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Abstract

We develop a method based on concept of exergy-return on exergy-investment (ERoEI) to determine the energy efficiency and CO_2 footprint of polymer and surfactant enhanced oil recovery (EOR). This integrated approach considers main surface and subsurface elements of the chemical EOR methods. The main energy investment in oil recovery by water injection is mainly related to circulation of water with respect to exergy of the oil produced. At large water cuts of >90%, more than 70% of the total invested energy is spent on pumping the fluids. Consequently, production of barrels of oil is associated with large amounts of CO_2 emission for mature oil fields with large water cuts. Our analysis shows that injection of polymer increases the energy efficiency of the oil recovery system. Because of additional oil (exergy gain) and less water circulation (exergy investment), the project-time averaged energy invested (and consequently CO_2 emitted) to produce one barrel of oil from polymer flooding is less than that of the water flooding at large water cuts. We conclude that polymer injection into reservoirs with high water cut can be a solution for two major challenges of the transition period: (1) meet the global energy demand via an increase in oil recovery and (2) reduce the CO_2 footprint of oil production (more and cleaner oil). For surfactant-polymer EOR, the extent of improvement in energy efficiency depends on the incremental gain and the simplicity of the formulations.

Introduction

With the assumption of no major breakthrough in development of renewable energy sources, a large fraction of the global energy demand will be supplied by (1a) further extraction of hydrocarbon fuels for the next few decades (1b) use of natural gas [1], (2) application of nuclear energy [2], and (3) hydroelectricity [3]. Improved wind, geothermal and solar renewable energy (currently accounting for 3.6% of the world energy consumption in regions of moderate insolation are only expected to give a small contribution to the near future energy demand, because of their low energy density [4].

Hydrocarbon fuels generate large amounts of carbon dioxide upon burning and therefore are perceived to be a major contributor to the anthropogenic climate change. Moreover, with the rise in the population of the world, more energy will be required to sustain the economic growth. Then, it is necessary for the oil and gas industry to come up with solutions to meet the (ever)-increasing energy demand in a more sustainable and cleaner manner, while renewable sources are made more accessible and affordable. Currently a significant portion of the fossil fuel energy production is used for fluid handling, refinery and production of fossil fuels, depending on the recovery mechanism [5,6]. The main costs are due to fluid circulation costs. In practice, it turns out that towards the end of the project, the fluid circulation costs even exceed the hydrocarbon energy produced [5,7].

While discovery of new oil and gas fields becomes scarce, the efficient extraction of oil from existing fields, particularly with enhanced oil recovery (EOR) methods, has become vital for providing more energy to the society [8,9]. EOR techniques are commonly applied when natural energy of the oil reservoir or the (secondary) water injection cannot effectively produce oil. The efficiency of water injection decreases when the mobility of the injected water is larger than that of the in-situ oil [10,11]. To overcome this shortcoming, water-soluble polymer molecules are added to the injected water to increase its viscosity, which reduces its mobility and thus improves the efficiency of the displacement process [8,12]. To extract the remaining oil trapped by the capillary forces, surfactants are sometimes added to lower the interfacial tension between oil and water. In a typical (surfactant) polymer EOR project, injection of chemicals starts when the water cut (water fraction in the total liquid produced) in the producers has reached a large value (referred to as tertiary recovery), although earlier injection of chemicals may be even more efficient [8,11,13]. Injection of chemicals (under tertiary mode) results in reduction of water cut and by definition increase of oil cut and hence the ultimate oil recovery.

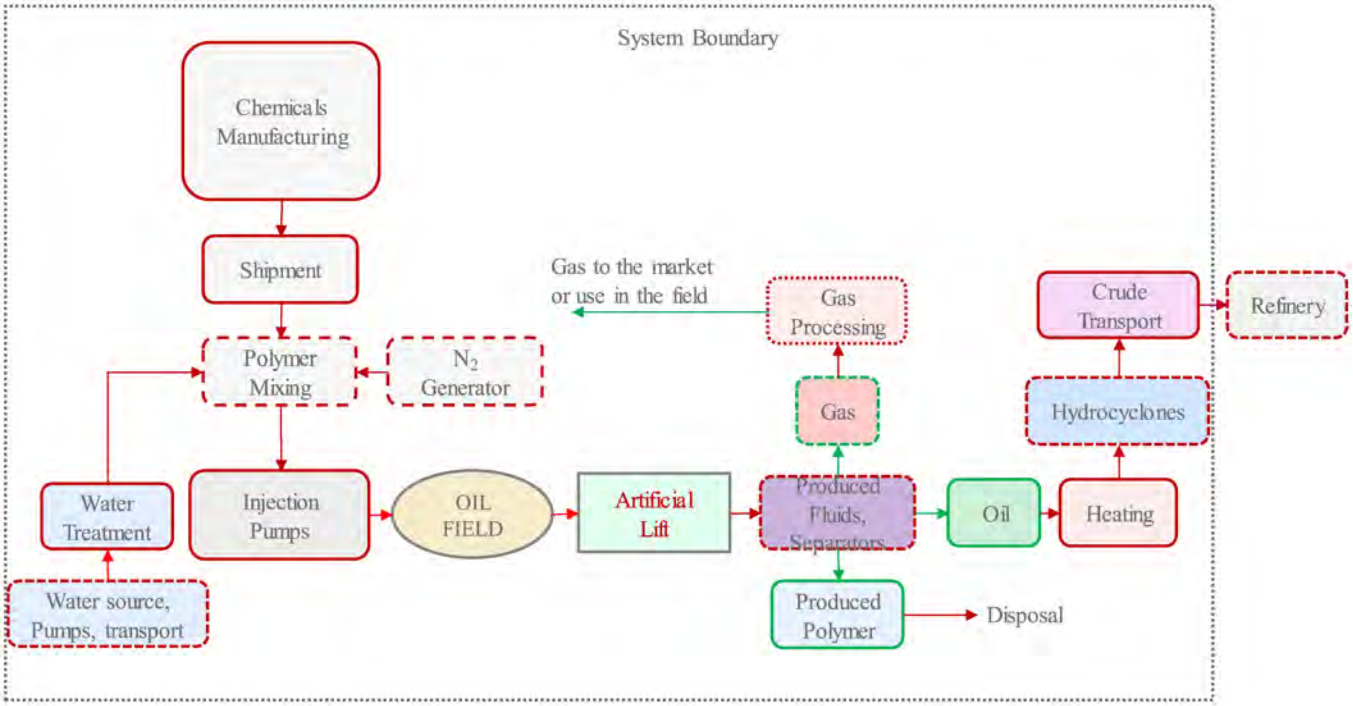

Figure 1—Schematic of the production cycle system and the selected boundary considered in this work for production of oil by polymer injection. The boxes with the broken lines are either not considered in the calculations or assumed to have negligible impact on the outcome. The red arrows are for the components with only exergy investiment, while the greem arrows contain part of the gained exergy.

There is a direct correlation between the CO_2 intensity of the oil production by water injection and field water cut. Above water cuts of 90% the, a large fraction of the energy obtained from oil is spent on handling the injected and produced water, which leads to large amounts of CO_2 emission [7,14]. Therefore, because of the wide application of water injection, reducing the carbon footprint of the aging or mature oilfields with

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large water cuts is an essential step towards cleaner or low-carbon production of hydrocarbons. Improving energy efficiency is a key to better emission performance, and can potentially deliver significant benefits to improve energy management, and the ensuing reduction of the greenhouse gas emissions [15]. This study examines the potential life-cycle impact of injecting polymer and surfactant into hydrocarbon reservoirs by considering the energy requirements of the process. In this paper, we develop a method based on the concept of exergy-return on exergy-investment (ERoEI) to determine the energy efficiency and the CO_2 footprint of polymer and surfactant EOR [16,17]. This integrated approach considers the main surface and subsurface elements of the chemical EOR process (see Figure 1). Such analysis provides information on the energy consumption (or CO_2 intensity) of each component, which can then be used optimize the whole system from the energy-efficiency perspective.

The structure of the paper is as follows. First, we explain different stages of a chemical EOR project and define the system and its boundary for the assessment. Next, we provide the details of the exergy calculations followed by a brief description of the method employed to forecast the amount of the oil produced by polymer and surfactant for the reservoir of interest. Afterwards the results of the analysis are explained as to the impact of different parameters on the exergy recovery factor. We also include real data and ensuing analyses for two reservoirs in the Middle East in which polymer is injected to improve the oil recovery. We end the paper with concluding remarks.

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System definition

Figure 1 depicts the main components of a chemical-EOR project. The analysis in this paper considers the exergy (material and process) required to manufacture the chemical (polymer and/or surfactant) and its transportation (in powder form and in large bags) to the project site. The distance between the chemical manufacturer and project site is assumed to be 7000km. The chemicals are mixed with the treated water to make up an injection solution with the desired viscosity. The energy consumption for the mixing is assumed to be negligible. The produced oil and gas are the exergy sources, which are shown by green arrows. The produced water initially does not contain the injected chemical; however, as time passes increasing amounts of chemicals can be produced. The produced water (with or without chemicals) should be treated before re-injection or disposal. For the surfactant polymer injection case, the treatment unit consists of a softening unit to remove the divalent cations. Generally, in chemical-EOR projects increasingly more energy is consumed at the production side to treat the produced (viscous) water, break the emulsions if present in the effluent, remove the chemicals from oil, etc. This is accounted for by assuming an additional 20% exergy requirements in the calculations (vs 10% in water injection). It is also assumed that 20% of the injected water is not back-produced or lost/consumed during the process. The liquids are assumed to be lifted using pumps in the producers. If the reservoirs contain viscous oil (as it is the case in this study), the produced oil is heated to a certain temperature before it is transferred to a hydrocyclone to remove the water and other dense components [18]. Finally, the oil is pumped to refineries to produce the final product, i.e., fuel.

Exergy streams

The exergy analysis of the system defined in Figure 1 is performed by considering the material (shown by green arrows) and work (red arrows) streams.

Material stream

The main source of exergy is the produced oil and gas. Similar to our previous studies [7,14], we assume an exergetic values of $Ex_{oil}^{ch} = 45.63\ MJ/kg$ for the produced crude oil and $Ex_{CH_4}^{ch} = 50\ MJ/kg$ for methane. The exergy of the produced water (with and without chemicals) is assumed to be negligible.

Work streams

Table 1 provides the relations used to calculate the exergy rate of the different components of the polymer-injection process. The details of the calculations for the processes common with the waterflooding (water treatment, pumping and lifting the liquids, heating, transportation, etc.) can be found in ref. [7]. The overall pump efficiency, η is assumed to be 36% [16].

Table 1—Summary of the required exergy for material and work streams

Material Stream	Specific Exergy [MJ/kg]	Work Stream	Specific Exergy [kJ/kg]
Crude oil	45.63	Injection pump $\left(\dot{Ex}_{liquid}^{pr,pump}\right)$	$Q\Delta P/\eta$
Gas (methane)	51.98	Artificial lift $\left(\dot{Ex}_{liq}^{th,lift}\right)$	$[Q\,(f_w\rho_w + (1-f_w)\rho_o)gh]/\eta$
Produced water	0.0	Water treatment	18 (5kWh/m^3)[19]
		Heating of crude oil $\left(\dot{Ex}_{oil}^{heating}\right)$	$m_{oil}\dot{\,}c_p\Delta T$
		Transport of oil to refinery	188 J/kg-km[20]
		Other process	20% (10%) of the total exergy for polymer/surfactant (water)
		Polymer manufacturing	123600
		Surfactant manufacturing	62000
		Water softening	50[21]

Polymer manufacturing

There are several polymers that can be used in polymer flooding; however, polyacrylamides are the most widely-used polymer types in EOR projects because of their low cost [8,9]. Polyacrylamides undergo hydrolysis (with the degree of hydrolysis depending on the conditions) and are therefore called hydrolyzed polyacrylamides or HPAMs. Polyacrylamides are produced by polymerization of acrylamides, which in turn are obtained via catalytic hydration of acrylonitrile. Consequently, to calculate the exergy and CO_2 footprint of polymer manufacturing, chemical exergy of the material and energy streams of these processes should be considered. The practical exergy of polyacrylamide is simply calculated by the sum of the cumulative exergy consumption of each material multiplied by the amount that is required for the production of one ton of polymer. The details of the procedure is explained in Appendix 1. The practical exergy of manufacturing of the HPAM polymers is calculated to be 123.6 MJ/kg-polymer. The CO_2 emission is estimated by calculating the CO_2 emission of each material stream, which is done by multiplying the fraction of the cumulative exergy consumption that comes from fossil fuels by the CO_2 emission of a fossil fuel, i.e., natural gas, oil and coal with respective estimated CO_2 emission of 0.055, 073, and 0.088 kg-CO_2/MJ [17]. This gives a CO_2 emission of 3.25 (gas), 4.72 (oil), and 6.35 (coal) kg CO_2 per kg polymer, depending on the type of consumed fossil fuel.

Surfactant manufacturing

Schowanck et al. (2018) provide life-cycle assessment and greenhouse gas emission for the production of common surfactants used in European detergents and personal care products using the data from 16 major surfactant manufacturers. We take linear alkylbenzene sulphonic acid as the proxy for surfactants used in EOR projects. The total energy consumption for these surfactants is 62 MJ/kg, and their manufacturing results in total CO_2 emission of 1.75 kg CO_2 per kg surfactant [23]. In the manufacturing of these surfactants, different sources of primary energy from renewable and fossil fuels are used (although contribution of

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renewables are not significant). The CO_2 emissions from the fossil fuels used in the manufacturing process is about 1.56 kg CO_2/kg-surfactant. The reported numbers are the average values for several surfactant-manufacturing companies.

Exergy Recovery Factor

The rate exergy recovery factor, Ex_{RF}, is a measure of sustainability of the system and is defined as the ratio between the net and gross exergy gains, i.e.,

$$Ex_{RF} = \frac{Ex_{gained} - Ex_{invested}}{Ex_{fuel}} \tag{1}$$

For production of oil by polymer injection, eq. (1) can be re-written as

$$Ex_{RF} = 1 - \frac{Ex^{manufacturing}_{chemicals} + Ex^{pr,pump}_{water} + Ex^{pr,lift}_{fluid} + Ex^{pr,trans}_{oil} + Ex^{pr,treatment}_{water} + Ex^{pr,heating}_{oil} + Ex^{pr,other}}{Ex^{ch}_{oil} + Ex^{ch}_{CH_4}} \tag{2}$$

The cumulative exergy recovery factor is calculated from

$$Exc_{RF} = \frac{\int_0^t \left(Ex_{gained} - Ex_{invested}\right)dt}{\int_0^t Ex_{fuel}dt} \tag{3}$$

Production forecast

A synthetic reservoir model, called "Egg Model", with the properties summarized in Table 2 is used to generate the oil-recovery histories for water, polymer, and surfactant-polymer injection. This geological model has four producers and eight injectors. The reservoir has a constant porosity of 20% and varying permeability of 80-7000mD. More details on the geological model can be found in refs. [14,22]. Each grid block is 8 by 8 m with a height of 4 m. The model consists of 8 injectors and 4 producers. The injectors have a constant flow rate and a maximum injection pressure constraint, and the producers operate at constant bottom-hole pressure. The initial pressure of the reservoir is 90 bar. The producers are operating at a bottomhole pressure of 65 bar and the injectors have a rate constraint of 79.5 m^3/day with a maximum allowable pressure of 140 bar.

Table 2—Reservoir and fluid properties for the base case

Symbol	Variable	Value	Unit
φ	Porosity	0.2	-
c_w	Water compressibility	1.0×10^{-10}	Pa^{-1}
μo	Oil viscosity	0.10	Pa s
μ_w	Water viscosity	6.5×10^{-4}	Pa s
k^0_{ro}	End-point relative permeability, oil	1.0	-
k^0_{rw}	End-point relative permeability, water	0.5	-
n_o	Corey exponent, oil	1.8	-
n_w	Corey exponent, water	2.7	-
S_{or}	Residual oil saturation	0.3	-
S_{wc}	Connate-water saturation	0.09	-
P_{init}	Reservoir initial pressure	90	bar

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In the polymer injection (PI) case, injection of polymer solution with viscosity of 15cP (concentration of 1200ppm) started once the overall water cut in the field reached 90%. In the surfactant-polymer injection (SP) case, when the water cut reached the value of 90%, 0.30 pore volume of surfactant-polymer mixture (with surfactant concentration of 3000ppm and polymer viscosity (concentration) of 50cP (2800ppm)). The brine used for preparing the surfactant solution contained no divalent ions. This was followed by injection of a polymer-only chase with viscosity of 50cP (concentration of 1800ppm). In the design of this process, because of presence of alkali in the surfactant-polymer slug, more polymer concentration was required to obtain viscosity of 50cP.

Results and discussion

Figure 2 shows the simulated oil-recovery-factor and water-cut (f_w) histories for the polymer- and water-injection cases. The oil recovery factor (dashed line) is defined as the volumetric ratio of cumulatively produced oil and the initial oil in the reservoir. In the water-injection (WI) case, the water cut (the ratio between the produced water and total liquid production) keeps increasing because production of the oil decreases with time. After about two pore volumes of water injection, the water cut reaches the value of 96%.

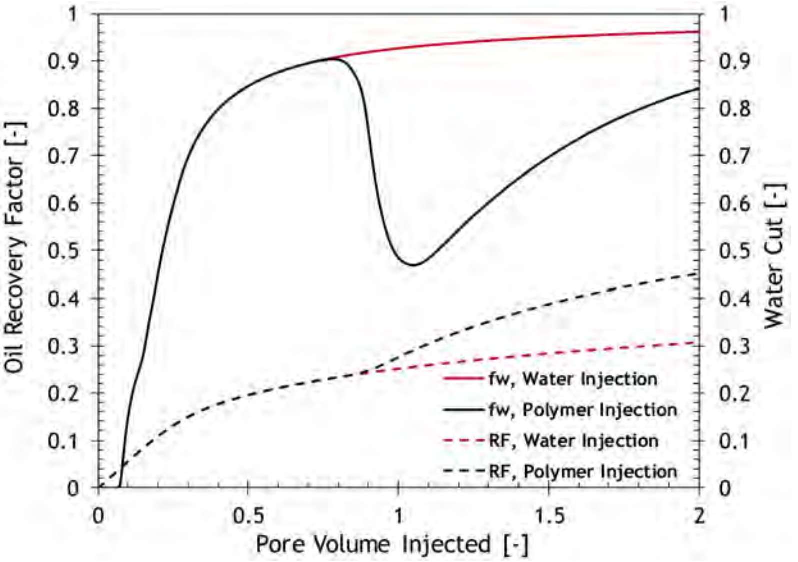

Figure 2—The oil recovery factor (RF) and water cut (f_w) histories for water and polymer injection.

Figure 3 shows the exergy invested to produce one barrel of oil (and its corresponding CO_2 emission) as a function of the water cut for the water-injection case. The unit CO_2 emission (kgCO_2/bbl oil) is the product of the unit exergy invested and the average emission rate of the electricity production in the location of the project, which is assumed to be the Middle East (650 gCO_2/kWh) [24]. The major exergy investment in water-injection projects relates to the circulation of water [7,14]. As a result, the unit exergy investment strongly depends on the water cut. For f_w>90%, small increase in the water cut leads to significant exergy dissipation or loss due to handling of excessive amounts of water. Accordingly, at large water cuts the unit CO_2 emission becomes considerable. For example, from Figure 3 for f_w=96% the unit CO_2 emission is ~100 kg/bbl of oil. For comparison, the specific CO_2 emission of crude oil is about 73 gCO_2/MJ or 3.14 kgCO_2/kg oil. Assuming an oil density of 850 kg/m^3, burning one barrel of oil will approximately produce 425 kg of CO_2. This implies that the indirect CO_2 emissions resulting from production of oil at high water cuts could become comparable to direct CO_2 emissions from combustion of the oil. Therefore, by operating oil reservoirs at lower water cuts release of large amounts of CO_2 could be avoided. The optimum operating

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conditions of an oil field (in terms of maximum net present value or minimum CO_2 emission) does not necessarily lead to maximum oil production from the reservoir [14]. Such optimum operations also leaves more oil in the reservoir, which can later be produced by a technique with comparatively smaller CO_2 footprint such as polymer flooding, as discussed next.

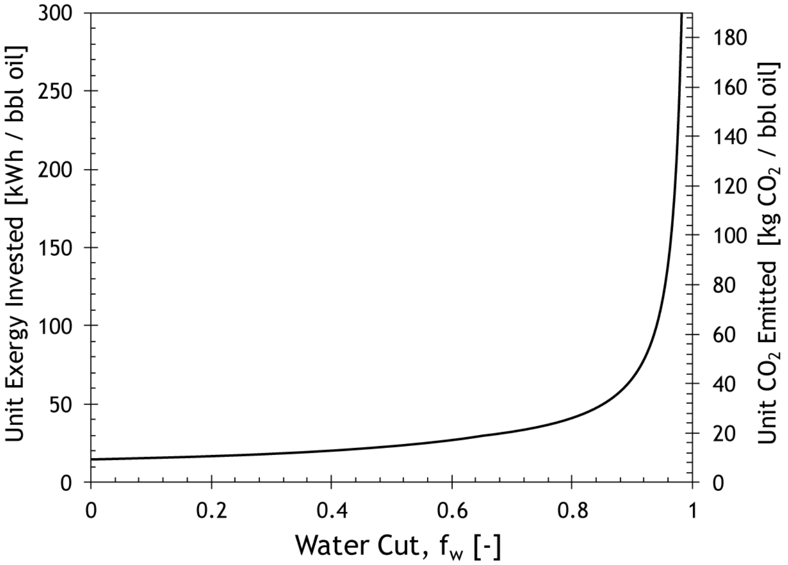

Figure 3—Unit exergy consumed and CO_2 emitted as functions of water cut for the water-injection case.

Injection of polymer results in reduction of water cut, as shown in Figure 2. In the case considered here, polymer injection starts when f_w=90%. The higher viscosity of the injected polymer compared to water results in more efficient extraction of oil from the reservoir; for instance, after injection of 1 PV of polymer the recovery increases from 22% to 41%. The water cut goes through a minimum and once the polymer front reaches the producer the water cut starts to increase. Eventually the amount of the oil produced by the polymer becomes negligible and f_w becomes very large.

Figure 4 compares the history of the rate exergy recovery factor for WI and PI cases. For the WI case, the rate exergy recovery factor (Eq. 2) keeps decreasing because as time passes more energy is required to recover oil. After 2 PV of total injection about 9% of the oil exergy is invested for producing it. With the injection polymer, the exergy recovery factor suddenly decreases, because of the larger exergy of the large manufacturing exergy of the polymer compared to the exergy gain from oil. However, once the oil bank created by the injected polymer solution arrives at the producers, the exergy gain from oil surpasses the exergy investment and therefore the exergy recovery factor increases. The maximum exergy recovery factor in Figure 4 corresponds to the minimum in the water cut for the PI case in Figure 2, which reemphasizes the negative impact of circulation of large volumes of water on the energy efficiency of the oil production systems. The area enclosed between the dashed line (decline curve for waterflooding) and the polymer injection is the incremental exergy gain (the area above the dashed line) or loss (area below the dashed line). The net exergy recovery is the difference between the upper area and the lower area. It is possible to get a negative net exergy recovery for polymer flooding compared to water flooding, especially when the injection of polymer does not efficiently reduce the water cut.

Figure 5 compares the unit exergy invested (left) and the unit emitted CO_2 (right) of WI (dashed red curve) and PI (solid green curve) cases. For the WI case, the unit exergy investment and the unit CO_2 emission keeps increasing in accordance with the increase in volumes of injected and produced water. With the start of the polymer injection, the exergy investment also increases, which results in larger unit CO_2 emission. This is due to exergy investments in manufacturing and shipment of the injected polymer. However, once

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the injection of polymer reduces the water cut, both exergy investment and CO_2 emissions are reduced. For example, at about one pore volume of total injection, the unit CO_2 emission decreases to 20 kgCO_2/bbl from the base case of 55 kgCO_2/bbl. Figure 6 presents the fractions of the unit exergy invested and unit CO_2 emitted for the PI case. At the start of the polymer injection, the energy invested on artificial lift and pumping comprises 68% of the exergy consumed for producing the oil. Of the other parts of the invested energy water treatment is a large contributor. A large invested exergy is reflected in a large contribution to greenhouse gas emission. Polymers act to reduce the cumulative pump costs. After 0.3 PV of polymer injection, about 42% of the total exergy is invested in polymer manufacturing and shipment. However, after breakthrough of the polymer bank, exergy investment in handling of the fluids increases again and the share of polymer exergy decreases. It is interesting to note that despite the large exergetic cost of the injected polymer, the related CO_2 emission is not in direct relation with the exergy investment. For example, at 0.3 PV of polymer injection, the polymer-related exergy investment is about 42%, while only 9% of the total CO_2 emission is due to the injected polymer. This is mainly because the injected polymer does not oxidize in the reservoir. It is either retained in the reservoir (via adsorption and mechanical entrapment) or degraded, and in case of production it is disposed.

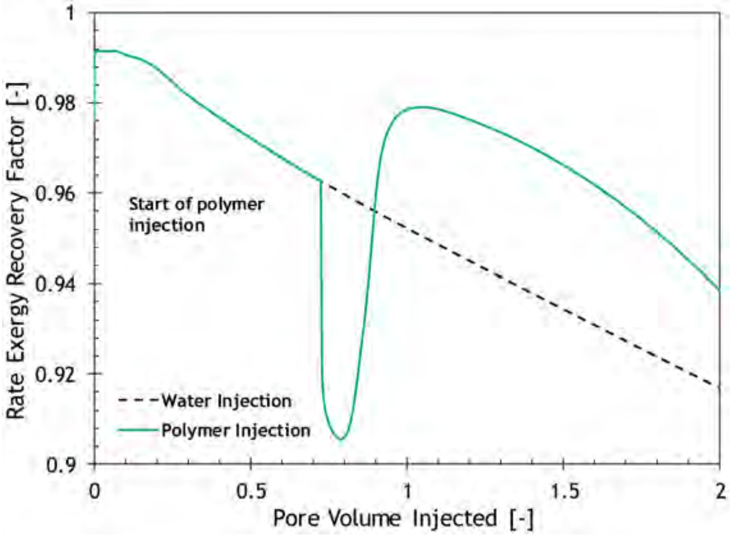

Figure 4—History of the rate exergy recovery factor for polymer (solid line) and water-injection (dashed line) cases.

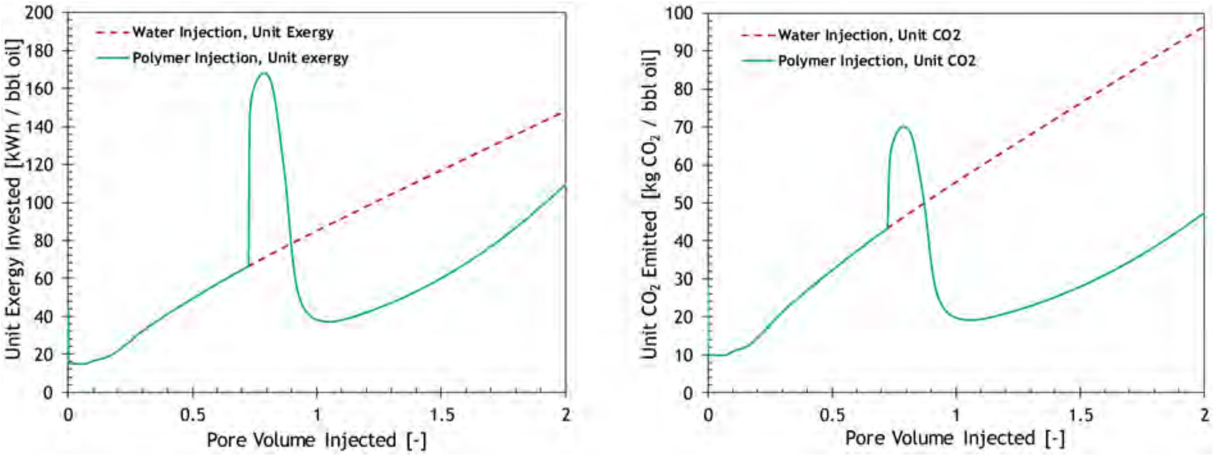

Figure 5—Histories of the unit energy consumed (left) and unit CO_2 emitted (right) for water injection (dashed line) and polymer injection (solid line) cases.

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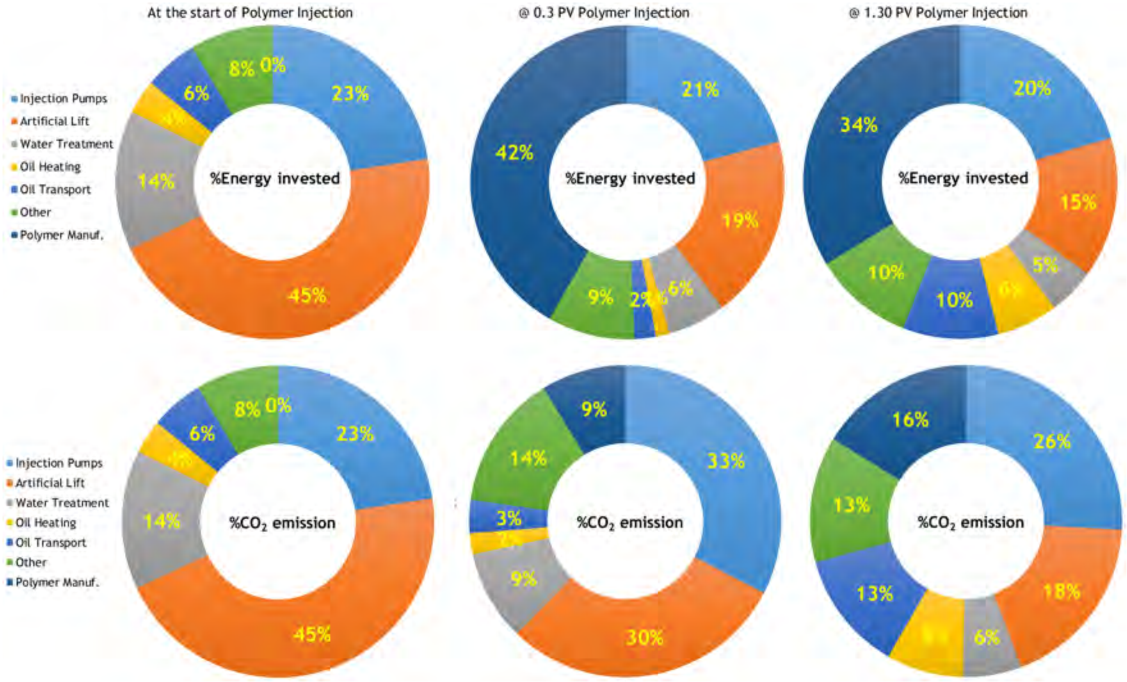

Figure 6—Fractions of exergy invested and CO$_2$ emission at different time intervals for water and polymer injection cases.

Figure 7 and Figure 8 show examples of these calculations for two fields in the Middle East. The field example in Figure 7, is a reservoir with a strong bottom aquifer. This figure plots the ratios of the CO$_2$ emitted and exergy invested between polymer injection and natural aquifer drive. Therefore, no water is injected into the reservoir. In this case, polymer EOR has larger exergy investment, because it requires pumping of significant volumes of polymer-containing water. However, injection of polymer, leads to reduction in exergy investment in lift pumps and excessive water treatment. This combined with the fact that polymer does not produce CO$_2$ in the reservoir (no oxidation) eventually results in smaller CO$_2$ footprint for the PI case compared to the aquifer-drive production scheme.

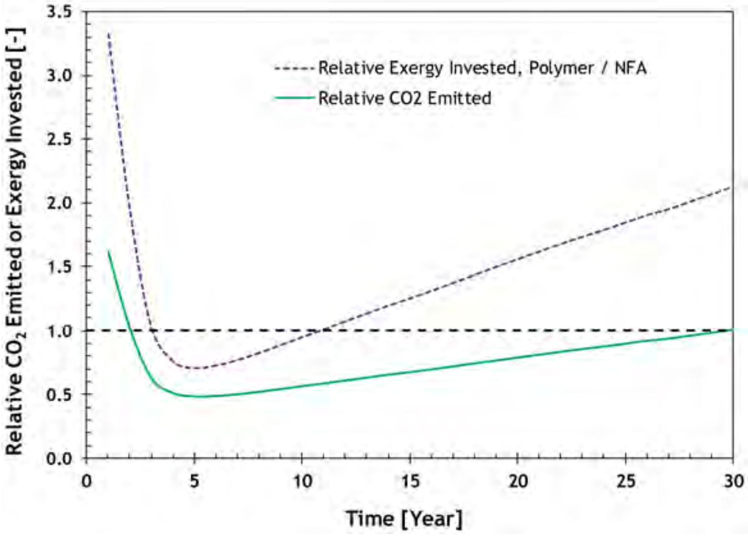

Figure 7—History of relative exergy invested and CO$_2$ emitted for field A in the Middle East. The calculations are based on simulation results. NFA stands for no further action, i.e., production by natural aquifer drive.

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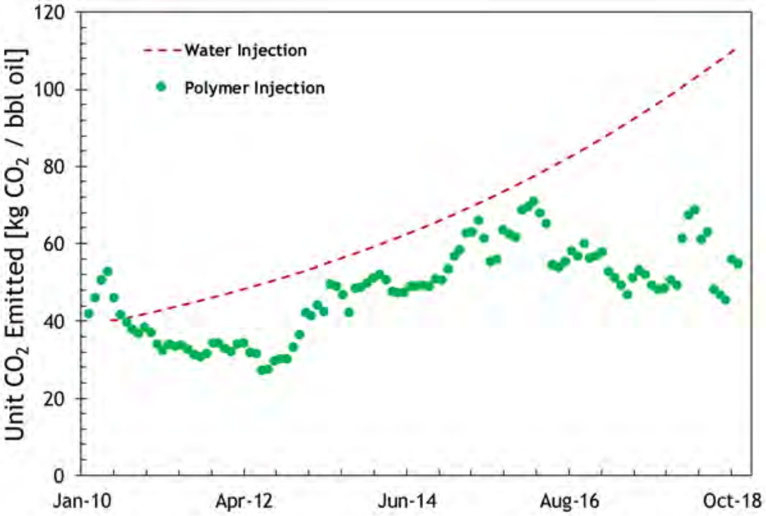

Figure 8—History of CO_2 emitted for field B in the Middle East. The calculations are based on the data from one injection pattern in the field.

Figure 8 uses the oil recovery results of a polymer injection pattern in another field in the Middle East. Water injection was the main recovery mechanism for this reservoir until the water cut reached value of 95%. At this point, injection of polymer started, which resulted in water-cut reversal, similar to Figure 2. The dashed line and the circles in Figure 8 compare the unit CO_2 emission for water injection (in case it continued) and polymer injection. The polymer injection project has a significantly smaller carbon footprint.

Figure 9 shows the impact of injecting surfactant/polymer on oil recovery and water cut in comparison with the water injection. The characteristics of the oil recovery is similar to that of the polymer flooding, i.e., injection of surfactant/polymer leads to formation of an oil bank. As a result, the water cut first decreases (more significantly than polymer injection) and after breakthrough of the chemicals the water cut starts to increase. The history of the exergy recovery factor for the surfactant-polymer injection, shown in Figure 10, is similar to that of the polymer injection. For the surfactant-flooding, the first deviation from water flooding (dashed line) occurs when soft water is injected to remove the divalent ions. With the injection of the chemicals, the rate exergy recovery factor significantly decreases, which is because of the large exergy invested in manufacturing of the chemicals. To maintain stable displacement larger viscosity (or polymer concentration) is required in surfactant/polymer injection [12]. Moreover, manufacturing of the HPAM polymer is exergetically two times more expensive than that of the surfactant. Therefore, the exergy recovery factor for the SP case is smaller than that of the PI case. Nevertheless, injection of SP extracts more oil and consequently with the breakthrough of the oil bank the exergy recovery rises above the WI case. Similar to the PI case, the maximum in the exergy recovery factor corresponds to the minimum in the water cut.

Figure 11 presents the unit exergy invested and the calculated CO_2 footprint of the SP case. The difference between the area enclosed above and below the water-injection case (dashed line) provides the net exergy (in the left figure) and the net CO_2 emission (in the right figure). Even though the net unit exergy invested can be negative for the SP flooding, since majority of the invested exergy is in the form of material it will not necessarily emit more CO_2 than water injection at large water cuts. In the case investigated here, application of SP leads to saving of large quantities of CO_2. For example, continuation of water injection at 2 PV results in 95kg/bbl of produced oil, while this number is less than 25 kg/bbl for SP flooding (similar to that of the polymer flooding). The extent of CO_2 emission in the surfactant/polymer process depends largely on the amount of the chemicals injected. For example, if an alcohol is used in the surfactant formulation as a co-solvent, the net CO_2 emission could also be negative.

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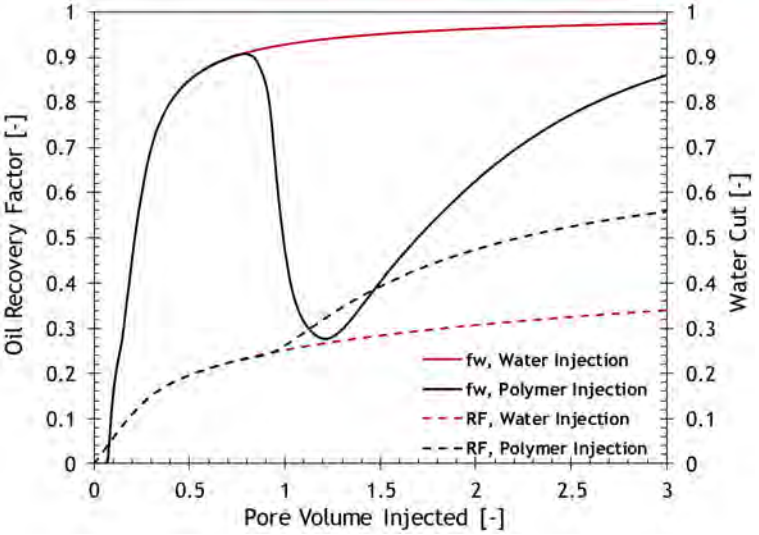

Figure 9—The oil recovery factor (RF) and water cut (f_w) histories for water and surfactant-polymer injection.

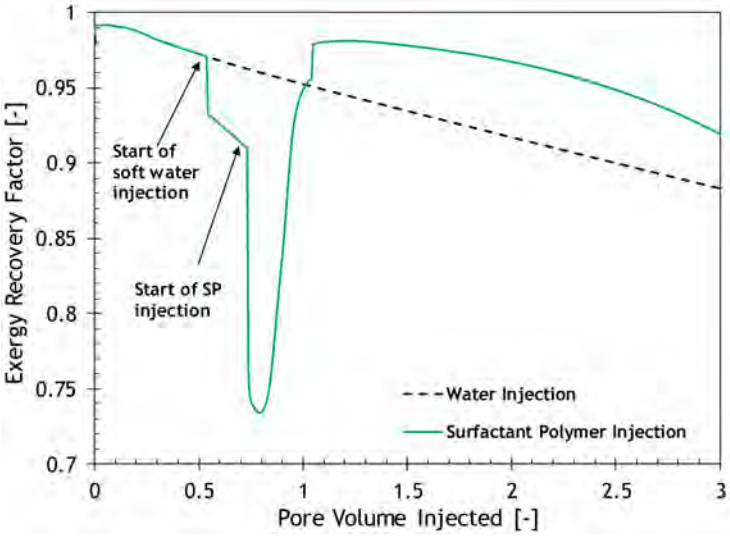

Figure 10—History of the rate exergy recovery factor for surfactant-polymer (solid line) and water-injection (dashed line) cases.

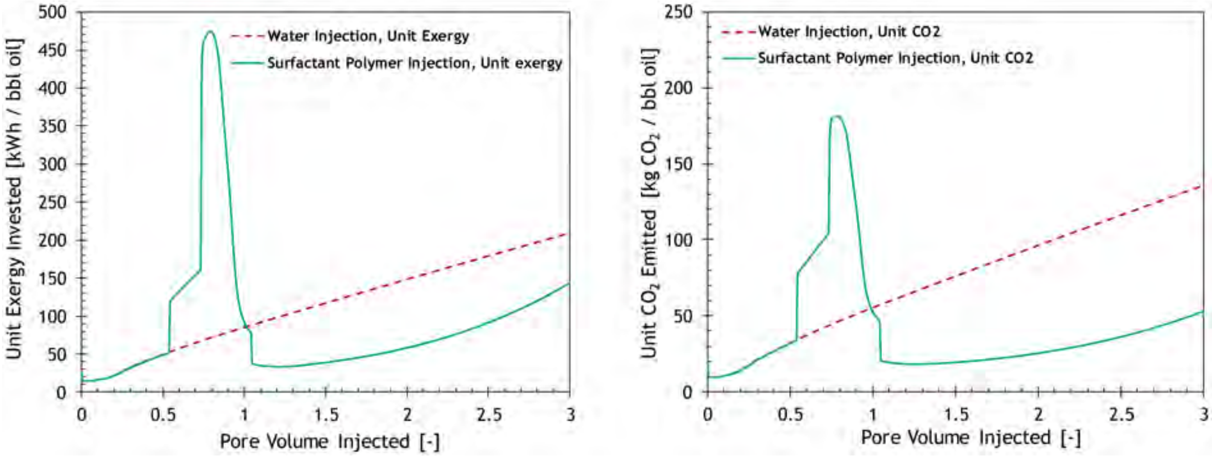

Figure 11—Histories of the unit energy consumed (left) and unit CO_2 emitted (right) for water injection (dashed line) and surfactant-polymer injection (solid line) cases.

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Figure 12 compares the cumulative exergy recovery for water-, polymer- and surfactant/polymer-injection cases. For the geological realization and injection compositions considered considered here, at the end of the respective projects, the cumulative exergy recovery factors of the three processes are similar. It is notable that, in the cumulative sense, only minor fraction of the exergy gained from oil (about 3%) is invested to produce it.

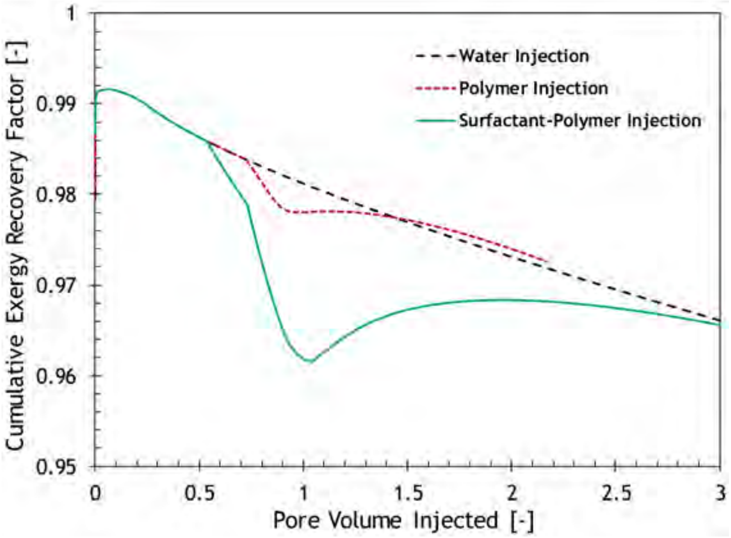

Figure 12—History of cumulative exergy recovery factor for water-, polymer- and surfactant/polymer-injection cases.

Conclusions

The dilemma of reducing of CO_2 emission from fossil fuels combined with (ever)-increasing global-energy demand has increased the efforts in development of low-carbon energy sources. During the transition from fossil fuel to renewable energy, the existing hydrocarbon fields should be developed in a more sustainable and energy-efficient manner. In this study, we develop a method based on the concept of exergy-return on exergy-investment (ERoEI) to analyze the life-cycle impact of polymer and surfactant enhanced oil recovery (EOR). This integrated approach considers both surface and subsurface elements of the oil-production systems and can be used to determine energy efficiency and CO_2 footprint of a unit volume of oil produced by chemical EOR. Numerical simulations were performed to quantify the additional oil gained by injection of chemicals. The injection of the chemicals started when the water cut in the field reached 90%. The following conclusions are drawn from this study:

- The exergy concept facilitates the assessment of the life-cycle efficiency of chemical enhanced oil recovery projects.
- The exergy recovery factor for chemical EOR decreases with time. This indicates that the process exergy requirements to produce the exergy increases with time.
- The practical exergy of manufacturing hydrolyzed polyacrylamide (HPAM) polymers is estimated to be 123.6 MJ/kg. This gives a CO_2 emission of 3.25 (gas), 4.72 (oil), and 6.35 (coal) kg CO_2 per kg polymer.
- Injection of polymer increases the energy efficiency of the oil recovery system. Because of additional oil (exergy gain) and less water circulation (exergy investment), the project-time averaged energy invested to produce one barrel of oil from polymer flooding is less than that of prolonged water flooding because of large water cuts.
- Exergy investment in some chemical EOR projects might be larger than that of the waterflooding; however, because a major fraction of exergy investment is in the form of materials, the CO_2

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footprint per barrels of oil produced from these projects are considerably smaller than those produced by water injection at large water cuts.

- Polymer injection into reservoirs with high water cut can be a solution for two major challenges of the transition period: (1) meet the global energy demand via an increase in oil recovery and (2) reduce the CO_2 footprint of oil production (more and cleaner oil).
- For surfactant EOR, the extent of improvement in energy efficiency depends on the incremental gain and the simplicity of the formulations. However, in many cases the oil produced by surfactant EOR will be cleaner than the oil produced by water injection at large water cuts.

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Appendix 1

Table 3 and Table 4 show the material and energy streams for the production of acrylonitrile and polyacrylamide, respectively. The exergy required for the production of acrylonitrile is estimated to be 78.9 MJ/kg [25,26]. Phosphoric acid has a chemical exergy of 980 kJ/kg. Assuming a production efficiency of 33%, a value of 3.0 MJ/kg is calculated [27,28]. However, by including all the exergy consumption in the life cycle of phosphoric acid, an exergy value of 47.65 to 57.65 MJ/kg is obtained, of which 31% is fossil fuel [29]. A large fraction of this value accounts for the environmental losses due to land use. For sodium hydroxide, we use a value 27.99 MJ/kg, of which 39% is fossil fuel (5). For activated carbon, which can be produced from coal or biomass, we follow Bayer et al. [30] assuming 1600 kWh plus 12 tonnes of steam consumption (produced by burning 330 m^3 of natural gas to produce 1 ton of activated carbon from coal). Assuming average exergy values of 500 kJ/mol and 800 kJ/mol, respectively, for coal (CH) and natural gas (CH_4), the average exergy of activated carbon is estimated to be 116.9 MJ/kg. The chemical and practical exergy of copper are reported to be 0.172 MJ/kg and 66.7 MJ/kg, respectively [31]. The exergetic efficiency of hydrogen production by steam reforming process is around 70% [32]. This gives a practical exergy of 168.6 MJ/kg or 9.46 MJ/m^3 (at standard condition) for hydrogen. Depending on the environmental condition, an exergy value of 1 kJ/kg (or 1 MJ/m^3) is expected for the cooling water [33]. The exergy of steam is calculated based on the the heat of vaporization of water, which is 2257 MJ/ton. We round the number to 2500 MJ/ton to include a small heat loss. We also assume that the required heat is provided from the combustion of natural gas. For mineral oil, which is usually an alkane, we assume an average chemical exergy of 53.6 MJ/kg.

Table 3—Material and exergy required for manufacturing of acrylonitrile by catalytic hydration [34,35]

Material	consumption (unit/ton)	unit	exergy	exergy unit	Total (MJ/ton acrylamide)
Acrylonitrile	0.7616	tonne	78.9	MJ/kg	60090.24
Activated carbon	0.0158	tonne	116.9	MJ/kg	1847.02
Cu-Cr	0.0018	tonne	66.7	MJ/kg	120.06
Hydrogen	65.5945	Nm3	9.46	MJ/Nm3	620.52397
Cooling water	159.397	m3	1	MJ/m3	159.397
electricity	133.6	kWh	9	MJ/kWh	1202.4
inert gas	304.171	Nm3	0		0
process water	1.33526	m3	0		0
steam	4.878	tonne	2500	MJ/tonne	12195

The practical exergy of polyacrylamide is simply calculated by the sum of the cumulative exergy consumption of each material multiplied by the amount that is required for the production of one ton of polymer. This gives a value of 123.6 MJ/kg for HPAM polymer. The CO_2 emission is estimated by calculating the CO_2 emission of each material stream, which is done by multiplying the fraction of the cumulative exergy consumption that comes from fossil fuels by the CO_2 emission of a fossil fuel, i.e., natural gas with an estimated CO_2 emission of 0.055 kg/MJ or coal with a CO_2 emission of 0.088 kg/MJ. This gives a CO_2 emission of 3.25 (gas), 4.72 (oil), and 6.35 (coal) kg CO_2 per kg polymer, depending on the type of consumed fossil fuel.

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Table 4—Material and exergy streams for the production of one ton of polyacrylamide [34,35]

Material and energy	Amount	Unit	CExC	Unit	% fuel
acrylamide	1.0222	tonne	76.23	MJ/kg	0.41
caustic soda (NaOH)	0.10647	tonne	28	MJ/kg	0.45
Mineral oil	0.6782	tonne	53.6	MJ/kg	0.4
Phosphoric acid	0.04719	tonne	25	MJ/kg	0.31
POE laurylether	0.06152	tonne	53.6	MJ/kg	0.4
Sodium bisulfite	0.00016	tonne	28	MJ/kg	0.5
sodium bromate	0.00008	tonne	28	MJ/kg	0.5
sorbitol monooleate	0.06073	tonne	-	-	1
Cooling water	458.163	m3	1	MJ/m3	1
electricity	116.845	kwh	9	MJ/kwh	1
steam	0.158	tonne	2500	MJ/tonne	1

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