

# Indian Institute of Technology Gandhinagar



**ES211 Project Report**  
**24 November 2021**

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Exergy Analysis Of CO<sub>2</sub> - EOR and CCS

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# Exergy Analysis Of $CO_2$ -EOR And CCS

## Introduction:

The concentration of carbon dioxide in the atmosphere is increasing second by second, so as one reads this paper. It is not one of the desired gases in the atmosphere as it increases global warming and hence, the global temperature. One of the primary and significant sources of carbon dioxide release is the combustion of fossil fuels for a multitude of processes, essentially energy production. With the increasing population, the need for energy was increasing, is increasing, and will increase. To satisfy this hunger, we have come up with several ice-breaking technologies, but none as cheap as burning fossil fuels. Also, these technologies are often limited to specific regions, limiting their spread. As we have learned that there is a cost one has to pay in terms of either the efficiency or the production cost; in India, fossil fuels are and shall remain a prime source of energy production over the next few years. Moreover, this means that there is a need to curb the rising carbon dioxide levels in the atmosphere.

One such method to control carbon dioxide emissions has been in effect in several parts of the world in the oil and gas industry for a considerable time. The industry has been producing, obtaining, moving and infusing carbon dioxide for such a process for the last thirty to forty years. It is the Enhanced Oil Recovery process. It not only uses carbon dioxide and hence reduces its content, but it also increases the lifetime of the oil fields while enhancing the rate of oil recovery. Taking advantage of the dissolution property of carbon dioxide, fissures and pores in the rock structure are fed in with compressed carbon dioxide. These then swell up inside, exerting pressure on the oil and forcing it out. The carbon dioxide mixed with this oil is extracted and reused for a similar cycle. This has increased the efficiency by around 20%.

## System Definition:

The first step would be to transport the produced carbon dioxide to the field site, say power plants. From the thermodynamics point of view, it would be better to compress it to carry it over long distances. This would save on the cost as well as energy. Upon reaching the plant, a compressor compresses it further so as to reverse any effects of transport. Due to its low density, it travels through the fissures and goes into the oil-producing site. Then part of it remains inside while part of it comes out along with oil as a mixture. This mixture is then separated, and the pump pumps oil from the extraction to the oil refinery for further processing. The carbon dioxide separated from the oil by the separator is supplemented by the additional required amount of fresh carbon dioxide for another similar cycle. Hence the system, or thermodynamically speaking, the control volume, consists of the components starting from its initial compression for travel to the step where the pump sends oil to the refinery.

## Why Exergy Analysis?

Entropy is a good measure for checking the irreversibility of the system. But we can't use it for checking the efficiency. For the heat engines and compressors, we were able to get the efficiency according to system by using  $\eta = \frac{W}{Q_H}$  or similar formulae. But they had their own limitations. They couldn't give the measure when only one system and substance or available. In other words, the formulae weren't universal.

The concept of exergy was first introduced by MIT in 1940's, and named as 'availability'. It denoted the maximum amount of energy that could be extracted from the system. The term exergy was introduced by Zoran Rant by combining the Greek word for 'from' *ex* and 'work' *ergon*. Another reason that drove us for using exergy was the excitement to learn something new and out of the syllabus. See appendix for more information on exergy.

## Exergy analysis:-

Here, we will describe the exergy streams and material relevant to  $CO_2$  storage through  $CO_2$  enhanced oil recovery. To perform the exergy analysis, the exergy of the work and material streams should be first calculated for the defined system in Fig. 1

### Exergy streams:-

We can see the main exergy streams of a  $CO_2$  EOR project in figure 1. Here, we expand each stream and calculate its corresponding exergy. The streams can be broken down into material and work streams.

### Material streams:-

The chemical exergy of crude oil depends on its composition and it is generally assumed to be its lower heating value (LHV). The following equation correlates the chemical exergy of oil to its specific gravity (SG).

$$LHV \left[ \frac{MJ}{kg} \right] = 55.5 - 14.4SG$$

- (1)

Assuming  $SG=0.70$ , the exergy of the crude oil is 45.5 MJ/kg. We assume that the gas released from oil is methane. The chemical exergy of  $CH_4$  is  $Ex_{CH_4}^{ch}=831.65$  kJ/mole or 51.98 MJ/kg. [1,2] When  $CO_2$  is injected into the reservoir, the produced gas will contain  $CO_2$ . However, the chemical exergies of  $CO_2$  and the produced water are neglected because their chemical exergy has a negligible impact on the final results; their exergy values are at least four factors of ten times smaller than that for oil.

### Work stream:-

The exergy of work streams identified in figure 1 are as follows:-

Exergy of  $CO_2$  capture:-

The  $CO_2$  capture methods (from mixtures containing carbon dioxide, methane, nitrogen) consume large amounts of energy.[3] Let us assume that  $Ex_{capture}^{pr}=4000$  KJ/kg  $CO_2$ , which is the average exergy value required for separating  $CO_2$  from flue gas in the chemical absorption of  $CO_2$  using an aqueous solution of MEA (mono-ethanol-amine), today's predominant carbon-capture technology. Capture costs can be reduced by using membrane technology, but this is not widely used, being insufficiently mature.

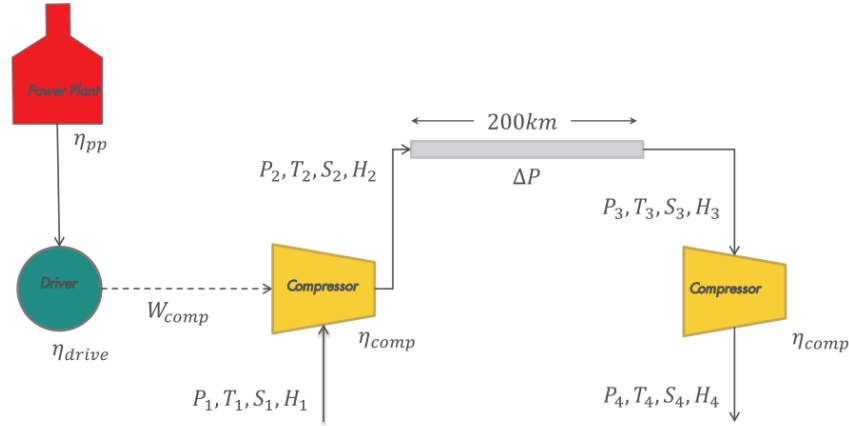


Fig. 3. Transport of  $CO_2$  by pipeline and reservoir injection.

Exergy of  $CO_2$  transport, compression and injection:-

To calculate the exergy of  $CO_2$  transport, compression, and injection, we followed the following procedure. We assume that  $CO_2$  is transported through a 200 km long pipeline system from a source power plant to the sink oil reservoir. The captured  $CO_2$  enters the transport compressor at a known temperature  $T_1$  and pressure  $p_1$  and leaves it at the elevated temperature  $T_2$  and pressure  $p_2$ . Compression is an isentropic (adiabatic) process, or the entropy of the streams remain constant. Similarly, the  $CO_2$  enters the injection compressor at a temperature  $T_3$  and pressure  $p_3$  and exits at the desired pressure  $p_4$ . The minimum exergy requirements of the two adiabatic compression stages are the enthalpy differences between the input and output streams at constant entropy, which we call the theoretical exergy of compression. For the practical exergy value, i.e., a state of the art compressor, the efficiencies of the compressor, electrical driver and the power plant should also be considered. Thus

$$Ex_{CO_2}^{pr, trans} = \frac{Ex_{CO_2}^{th, comp 1}}{\eta_{comp} \eta_{driver} \eta_{pp}} = \frac{H_2(S_1(T_1, P_1), P_2) - H_1(S_1(T_1, P_1), P_1)}{\eta_{comp} \eta_{driver} \eta_{pp}} \quad - (2)$$

and

$$Ex_{CO_2}^{pr, inj} = \frac{Ex_{CO_2}^{th, comp 2}}{\eta_{comp} \eta_{driver} \eta_{pp}} = \frac{H_4(S_1(T_1, P_1), P_4) - H_3(S_1(T_1, P_1), P_3)}{\eta_{comp} \eta_{driver} \eta_{pp}} \quad - (3)$$

The total practical exergy of compression is the sum of the exergy of compression for transport and for injection, i.e.,

$$Ex_{CO_2}^{pr, comp} = Ex_{CO_2}^{pr, trans} + Ex_{CO_2}^{pr, inj} \quad - (4)$$

The following steps are taken to calculate the exergy of  $CO_2$  transport and injection.

1. Isentropic compression is assumed for all streams, i.e.,  $S_2 = S_1$  and  $S_3 = S_4$ .
2. For stream 1, the values of enthalpy and entropy are calculated by using Cantera.

3. The pressure drop in the pipeline is calculated using the panhandle equation suggested by R.H. Perry and D.W. Green. The pipe diameter is calculated by assuming a maximum allowable velocity for the gas stream (here, a 20-inch diameter pipeline).
4. We assume a pressure for the gas stream at the outlet of the transport pipeline, e.g.,  $p_3=80\text{bar}$ . The pressure of stream 2 ( $p_2$ ) is then  $p_2 = p_3 + \Delta P_{pipe}$ .
5. For the calculation of the theoretical compression exergy, we consider a multistage compressor with inter-stage cooling where the pressure of the output stream from each stage is calculated using the pressure ratio of typical compression processes ( $P_2/P_1= 3.0\text{-}4.5$ ) for a centrifugal compressor. [3] The input temperature to each stage is  $T_1$ .
6. The enthalpy of the output streams from each compression stage is calculated for the known pressure and entropy.
7. The isentropic compression work for each case is the difference in enthalpy  $\Delta H$  between the input and output streams.
8. We use a typical current values for the compressor efficiencies and the power generating efficiencies, i.e.,  $\eta_{pp} = 0.40$ ,  $\eta_{drive} = 0.90$ ,  $\eta_{comp} = 0.70$ .

The injection pressure  $p_4$ , as well as the  $CO_2$  injection rate, are taken to be 280 bar and  $\sim 30,000$  m<sup>3</sup>/d (at reservoir conditions). The results of the compression exergy requirements in the transport and injection compressors are given in Table 1.

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**Compression exergy in the transport and injection of  $CO_2$ .**

	Transport	Injection	Unit
$P_{in}$	1	80	bar
$P_{out}$	80	280	bar
Max pressure ratio	3	3	
$\eta_{comp}$	0.70	0.70	
$\eta_{driver}$	0.90	0.90	
$\eta_{powerplant}$	0.40	0.40	
$Ex_{CO_2}^{th,comp}$	354	59	kJ/kg $CO_2$
$Ex_{CO_2}^{pr,comp}$	1405	235	kJ/kg $CO_2$

Exergy of oil transport to the refinery:-

For calculating the exergy of oil transport, an average flow rate of 2.88 kg/s, the diameter of pipeline three inches, the average flow speed of 0.8 m/s, an initial pressure of 200bars, and a transporting distance of 200 km to the refinery were assumed.

Using the Darcy–Weisbach equation for fluid pressure drop in pipeline transportation, taking into account that at the end of the pipeline, the crude oil need only be at a slightly higher pressure than atmospheric, a pressure loss of  $\Delta P = 196$  bar is calculated. The theoretical pumping exergy required for the pumps to transport the crude oil under the above conditions is given as an approximation by:

$$Ex_{oil}^{th,trans} = Ex_{pump} = \dot{Q}\Delta P$$

- (5)

where  $\dot{Q} \left[ \frac{m^3}{s} \right]$  stands for the flow rate of the crude oil through the pipeline and  $\Delta P$  [Pa] is the pressure drop in the pipeline. The practical pumping exergy is calculated by including the mechanical efficiency of the pump (80%), and efficiency of the electrical driver (90%), and the power plant (45%), i.e.,

$$Ex_{oil}^{pr,trans} = \frac{Ex_{oil}^{th,trans}}{\eta_{pump} \eta_{driver} \eta_{pp}} = \frac{\dot{Q} \Delta P}{\eta_{pump} \eta_{driver} \eta_{pp}}$$

- (6)

This amounts to a value of  $Ex_{oil}^{pr,trans} = 2.6 kJ/s$ , which in turn, normalized over the lifetime of the project and the total amount of oil transported amounts to 75.4 kJ/kg of oil transported.

Exergy of gas ( $CO_2/HC$ ) separation:-

The separation of the gases from the liquid oil is assumed to take place in a gravity separator vessel; therefore, there is no need to spend exergy in this step. The subsequent separation of the  $CO_2$  from the hydrocarbons in the gaseous mixture is assumed to  $Ex_{CO_2}^{pr,sep} = 2500 kJ/kg$  of  $CO_2$  captured.

## Exergy recovery factor:-

We define the exergy recovery factor,  $Ex_{RF}$ , as the ratio of the produced exergy corrected for material and process exergy requirements for its extraction and to the gross exergy of the source, i.e.,

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

- (7)

$Ex_{gained}$  is the exergy of the final product (within the selected boundary),  $Ex_{invested}$  is the amount of exergy invested in producing hydrocarbons, and  $Ex_{fuel}$  is the amount of exergy stored in the hydrocarbon reservoir. [4] For the case considered here, i.e. a  $CO_2$  EOR project with CCS option, Eq. (7) becomes

$$Ex_{RF} = \frac{(Ex_{oil}^{ch} + Ex_{CH_4}^{ch}) - (Ex_{CO_2}^{capture} + Ex_{CO_2}^{comp} + Ex_{CH_4}^{comp} + Ex_{water}^{treat} + Ex_{CO_2}^{sep} + Ex_{oil}^{trans})}{Ex_{oil}^{ch} + Ex_{CH_4}^{ch}}$$

- (8)

## Calculation Of Oil Recovery

LW Lake and MP Walsh have developed a remarkable procedure to calculate oil recovery when  $CO_2$  is injected with water to displace oil in a 1-D porous medium. The procedure ignores  $CO_2$  dissolution in water and oil for simplicity. But we need water-solvent and water-oil fractional-flow functions.

Fractional-flow Function for phase  $i$  displacing phase  $j$  is,

$$f_{ij} = \frac{1}{1 + \frac{1}{M_{ij}}}$$

- (9)

$$M_{ij} = \frac{k_{r_i}}{k_{r_j}} \cdot \frac{\mu_j}{\mu_i}$$

- (10)

where,

$M_{ij}$  → Mobility ratio

$k_{r_i}$  → Relative Permeability of phase i

The relative permeability is calculated using a Corey-type model. [5] Figure-4 shows a few fractional flow curves for water-solvent and water-oil pairs.

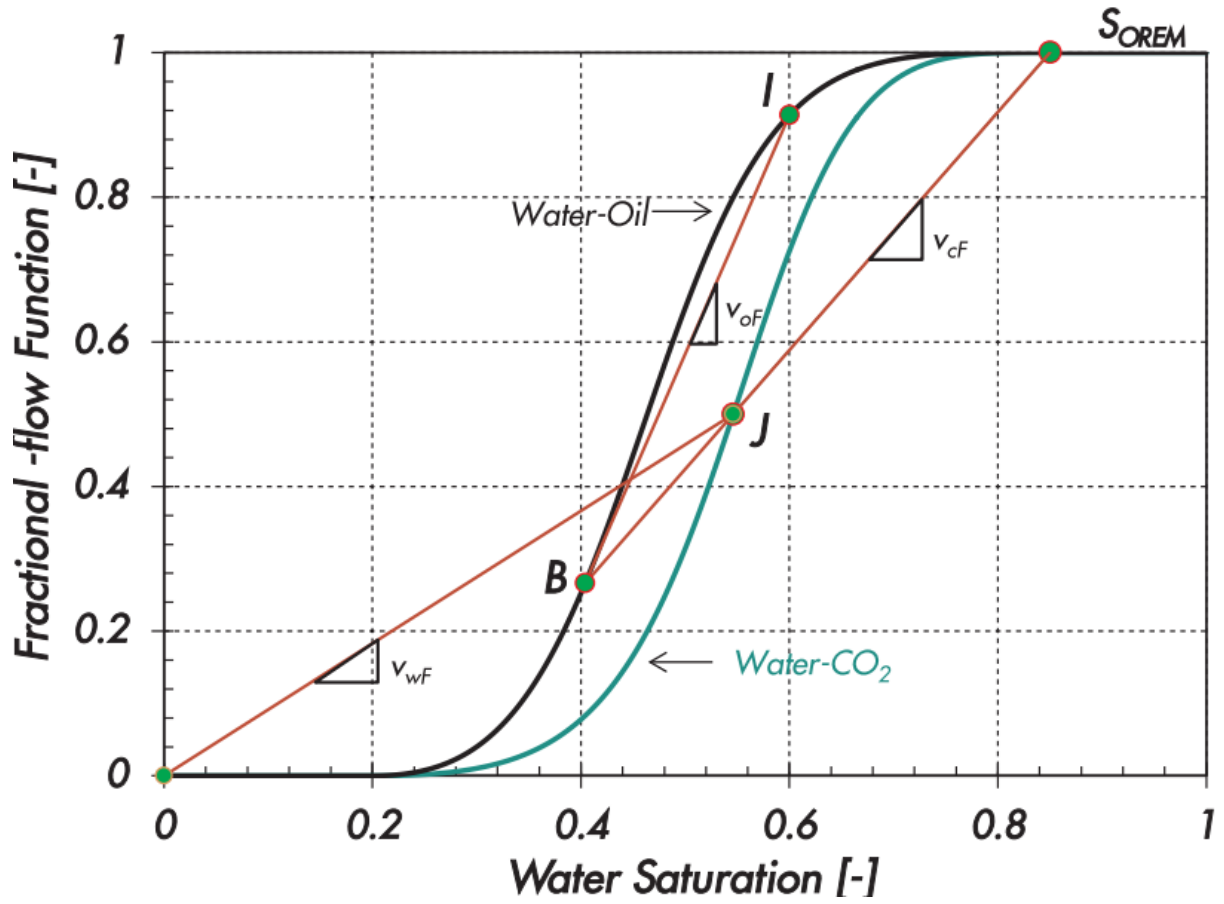


Figure 4: Oil Displacement by Miscible  $CO_2$ .  $S_{OREM}$  is the remaining oil saturation.

In The Graph,

$v_{cF}$  → Specific Velocity of  $CO_2$

$v_{oF}$  → Velocity of Oil Bank

$v_{wF}$  → Velocity of Water Front

The inflection point 'J', is determined using WAG ratio,  $W_R$ :

$$f_{wJ} = \frac{W_R}{1 + W_R}$$

- (11)



For optimal WAG ratio, we need to chose J such that  $v_{cF} = v_{wF}$ .

Mollaie A, Delshad M, Farajzadeh R, Wassing LB, and Lake LW developed a method named '**Modified Koval Method**' for upscaling the result obtained from this analytical method. On Upscaling, the solvent and oil-bank fronts become distorted due to heterogeneity of porous medium and adverse mobility ratio and gravity effects. The extent of distortion is quantified with the help of two Koval factors,  $K_{oB}$  for the oil bank and  $K_S$  for solvent. The factors are functions of the Dykstra-Parsons coefficient. The critical consequences of this distortion include the early breakdown of oil and solvent banks, smaller oil cuts, and more time required for production. (Fig-5)

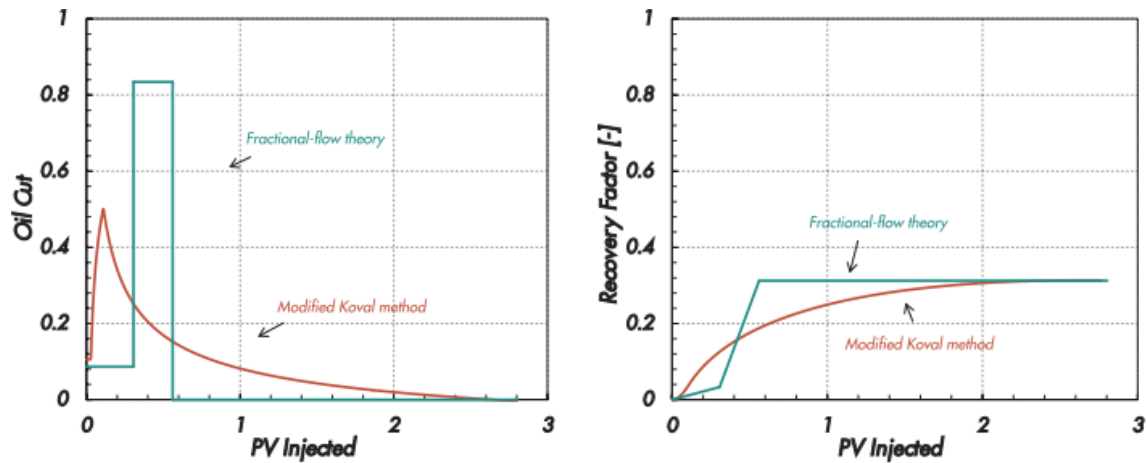


Figure-5: Analytical curves (Green ones) upscaled by taking  $K_{OB} = 10$  and  $K_S=5$  (red ones)

Data for  $K_{OB}$  and  $K_S$  values have been obtained by matching several old large scale applications of EOR with the modified Koval method. Based on these values and using the reservoir and fluid properties (Table 2), we can create three production cases (Figure 6).

Parameter	Value	Description
$n_w$ ( $n_{ws}$ )	2	Water (water-solvent) Corey exponent
$n_o$ ( $n_{os}$ )	3.5	Oil (oil-solvent) Corey exponent
$k_{rw}^e$	0.325	Water end-point relative permeability
$k_{ro}^e$	0.66	Oil end-point relative permeability
$S_{ori}$	0.50	Initial oil saturation before CO <sub>2</sub> injection
$S_{orw}$	0.30	“remaining” oil saturation to water
$S_{ors}$	0.20	“remaining” oil saturation to CO <sub>2</sub>
$S_{wc}$	0.20	Connate water saturation
$\mu_s$	0.1	CO <sub>2</sub> viscosity (cP)
$\mu_w$	1	Water viscosity (cP)
$\mu_o$	2	Oil viscosity (cP)
WAG ratio	2:1	CO <sub>2</sub> :water
Reservoir pore volume	$1 \times 10^8 \text{ m}^3$	
Injection rate	0.1 PV/year	
$B_o$	1.2	

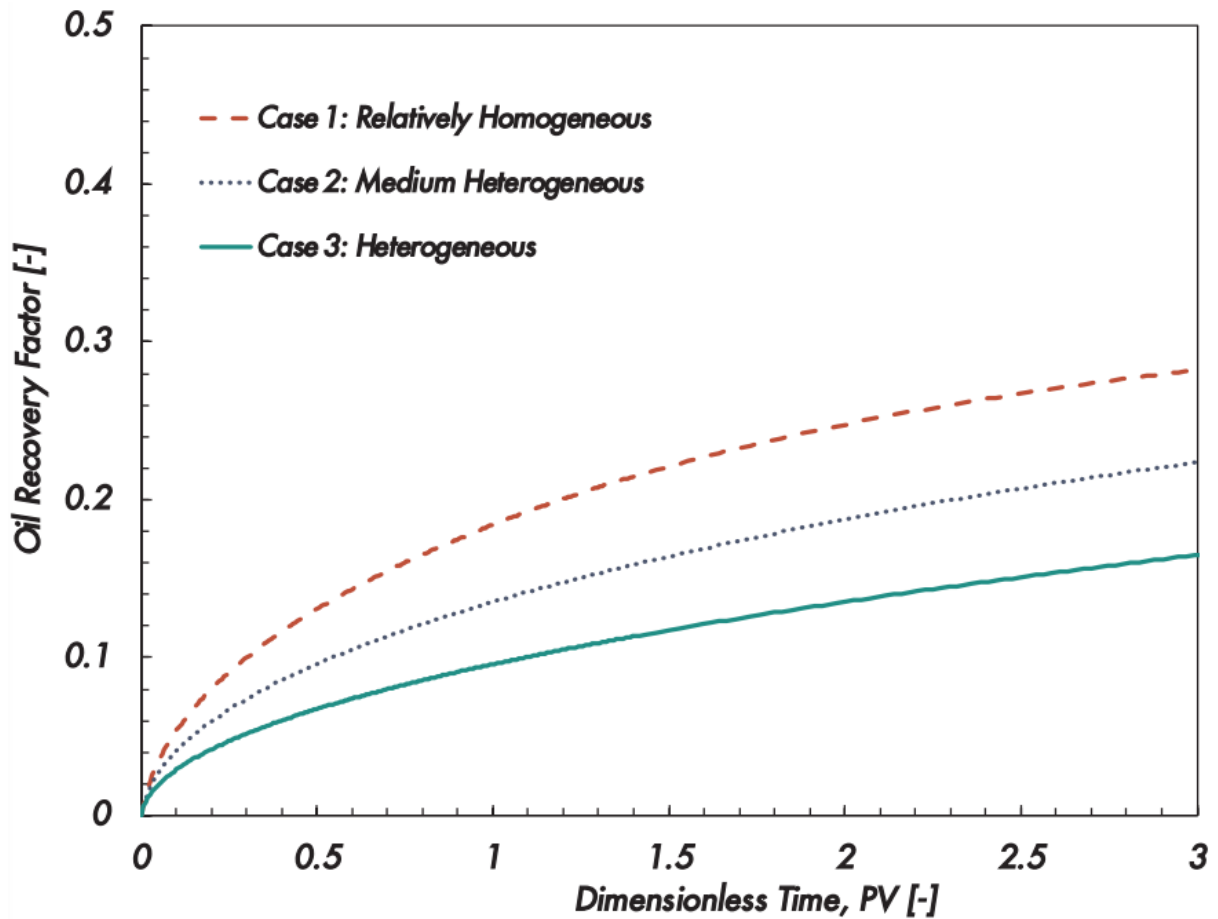


Figure-6. Oil Recovery Factor for three cases. Data summarized out of 37 Large-scale  $CO_2$  EOR Projects.

We can see that amount of oil produced by injected  $CO_2$  decreases with increasing heterogeneity. In other words, on increasing reservoir heterogeneity,  $CO_2$  utilization factor increases. The recovery factors from projects like these generally range between 5 and 25%, with an average of 13% after three cycles.

## Results and Discussions

### Exergy analysis of $CO_2$ Capture and Storage

In standalone CCS,  $CO_2$  is captured and transported underground for storage. The captured  $CO_2$  is compressed according to the requirements of the storage sites. The minimum required exergy to store a unit mass of is given by:

$$\dot{e}x = \dot{e}x_{capture} + \dot{e}x_{compression} + \dot{e}x_{transport}$$

For our project, we will take the specific energy of CCS to be around 5.5MJ/kg  $CO_2$ . We will also neglect any  $CO_2$  losses. The amount of  $CO_2$  generated in a process depends on the fuel that was used. The heating values of the significant fuels are:

1. Natural Gas or methane( $CH_4$ ) = 50MJ/kg
2. Oil( $CH_2$ ) = 42.85MJ/kg
3. Coal( $CH$ )=38.46MJ/kg

## Specific $CO_2$ Emission

Thus the specific  $CO_2$  are calculated as:

1. Natural Gas: combustion reaction:  $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$   
gives us:

$$\frac{44kgCO_2}{16kgCH_4} \times \frac{1kgCH_4}{50MJ} = 0.055 \frac{kgCO_2}{MJ}$$

2. Oil: Similar calculations give us:

$$0.073 \frac{kgCO_2}{MJ}$$

3. Coal: similarly we get

$$0.88 \frac{kgCO_2}{MJ}$$

Now assuming  $CO_2$  is stored at specific exergy of 5.5MJ/kg, we calculate the exergy of multistep capture:

1. For methane, the fraction of energy produced that is used up in a single storage step of  $CO_2$  is  $5.5 \times 0.055 \times 100\% = 30.25\%$ . This usage of methane energy also releases some  $CO_2$  which is needed to be captured. The exergy cost in storing this is met with by producing even more methane. This is mathematically represented by:

$$\Sigma(1 + 0.3025 + (0.3025 \times 0.3025) + \dots) = 1/(1 - 0.3025)$$

$$= 1.433 \frac{\text{exergy } CH_4 \text{ multiple steps}}{\text{exergy } CH_4 \text{ single step}}$$

This shows that 43% of the energy produced from methane would be used for storing the  $CO_2$ . So the total exergy consumption is

$$1.433 \frac{\text{exergy } CH_4 \text{ multiple steps}}{\text{exergy } CH_4 \text{ single step}} \frac{\text{actual MJ}}{\text{required MJ}} \times 5.5 \frac{MJ}{kgCO_2}$$

$$= 7.88 \frac{MJ}{kgCO_2}$$

2. For oil, the the fraction of energy produced that is used up in a single storage step of  $CO_2$  is  $(5.5 \times 0.073) \times 100 = 40.15\%$ . Like methane, this also produces some  $CO_2$  which is captured. The compensated exergy is given as

$$\Sigma(1 + 0.4015 + (0.4015 \times 0.4015) + \dots) = 1/(1 - 0.4015) = 1.671 \frac{\text{exergy oil multiple steps}}{\text{exergy oil single step}}$$

Total exergy consumption is

$$1.671 \frac{\text{exergy oil multiple steps}}{\text{exergy oil single step}} \frac{\text{actual MJ}}{\text{required MJ}} \times 5.5 \frac{MJ}{kgCO_2} = 9.19 \frac{MJ}{kgCO_2}$$

3. Similarly for coal, the compensation gives:

$$1.671 \frac{\text{exergy oil multiple steps}}{\text{exergy oil single step}} \frac{\text{actual MJ}}{\text{required MJ}} \times 5.5 \frac{MJ}{kgCO_2} = 9.19 \frac{MJ}{kgCO_2}$$

So total exergy consumption in case of coal is

$$1.937 \frac{\text{exergy coal multiple steps}}{\text{exergy coal single step}} \frac{\text{actual MJ}}{\text{required MJ}} \times 5.5 \frac{\text{MJ}}{\text{kgCO}_2} = 10.65 \frac{\text{MJ}}{\text{kgCO}_2}$$

## Total CO<sub>2</sub> Emission

1. For methane: The exergy required for storing 1kg of CO<sub>2</sub> produced by a methane burning powerplant is 7.88 MJ/kg-CO<sub>2</sub>. But during this storage, the amount for CO<sub>2</sub> generated is

$$1.43 \frac{\text{exergy CH}_4 \text{ multiple steps}}{\text{exergy CH}_4 \text{ single step}} \times 0.055 \frac{\text{kgCO}_2}{\text{MJ} - \text{CH}_4} = 0.0788 \frac{\text{kgCO}_2}{\text{MJ} - \text{CH}_4}$$

2. For Oil: Similarly, the amount of CO<sub>2</sub> produced for storing 1kg of CO<sub>2</sub> from oil burning is:

$$1.67 \frac{\text{exergy oil multiple steps}}{\text{exergy oil single step}} \times 0.073 \frac{\text{kgCO}_2}{\text{MJ} - \text{CH}_2} = 0.122 \frac{\text{kgCO}_2}{\text{MJ} - \text{CH}_2}$$

3. Similarly for coal, the amount of CO<sub>2</sub> is:

$$1.937 \frac{\text{exergy coal multiple steps}}{\text{exergy coal single step}} \times 0.088 \frac{\text{kgCO}_2}{\text{MJ} - \text{CH}} = 0.17 \frac{\text{kgCO}_2}{\text{MJ} - \text{CH}}$$

Thus, it shows that per kg of CO<sub>2</sub> stored from methane, oil and coal burning respectively, 0.433, 0.671 and 0.937 kg of CO<sub>2</sub> is released. Assuming complete capture of CO<sub>2</sub>, the efficiency of CCS only projects are:

1. (100-93.7)%=6.3% for coal
2. (100-67.1)%=32.9% for oil
3. (100-43.3)%=56.7% for methane

This efficiency is further decreased if we take a more practical CO<sub>2</sub> capture efficiency of around 90%. This gives us 45.6% for methane, 21.8% for oil and -4.8% for coal, which means capturing CO<sub>2</sub> produced by coal powerplants results in a net emission of CO<sub>2</sub> into surroundings. To reduce the impact of CO<sub>2</sub> emission, it is necessary to use fuels that emit lesser carbon-containing gases.

## Exergy analysis through Enhanced oil recovery

In this section, to utilize the produced gas, we will introduce three scenarios. In the first scenario(denoted by S1 or Scenario 1), all the gas goes directly into the reservoir without any exergy consumption. However, From Eq.(8), it comes out at the cost of losing the exergy gain. Scenario 2(S2) assumes that only CO<sub>2</sub> is injected into the reservoir, and generated methane is separated. In Scenario 3(S3), Although this is not a practical scenario, fresh CO<sub>2</sub> is continuously given in the project. In S3, it is just an assumption. This paper concludes that it is possible to use exergy analysis to optimize CO<sub>2</sub> EOR processes by considering several factors such as exergy consumption, oil recovery factor, exergy recovery factor, and exergy consumption between the CO<sub>2</sub> injection and gas separation. The first and essential thing that one needs to do for this study quantifies the exergy recovery factor of CO<sub>2</sub> EOR. The problem with CO<sub>2</sub> EOR is the lack of knowledge about the exergy content of CO<sub>2</sub>. This study performed an analysis of the exergy recovery factor to help answer this question.

The most efficient method for  $CO_2$  compression is using a gas separation process. Gas separation is so efficient because it can separate  $CO_2$  with high purity and low cost. The main expense in this process is the feeding system that pressurizes the gas to keep it in liquid form. Exergy is the measure of the chemical potential exergy for a thermodynamic system under specified conditions. Exergy analysis of  $CO_2$  Enhanced oil recovery(EOR) is an emerging technology that has been shown to increase oil production by 30% without high-pressure injection. The exergy recovery factor of  $CO_2$  EOR is around 80% which means that with  $CO_2$  EOR, 80% of the exergy released by injecting gas into the reservoir is recovered. Gas separation affects the exergy efficiency of  $CO_2$  EOR because it leads to a reduction in pressure and a drop in oil flow rates.

If we use the  $CO_2$  for thermal cracking and reforming, we can achieve a high exergy-recovery factor. However, we can only get a low exergy-recovery factor if we use the  $CO_2$  for enhanced oil recovery. Exergy is a measure of exergy content in terms of work and heat. Carbon dioxide is an artificially produced gas and is used in different industries for various reasons. Carbon dioxide has high solubility and is a suitable solvent for oil. This results in more oil being recovered from the well when  $CO_2$  is injected into the reservoir. This paper aims to provide theoretical analysis on the exergy-recovery factor for the carbon dioxide enhanced oil recovery(EOR) process and how  $CO_2$  is utilized by oil recovery. The exergy-recovery factor depends on various factors such as  $CO_2$  utilization, rock heterogeneity, volumetric gross  $CO_2$  utilization, etc.  $CO_2$  enhanced oil recovery is not a widely adopted process. It is not very widely used for economic constraints, the need for more research, and limited applicability. It can be used in specific circumstances where there are low permeability reservoirs.  $CO_2$  enhanced oil recovery procedures are often limited in secondary or tertiary operations where the reservoir pressure is very low, or other limitations inhibit production with conventional methods. The exergy gain of  $CO_2$  - enhanced oil recovery depends on the volumetric gross  $CO_2$  utilization (VCGU), which has an inverse relationship with  $CO_2$  utilization (OCU).

In Eq.(6), the exergy-recovery factor (ExRF) is calculated according to the oil-recovery histories.  $CO_2$  is directly supplied from an oil-fueled power plant. Along with the time, the exergy recovery factor gradually decreases, which indicates and leads us in the direction that more exergy is required as the lifetime increases. For all of that, the causes ate exergy gain and exergy investment. From Fig.(7), it is clear that the exergy-recovery factor is a vital function of the heterogeneity of the reservoir, and, for a given time, its value decreases with an increase in reservoir heterogeneity. For a particular time, the exergy recovery factor becomes negative(shown with a red dot in Fig.7). Now coming to the thermodynamically perspective, beyond this time, the project cannot become sustainable. In Fig.(8), exergy recovery factors of the three cases are plotted as a function of the (volumetric) gross  $CO_2$  utilization factor. The most exciting feature of the analysis is that the exergy recovery factor and the  $CO_2$  utilization factor are interconnected.

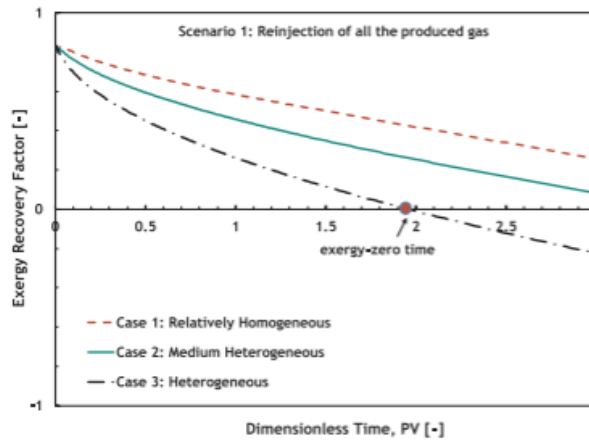


Figure-7: Exergy Recovery Factor as a function of time

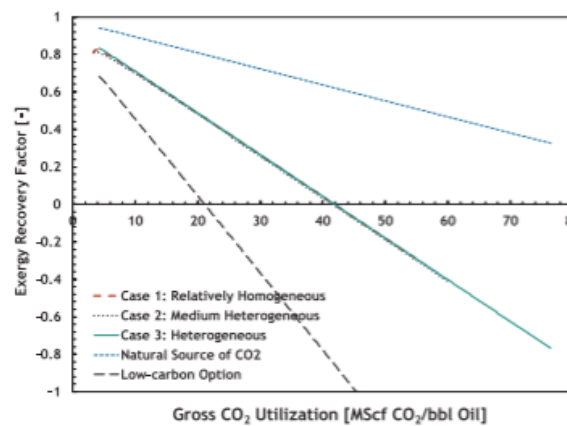


Figure-8: Exergy Recovery Factor as function of gross  $CO_2$  utilization factor for the three cases

In the practical world, there is an assumption that the natural source of  $CO_2$  has zero capture exergy. The most favorable process from the exergy perspective is utilizing the natural sources of  $CO_2$  for extracting oil. By Fig.(9), Although for the natural source of  $CO_2$  the exergy recovery factor is very large, so is its  $CO_2$  footprint (480–550 kg  $CO_2$  /bbl for  $CO_2$  utilization factor of 4–2 bbl oil/ tonne  $CO_2$ ). The difference between the two curves with open symbols in Fig (9) is the amount of  $CO_2$  stored in the  $CO_2$  EOR process when  $CO_2$  is supplied from an anthropogenic source (or captured). Compared to the natural source of  $CO_2$  , the  $CO_2$  coming from the anthropogenic source has on average 30–40% less exergy. To improve the climate change condition of  $CO_2$  , we can use the advantage of this project. It is easy to store more than 400 kg of extra carbon dioxide per barrel of oil produced through this.

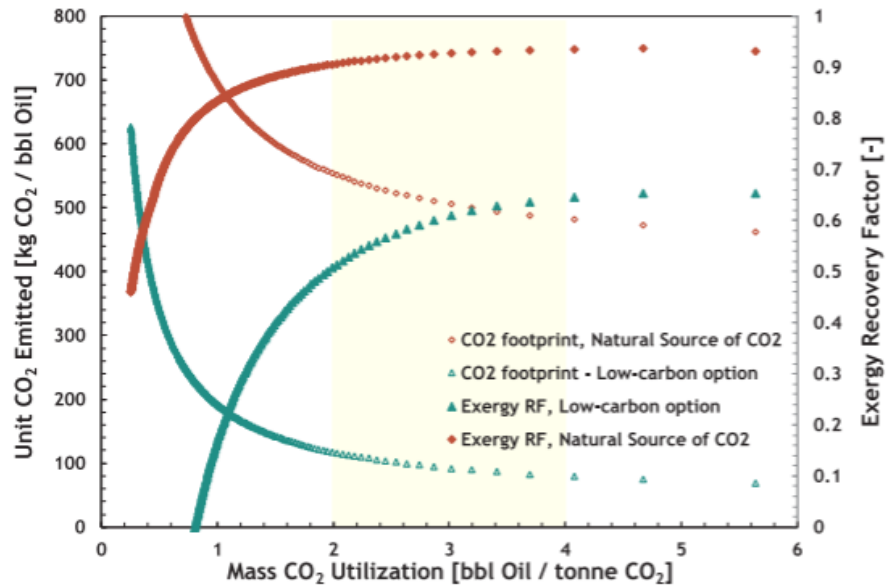


Figure-9: Exergy recovery factor as a function of gross mass  $CO_2$  utilization factor

The exergy of a system is the work that can be extracted from the system. It is a measure of how much exergy it takes to heat water at 1 degree Celsius. The less work it takes to heat water, the better. In this section, we will look at an example of how the  $CO_2$  Enhanced oil recovery gas separation method may affect the exergy recovery factor. The amount of exergy released in a certain process depends on what is happening with the molecules in the process. For example, when methane and oxygen burn together and form carbon dioxide and water, they release exergy, while when methane and oxygen combine into ethane and hydrogen, they use up exergy. Increasing  $CO_2$  emissions and their effects on the environment is a concern that we cannot ignore. There are various methods to capture and store the emissions before they reach the atmosphere. One such method is by using  $CO_2$  Enhanced Oil Recovery. It is a process of inserting  $CO_2$  into an oil reservoir, which helps to raise the pressure, increasing the production rate of oil from the well. A gas separation method is used to separate methane from  $CO_2$ . Methane is then burned, which leads to the  $CO_2$  being released into the atmosphere. The exergy recovery factor is changed by gas separation. The gross mass  $CO_2$  utilization factor also changes with the separation of methane, leading to more  $CO_2$  in oil combustion.

Fig(10) shows the effect of gas separation on the exergy recovery factor. There is a little problem because the gas separation is energetically expensive due to the high specific exergy of methane(2.5 MJ/kg). Here Fig(11) shows the connection between exergy recovery factor and mass  $CO_2$  utilization factor. At present,  $CO_2$ , extracted from natural sources, is used in  $CO_2$  enhanced oil recovery projects because we can get pure  $CO_2$ . Therefore, little exergy is consumed. This effect can be seen in Fig.(10). The solid black line in Fig.(10) indicates the effect of exergy of capture on the exergy outcome of the  $CO_2$  EOR project for Scenario 2.

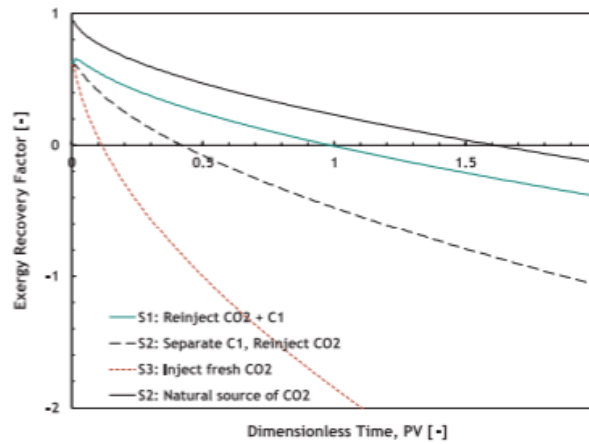


Figure-10: Effect of gas separation on exergy recovery factor for case-II

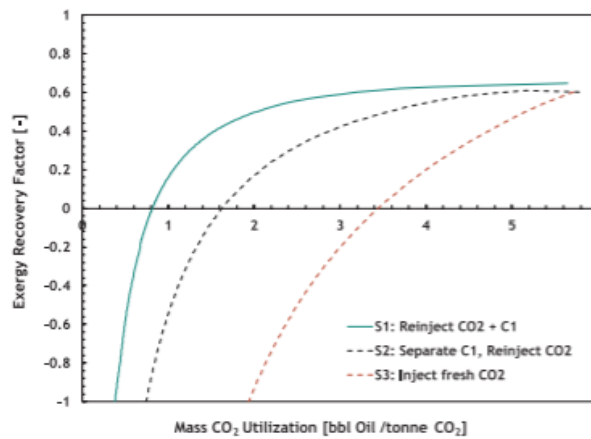


Figure-11: Exergy recovery factor as function of gross mass  $CO_2$  for case-II

## Concluding Remarks

In this paper, we analysed and understood circumstances that are exergetically efficient to store  $CO_2$  through enhanced oil recovery (EOR). We explored several large scale examples of  $CO_2$ -EOR with a modified Koval method to estimate the oil production cases. Our system included  $CO_2$  capture, initial compression at capture site, transport to oil field, re-compression in oil field, water injection, separation of gas stream, and oil and gas production from the reservoir. We can draw the following conclusions from this study:

- We can assess the life cycle of  $CO_2$ -EOR using the exergy concept. The carbon footprint of each stage can also be quantified.
- The exergy recovery factor decreases with time. This factor is the ratio between produced exergy corrected for material and process exergy requirements for its extraction.
- Depending on the fuel type, around 0.43-0.94 kg of  $CO_2$  is re-emitted into the atmosphere per kg of  $CO_2$  stored.
- For CCS to be efficient, we need to
  - Reduce exergy consumption in  $CO_2$  separation
  - Use low carbon source of energy



- Thermodynamically,  $CO_2$  EOR with CCS is unsustainable as the process consumes more exergy than the exergy produced from oil.
- Currently,  $CO_2$  utilization factor is around 2-4 bbl-oil/t $CO_2$  in most of the factories. For that much  $CO_2$  utilization range, about half of the exergy produced from oil will need to be invested for  $CO_2$  capture.
- Although there is less exergy extraction using  $CO_2$ -EOR method, it leads to the storage of more than 400 kg of extra  $CO_2$  per barrel of oil.
- The highest exergy recovery factor is obtained when we reinject the production gas stream to the reservoir without separation.

To conclude, We need to improve the  $CO_2$  utilization factor by using performance and mobility control techniques to reduce the  $CO_2$  footprint of  $CO_2$ -EOR projects.

## Appendix-A: Exergy

The exergy is the amount of useful work available in the system with reference to dead state. The dead state is defined as the one which is in thermal and mechanical equilibrium and at rest relative to the environment.

In other words, the exergy is the maximum theoretical work obtainable from the overall systems consisting of a system and the environment as the system comes into equilibrium with the environment. (passes to dead state)

This exergy is a function of temperature, pressure, composition, potential energy and kinetic energy of substance and dead state. The exergy of the dead state is zero.

For our Calculations, we can take dead state at  $T_o = 298.15\ K$  and  $P_o = 1\ bar$ .

Also,

$Ex \rightarrow$  Exergy of System (J)

$\dot{Ex} \rightarrow$  rate of change of exergy(J/s)

$ex = \frac{\dot{Ex}}{\dot{m}} \rightarrow$  Specific Exergy (J/kg)

Thus, exergy transfer for material streams is,

$$\dot{Ex} = \dot{Ex}^{ke} + \dot{Ex}^p + \dot{Ex}^{ph} + \dot{Ex}^{ch}$$

where,

$\dot{Ex}^{ke} = \frac{\dot{m}V_0^2}{2} \rightarrow$  kinetic exergy rate

$V_0 \rightarrow$  Speed of stream

$\dot{m} \rightarrow$  mass flow rate

$\dot{Ex}^p = \dot{m}gZ_0 \rightarrow$  Potential exergy rate

$g \rightarrow$  acceleration due to gravity

$Z_0[m] \rightarrow$  Stream altitude above sea level

$\dot{Ex}^{ph} [J/s] \rightarrow$  Thermo-mechanical exergy

$\dot{Ex}^{ch} [J/s] \rightarrow$  Chemical Exergy

Now,

$$ex^{ph} = h - h_0 - T_0(s - s_0)$$

Taking ideal gas assumption with constant heat capacity  $C_P$ ,

$$ex_{gas}^{ph} = C_P T_0 \left( \frac{T}{T_0} - 1 - \ln \frac{T}{T_0} \right) + R T_0 \frac{P}{P_0}$$

Assuming constant heat capacity  $c$  for solids and liquids,

$$ex_{is}^{ph} = c \left[ (T - T_0) - T_0 \ln \frac{T}{T_0} \right] - v_m (P - P_0)$$

where  $v_m [m^3/mol] \rightarrow$  molar volume of substance at temperature  $T_0$

$$\dot{Ex}^{ch,0} = \Delta_f G^0 + \sum_{el} n_{el} \dot{Ex}_{el}^{ch,0}$$

where,

$\Delta_f G^0 \rightarrow$  Standard Gibbs energy of formation [J]

$n_{el} \rightarrow$  number of moles of element per unit compound

$\dot{Ex}_{el}^{ch,0} \rightarrow$  Standard chemical exergy of element [J/mol]

The chemical exergy of a mixture with composition  $x_i$  is,

$$\dot{Ex}^{ch} = \Delta_{mix} H + \sum_i x_i \dot{Ex}_i^{ch,0}$$

where  $\Delta_{mix} H$  is enthalpy of mixing.

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