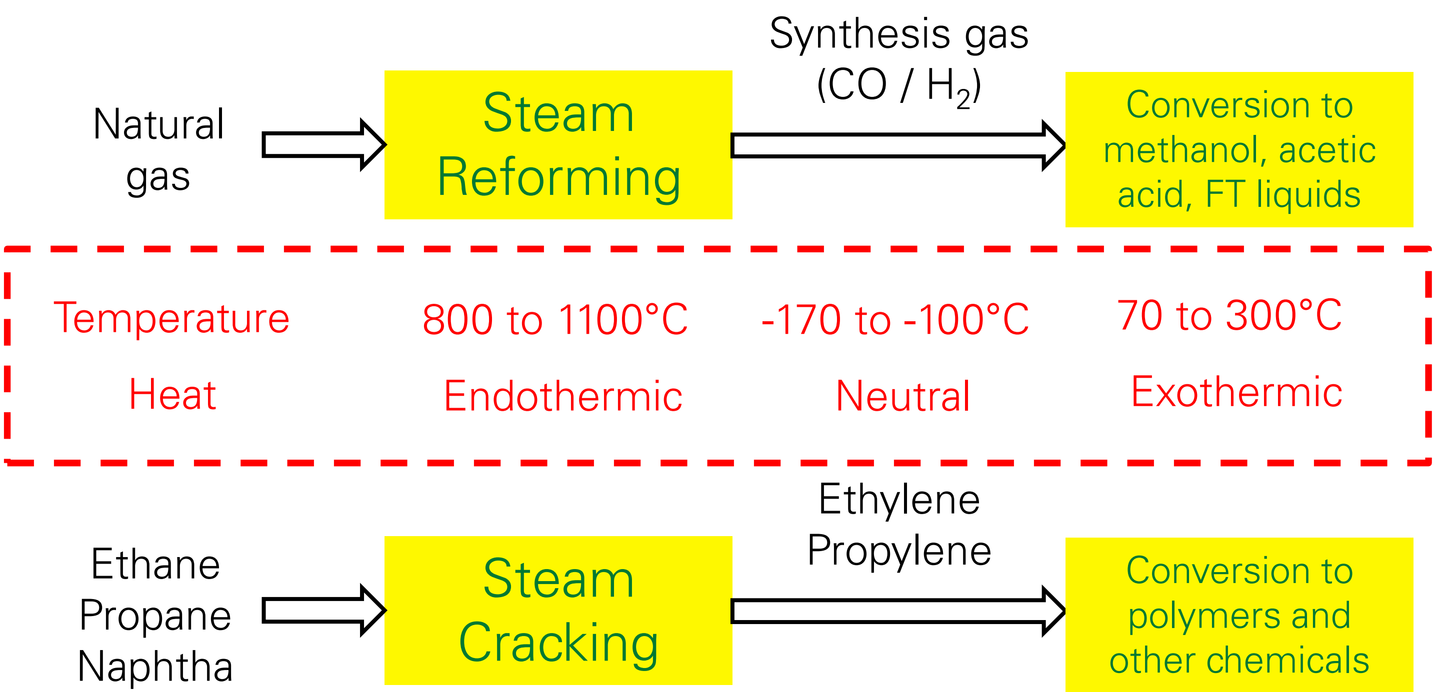
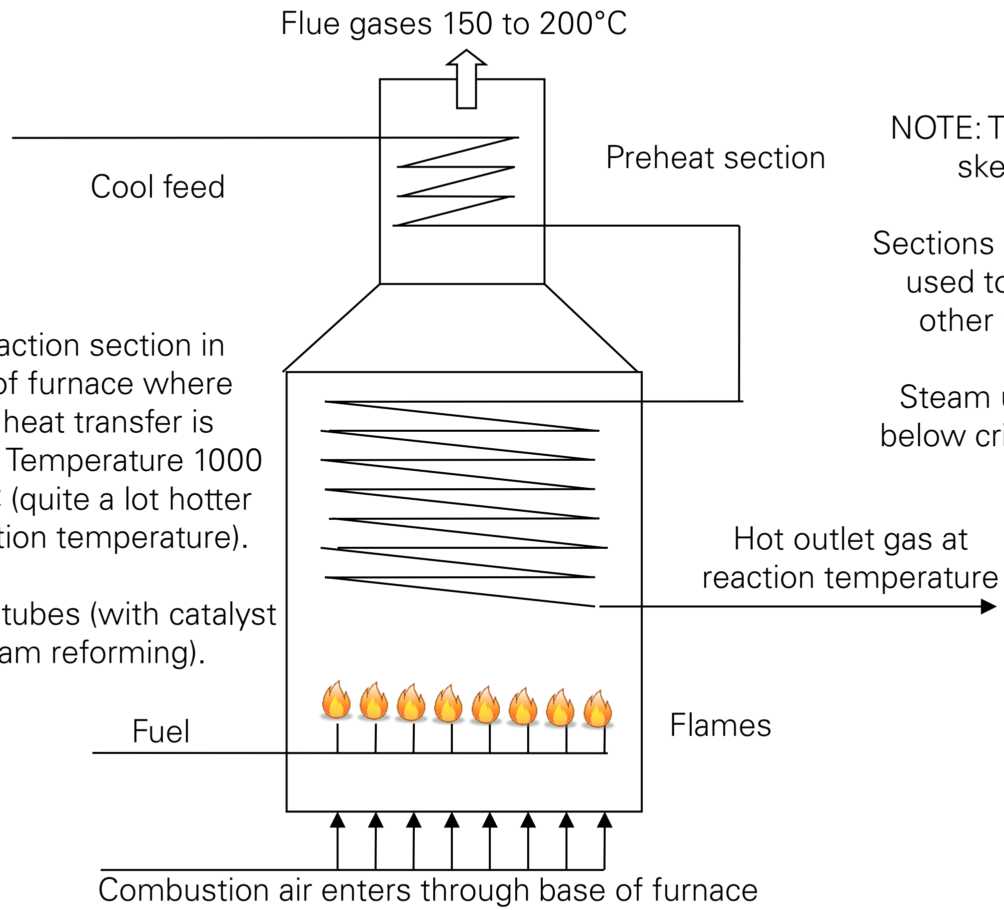


An excess of heat produced at low temperature, and a demand for heat at high temperature

High temperature processes



Main reaction section in section of furnace where radiant heat transfer is dominant. Temperature 1000 to 1400°C (quite a lot hotter than reaction temperature).

Reaction in tubes (with catalyst for steam reforming).

NOTE: This is a simplified sketch diagram.

Sections of furnace are also used to raise steam for other process needs.

Steam usually limited to below critical temperature.

High temperature processes

High temperature processes

- As in all process design, there are compromises.
  - There is a substantial temperature difference between the firebox temperature and the reaction temperature. Closing this gap would require thinner or more conductive tubes.
  - Air flow is normally only controlled by manually adjusted "registers" rather than control valves, so heat distribution in the firebox is often uneven.
- Heat recovery is constrained.
  - The stack outlet temperature may seem high, but this is as low as is normally economic.
  - Process stream heat recovery can be constrained by the process chemistry: for steam cracking, rapid cooling is needed to stop the reaction; for steam reforming, the gas must be rapidly cooled through the range 300 to 850°C to avoid metallurgical problems.

High temperature processes

- In summary:
  - the front-end endothermic reactions used in petrochemicals manufacture use fired heaters to achieve the required temperatures;
  - effective heat recovery from both the process stream and the furnace flue gases is a critical part of achieving high process efficiency and good economic operation;
  - there are significant process constraints due to the chemistry of these reactions.

Cryogenic processes

- The products of these high temperature processes are light gases and are generally separated by distillation at cryogenic conditions.
  - Key separations are $H_2/CH_4/C_2H_4/C_2H_6$ for steam cracking, $H_2/CO/CH_4$ for steam reforming.
    - Typical temperatures are from -100°C to - 170°C.
  - Energy is provided as the shaft work into the refrigeration compressors, often using steam turbines supplied with steam from the high temperature sections.
  - Technologists have long sought alternatives to these separations, such as absorption, adsorption, or membrane systems, to avoid the large swings in process temperature.

Cryogenic processes

- The coldest parts of these processes (along with air separation processes, which have similar needs) are carried out in “cold boxes” and make very extensive use of multi-stream plate-fin heat exchangers to achieve very high efficiency of the heat exchange sections.
- These pack the many heat exchangers into a single protected volume to minimise heat gain from the environment.

Hot and cold integration

- In summary:
  - steam generated from the "hot" waste heat from the high temperature processes is used to power refrigeration processes (and often other compression needs);
  - there is often sufficient high temperature heat also to generate and export power;
  - medium temperature heat (100 to 250°C) is used for other process needs, for example non-cryogenic distillation column reboilers;
  - process integration considerations and "pinch" analysis are part of the normal design process: most processes are well integrated as far as process and material constraints allow.

Downstream processes

- The reactive intermediates are used in a huge variety of downstream conversion processes.
- Three common types are:
  - polymerisation reactions – polyethylene, polypropylene, polystyrene, and so on; these represent by far the largest volume of chemicals manufactured.
  - selective oxidations – terephthalic acid, ethylene oxide, propylene oxide, adipic acid, acrylonitrile, vinyl acetate, and maleic anhydride; many of these are reacted further to polymers.
  - conversions of syngas components to make methanol, acetic acid, ammonia *etc*.
- There are other reaction types, but the above cover over 95% of the volume of the petrochemical industry.

Downstream processes

- Polymerisation reactions are very exothermic and mainly take place at less than 120°C, making effective use of the heat evolved very difficult. In general, the heat is rejected to cooling water.
- Selective oxidation reactions are also very exothermic but take place at higher temperatures (typically between 180 and 350°C). In most of these processes, heat is recovered effectively from the reaction step and used for preheat and purification processes, and, in some cases, heat or power can be exported.
- Syngas conversion have broadly similar characteristics to the oxidations, but are less exothermic.

- In summary, much of the heat put into the high temperature processes is rejected at low temperatures in the downstream processes.

Other parts of the chemical industry

- Although the focus here has been on petrochemicals, there are similarities in other areas of bulk chemicals manufacture.
- In the Chlor-Alkali industry, the initial step involves very high grade energy (as power used for electrolysis of salt), with subsequent reactions using sodium hydroxide and chlorine being exothermic and conducted at modest temperature.

Conclusions

- The chemical and petrochemical industries contain a very diverse range of different processes, and are very large energy users. Improvements in process efficiency through integration will lead directly to reduction in GHG emissions.
- There are many mature and well-integrated technologies, but opportunities still exist for technology vendors and operators to make improvements (particularly for new build) in energy efficiency by process integration. Increasing carbon price may tip the balance towards doing more integration.
- Some very large exergy losses exist in processes, but these will probably require different technological breakthroughs, as well as process integration analysis, to address.
- Chemical and petrochemical processes will continue to be very large producers of lower grade heat. This can probably only be effectively used outside the petrochemical site (*e.g.* for district heating).