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Perspective

Review of Electric Cracking of Hydrocarbons

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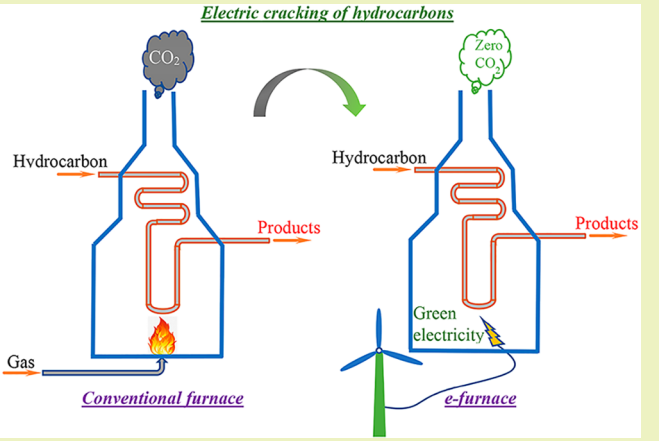
ABSTRACT: The cracking of hydrocarbons is a highly energy-intensive process with large CO_2 emissions. Industrial steam crackers use gas-fired furnaces, which produce a global CO_2 emission of about 366 Mt/year. Modern crackers have been improved through the years to increase performance and reduce greenhouse emissions. However, the improvements are limited, and the required future CO_2 emission reductions cannot be achieved with the present designs. Electrification is a promising option to make cracking processes more sustainable, especially if renewable electricity is used. Electric heating will result in energy savings as flue gas losses are avoided, while CO_2 emissions will be reduced radically if renewable electricity is used. This paper evaluates the current state of electric cracking and identifies potential electric heating technologies for the electrification of cracking processes. Various electric heating technologies are reviewed, an extensive literature search is conducted on their application in cracking processes, and industrial applications of electric cracking are compiled. The study shows that resistance (Ohmic) heating is a promising electric heating technology for steam cracking of naphtha. The technology is relatively easy to scale up and can be used to retrofit existing crackers. The cost of electric cracking is expected to be higher than conventional cracking, mainly due to the current electricity price being higher than the gas price. However, the cost of naphtha represents about 80% of the ethylene production cost, so possible selectivity improvements could reduce the overall cost through lower feedstock consumption. The electrification of the cracking processes can be stimulated by guaranteeing sufficient availability of renewable electricity and by introducing a CO_2 tax.



KEYWORDS: *Electrification, Cracking, Pyrolysis, Hydrocarbons, Naphtha, Sustainable, Energy, CO_2 Emission*

INTRODUCTION

In cracking processes, hydrocarbon molecules are broken down into smaller molecules by using thermal energy. These processes can be carried out with or without a catalyst. The most energy-consuming industrial cracking processes occur in refineries and naphtha crackers. There are different types of industrial cracking processes, such as steam reforming of methane (SMR), fluid catalytic cracking (FCC), and steam cracking. SMRs are used for producing hydrogen from methane; FCCs are used in refineries for the conversion of large molecular hydrocarbons into olefins, gasoline, and other products; and steam cracking is used to convert saturated hydrocarbons into unsaturated hydrocarbons. Steam cracking is the primary industrial process for producing olefins like ethylene and propylene.

Most cracking processes are energy-intensive thermal processes and mainly use natural gas combustion to produce the required heat for the reaction. The use of natural gas generates large quantities of CO_2 emissions. In this paper, some cracking processes will be presented, with a focus on steam cracking of naphtha as a typical energetic intensive cracking process.

The main product of the naphtha steam cracking process is ethylene, with a global production of 183 Mton in 2019 and an annual increase of about 4−5%.[1] Ethylene is the basic chemical for the plastics industry. It forms the feedstock for many chemical products, like polyethylene, ethylene oxide, ethylene dichloride (which is used to produce PVC), and ethylbenzene (which is used to produce polystyrene).[2] Steam cracking of naphtha consumes about 30% of the total energy use in the chemical industry in The Netherlands.[3]

Steam cracking of naphtha is inefficient as only 30% of the furnace energy input is used for the cracking reaction.[4] The

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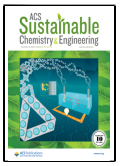

heat in the product gas leaving the furnace is recovered in the transmission line exchanger (TLE) by generating high-pressure steam. Most of the remaining heat leaves the furnace in the form of hot flue gas, of which the heat is recovered in the convection section for superheating of steam, preheating of feed, and preheating of boiler feedwater. This results in an overall efficiency of about 94% for the furnace. However, most of this overall efficiency is not related to energy embodied in the product flow but to energy embodied in the byproduct steam. This steam is currently used to drive compressors, but it would be much more efficient to avoid these flue gases in the first place. This can be achieved by electrification of the cracker and driving the compressors with electricity (since electromotors have a much higher efficiency than steam turbines). This would strongly increase the overall efficiency (in terms of final energy, and if renewable electricity is used, also in terms of primary energy).

Industrial steam crackers produce about 1.8−2 tons of CO_2 per ton of ethylene.[3] This results in a global CO_2 emission of about 366 Mt/year. In addition, NO_x emissions are also significant due to the high temperature pyrolysis.[3]

Using renewable electricity for the electrification of chemical processes is an important option to make the chemical industry more sustainable.[5−9] Specifically for cracking, electric heating will result in significant energy savings as the feedstock is heated directly without flue gas losses. The scope 1 CO_2 emissions will be reduced radically by using renewable electricity and by increasing energy efficiency and could be reduced to almost zero if the separation processes also can be electrified (e.g., by using electrically driven compressors). Only the small CO_2 emissions caused by decoking cannot be avoided (yet).

In the current discussions within the framework of climate change, there is serious interest from the petrochemical industry in electrical cracking. However, analysis of the literature shows a lack of knowledge about electrification of hydrocarbon cracking processes. Only two industrial-scale electric crackers have been built. These reactors are the Huels- and the DuPont-arc/plasma reactors. The Huels reactor is used to produce acetylene from different hydrocarbons, including natural gas as a feedstock.[10−12] The DuPont reactor is similar to the Huels reactor and produces acetylene from liquid hydrocarbons,[11,12] with a similar power scale of about 10 MW. These two plants were stopped due to the decreasing market demands for acetylene.[13]

The objective of the present study is to evaluate the current state of technology in the field of research, innovation, and application of electrical cracking and the identification of potential electric heating technologies which can be applied for the electrification of cracking processes. To this end, an extensive literature search is conducted in the field of electric cracking of hydrocarbons. An exploration of the different electric heating technologies, their physical principle, industrial applications, advantages, performance, challenges, and the temperature level that can be achieved, is undertaken. Additionally, an overview of industrial applications of electric cracking is compiled. This is done to answer some important questions for electric cracking like the state of the art, the respective strengths and weaknesses, the match with the user requirements, and the research questions for further development of the technology.

This paper is organized as follows: First an overview is presented of the most important cracking processes, followed by an overview of the different electric heating technologies. Subsequently, a literature overview is presented related to electric cracking in research, patents, and in industrial applications. Next, a case study concerning the electrification of the steam cracking of naphtha is presented, including the economics and feasibility. Finally, conclusions are drawn.

CRACKING PROCESSES

In cracking processes, hydrocarbon molecules are broken down into smaller, more useful molecules. The cracking process takes place at high temperatures and uses heat produced by the combustion of fossil fuels, leading to large CO_2 emissions. There are many different cracking processes which are used in the chemical industry and the refinery sector, and some examples are presented shortly in the following sections.

Steam Methane Reforming (SMR). SMR is a cracking process whereby methane reacts with steam at a high temperature (800 °C) in the presence of a catalyst to produce hydrogen. Hydrogen is used in many chemical and refinery processes, like ammonia production and hydrogenation reactions. SMR is an endothermic process and thus requires heat to proceed according to the reactions:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \left(\Delta H = 206 \frac{kJ}{mol}\right) \quad (1)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \ (\Delta H = -41 \text{ kJ/mol}) \quad (2)$$

The combination of the two reactions gives

$$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2 \ (\Delta H = 165 \text{ kJ/mol}) \quad (3)$$

Reaction 2 is the so-called water−gas shift reaction (WGS), where the CO formed in reaction 1 is converted to CO_2 and H_2. Worldwide, SMR is the principal technology used to produce hydrogen (95% of the world's production).

The SMR reaction takes place inside catalytic tubular reactors placed in a gas-fired furnace, as illustrated in Figure 1. The feedstock consists of a mixture of methane and steam, which passes through the hot reactor tubes. These tubes contain a catalyst, converting the feed to syngas. SMR produces 6.6−9.3 tons of CO_2 per ton of H_2.[6] The typical

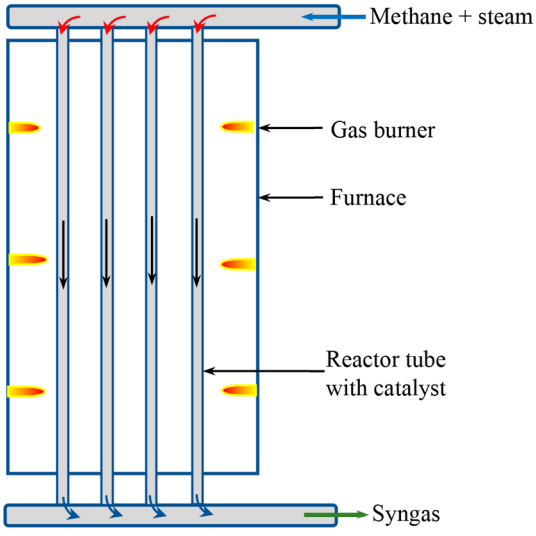

Figure 1. Illustration of a SMR reactor.

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specific energy consumption for SMR is in the range of 12.3−13.8 MJ/Nm^3 H_2.[14]

Fluid Catalytic Cracking (FCC). FCC is a cracking process which is mainly used in oil refineries for the conversion of heavy hydrocarbon molecules into gasoline and other products. FCC is endothermic and is used in about 50% of the refineries.[15] A schematic illustration of the FCC cracking process is shown in Figure 2. The feedstock is preheated and

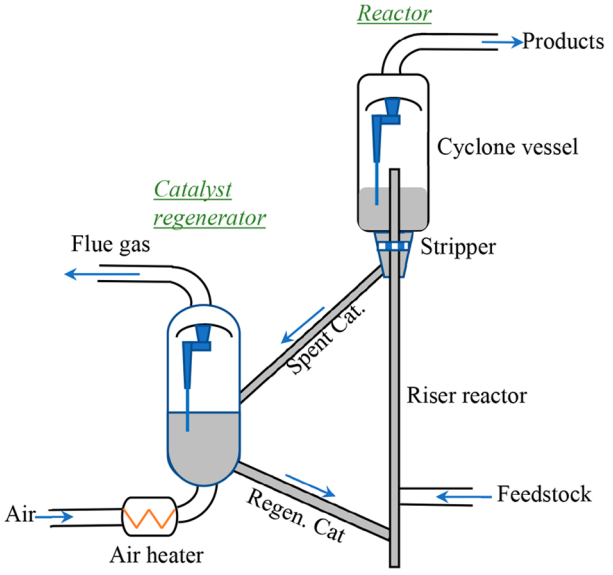

Figure 2. Schematic illustration of the FCC cracking process.

then mixed with a finely powdered catalyst (zeolite) in the bottom of the reactor at a temperature of about 550 °C. The powdered catalyst behaves like a fluid and flows with the cracking products. The product gases are transported up in the riser reactor. The residence time in the riser is on the order of seconds. The products are refined downstream. The catalyst is extracted from the product mixture and regenerated in the regenerator by burning off the deposited carbon in air at about 650−750 °C. The catalyst is then recycled and reused. A fraction of the feedstock is burned in the regenerator to produce the required heat for the cracking process. The temperature, residence time, and type of catalyst determine the product composition (selectivity).

Hydrocracking. Hydrocracking is an endothermic catalytic cracking process which takes place in the presence of hydrogen. The process uses hydrogen gas at high pressure (103−138 bar) and high temperature (288−385 °C), and a catalyst.[16] Hydrocracking is used for the upgrading of a large variety of petroleum fractions. The addition of hydrogen improves the ratio of hydrogen to carbon, removes impurities like sulfur, and limits the coke deposition on the catalyst. Hydrocracking is a two-step process which combines catalytic cracking and hydrogenation. The catalyst consists of fine platinum particles on silica or alumina. The cracking products range from heavy diesel to light naphtha, and they are separated by fractionation. A hydrocracking unit consists of a furnace, a reactor section, and a fractionation section. The hydrocracking process can either be a one- or two-stage process with or without recycling.[16] Figure 3 shows configurations of the one- and two-stages hydrocracking with recycling. In the one-stage configuration, the feed is mixed with hydrogen and routed through the reactor. The cracking products are separated in the fractionation column. In the two-stage process, hydrotreating and partial cracking occur in the first stage. The cracking products from the first stage are separated in the fractionator, and the residual oil is fed to the second stage for further cracking. The products from the second stage are passed to the fractionator for separation.

Visbreaking. Visbreaking is a relatively low severity noncatalytic cracking process where large hydrocarbon molecules are broken into short molecules, reducing the viscosity of the feedstock.[17,18] The feedstock (crude oil residue or tar sand bitumen) is cracked at 470−520 °C and at atmospheric pressure. The residence time in the reactor is in the range of 1−3 min. The cracking products are quenched with cool oil to avoid overcracking. Subsequently, the products are flashed in a distillation tower. The products consist of gas, naphtha, gas oil, and furnace oil. The composition depends on the type of feedstock. A typical yield composition is gas 1−2%, naphtha 2−3%, gas oil 5−7%, and furnace oil 90−92%. There are two types of visbreaking processes: the coil type, which operates at high temperature (455−520 °C) and short residence time, and the soaker type, which operates at a lower temperature (480 °C) and longer residence time. The majority of the visbreaking reactors are of the soaker type. In the coil type, the feedstock is cracked in a furnace, and the cracking products are quenched and distilled in a fractionator. In the soaker type, the furnace operates at a lower temperature,

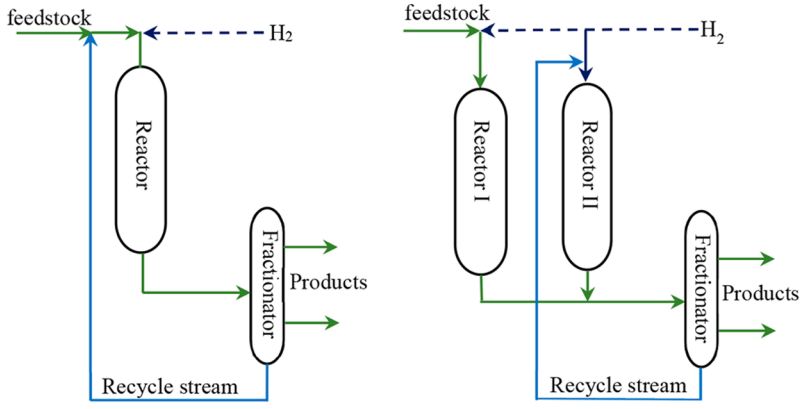

Figure 3. Illustration of one-stage (left) and two-stage (right) hydrocracking.

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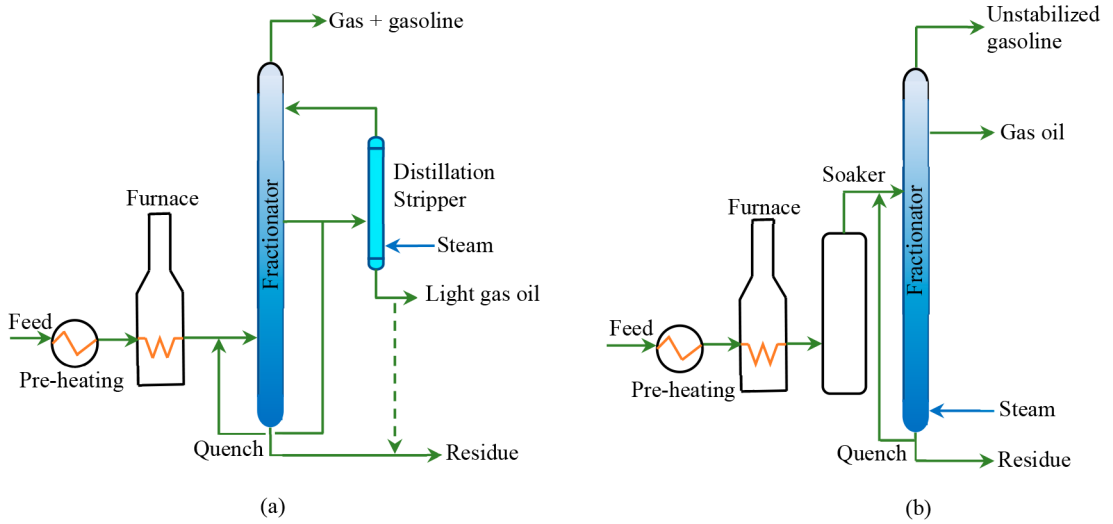

Figure 4. Illustration of visbreaking process. (a) Coil visbreaking and (b) soaker visbreaking.

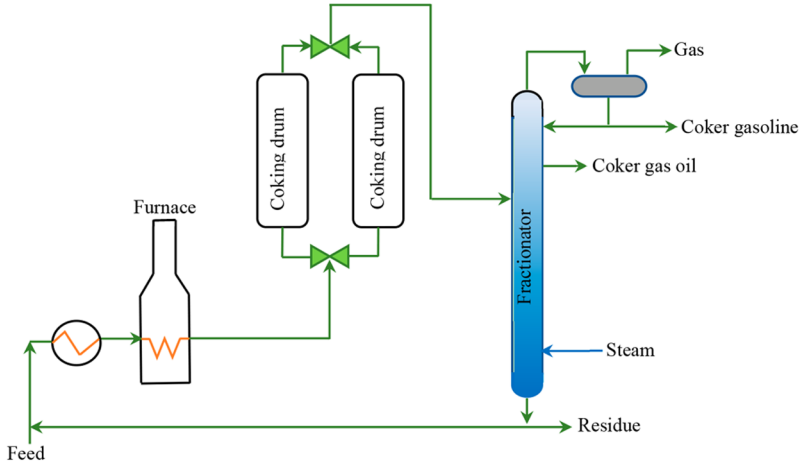

Figure 5. Illustration of the coking process.

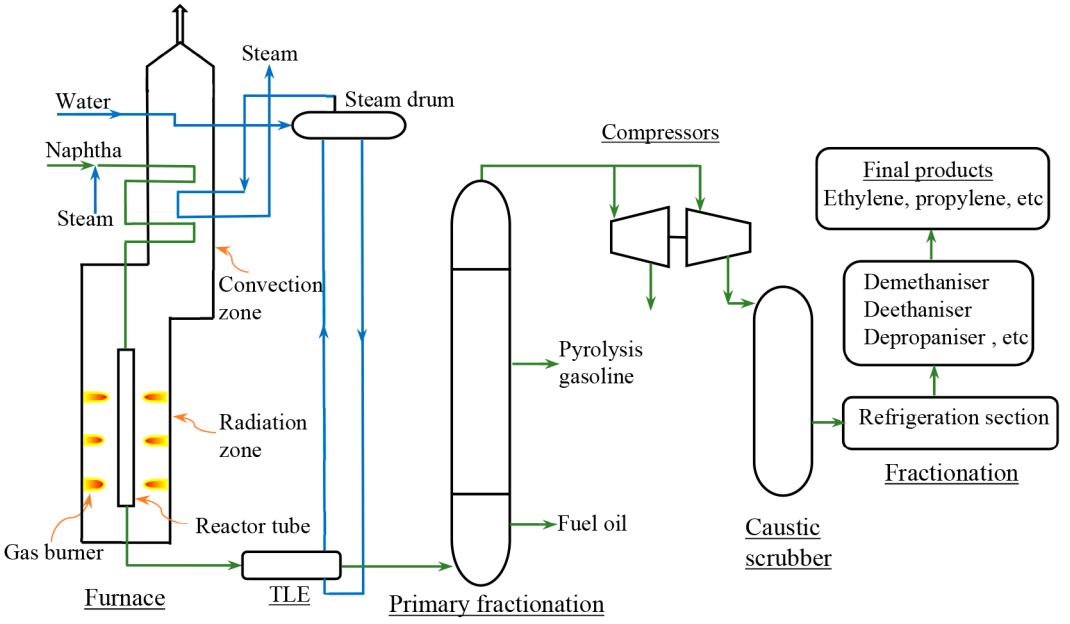

Figure 6. Illustration of a naphtha cracker plant.

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and a soaker drum at the outlet of the furnace controls the residence time to obtain the desired products while reducing the coke deposition in the reactor.[17,18] The products from the soaker drum are quenched and distilled in a fractionator. Illustrations of the coil and soaker processes are shown in Figure 4.

Coking. Coking is a severe thermal cracking process used to convert heavy residues into lighter products and coke.[18] Residues from vacuum distillation and other hydrocarbon residues are cracked to produce fuel gas, LPG, naphtha, gas oil, and coke. There are two types of coking processes: delayed coking and continuous coking. Three types of coke can be produced: sponge-, honeycomb-, or needle-coke, depending on the reaction conditions. An illustration of the delayed coking process is shown in Figure 5. In delayed coking, the feedstock is heated in a furnace at a high temperature (480−500 °C) and low pressures (1.7−5 bar).[18] The hot feedstock is then passed to drums, where it remains for about 24 h until the reaction is completed. Products from the drums are routed to a fractionator where the light products are separated. The heavier products from the fractionator are routed to the furnace for recycling.

At least two drums are used to maintain continuous operation. The coke is removed from the drum by using an auger which rises from the bottom of the drum.[18]

Steam Cracking of Naphtha. Steam cracking of naphtha has been applied since the 1960s. Naphtha is the lightest nongaseous product from the refining of crude oil. Light naphtha has a boiling temperature in the range of 30−90 °C, and heavy naphtha has a boiling temperature in the range of 90−200 °C. The composition of the naphtha depends on the used raw oil and the refining process. It contains mainly (iso)pentane, (iso)hexane, and (iso)heptane, together with smaller fractions of the corresponding cycloparaffins (naphthenes) and a small fraction of aromatics.[4]

The steam cracking process consists of four steps, as shown in Figure 6: (1) pyrolysis, (2) primary fractionation, (3) compression, caustic scrubbing and drying, and (4) fractionation.[19]

Steam cracking of naphtha takes place in tubular reactors in the presence of steam at about 850 °C. The tubular reactors are heated in a gas-fired furnace. Naphtha is first preheated using heat from the flue gases in the convection zone, next thorough mixed with dilution steam, and then further heated to temperatures in the range 500−680 °C. Subsequently, the mixture enters the tubular reactors in the radiant zone where under controlled residence time (0.1−0.5 s), temperature profile, and partial pressure, it is heated up to about 850 °C. During this short residence time, naphtha is cracked to produce ethylene and other products. The cracking reaction is highly endothermic. The cracking products leaving the tubular reactor at 850 °C are rapidly (0.1−0.5 s) quenched to avoid their degradation/recombination. The rapid quench first takes place in the transfer line heat exchanger (TLE), where the temperature decreases to about 450 °C. The extracted heat is used to produce steam which is superheated in the convection zone to produce high-pressure steam (6−12 MPa). This high-pressure steam is used to drive the turbines of the compressors downstream. The products leaving the TLE are further quenched using oil, and the gaseous- and liquid-components are separated in the primary fractionation. Next, the gases are compressed, cleaned, and dried. Cryogenic fractionation is used to separate hydrogen, methane, the C2 fraction, the C3 fraction, and other gaseous components. The C2 fraction is subsequently split into ethylene and ethane (deethaniser), and the C3 fraction into propylene and propane (depropaniser). The ethylene and propylene are the main products. Methane is generally recycled back to the furnace as fuel, while ethane and propane are fed back to the cracker as a feedstock. The hydrogen is used for the hydrogenation of coproduced acetylene to ethylene.

The composition of the cracking products depends on the severity (temperature) of the cracking process. Ethylene is the main product, but other products like propylene, butadiene, and benzene are also produced. A typical composition of the cracking product is ethylene (30%), propylene (14%), benzene (5%), toluene (3%), hydrogen (1%), and methane (16%).[2]

The specific energy consumption (SEC) for the production of ethylene from naphtha is in the range of 26−31 GJ/ton of ethylene.[3] Best cases are given in Table 1,[20] showing typical SEC values of 18−21 GJ/ton ethylene. From this energy use, only about 6.7 GJ/ton is used for the cracking reaction (stoichiometric heat of reaction), which is about 30% of the total SEC involved.

Table 1. Energy Consumption for Naphtha Steam Cracking Per Ton Ethylene[20a]

	Technip-Coflexip	ABB Lummus	Linde AG	Stone & Webster	Kellog Brown & Root
ethylene yield wt %	35%	34.4%	35%	no data found	38%
Energy use GI/t Ethylene	Best: 18.8−20	Best: 18 (w/ gas turbine)	Best: 21	20−25	no data found
	Typical: 21.6−25.2	Typical: 21			

[a]Note that these specific energies are given per ton of ethylene. Since naphtha cracking typically results in about 30% of ethylene, the specific energy per ton of naphtha cracked is only 30% of the given values in Table 1.

ELECTRIC HEATING

All of the cracking processes discussed above are endothermic thermal processes, and they require heat to proceed. In general, heat is generated by burning gases, which produce large CO_2 emissions. The electrification of the heating processes using renewable electricity is an important option to reduce these CO_2 emissions. Electric heating methods using renewable electricity have a high potential for improving the environmental and economic performance of the industry. It seems aberrant to use electric energy produced from fossil fuels to produce low-quality heat, but this becomes less relevant when renewable electricity is used.

Electric heating methods use electricity to provide heat to processes. They are applied for heating, drying, curing, melting, forming, hardening, and welding. Electric heating has many advantages compared to fossil fuel combustion; it is clean, pollution free, easy to control, generates uniform heating, and has high efficiency,[21,22] flexibility, precise temperature control, direct heat transfer to feedstock with less heat losses, modular construction, and more compact design for reactors.[6−9]

Electric heating methods use electric current or electromagnetic radiation to heat materials. The heating can be direct or indirect. In direct heating, heat is generated inside the material by passing an electrical current through the material

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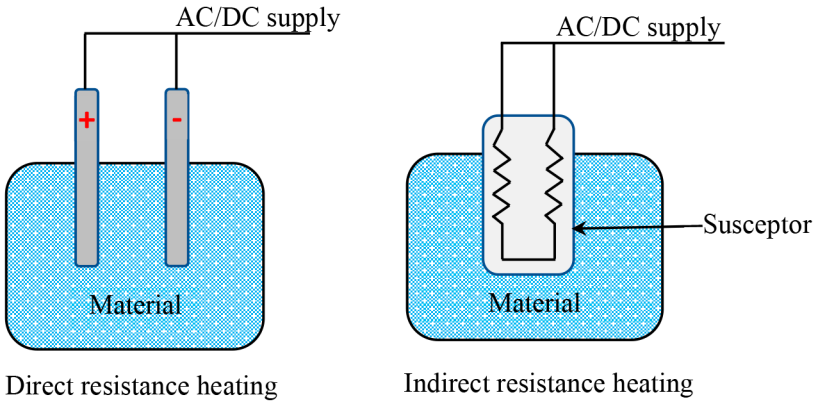

Figure 7. Illustration of direct resistance heating (left) and indirect resistance heating (right).

or by inducing an electrical current, dipole excitation, or electron excitation within the material (e.g., induction, radio frequency, microwave, or infrared). Indirect heating methods use one of these methods to heat a susceptor which transfers the heat to the material.

Electric Heating Technologies. The electric heating technologies used in industry are *resistance-, electric arc-, plasma-, electron beam-, laser-, electromagnetic- (infrared, ultraviolet, induction, and dielectric heating), and shock wave-heating.* Note that shock waves can be generated in a gas using electrical energy as will be discussed later.

Electron beam and laser heating could in theory be used for cracking processes, but their complexity, application difficulty to large volume flows of low density gas, and their costs are a challenge. UV-heating is also not suitable for cracking applications due to limited absorption in the gas phase. These electric heating technologies will be ignored in the rest of this paper.

A short description of the remaining electric heating technologies and their industrial applications is given in the following.

Resistance Heating. In resistance heating, heat is generated by passing an electric current (AC or DC) through an electric resistance, causing an increase in temperature. Resistance heating can be direct or indirect. An illustration of both methods is shown in Figure 7. In direct resistance heating, a material is directly heated by passing a current through it. It is applied in the glass industry, for welding of steel tubes and pipes, and in electrode boilers. In indirect resistance heating, an electrical current is passed through a susceptor which transfers the heat to the material. Resistance furnaces are used for holding molten iron and aluminum. Indirect resistance heaters are used for a variety of applications like heating water and sintering. Temperatures up to 3000 °C can be reached with resistance heating. In principle, resistance heating can also be used for the pyrolysis of hydrocarbons,[6,23−27] but so far, this is only carried out at laboratory scale.

Electromagnetic Heating. In electromagnetic heating, electromagnetic waves are absorbed by the material to be heated. This generates heat directly in the material, which limits the losses to the surrounding. There are three different types of electromagnetic heating which are characterized by the frequency range used: (1) induction heating, (2) dielectric heating (radio waves, microwaves), and (3) infrared heating.

Induction Heating. Induction heating occurs when an electrically conductive material is placed in an alternating magnetic field. This is realized by placing the material inside a coil which carries a high-frequency (50 Hz to 500 kHz) alternating current. The alternating field generates eddy currents in the material, which by dissipation generates heat. Induction heating is limited to metals due to the required high conductivity and is typically applied in foundry melting and casting of metals. However, like resistance heating, induction heating can be direct or indirect, which means that indirect induction heating can be used to heat nonconductive materials as well. Temperatures up to 3000 °C can be reached with power densities of about 50 MW/m^2 and efficiencies in the range of 50−90%. Induction heating is illustrated in Figure 8. Indirect induction heating can be used to heat liquids in vessels and pipelines in the petrochemical industry and for the pyrolysis of hydrocarbons.[28,29]

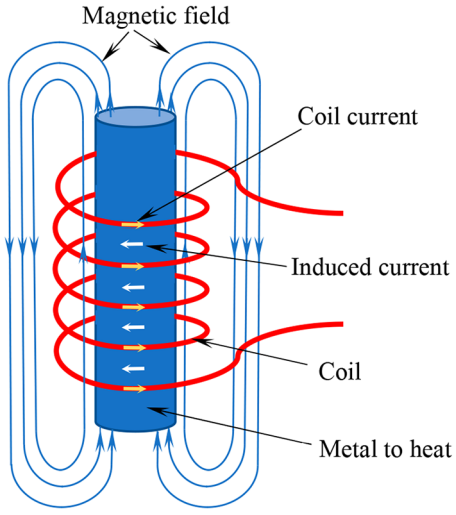

Figure 8. Schematic illustration of induction heating.

Dielectric Heating. Dielectric heating uses electromagnetic radiation for the heating of materials that have low electric conductivity but have sufficient polarity. The polarized molecules (e.g., water) in the material oscillate with the frequency of the electromagnetic field. This induces molecular friction, which generates heat, increasing the temperature of the material. The advantage of dielectric heating compared to conventional heating is that heat is generated inside the

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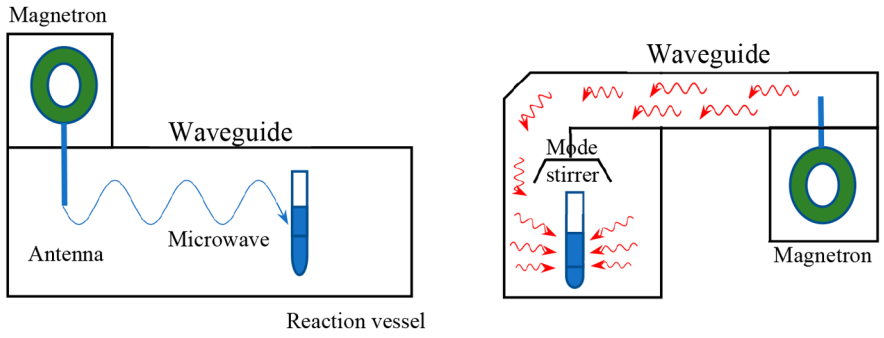

Figure 9. Single mode microwave heater (left) and multimode microwave heater (right).

material, which is rapid, homogeneous, and more efficient. Microwave (MW) and radio frequency (RF) heating use this principle. The difference between microwave and radio frequency is the frequency range used. Lower frequencies typically have a larger penetration depth.

Microwave (MW) Heating Systems. Microwave heating uses electromagnetic radiation in the microwave range (200 MHz to 3 GHz) to heat dielectric materials. Two frequencies are used in the industry 900 MHz and 2.45 GHz. There are two types of microwave heating systems: single mode and multimode as shown in Figure 9. Single mode heaters focus high powers to a small volume, while a multimode heater is used to heat large volumes. The most well-known application of microwave heating is the household oven (multimode), illustrated in Figure 9.

Microwave heating is applied in industry for drying textiles and polymers, food processing, and drying and sintering ceramics. Microwave heating systems are rapid, have high efficiency and high energy densities, and are easy to control. Temperatures up to 2000 °C can be achieved depending on the material. Power densities of about 500 kW/m^2 can be obtained with efficiencies of about 80%. Microwave furnaces do not supply a high temperature directly but rather provide microwave power to be absorbed by the material to be heated, thereby attaining the desired temperature. For materials that do not absorb microwaves well, susceptor materials that absorb microwave energy can be used.[30] The susceptor then transfers the heat to the material. Hydrocarbons with low microwave absorption can be mixed with a susceptor (e.g., a catalyst) with high microwave absorption, and pyrolysis can take place on the catalyst surface. Heavy hydrocarbons like *n*-hexadecane are pyrolyzed to products like olefins and alkanes, and temperatures up to 700 °C have been achieved.[31] Priecel et al. discussed the use of microwave heating for chemical transformations, and they addressed some issues related to the industrial utilization of microwave heating and the upscaling of such technology.[32] They also give some examples of industrial applications.

Radio Frequency (RF) Heaters. Radio frequency heating is similar to microwave heating but uses lower frequencies in the range of 10−100 MHz. Radio frequency waves are longer than microwaves and are suitable to heat larger volumes (larger penetration depth). The most used heating frequencies are 13.56 and 27.12 MHz. The main industrial applications of radio frequency heating are in the production of plasmas for semiconductor processing and in drying processes in the food and paper industries. Several configurations are possible, depending on the application. An illustration of an RF-dryer is given in Figure 10. This plate electrode heater consists of two parallel electrodes coupled to an RF-generator. The material to be heated passes between the two electrodes.

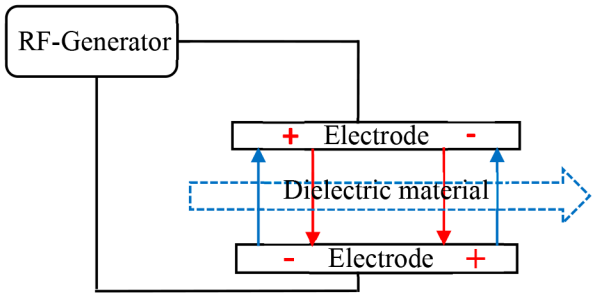

Figure 10. Illustration of a RF-dryer.

RF-radiation is presently also used for the heating and extraction of heavy hydrocarbons (kerogen, oil shale, tar sand, heavy oil, etc.) from the soil, using the large penetration depth to heat these materials, thereby lowering their viscosity for easier extraction.[33] This is discussed in more detail later.

Infrared (IR) Heating. Infrared heating uses electromagnetic frequencies in the range 30−400 THz to heat and process materials. When an electrical current is passed through an electric resistance, it heats up and emits infrared radiation that can be used for heating. Infrared heating is typically used for heat treating surfaces, curing coatings, and drying materials.[34] The material to be heated must be able to absorb infrared radiation. Therefore, it is necessary to determine the IR-wavelength range the material can absorb. Infrared heaters are characterized by the wavelength they emit: short-, medium-, or long-waves. Temperatures up to 2600 °C can be reached with short waves, and power densities in the range of 300 kW/m^2 can be achieved with efficiencies in the range of 60−90%. An industrial electric IR-heating system typically consists of an emitter and a controller, as shown in Figure 11.

Electric Arc Heating. Electric arc heating uses an electric arc to heat materials. Industrial arc furnaces are applied in foundries for the production of steel from scrap iron.[22] Three types of arc furnaces are used: direct, indirect, and submerged. In direct arc furnaces, steel or iron scrap is melted by an electric arc which is generated between an electrode and the metal charge. Indirect arc furnaces use an arc that is generated between two carbon electrodes placed above the charge, and heat is transferred to the charge by radiation. Indirect arc furnaces are used in the production of copper alloys. In submerged arc furnaces, the electrodes are submerged in the charge (ore and coke) that is fed from the top. Such furnaces are typically used in reduction processes and are used to

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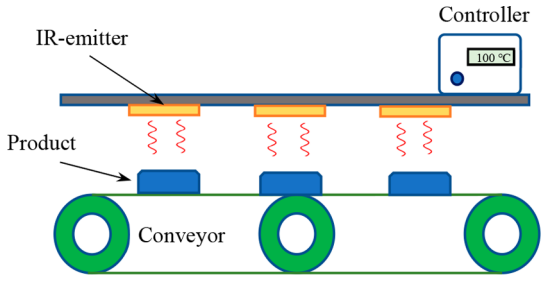

Figure 11. Illustration of an electric IR-heating system electric arc heating.

produce, e.g., ferroalloys[35] and white phosphorus (Wöhler process). Temperatures up to 3000 °C can, in principle, be achieved by arc heating, although typical industrial electric arc furnaces operate at lower temperatures (1200−1800 °C, depending on application). Figure 12 shows an illustration of an AC-arc furnace used for the smelting of steel scrap.

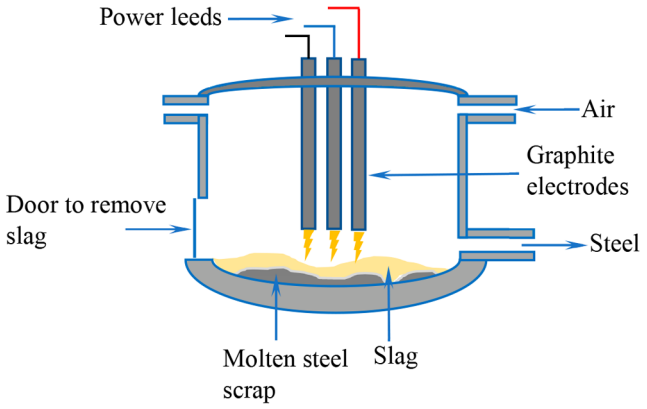

Figure 12. Illustration of an AC-arc furnace.

Plasma Heating. Plasma consists of ionized gas, in which the charged particles are accelerated by an electric field, transferring energy by impacting other particles. There are different ways to generate plasma. It can be generated by electric arc or by MW/RF.[36] In the case of arc-plasma, an electric arc is created between two electrodes to ionize a gas. The ionized gas can reach temperatures in the range of 3000−4000 °C and can be used to heat materials.

Industrial applications of plasma heating include melting of scrap and steels. Plasma processing is used in the titanium industry. Plasma is also used for processes like welding, cutting, and spraying of metal and ceramic coatings.

There are different parameters which characterize a plasma. In general, the plasmas are divided into two classes: thermal or hot plasma (>700 °C) and nonequilibrium plasma or cold plasma (<700 °C). In the first case, ions and electrons are in thermal equilibrium, while in the second case, the electron temperature is much higher than the ion temperature. Direct current arc torch, alternating current arc torch, and radio frequency (RF) plasmas are examples of thermal plasmas. Microwave plasma, corona discharge plasma, and dielectric barrier discharge plasma are examples of cold plasma.

Plasma can also be used for cracking gaseous materials such as evaporated hydrocarbons, as will be discussed later.[37] Figure 13 shows an illustration of a plasma torch generated by an electric arc between a cathode and an anode. The arc ionizes a gas (NG) to generate the plasma torch. This principle is used in the Huels arc/plasma reactor discussed later.

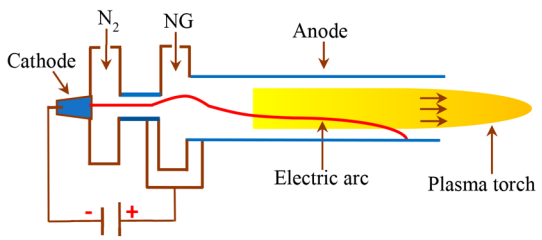

Figure 13. Illustration of an arc-plasma torch.

Ultrasonic Heating. Ultrasonic sound waves are used in ultrasonic welding, ultrasonic cleaning, and sonochemistry. Ultrasonic welding is applied for plastics and metals where local melting is generated by means of friction generated at the interface. Ultrasound can be used to heat liquids by cavitation. Cavitation is the physical process where an ultrasound wave creates a large number of microbubbles in a liquid which expands and contracts, and at the end implodes. A sound wave consists of periodic compression, displacement, and expansion of a liquid. During expansion, the low pressure vaporizes the liquid forming microbubbles. The sound wave causes the bubbles to grow during an expansion and contraction during compression. At a given critical diameter, the bubbles implode, releasing a large amount of energy. As a result, local high temperatures (5000 °C) and high pressures of several hundred atmospheres can be achieved.[38,39] Typically, cavitation uses ultrasound waves in the range of 20−40 kHz. An illustration of the cavitation process is shown in Figure 14.

Shock Wave Heating. Shock waves can be used for the heating of gases by converting kinetic energy into heat. The shock tube is an example, which is a tube divided into two sections by a diaphragm as shown in Figure 15. The first section is the driver, which contains a low molecular weight and high-pressure gas (H_2, He), and the other part is the test section which contains the reactants at low pressure.[40] The suppression of the diaphragm creates a shock wave in the low-pressure part. The shock wave propagates through the reactants in the driven section and then reflects at the right closed-end wall of the shock tube, causing further compression and heating of the reactants. A position-time graph illustrating the effect is shown in Figure 15. The horizontal axis is the position along the shock tube, and the vertical axis is the time axis. At the right closed end of the tube is the location where the reaction takes place. The shock wave heats the reactants (>800 °C) in a very short time (ms).

Another way to produce a shock wave is by the deceleration of a supersonic flow which results in a rapid increase in the temperature. This principle is applied in a laboratory setup for the pyrolysis of ethane to produce ethylene which achieved a product yield of more than 70%.[40−43]

This shock wave principle is also applied in the rotor dynamic reactor (RDR) to crack hydrocarbons.[44−46] An illustration of the RDR is shown in Figure 16. The RDR consists of a toroidal duct with a rotor that rotates between two stationary vane cascades (diffuser and nozzle). The vane cascades are configured to route the feedstock in a helical trajectory as illustrated by red arrows in Figure 16. While flowing within the toroidal duct between the inlet and outlet, the feedstock is successively accelerated by the rotor blade and decelerated by the nozzle blades creating shock waves which

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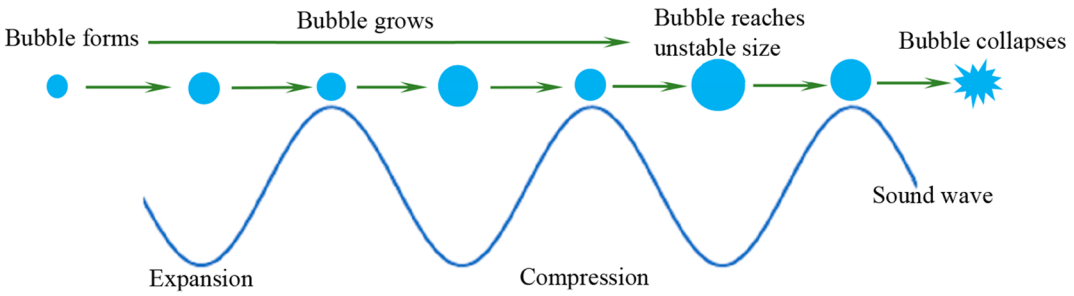

Figure 14. Illustration of the cavitation process.

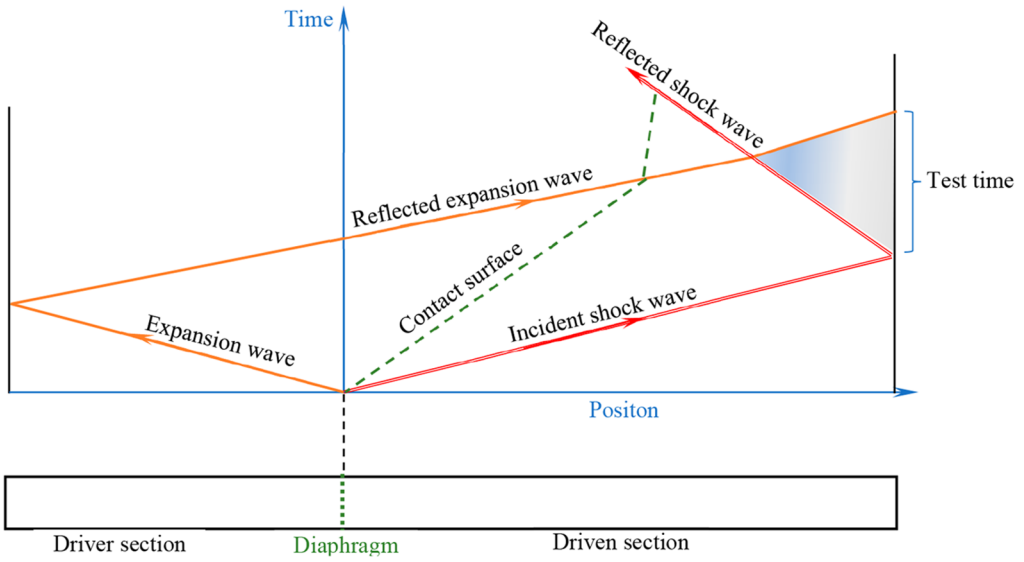

Figure 15. Illustration of shock tube (bottom) and time-position graph (top).

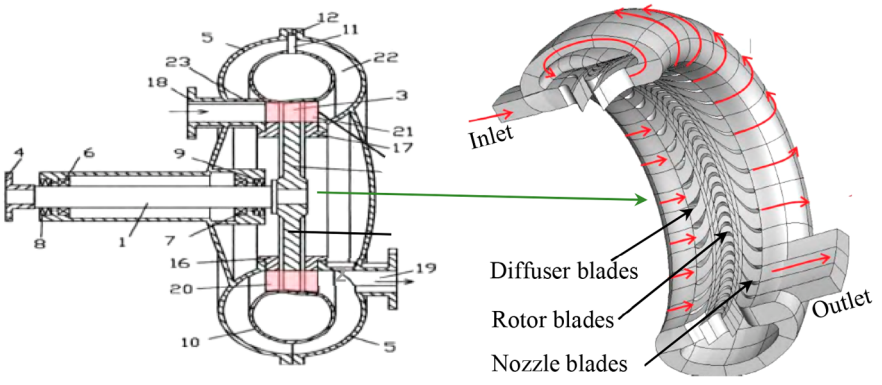

Figure 16. Illustration of the RDR reactor.[44] Rotor shaft (1); rotor, diffuser, and nozzle (2), rim (3); casing (4), toroidal duct (10); inlet port (18), exit port (19). Reproduced from Web site of CoolBrook.[45] Copyright Coolbrook.

convert kinetic energy into heat. As a result, during the helicoidal flow, the temperature of the feedstock increases gradually to reach temperatures above 1000 °C in a few milliseconds.[45,46]

LITERATURE REVIEW

A literature search was carried out on patents and scientific papers related to electric cracking of hydrocarbons. The result of the search is discussed in the following.

Patents. Figure 17 shows the number of patents per year for the different heating technologies. From the year 1894 up to 1980, most patents concern resistance and arc/plasma heating. Since about the year 1980, there is more interest in other heating methods like microwave, shock wave, and ultrasound. Most patents are related to arc/plasma cracking, which is mainly used in the production of acetylene. The first arc patent goes back to 1930.

The chronological history of the arc/plasma patents shows how the technique has evolved over time to make this method more feasible and efficient. The arc is rotated magnetically to avoid hot spots on the electrodes and to avoid carbon deposits. Also, improvements are introduced by some patents on the chemical conversion efficiency. In the first set-ups, the mass flow rate of feedstock was limited due to the stability of the arc,

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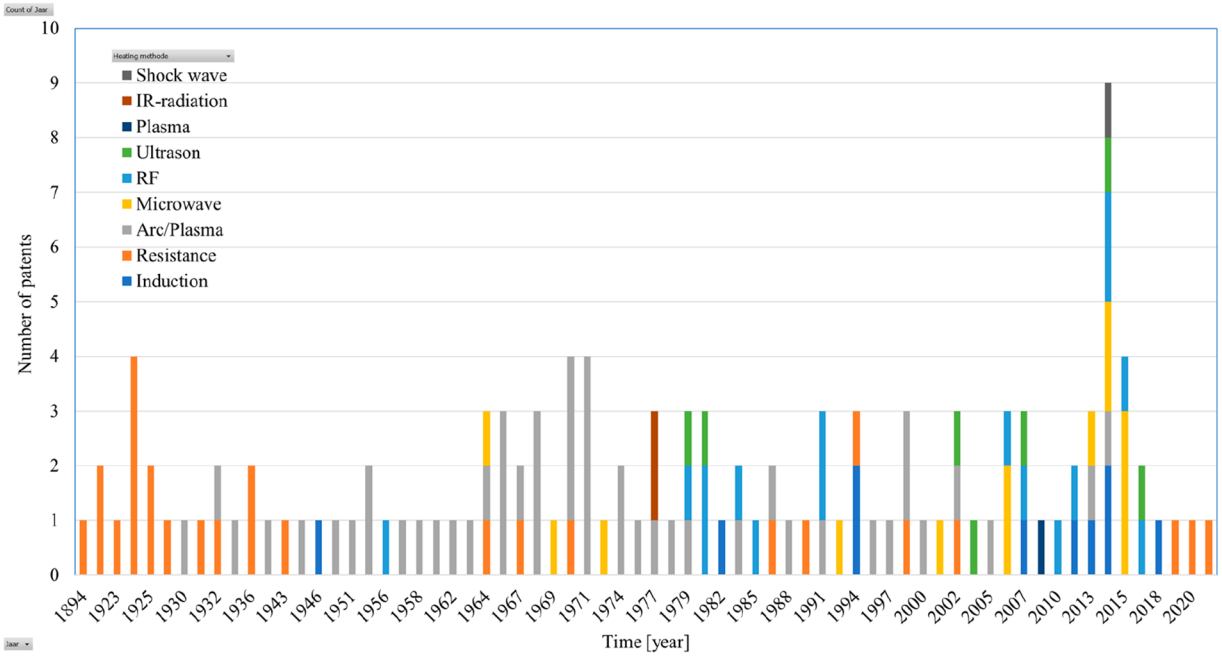

Figure 17. Number of patents per year for the different electric cracking technologies.

as the arc was extinguished at high flow rates. This resulted in low conversion efficiency. Solutions to improve the heating of feedstock are done, for example, by swirling the reactant gas in counter flow to heat carrier gas plasma (mixing). Also, a gas such as hydrogen or argon can be ionized by an electric arc, and the resulting hot gas (plasma torch) can be used for the pyrolysis of large volumes of feedstock to produce high yields. Some patents describe arc plasma generators that employ concentrically placed circular electrodes which operate at powers in the megawatts range and under high gas pressures to produce continuous plasma discharge for industrial applications.

In terms of the number of patents, electrical resistance heating comes in second place after arc/plasma heating. The described methods are simple to implement and can easily be upscaled. A number of patents discuss the use of indirect induction heating for the cracking of hydrocarbons. Since induction generates heat in materials by a changing magnetic field, it can generate heat in materials not physically connected to the electric supply. This allows for the heating up of packed beds filled with highly conductive metallic particles, while a hydrocarbon gas is flowing through, allowing for a very large heat transfer area. This allows for high rates of heat input, whereby the reaction is accomplished at higher temperatures and in a shorter time than is possible by conventional practice. The heat transfer is so rapid that the temperature difference between the heated bed and the feedstock is small, which minimizes the carbon deposition.

The patents related to microwave and radio frequency pyrolysis come in third place after resistance and induction heating. Microwaves are typically used indirectly to generate plasma for the heating of reactants. The majority of the patents related to RF radiation heating are concerned with the dielectric heating of oil sands, bitumen, or shale oil production in petroleum upgrading. This is due to the fact that RF radiation has a longer wavelength and is thus more appropriate to heat large volumes. However, this also makes the technology less appropriate for hydrocarbon cracking, where small volumes are heated to high temperatures.

Several patents discuss the upgrading of heavy oil using ultrasonic cavitation. The high temperatures and high pressures resulting from cavitation cause cracking of the hydrocarbons. High temperatures of up to 5000 °C and high pressures of about 50 MPa can reached. However, whether ultrasound can also be used for the cracking of lighter and more volatile oil fractions is presently not clear.

Finally, an interesting patent discusses the use of the rotor dynamic reactor (RDR), which is discussed later, to crack naphtha.[44] A picture of the RDR is shown in Figure 18.

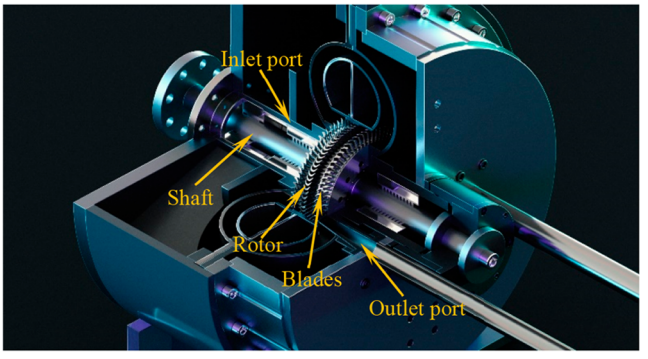

Figure 18. A picture of the RDR. Reproduced from Web site of CoolBrook.[45] Copyright Coolbrook.

Research Papers. Different electric cracking methods are discussed in the literature, scattered over many research papers. Laboratory scale set-ups are used to study the feasibility of electric heating methods for the pyrolysis of different hydrocarbons, or electric heating is used for convenience because of the ease of control and to avoid the flue gas involved in the conventional combustion heating methods. In the following, some representative papers are discussed.

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Resistance/Induction Heating. In many research papers, laboratory set-ups are discussed that use resistance heating for the study of the cracking of hydrocarbons.[23−28] These set-ups are mainly used for the study of the effect of the operating parameters on the production yields and coke deposition. Bajus et al. studied the thermal decomposition of heptane in the presence of steam in a flow reactor with a large inner surface.[23] The experiments were performed using an electrical resistance heated furnace at atmospheric pressure in a temperature range of 680−760 °C. Pinter et al. used a resistance heated furnace for the pyrolysis of different feedstocks, including naphtha in a laboratory scale setup.[24] The reactor tube consists of a Cr−Ni-steel tube of 85 cm long and 24 mm diameter. The maximal temperature is 950 °C. The setup also includes a cooling system (quench) placed directly after the furnace. Salari et al. conducted experiments with an electrically heated cracking setup to study the coking rate in the pyrolysis of naphtha.[25] The experiments are conducted at atmospheric pressure and at a temperature of about 860 °C. This setup is also used by Sadrameli et al. to validate modeling results for naphtha cracking experiments.[26,27] Wismann et al. used a laboratory scale reactor to study the electrification of steam-methane reforming.[6] They claim that direct resistive heating is scalable to industrial scale. The laboratory-scale setup consists of a FeCrAl-alloy reactor tube with a coating of catalyst on its internal wall. The ends of the tube are connected to two copper electrodes to apply a DC-current to the tube, as shown in Figure 19. It is shown that the good heat transfer in

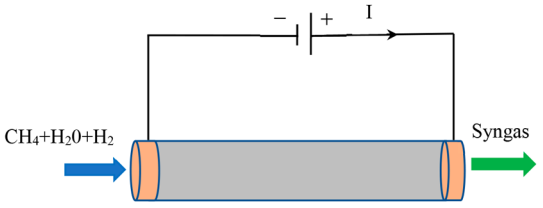

Figure 19. Laboratory-scale resistance heated SMR reactor.

the reactor drives the reaction at thermal equilibrium, increases catalyst utilization, and limits the production of undesirable byproduct. It is concluded that resistance heating can lead to a compact industrial reactor design, potentially 100 times smaller than conventional reformers.[6] Balakotaiah et al. discussed the use of modular reactors with resistance heating.[47] The module consists of a number of basic units with parallel wires, parallel strips, wire meshes, metallic monoliths, or parallel tubes which can be heated by an electric current. The system can be scaled up by using more modules. This makes the system modular and flexible. They showed that the thermal efficiency and conversion can be higher than for a conventional furnace based method. Shekunova et al.[48] studied the cracking of C1−C4 associated petroleum gases to ethylene and propylene in the presence of different material electrically heated metal wire coils in the temperature range of 300−600 °C. It was shown that the alkene yield depends on the coil material with a yield increase in the order tungsten > molybdenum > nichrome.

Arc/Plasma Cracking. Much attention has been given to arc/plasma cracking in the literature. Most literature focuses on the production of acetylene. The interest in arc/plasma heating is due to its unique properties, such as high energy density, high efficiency, and high temperatures. An electric arc/plasma can be used to pyrolyze hydrocarbons at very high flows and a very short time. Feedstocks can be gaseous, liquid, or solid hydrocarbons. In 1971, Abrahamson designed and built a 3 kW electric arc discharge reactor for the production of acetylene.[49] The electric arc generated between an anode and a cathode is used to ionize hydrogen, which is used to convert propane to acetylene and the products are rapidly quenched. Ward modified and scaled up the reactor of Abrahamson to 30 kW.[50] An illustration of a reactor similar to that used by Ward is shown in Figure 20.

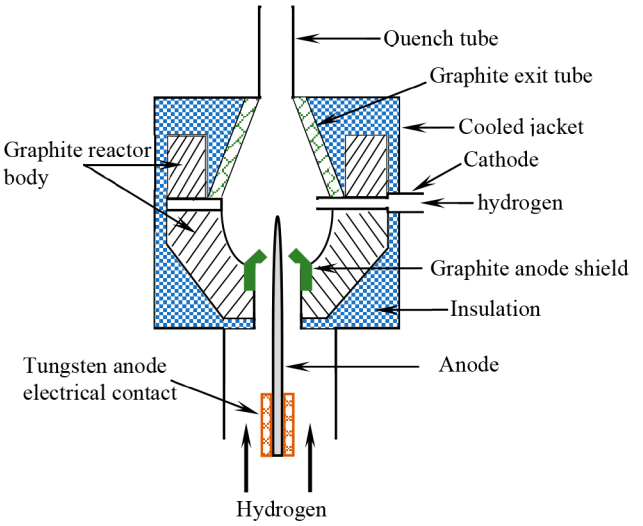

Figure 20. Illustration of an electric arc reactor.

Safronov et al. discussed the design and construction of a three-phase AC plasma torch with a power of up to 500 kW and a temperature of up to 5000 °C.[51] The reactor is used for different plasma chemical processes like pyrolysis of hydrocarbons. Yan et al. built a 5 MW hydrogen plasma reactor for coal pyrolysis, which operated under high temperature with a residence time of milliseconds.[52,53] Fincke et al. explored plasma conversion of natural gas to acetylene.[8] A laboratory setup was built and tested, and a better selectivity for acetylene and improved process conversion efficiency were demonstrated compared to the conventional cracking process. The improvements were achieved due to efficient injection and mixing of reactants with plasma gases and minimization of temperature gradients in the reactor. Methods for upscaling and possible improvement of the economics are also discussed. Jahanmiri et al. used a nanosecond pulsed dielectric barrier discharge (DBD) plasma reactor to investigate the conversion of heavy naphtha.[54] The effect of applied voltage, pulse frequency, and inner electrode material on the quantity and quality of products has been examined. The results show that these parameters affect the energy efficiency of the plasma cracking process. The product distribution during the process is C2 > C1 > C3. Khani et al. studied the cracking of heavy *n*-hexadecane using a cylindrical DBD-reactor.[55] Results show that the use of methane as plasma gas instead of air improves both conversion and cracking percentage. It is also shown that increasing the applied voltage and working gas flow rate enhances the conversion and cracking percentages. The highest conversion percentage obtained is 84%. Prieto et al. published work on the use of a plate−plate nonthermal plasma reactor driven by a high AC-voltage (9 kV) for the conversion of heavy oil into light hydrocarbon olefins.[56] The parameters studied

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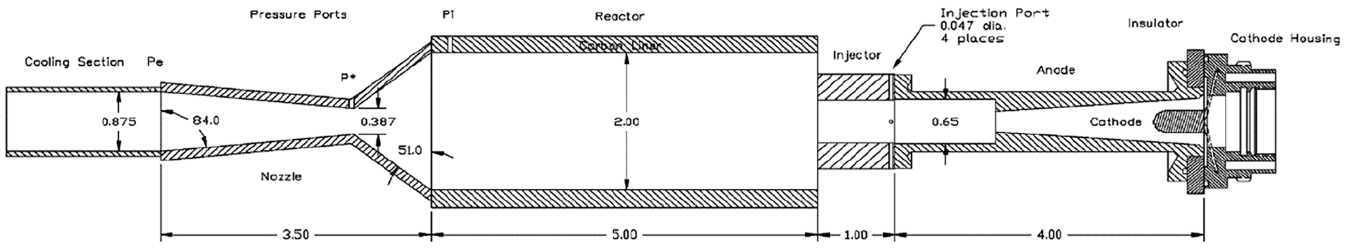

Figure 21. Illustration of the thermal plasma reactor. Reproduced with permission from ref 12. Copyright 2002 from Elsevier.

were the gap distance between the electrodes, the carrier gas flow, and the applied power. Results indicate that the reactions occurring in the process of heavy oil conversion have an important selective behavior. The products obtained were C1−C4 hydrocarbons with ethylene as the main product. Matsui et al. investigated a plate electrode plasma reactor for fuel reforming of different liquid-phase hydrocarbons at room temperature.[57] They placed aluminum or copper chips between the plate electrodes in a vessel filled with oil. A plasma was generated between the chips and the plate electrodes to convert the liquid hydrocarbons to gas and solid phases. The application of a pulsed, high square voltage results in the formation of coke and gaseous products. Hydrogen gas concentration in the produced gas was about 60−70% when the electrodes and chips consisted of aluminum. The production rate was proportional to the input energy. The selectivity to CH_4 was higher than that to C_2H_4 when 2,2,4-trimethylpentane was used as feedstock. The selectivity toward C_2H_4 and C_2H_2 was higher than that toward CH_4 when other feedstocks were used. When the electrodes and chips were made of copper, the production rate was only half of that obtained by aluminum electrodes. Yan et al.[58] discussed the use of H_2/Ar plasma to pyrolyze *n*-hexane, cyclohexane, and toluene. The effect of the type of feedstock and operating conditions like specific input power and residence time on the reaction performance was evaluated. The experiments show that the nonaromatic hydrocarbons have better chemical reactivity than partially aromatic substances. The results also demonstrate that the pyrolysis reactions are completed within 0.8 ms in the Ar/H_2 plasma, independent of the feedstock. The increase of the input power increases the conversion and thus raises the yield of acetylene. At a specific input energy of 4.7×10^4 kJ per kg of feedstock, the *n*-hexane conversion is more than 90%, and the yield of acetylene is 70%. When *n*-hexane is used as the feedstock, a small amount of coke is formed. The improvements of the specific energy requirement of this process are also discussed. Anderson et al. investigated the conversion of natural gas to liquid transport fuel through acetylene as an intermediate.[12] Methane is first converted to acetylene using a thermal plasma reactor with a power of 60 kW. The aim of the study is to improve the methane conversion efficiency, acetylene yield, selectivity, and specific energy use measured in the original Huels and DuPont reactors.[10−12] The study shows conversion efficiencies which reach 100% with an acetylene yield in the range of 90−95% and carbon production of 2−4%. These results show an improvement compared to the original Huels process which has a conversion efficiency of 70.5% and an acetylene yield of 51.4%, and the DuPont process, which has an acetylene yield of 51.4%. An illustration of the thermal plasma reactor used by Anderson et al. is shown in Figure 21.

Ganieva et al.[59] used an arc plasma to crack heavy hydrocarbons into light products. The analysis of the product shows that they are composed of 25% hydrogen, more than 40% ethylene, and about 7% ethane. The solid deposit on the electrodes is also analyzed using IR spectroscopy and electron microscopy. A review on the plasma-chemical production of acetylene from hydrocarbons in Russia is given by Bilera et al.,[60] and a state of the art of the industrial applications of plasma for the production of petrochemicals and hydrogen is discussed by Slovetskii.[61] Beiers et al.[62] studied the pyrolysis of hydrocarbons in a hydrogen plasma at atmospheric pressure and temperatures in the range 1000−2000 °C. It is found that the product distribution depends on the used hydrocarbon. The thermodynamic equilibrium cannot be achieved during a residence time of a few milliseconds.

Microwave Plasma Cracking. Microwaves can be used directly for the heating of the feedstock or can be used indirectly by ionizing a gas (e.g., argon) to generate plasma for cracking. For the cracking of hydrocarbons, the focus has been on the latter option. Some experimental laboratory set-ups have been built to evaluate the feasibility of this method. Shulman et al. developed a laboratory scale microwave plasma cracker as illustrated in Figure 22. The setup uses ethane as a

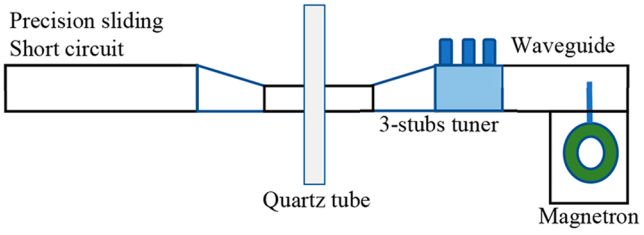

Figure 22. Microwave plasma reactor.

feedstock and argon as plasma gas. A microwave guide focuses the microwave radiation from a microwave generator onto a quartz tube which contains the argon gas and the feedstock (ethane). The microwave radiation ionizes the argon gas and generates a plasma within the tube which cracks ethane. It is claimed that the setup can be easily scaled up, and a concept for the upscaling of the system is proposed.[9]

Oberreuther et al. used a microwave reactor for the reforming of carbon dioxide with methane to produce syngas.[63] They use a commercially available plasma reactor which uses a microwave plasma source.[64] The system operates at 2.45 GHz with microwave power up to 6 kW. The thermal efficiency of the reactor is about 90%, and temperatures up to 1000 °C can be reached. Based on the experimental results, a feasibility study is made for a pilot plant which shows that a number of 36 sources with a total energy supply of 75 kW is needed to produce 20 Mm^3/year of syngas. A similar plasma

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reactor was used by Belov et al. to study the dissociation of CO_2 at different pressures.[65] The aim of the study is to identify the most appropriate conditions for the scaling up of the CO_2 dissociation reaction. An illustration of the microwave plasma reactor used by Belov et al. is shown in Figure 23. CO_2 gas is supplied to the discharge tube, where a microwave induced plasma discharge in pure CO_2 leads to the dissociation of CO_2 to CO and O_2.

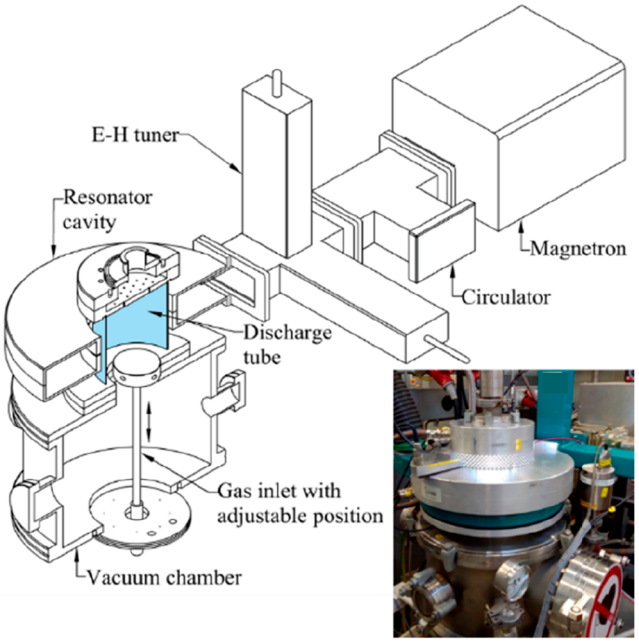

Figure 23. Illustration of the MW plasma reactor. Reproduced with permission from ref 65. Copyright 2018, from Elsevier.

Mora el al.[37] studied the conversion of three different alkanes (*n*-pentane, *n*-hexane, and *n*-heptane) using an argon microwave (2.45 GHz) plasma at reduced pressure, using a reactor similar to that shown in Figure 22. It is found that the microwave power and hydrocarbon flow rate are critical for the conversion and selectivity. The main gaseous products of the cracking process are hydrogen and ethylene.

In the last few years, there has also been more interest in using plasma reactors for the production of hydrogen. Plasma reactors have many advantages, like high conversion efficiencies and the possibility to operate with different hydrocarbons.[66−74]

RF Heating. RF radiation is typically applied for uniform dielectric heating of large volumes of hydrocarbons. It is used for the heating of oil sands, bitumen, or shale oil production in petroleum upgrading at temperatures between 150 and 500 °C.[75,76] The heating decreases the viscosity of the heavy hydrocarbons, which can therefore be more easily recovered. Two methods are used to generate the RF radiation in the hydrocarbon site to be heated. One method consists of placing an in situ borehole RF-radiating antenna deep in the hydrocarbon site, and the second method uses two parallel electrodes, as shown in Figure 10. The temperature levels which can be achieved by dielectric RF heating are not high enough for the cracking of hydrocarbons.[75,76]

Ultrasonic Cracking. The application of ultrasound in the chemical industry (sonochemistry) is discussed in many papers.[77−84] Nesterenko et al. demonstrated the potential of using cavitation for the cracking of hydrocarbons.[77] Suslick et al. use high-intensity ultrasound to crack alkane solutions by means of sonolysis.[78] The products of *n*-decane sonolysis are hydrogen, methane, acetylene, and a series of alkenes. It is observed that the reaction is similar to high-temperature (>1200 °C) alkane pyrolysis. Cataldo et al. showed that sonolysis of benzene and toluene at room temperature splits the aromatic ring to form acetylene and other products.[79] Riesz et al.[80] and Misik et al.[81] study the radicals produced during the sonolysis of different organic liquids, including *n*-alkanes. Lin et al. investigated the conversion of asphaltenes to lighter products using cavitation with surfactants.[82] It was found that 35% of the asphaltene was converted into gas oil and resin after 15 min of sonolysis at normal temperature and atmospheric pressure. Hosseini et al. studied the cracking of heavy petroleum residue using ultrasound.[83] It is found that lighter products like benzene are formed, and it is concluded that sonolysis can help crack heavy petroleum into lighter elements. Price et al. explored the sonolysis of hydrocarbons.[84] They observed the formation of solid carbon particles, which are a mixture of amorphous and graphite carbon. The mass of the carbon product increases with the C/H atomic ratio of the feedstock undergoing cavitation. Fan et al. investigated the ultrasound cracking of tar sand and bitumen.[85] The product distribution and coke formation for conventional thermal cracking (CTC) and ultrasound thermal cracking (UTC) are compared for an ultrasound frequency of 20 kHz, ultrasonic power of 2 kW, reaction time of 2 h, and reaction temperature in the range of 400−440 °C. The results show that UTC can significantly increase gasoline and diesel yield and significantly reduce vacuum gas oil yield and residue. Dunn et al. investigated the conversion of asphaltenes into asphaltene products using ultrasound.[86] They discovered that dehydrogenation and cracking reactions occur simultaneously in

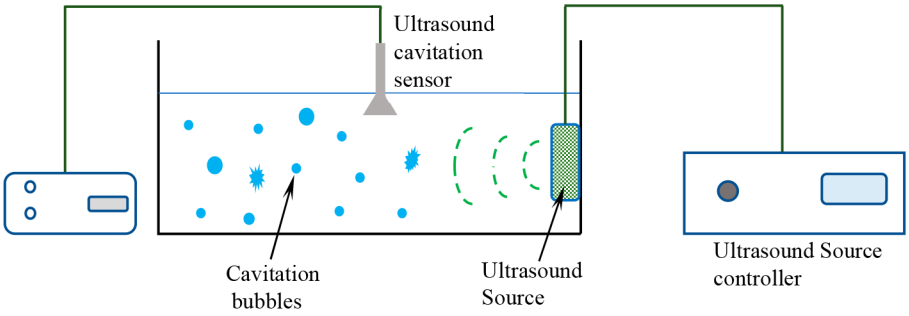

Figure 24. Schematic illustration of a sonoreactor.

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ultrasonic cracking. Son et al. investigated the cavitation energy distribution in a large-scale sonoreactor at different frequencies.[87] An illustration of a setup similar to that used by Son et al. is shown in Figure 24. It is worthwhile to notice that cavitation can only take place in liquids, so this technology seems more appropriate for heavier hydrocarbons than for naphtha.

Shock Wave Heating. As discussed previously, shock waves can be used for the cracking of hydrocarbons. The shock wave subjects the hydrocarbons to high temperatures (>800 °C) in a short time (ms). Kaminski et al. study the decomposition of propane using a shock tube in the temperature range 700−810 °C, while the pressure of the carrier gas varies from 1.3 to 1.9 bar, and the reaction time is in the range 0.2−1.4 s.[88] The reaction products are hydrogen, methane, ethane, ethylene and propylene. Olson et al. studied the decomposition of ethane in the temperature range 1027−2227 °C with argon as carrier gas.[89] It was found that for the dissociation reaction $C_2H_6 + M \rightarrow 2CH_3 + M$, the rate is the same for M = Ar and M = C_2H_6. Laskin et al. investigate the decomposition of benzene in a single-pulse shock-tube.[90] In the temperature range 1127−1727 °C, the main products are C_2H_2 and C_2H_4. Tohru et al. studied the decomposition of acetylene and ethylene diluted in argon by using a shock tube in the temperature range 1527−2327 °C.[91] It was found that C_2H_4 decomposes to C_2H_2 and H_2. The dissociation of C_2H_4 using a shock wave was also studied by many other research groups.[92,93] Tohru et al. investigated the decomposition of butane diluted in argon in a shock wave in the temperature range 1029−1337 °C at 0.5 atm.[94] UV-absorption measurements show the formation of C_2H_2 and C_2H_4. Mizerka et al. studied high temperature decomposition of ethylbenzene using a shock wave with the laser schlieren technique.[95] Mixtures of 1 and 2% ethylbenzene in krypton as carrier gas were studied in the temperature range 1027−1527 °C and pressure range 0.073−0.73 bar. They observe dissociation into benzyl and methyl radicals. Al-Alami et al. investigate the decomposition of propane in a shock wave in the temperature range of 1127−2027 °C.[96] They observe that the reaction $C_3H_8 \rightarrow CH_3 + C_2H_5$ takes place. Cassady et al. studied the decomposition of ethane by using a shock wave.[97] The reaction products are ethylene, methane, and acetylene for the temperature range 905−1254 °C and pressure range 3.1−4.2 atm.

Shock waves are also generated in the rotor dynamic reactor (RDR), which can be used to crack naphtha.[44−46] It is claimed that the RDR will produce about 25% more ethylene yield than a conventional steam cracker.[46]

INDUSTRIAL APPLICATIONS

This section gives an overview of the known industrial applications of electric cracking of hydrocarbons. Also, suggestions are made for the application of the different electric cracking methods in industry.

Resistance/Induction Heating. To date, there are no industrial applications of resistance/induction heating for the cracking of hydrocarbons. Nevertheless, the tubes in conventional naphtha cracking furnaces could, in principle, be heated by electric resistance or by induction. Electric resistance elements can be directly placed on the cracking tubes, or the electric resistance of the tube itself can be used for heating by passing an electric current through the tube wall, as shown in Figure 19.[6] Alternatively, instead of direct electric heating of the tubes, the gas burners which populate the inside walls and floor of the conventional furnaces can be replaced by electrical heating elements, as shown in Figure 25. It is worth noting that

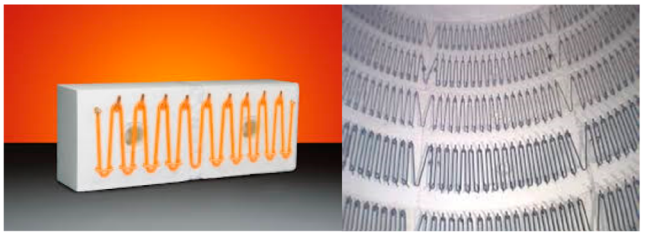

Figure 25. Electric heating elements (left). Electric modules placed on the inside wall of an electric furnace (right). Reproduced from Fibrothal heating modules and insulation systems Web site of Kanthal. Copyright 2022 Kanthal.

the cracking reaction requires heat fluxes at the reactor coil higher than 30 kW/m^2. The electric modules can provide heat to the cracking tubes by radiation, and they can provide heating power of about 70 kW/m^2 for a furnace temperature of 900 °C.[98] The advantage of this heating method is that it can easily be applied to retrofit conventional cracking furnaces. Other resistance heating reactor concepts which can potentially be scaled up for industrial applications are discussed in refs 47 and 48.

In a similar way, induction heating can also be applied to heat up the tubular reactors. A metal coil which carries a high-frequency electric current can be placed around each tube or around a number of tubes to induce an electromagnetic field around the tubular reactors, causing an electric current within them, generating heat, as shown in Figure 8 and Figure 26.

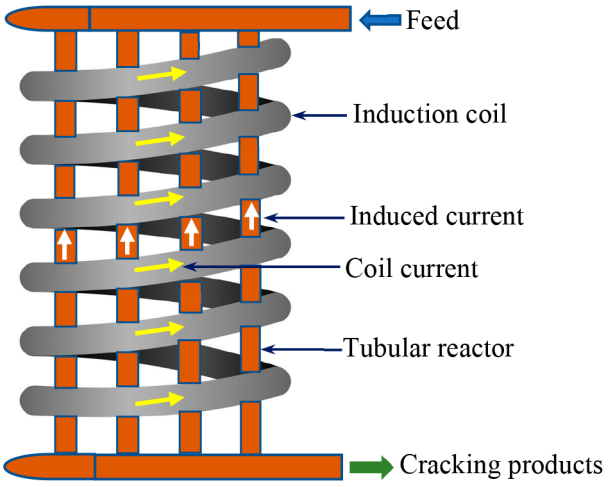

Figure 26. Induction heating of the cracking tubes.

Arc/Plasma Heating. Despite extensive research, there are presently no commercial reactors based on plasma technology for the cracking of hydrocarbons. In general, the application in industrial processes is limited to processes requiring high temperatures not achievable by conventional heating methods. Arc/plasma heating has mainly been applied in the cracking of methane to acetylene. In the past, two large-scale arc plasma technologies were developed: the Huels plasma reactor and the DuPont plasma reactor. Large scale plasma reactors are also developed by Westinghouse Plasma Corporation.[10−12,99]

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The production of acetylene from hydrocarbons by means of an electric arc started in 1920 in Germany by BASF and was further developed by Huels. The Huels electric arc/plasma plant was inaugurated in 1930, and the production capacity in 1965 was 130 kton/year of acetylene, 60 kt/year of ethylene, and 350 Mm^3/year of hydrogen, using 19 reactors.[100] The cracking process in the Huels reactor consists of three steps:[10] first, the plasma gas (hydrogen) is injected tangentially into the reactor and ionized at high temperatures of 3500−4000 °C by a DC-high voltage electric arc (7.1 kV, 1.2 kA, 8.5 MW) or in a three-phase high current electric arc (1.4 kV, 4.2 kA, 10 MW). The generated plasma is then mixed with the feedstock to be cracked. After that, the cracking products at 1000−1200 °C are quenched rapidly to about 300 °C using water or crude oil residues. An illustration of the Huels reactor is shown in Figure 27.

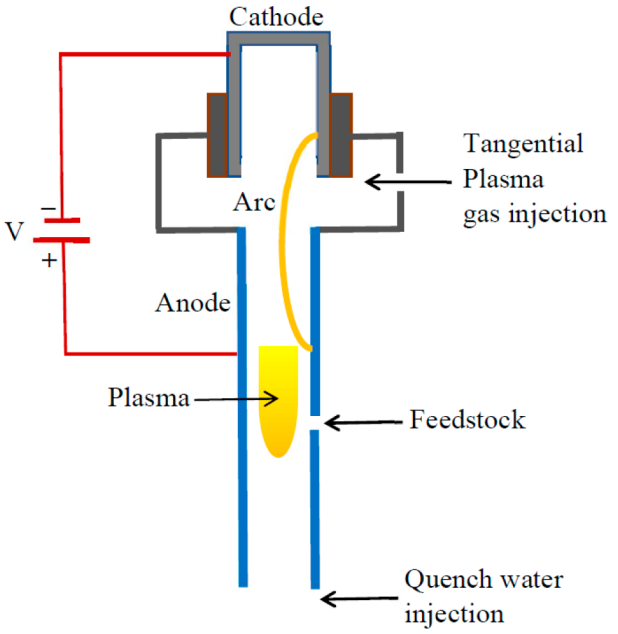

Figure 27. Schematic illustration of a Huels arc/plasma reactor.

The thermal efficiency of the Huels reactor is in the range 85−92%. The reactor operates at 1000−1200 °C, and the residence time is in the order of milliseconds. The reactors used in the Huels process are 100 mm in diameter and 1.5 m in length. The Huels arc/plasma plant was stopped in 1993 because of the decrease in global acetylene demand.[13] The Huels reactor reached a combined yield of acetylene and ethylene of about 80% using naphtha as feedstock (with recycling), which is much higher than for conventional crackers.[10] This is relevant because in conventional naphtha cracker plants, also an acetylene fraction is produced that is typically hydrogenated to ethylene by using the hydrogen fraction that is produced in the cracking.

DuPont developed an arc/plasma plant which operated from 1963 to 1968. The plant supplied acetylene, produced from liquid hydrocarbons, to a neoprene plant.[62] The Dupont reactor has a similar size as a Huels reactor (9 MW). The difference between the Huels and DuPont reactor is in the way the arc is stabilized. In the Huels reactor, the arc is stabilized by tangential injection of the plasma gas (hydrogen), while in the DuPont reactor, the arc is magnetically rotated. The DuPont reactor has a better performance than the Huels reactor; the acetylene yield and specific energy are 70% and 8.8 kWh/kg acetylene for Dupont reactor and 50% and 12.1 kWh/kg for Huels reactor.[62]

Westinghouse also developed an arc/plasma reactor using a magnetically rotating arc.[8] The system is applied for the gasification of biomass to produce syngas, but it is probably also appropriate for the cracking of hydrocarbons.

Microwave Heating. Microwave cracking of hydrocarbons depends on the absorption of microwave energy. A distinction must be made between three microwave heating processes:

- Direct absorption of microwave power by the feedstock to be heated, which depends on the dielectric properties of the feedstock[31,32]
- Indirect heating by using a susceptor which absorbs the microwave power[31,32]
- Microwave power is used to generate plasma in a gas, which is subsequently used for the heating/cracking of the feedstock[9]

In recent years, dielectric microwave heating has been getting more attention from the industry, mainly for drying purposes.[101−105] To date, there are no industrial applications of microwave for the cracking of hydrocarbons. However, experimental work at laboratory scale shows the possibility of cracking hydrocarbons using microwave power mainly by using the second or third heating methods. Some of these works are presented and discussed previously.

Ultrasound Heating. There are many industrial applications of ultrasound, ranging from ultrasonic cleaning applications to advanced sonochemistry.[38,39] Sonochemistry is concerned with the effect of ultrasonic sound waves on chemical reactions. These technologies make use of the cavitation induced in liquids by ultrasound. Reviews and discussions of the different applications can be found in the literature.[77−85] Research in this field is mainly at the laboratory scale, but the sonoreactor of Figure 24 could be scaled up by using a larger bath with a multitude of ultrasound sources or by using multibaths. However, as mentioned before, the technology of cavitation induced cracking can only be applied in liquids, making the technology more suitable for longer hydrocarbons than for naphtha.

Shock Wave. A shock wave reactor can be used for the cracking of hydrocarbons on an industrial scale. The RDR reactor can heat the feedstock directly to a high temperature in a very short time, resulting in a high yield and lower specific energy use. An electric motor is used to drive the reactor rotor. Just as for other electrified cracking methods, no scope 1 or 2 CO_2 emissions occur if renewable electricity is used (apart from those caused by possible decoking). Coolbrook used a small RDR bench sale reactor which cracked 20 kg/h of naphtha. Coolbrook indicates that the residence time for this reactor is in the range of 20−50 ms, and about 25% more ethylene yield is produced than in conventional steam cracking. They intend to build an upscaled RDR-pilot unit which can crack 400 kg/h of naphtha.[46] The unit will crack 450 tons of hydrocarbons, and it will be used to demonstrate the techno-economic potential for this new technology and study the yields from different feedstocks, determine the upscaling issues, evaluate CAPEX and OPEX, validate modeling results and evaluate the reliability of the reactor.[45,46] The simulation of a full scale RDR cracker shows that ethylene yield is 38.3%, which is 25% higher than for a conventional steam cracker (30.8%).[46] The coke formation would be less

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than in conventional steam crackers because in the RDR reactor, the feedstock is heated directly instead of via a hot wall. Therefore, the surface temperature is less than the surface temperature of the conventional coil, reducing coking at the surface. The production of 1 Mton/year of ethylene would require 7−16 RDR reactors, using electrical motors in the range of 20−40 MW. Furthermore, Coolbrook indicates that an RDR cracker is much more compact than a conventional cracker; the size would be about 20% of the size of a conventional steam cracker for the same production capacity as shown in Figure 28.

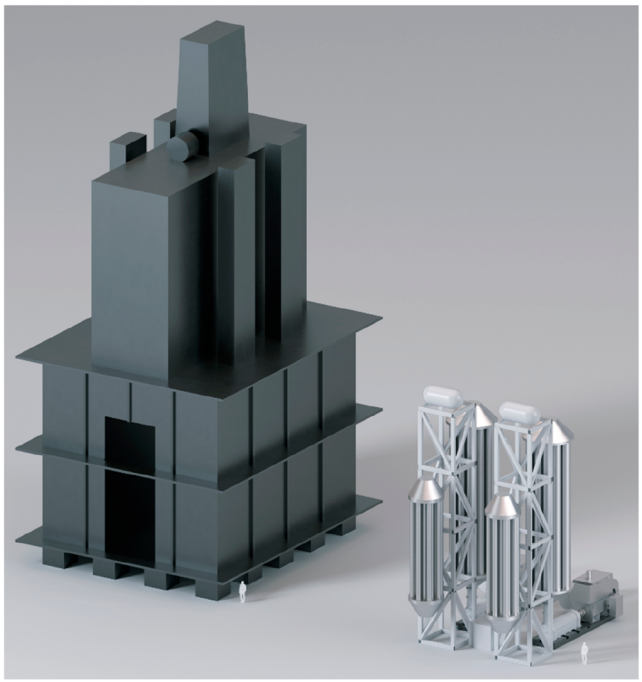

Figure 28. Illustration of the size the conventional cracker (left) and the RDR cracker with TLE-heat exchangers (right) for the same capacity. Reproduced with permission from ref 46. Copyright 2021 CoolBrook.

CASE STUDY: EVALUATION OF ELECTRIC CRACKING METHODS FOR STEAM CRACKING

As a representative case study for cracking of hydrocarbons, the electrification of the steam cracking of naphtha is presented. By considering the operational conditions for the naphtha steam cracking process and the results from the preceding sections, the different electric heating methods can be evaluated as a potential candidate for the electric cracking of naphtha. To obtain the most promising technology, it is first relevant to consider which electric heating technologies have been demonstrated on the scale of a naphtha cracking furnace. A typical naphtha cracking furnace has about 100 MW of heating power (with a plant having multiple parallel furnaces). Considering that in a conventional cracker, about 50% of the energy is in the flue gases that can be avoided in an electric furnace, the scale of a corresponding electric furnace would be about 50 MW.

Literature indicates that large-scale electric furnaces are typically electric arc furnaces (up to 175 MW[106]) or induction furnaces (up to 42 MW[107]). Resistance heating furnaces have been built with power up to about 8 MW,[108] while microwave or other technologies are typically below 1 MW. Furthermore, compressors are built over a wide range of powers, the largest having powers up to 100 MW,[109] indicating a large upscaling potential for the RDR concept.

From the largest four types of furnaces, resistance heating is probably the type of heating that can be most easily applied in conventional furnaces (as a retrofit or boosting), while induction heating or electric arc would require larger furnace modifications.

- For retrofitting, therefore, resistance heating seems the most appropriate method for the electric cracking of naphtha. A convenient method for implementation could be to replace the gas burners, which populate the inside walls of the furnace with electric heating elements. Since the heat transfer in the cracking section is mostly by radiation, the difference between electric heating elements and gas heating elements on heat transfer would probably be limited.
- For greenfield implementation, the situation is less clear; the best option would probably be the option with the highest selectivity, as this is very important for the economic feasibility of a cracker, as argued later in this paper. This requires further investigations to compare the selectivity of resistance heating, induction heating, electric arc plasma, and shockwave.

R&D Challenges for Retrofit. There are several R&D challenges for the implementation of a new electric heating method. The method needs to be tested and demonstrated before it can be applied in industry. Some of the R&D challenges are discussed in the following section.

Implementation of Resistance Heating. Electric naphtha cracking by resistance heating can be realized in two ways as discussed in the foregoing section. These two methods have to be evaluated from a techno-economic point of view to select the most appropriate one.

Optimization of the Cracker Design. In addition to the optimization of the process conditions, the design of the resistance cracker is an important issue. The system must be designed considering the optimal operating conditions, the CAPEX and OPEX, operational flexibility, and upscaling of the system.

Optimization of Cracking Plant Heat Integration. Next to optimization of the cracker design, an optimization study of the whole production process for naphtha cracking, including preheating requirements and downstream separation steps, is required because the heat flows in the conventional cracking process are highly integrated with the other processes in the plant. For example, the steam produced in conventional crackers is used to drive the turbines of the compressors; if the cracker is electrified, the compressors will be driven by electrical motors.

ECONOMIC FEASIBILITY

The cost for electric naphtha cracking in GJ/ton of ethylene is expected to be higher than the cost for conventional cracking. The CAPEX is expected to be lower, but the OPEX increases significantly due to a combination of the significantly higher price for electricity compared to gas, which is, however, partly compensated by increased efficiency due to reduced furnace losses and more efficient electric motors. However, the cost of the feedstock (naphtha) represents about 80% of the total cost of the produced ethylene.[99] Therefore, it is important to

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increase selectivity as improved use of the naphtha will more than compensate for higher OPEX costs. The Huels process, which uses an arc-plasma achieved yields of acetylene and ethylene of about 80% using naphtha as a feedstock with recycling.[10] If the acetylene could be converted to ethylene with hydrogenation, the resulting selectivity would be much higher than that of conventional crackers. Such high selectivity will significantly reduce the specific OPEX costs per ton of ethylene produced. The electrification of the cracking processes can be stimulated by guaranteeing sufficient availability of renewable electricity and by the introduction of a CO_2 tax.

CONCLUSIONS

The electrification of cracking processes is a serious option to make the cracking processes more sustainable, especially if renewable electricity is used. As an example, the electric steam cracking of naphtha could result in significant energy savings of up to 50% as the feedstock is heated directly, and no flue gas losses are involved. The scope 1 and scope 2 CO_2 emissions can be reduced to almost zero by exclusively using renewable electricity (only the small CO_2 emissions caused by decoking cannot be avoided yet).

The review of the patents related to electric cracking of hydrocarbons shows that from 1894 up to 1980, most patents concern resistance and arc/plasma heating. Resistance heating is discussed in many patents as a mean for the cracking of hydrocarbons. Arc/plasma cracking is mainly used in the production of acetylene which requires a high temperature that cannot be realized by conventional heating methods. Most patents related to RF-radiation heating are concerned with the dielectric heating of oil sands, bitumen, or shale oil production since RF-radiation technologies are especially suitable for heating larger volumes due to the large penetration depth related to the long wavelength. Since about the year 1980, other heating methods appear more frequently in patents, like induction, microwave, and ultrasound. An interesting patent is the cracking of naphtha using shock waves (the RDR-reactor developed by CoolBrook).

The review of the research papers shows that many papers use resistance heating in laboratory set-ups to study the pyrolysis of hydrocarbons, due to the ease of use and good control options. These laboratory set-ups are typically used to study the effect of the operating parameters on the production yields and coke deposition in the reactor. The upscaling of such set-ups and their industrial application are only discussed in two papers. In addition, many plasma reactors are built and tested for the pyrolysis of hydrocarbons, generating the plasma by an electric arc or by MW/RF. Finally, some papers discuss the application of ultrasound for the cracking of hydrocarbons, and it is reported that by inducing cavitation in liquid alkanes, alkanes can undergo sonochemical reactions which are similar to high temperature (>1200 °C) pyrolysis.

Large-scale industrial applications of electric cracking are scarce. Resistance heating and induction heating are applied in many industrial applications like the glass and metal industries, and in electric boilers, but there is presently no industrial application in the field of cracking of hydrocarbons. The same holds for MW/RF and ultrasound heating. There have only been two large-scale electric crackers which used arc/plasma heating: the Huels and the DuPont plasma reactors operated for the production of acetylene. The DuPont reactor was operational from 1963 to 1968, and the Huels plasma plant was stopped in 1993 because of reduced market demand for acetylene.

For retrofitting naphtha crackers, the evaluation of the different electric heating technologies shows that resistance heating is probably the type of heating that can be most easily applied in conventional furnaces (as retrofit or boosting), while induction heating or an electric arc would require larger furnace modifications. Options for retrofitting naphtha crackers by resistance heating would be to replace wall burners with electric heating elements or to develop tubes that can be heated directly by electric current.

The OPEX cost of electric naphtha cracking is expected to be higher than for conventional cracking. This is due to the higher electricity price compared to the gas price. However, as the cost of naphtha represents about 80% of the cost of the production of ethylene, an improvement in the selectivity would strongly lower the specific costs. Therefore, performing more research on the selectivity of the different heating methods is highly relevant. The electrification of the cracking processes can be stimulated by guaranteeing sufficient availability of renewable electricity and by the introduction of a CO_2 tax.

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Notes

The authors declare no competing financial interest.

Biographies

Dr. Ir. M. E. H. Tijani studied physics at the Eindhoven University of Technology (TUE), and he received the M.S. degree in physics in 1996. He obtained a Ph.D. degree in physics from TUE in 2001. From 2002−2004, he was a postdoc at TUE and the Energy research Centre of The Netherlands (ECN). In 2005, he was appointed as a scientist at ECN. His research on thermoacoustics has been reported in many publications. Since 2018, he has been working for The Netherlands

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Organization for Applied Scientific Research (TNO) as a scientist. He is active in the field of thermoacoustics, electrification of industrial processes, and industrial energy savings. He is also a reviewer and referee for many professional journals.

Prof. dr. Herbert Zondag obtained his master's degree in solid state physics at Utrecht University in 1992 and his Ph.D. on fluid dynamics in 1997 at the Eindhoven University of Technology. After postdoc positions at the TU/e in the Department of Mechanical Engineering, he joined ECN, the energy research institute of The Netherlands, first in the unit for the built environment, and subsequently in the unit for industrial energy efficiency, which continued when in 2018, ECN merged with TNO. Meanwhile, from 2010 onwards, he has been a part-time professor on heat storage technology at the TU Eindhoven. He has over 20 years of experience in research and development on energy efficiency, for both the built environment and industry, and has worked on a wide range of topics, mainly related to heat storage and industrial processes.

Yvonne van Delft obtained her master's degree in chemical engineering at the Twente University in 1995. Yvonne started working as product developer at Sekisui Alveo, and after two years she joined ECN first as engineer in construction of prototypes and later as a researcher and project manager. In 2015, Yvonne started the Shared Innovation Program VoltaChem, a collaborative effort of research organizations and companies to accelerate innovation and implementation of industrial electrification. Along with that, she has coordinated research on Efficiency & Circularity for the TNO R&D roadmap CO_2 neutral industry. At this moment, Yvonne is senior project manager at TNO and coordinator of the EERA joint program on Energy Efficiency in industrial Processes. She has over 20 years of experience in research and development for the energy and process industry and has worked on a wide range of topics, including process engineering, industrial electrification, technology transfer, separation processes, and process intensification.

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