

Faculty of Chemical Engineering

PhD in Chemical Engineering

INVOLVING SAFETY IN THE OPTIMAL DESIGN OF CHEMICAL PROCESSES

PHD THESIS

To obtain the degree of Doctor of Science in Chemical Engineering presents:

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DISSERTATION

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SUMMARY

The economic factor is often the determinant one in the design of a chemical process; however, the current problem related to environmental damage and social problems, demands to include criteria that consider a sustainable design. The social and environmental impacts of a process can be measured from the risk that this has, due to the fact that when a catastrophe occurs, it causes the loss of human lives as well as damage to the ecosystem surrounding the process. The current trend in the design of a process consists in the formulation of Multi-objective optimization problems that allow to obtain an economic design involving low safe and of low environmental impacts. These formulations should allow us to find balanced solutions among these objectives, having as main attribute the selection of the best operating conditions, capacity and location, and in general the process design, taking into account the specifications and restrictions for each objective. The ideal is to formulate quantitative models based on the physical properties of the substances, allowing in this way to find numerical solutions that satisfy these three objectives. Thus, for the economic and environmental objectives, there are widely developed metrics, which are able to quantify the impact of a proposed solution. On the other hand, the metrics developed to measure the risk of a process allow to propose solutions that guarantee a lower consequence in the event that an accident is caused or the reduction of the frequency of occurrence of an accident. The way in which the concept of safety is incorporated in the design of a chemical process depends to a great extent on the type of process, the information available and the scope of the other objectives. The above indicates that the safety strategy to be used in the design of a process varies, being able to apply a combination of these or one, in greater proportion. In this way, the objective of this work is to show in detail how the concept of safety is involved since the design stage. The present work was divided into two works, where, in each work, a different problem is addressed. The first one is related to the process of production of syngas using shale gas as raw material; in this work, the main objective was to determine the best technology available to produce syngas, considering cost and safety as decision criteria. The second work consists in a multi-objective optimization problem, which accounts for selecting the best working fluid for the optimal operation of a Rankine cycle used for the conversion of geothermal to electrical energy. The idea is to select the best fluid between hydrocarbons and refrigerants, which provides the best efficiency, the lowest risk and environmental impact. In each of the two chapters explains in detail the manner in which each of the objectives are considered and their objective functions are formulated.

Keywords: Optimal design, safety, sustainability, optimization, processes.

RESUMEN

El factor económico es tradicionalmente el determinante en el diseño de un proceso químico; sin embargo, el problema actual relacionado con el daño ambiental y los problemas sociales, exige incluir criterios que consideren un diseño sustentable. Los impactos sociales y ambientales de un proceso se pueden medir a partir del riesgo que esto tiene, debido al hecho de que cuando ocurre una catástrofe, causa la pérdida de vidas humanas y daños al ecosistema que rodea el proceso. La tendencia actual en el diseño de un proceso consiste en la formulación de problemas de optimización multi-objetivo que permitan obtener un diseño económico que implique un bajo riesgo e impacto ambiental. Estas formulaciones deben permitirnos encontrar soluciones equilibradas entre estos objetivos, teniendo como principal atributo la selección de las mejores condiciones de operación, capacidad y ubicación, y en general el diseño del proceso, teniendo en cuenta las especificaciones y restricciones para cada objetivo. Lo ideal es formular modelos cuantitativos basados en las propiedades físicas de las sustancias, permitiendo de esta manera encontrar soluciones numéricas que satisfagan estos tres objetivos. Por lo tanto, para los objetivos económicos y ambientales, existen métricas ampliamente desarrolladas, que pueden cuantificar el impacto de una solución propuesta. Por otro lado, las métricas desarrolladas para medir el riesgo de un proceso permiten proponer soluciones que garanticen una menor consecuencia en caso de que se produzca un accidente o la reducción de la frecuencia de ocurrencia de un accidente. La forma en que se incorpora el concepto de seguridad en el diseño de un proceso químico depende en gran medida del tipo de proceso, la información disponible y el alcance de los otros objetivos. Lo anterior indica que la estrategia de seguridad a ser utilizada en el diseño de un proceso varía, pudiendo aplicar una combinación de estos o uno, en mayor proporción. De esta forma, el objetivo de este trabajo es mostrar en detalle cómo se involucra el concepto de seguridad desde la etapa de diseño. El presente trabajo se dividió en dos trabajos, donde, en cada trabajo, se aborda un problema diferente. El primero está relacionado con el proceso de producción de gas de síntesis utilizando gas de esquisto como materia prima; en este trabajo, el objetivo principal fue determinar la mejor tecnología disponible para producir gas de síntesis, considerando los costos y la seguridad como criterios de decisión. El segundo trabajo consiste en un problema de optimización multi-objetivo, que considera la selección del mejor fluido de trabajo para la operación óptima de un ciclo de Rankine utilizado para la conversión de energía geotérmica a energía eléctrica. La idea es seleccionar el mejor fluido entre los hidrocarburos y los refrigerantes, que proporciona la mejor eficiencia, el menor riesgo y el impacto ambiental. En cada uno de los dos capítulos se explica en detalle la manera en que se consideran cada uno de los objetivos y se formulan sus funciones objetivo.

Palabras Clave: Diseño Óptimo, Seguridad, Sustentabilidad, Optimización, Procesos.

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NOMENCLATURE

Scripts

- d distance of interest for risk assessment.
- h accident that can occur in the components of the Rankine cycle.
- i working fluid.
- j cycle component (turbine, condenser, pump and evaporator).

Sets

- I set for is the set of working fluids which is comprised of hydrocarbons and refrigerants.
- J set for equipment that integrates the binary power cycle.

Binary variables

- Y_i binary variable associated with the existence of the working fluid i .

Greek Symbols

- ξ recovery factor.
- δ operating lifetime of the cycle in years.
- ΔT_w temperature gradient.

Variables and Parameters

Annual Sale Revenue revenues due to sales of syngas, \$/year.

- α_i constant associated to the calculation of the emission flow rate for the compound i in the liquid phase.

BLEVE boiling liquid expanding vapour explosion.

- b_i constant associated to the calculation of the emission flow rate for the compound i in the liquid phase.

$\bar{C}_{R,U}^{out}$ set data of costs to technology U, \$.

$CRRISK_j$ individual risk due to a continuous release.

$CTR_{i,j}$ concentration in ppm at the distance d for working fluid i .

CP_w heat capacity of water.

D	carbon dioxide price, \$/kg.
DR	dry reforming.
$DRJF_{i,j}$	radiation dose for fluid i and unit j due Jet Fire in kW/m ² .
$DRPF_{i,j}$	radiation dose for fluid i and unit j due Pool Fire in kW/m ² .
$ENVIRONMENTAL_{MAX}$	maximum environmental impact.
$EPEC$	amount of gr CO ₂ /kWhr produced by the combustion of coal.
EP	energy price (heating or cooling) \$/MMJ.
EW	emissions of CO ₂ due to the use of water in the condenser.
FM_i	mass flow for the working fluid.
FC	fixed cost, \$.
$f_{H_2}^{SR-out}$	flowrate of hydrogen produced in SR, kmol/hr.
f_{co}^{SR-out}	flowrate of carbon monoxide produced in SR, kmol/hr.
$f_{H_2}^{POX-out}$	flowrate of hydrogen produced in the POX, kmol/hr.
$f_{co}^{POX-out}$	flowrate of carbon monoxide produced by POX, kmol/hr.
$f_{H_2}^{DR-out}$	flowrate of hydrogen produced in DR, kmol/hr.
f_{co}^{DR-out}	flowrate of carbon monoxide produced in DR, kmol/hr.
f_i	incident outcome frequency events/year.
$f_{R,U}^{inlet}$	set data of reactant flowrate R (D,O and S), kmol/hr.
$f_{SG,U}^{inlet}$	set data of shale gas flowrate SG, kmol/hr.
$f_{P,U}^{out}$	set data of flow rates to technology U, kmol/hr.
$f_{R,U}^{optimal}$	set data of optimal reactants flowrates to technology U, kmol/hr.

$F_r^{inlet-well}$	flowrate of shale gas to the mixer, kmol/hr.
$F^{Total-inlet-SG}$	total flowrate of shale gas to be converted into syngas, kmol/hr.
$f^{SR-inlet}$	flowrate of shale gas sent to SR, kmol/hr.
$f^{POX-inlet}$	flowrate of shale gas sent POX, kmol/hr.
$f^{DR-inlet}$	flowrate of shale gas sent to DR, kmol/hr.
f_j^l	frequency of occurrence of a continuous release in liquid phase.
f_j^g	frequency of occurrence of a continuous release in gas phase.
$f_{i,j,h}$	frequency of occurrence of accident h .
G	shale gas price \$/kg.
GVP	profits from energy sales.
GVP_{MAX}	maximum profits from energy sales.
GWP_i	global Warming Potential indicator.
H	working hours in a year, hr/yr.
$HAZOP$	hazard and operability.
HH_i	constant related to the calculation of toxic concentration for the fluid i .
$h_{3,i}$	enthalpy exchanger outlet.
$h_{2,i}$	enthalpy exchanger inlet.
$h_{1,i}$	enthalpy condenser outlet.
$h_{4,i}$	enthalpy condenser outlet.
h_{inject}	enthalpy of the brine at the inlet of the heat exchanger.
$h_{production}$	enthalpy of the brine at the outlet of the heat exchanger.
I	radiation intensity, kW/m ² .
$IR_{x,y}$	individual risk in the coordinates x,y.

$IRRisk_j$	individual risk due to an instantaneous release.
$IR_{i,j,d}^{IRRisk}$	risk due to an instantaneous release of the fluid a to the distance d .
$IR_{i,j,d}^{CCRRISK}$	risk due to a continuous release of the fluid a to the distance d .
$IR_{i,j,d,h}^{CCRRISK}$	risk due to a continuous release of the fluid a to the distance d , for the accident h .
$IR_{i,j,d,h}^{IRRisk}$	risk due to an instantaneous release of the fluid a to the distance d , for the accident h .
j_i	constant related to the calculation of the overpressure for fluid i .
$J_w^{SR-inlet}$	flowrate of water used in SR, kmol/hr.
$J_o^{SR-inlet}$	flowrate of oxygen used in POX, kmol/hr.
$J_d^{SR-inlet}$	flowrate of carbon dioxide used in DR, kmol/hr.
$k1$	constant Probit function.
$k2$	constant Probit function.
k_f	annualization factor, 1/yr.
$K6_i$	constant related to the calculation of the dose of radiation due Jet Fire for the fluid i .
$K7_i$	constant related to the calculation of the dose of radiation due Jet Fire for the fluid i .
$K8_i$	constant related to the calculation of the dose of radiation due Jet Fire for the fluid i .
$K11_i$	constant related to the calculation of the dose of radiation due Pool Fire for the fluid i .
$K10_i$	constant related to the calculation of toxic concentration for the fluid i .
$LC_{50i,j}$	lethal dose 50
$MCO2$	mitigation of CO ₂ due to the energy generated by the use of geothermal resources.

$MMBTU$	one million of British thermal unit.
m_{brine}	flow of brine inlet in the heat exchanger.
$NETPROFIT$	net profit in the production of syngas, \$/yr.
N_i	constant associated to the calculation of the emission flow rate for the compound i in the gas phase.
O	oxygen price \$/kg.
$OVCE_{i,j}$	overpressure due blast.
p	overpressure peak, N/m ² .
P	damage probability.
$P_{x,y,i}$	damage probability of outcome incident at coordinates x,y.
P^{SR-out}	operation pressure of the steam reformer reactor, MPa.
$P^{POX-out}$	operation pressure of the POX reactor, MPa.
P^{DR-out}	operation pressure of the DR reactor, MPa.
POX	partial oxidation.
P_U^{inlet}	set data of pressure to technology U, Pa.
$P_U^{optimal}$	set data of optimal pressures to technology U, Pa.
PM_w	molecular weight of water.
PM_i	molecular weight of each fluid.
PV	selling price.
P_j	operating pressure (Pa).
$P_{i,j,d,h}$	probability of affectation due to the effect of the exposure to the physical variable caused by an accident h in the position d .
$P_{i,j,d,h}^{CCRRISK}$	probability of affectation due a continuous release.
$P_{i,j,d,h}^{IRRisk}$	probability of affectation due an instantaneous release.

\dot{Q}_U^{out}	set data of heat added or removed to technology U, J.
<i>Price Syngas</i>	price of syngas, \$/kg.
Q^{SR}	external utility for SR, J.
Q^{POX}	external utility for POX, J.
Q^{DR}	external utility for DR, J.
<i>QRA</i>	quantitative risk analysis.
Q_c	heat added by brine.
$QG_{i,j}$	is the gas phase mass flow for each working fluid and process unit in kg/s.
$QL_{i,j}$	mass flow rate of liquid phase for each working fluid and process unit in kg/s.
q_i	constant related to the calculation of the overpressure for fluid <i>i</i> .
<i>r</i>	well of shale gas.
<i>Raw Material Costs</i>	costs of raw materials, \$.
$RCRisk_j$	individual risk of each element <i>j</i> .
<i>S</i>	water steam price \$/kg.
S_i	constant related to the calculation of the dose of radiation due Pool Fire for the fluid <i>i</i> .
<i>SR</i>	steam reformer.
<i>TEWI</i>	total Equivalent Warming Impact.
<i>TotalRisk</i>	total individual risk of the cycle.
$TotalRisk_{MAX}$	maximum total individual risk.
T_j	operating temperature (K)
<i>t</i>	time duration of the leak
<i>t</i>	exposure time, s.
$\dot{T}_U^{optimal}$	set data of optimal temperatures to technology U, K.

T_U^{inlet}	set data of temperature to technology U, K.
T^{SR-out}	operation temperature of the SR reactor, K.
$T^{POX-out}$	operation temperature of the POX reactor, K.
T^{DR-out}	operation temperature of the DR reactor, K.
<i>Technology Cost</i>	cost of technology, \$.
U_i	constant associated to the calculation of the emission flow rate for the compound i in the gas phase.
<i>Utilities Costs</i>	costs of external utilities, \$.
V_i	constant related to the calculation of toxic concentration for the fluid i
V	variable physical (overpressure, toxicity and radiation).
VC	variable cost, \$.
VCE	vapour cloud explosion.
W_i	power generated annually by the cycle in MW / year.
w_i	constant related to the calculation of the dose of radiation due Pool Fire for the fluid i .
$YDR_{i,j}$	probit value due to exposure to thermal radiation.
$YOVC_{i,j}$	probit value due to exposure to overpressure.
x_i	constant related to the calculation of the overpressure for fluid i .
x,y	coordinates.
Y	Probit value.
Z_i	constant associated to the calculation of the emission flow rate for the compound i in the gas phase.

CHAPTER 1

Introduction

1.1 Introduction

Throughout history a large number of accidents have been reported, which have left as a main consequence, the loss of human lives. The one that occurred in San Juan Ixhuatepec in 1984, which caused the death of more than 500 people. Another example is the explosion at the polyethylene plant in Pasadena, Texas in 1989. Several factors contribute to the occurrence of an accident, the human factor accounts for 88% of the causes, the design or engineering 10% and the remaining 2% corresponds to natural causes. If safety is involved as a simultaneous criterion from the design stage, it is possible to reduce or avoid the consequence associated with an accident. Poor design can cause the effects of an accident potentializing or increase the probability that it occur. In this sense, designs should be proposed that help to minimize the level of risk associated with the design of a chemical process from the design stage. However, it is necessary to mention that zero risk does not exist, that is, whenever there is a given process, there will be a hazard and with it a risk. In this way, when the risk in a given process is reduced, it is said that the risk of this process was reduced to an acceptable level, but not totally eliminated. There are currently four main approaches that aim to reduce risk at the design stage or in the process operation:

Passive: Passive safety systems are those that control hazards with process or equipment design features without additional, active functioning of any device. For example, a containment dike around a hazardous material storage tank limits a spill to an enclosed area because of the geometry and construction of the dike, and no action is required to provide this function.

Active: Active safety systems control hazards through controls and systems designed to monitor and maintain specific conditions or to be triggered by an event. Active systems include process controls, safety instrumented systems (SIS), and mitigation systems. A sprinkler system put in place to extinguish a fire is an example of an active system designed to minimize consequences. A control system that regulates solvent flow into a reactor vessel and prevents overflow is an example of a monitoring system.

Procedural: Procedural safety systems control hazards through personnel education and management. Such systems include standard operating procedures, safety rules and procedures, operator training, emergency response procedures, and management systems. For example, an operator may be trained to monitor the solvent level in a reactor vessel and to shut off the feeds to the tank if the volume exceeds a given quantity.

In general, inherent and passive strategies are the most robust and reliable, requiring the least monitoring or interaction to be effective, but incorporation of strategies from all tiers of the hierarchy should be considered and incorporated as needed for comprehensive PSM. Note that all process safety controls have the potential to reduce the probability or likelihood that a worst-case accident.

1.2 Inherent safety

Inherent safety is a concept, an approach to safety that focuses on eliminating or reducing the hazards associated with a set of conditions. A chemical manufacturing process is inherently safer if it reduces or eliminates the hazards associated with materials and operations used in the process. The process of identifying and implementing inherent safety in a specific context is called inherently safer design. A process with reduced hazards is described as inherently safer compared to a process with only passive, active, and procedural controls (CCPS, 2008b). The inherent approach to hazard control is to minimize or eliminate the hazard. Substituting water for a flammable solvent to eliminate the fire hazard is an example. CCPS identifies four ISP strategies to consider when designing or modifying a process (CCPS, 2008b). As adapted from that volume, one can:

Substitute: use materials, chemistry, and processes that are less hazardous;

Minimize: use the smallest quantity of hazardous materials feasible for the process, reduce the size of equipment operating under hazardous conditions, such as high temperature or pressure;

Moderate: reduce hazards by dilution, refrigeration, process alternatives that operate at less-hazardous conditions; reduce potential impact of an accident by siting hazardous facilities remotely from people and other property; or

Simplify: eliminate unnecessary complexity, design “user-friendly” plants.

As mentioned above, this approach is one of the most robust since it aims to reduce or eliminate risk rather than controlling it. Previously the processes were designed considering strategies associated with risk control (active and procedure). It is noteworthy that the approach taken in the development of the models presented in this work, to minimize the risk lies within this concept, because a model that minimizes risk from the design stage is proposed.

To measure the effectiveness of the application of a risk safety strategy, metrics are used related to the damage that a person may suffer in a certain position due to the effects of an accident. The methodologies that allow to know the value of this damage, are the risk analyzes. These can be quantitative or qualitative, a qualitative risk analysis is based on the identification of the hazards existing in a system and the determination of their causes, providing qualitative characteristics of the risks associated to a certain process, without quantifying the consequence. It is necessary to mention that to carry out a quantitative risk analysis, is an expensive and laborious analysis. An analysis of qualitative watering can I be practical or laborious, however, depending on the initial objectives can be achieved adequate results to identify hazards usually simple in comparison with quantitative requiring more information, methods of qualitative analysis more employees are HAZOP, CHECK LIST, WHAT IF, among others. The above qualitative methods identify the risks and their causes, however once all the risks have been identified, it is usually necessary to decide which risks are to be addressed, and to which risks it is necessary to give priority, since some risks represent stronger impacts than others and in industries it is not always possible to address all the existing risks. However, with qualitative methods it is not always obvious or simple to take these determinations, so one of the advantages of quantitative risk analysis (QRA), over qualitative is this since numerically the risks are identified and measured making it possible to weight them and in turn giving one more element to decide where it is more feasible to invest when the industry does not have enough capital to cover all the risks. The QRA provides more information about the risk being evaluated, as it is not only possible to determine the consequence but also the probability of an accident occurring. An QRA provides the numerical value that measures the risk, being able to know in this way the level of risk of a process and thus to compare it with another

1.3 Quantitative Risk Analysis (QRA)

Quantitative Risk Analysis (QRA), is a tool whose specific objective is the quantitative review of the risks that can arise in a process. This tool helps to quantify the different risks that may occur in a particular process industry, which is the most important reason for the application of Quantitative Risk Analysis methodology. Identify scenarios of incidents and their consequences and impact by probabilities and frequencies as well as the impact they generate they are broadly the requirements of a quantitative risk analysis. In the last 15 years, the ARC methodology has evolved greatly since it began in the aerospace, electronics and nuclear industries. The most extensive risk analyzes of potential catastrophes have been conducted in the nuclear industry. The QRA is a simple concept that offers methods to answer the following four questions:

- 1.-What can go wrong?
- 2.-What are the causes?
- 3.-What are the consequences?
- 4.-What is the probability that happen?

A relative application of QRA is the comparison of strategies for risk reduction. Some organizations also use QRA in an absolute sense to confirm that risk-related goals have been achieved: A greater risk reduction, beyond previous goals, may be appropriate where a cost-effectiveness analysis permits. The application of the entire set of QRA techniques involves a quantitative review of the hazards that can be encountered in a facility, ranging from frequent incidents of low consequences to large and unusual incidents using a uniform and consistent methodology. Once risk processes are identified, QRA techniques can help focus risk control studies. The major contributors to risk can be identified, and recommendations can be made and decisions made on corrective measures on an objective and consistent basis. QRA is an emerging technology within the CPI and there are variations of terminology in the published literature, which can lead to confusion. For example, while "risk" is defined as "a measure of economic or human loss in terms of possibility of the incident and magnitude of loss", readers should be aware that other definitions are also used. For example, Kaplan and Garrick (1981) have discussed an infinity of possible definitions of "risk". Thus, it is said that:

- Risk is a combination of uncertainty and damage.
- Risk is a ratio of hazards and safety measures.
- Risk is a triple combination of event, probability, and consequence.

In QRA, risk is defined according to the proposed scenario, the consequence and estimated frequency:

$$Risk = F(s, c, f)$$

Although a quantitative risk analysis evaluates the impact of the consequences of the incidents, it is used for other objectives such as the implementation of strategies for the reduction of risk and to confirm that an area is safe, it provides knowledge on which both must be reduced the risk to be considered acceptable and in this way the risk reduction is favored when a cost study is done effectively.

1.4 Justification

Safety approach used and the development of an adequate metric are the main factors that must be considered in the design of a safe process. In design and operation mode, the ideal is to use an approach that avoids or attacks the accident in the initiation stage, thus avoiding a propagation obtaining in this way a minor or null consequence. Inherent and passive approaches are considered the most robust, they generate more efficient designs, because they reduce or eliminate hazards. Once the safety approach to be used in the design has been selected, it is necessary to evaluate the performance of this. The above leads to generate a metric that additionally allows dimensioning and establishing the operating policies of a process. The metrics commonly used are social risk and individual risk, the main characteristic of these metrics, is that they allow precisely establish relationships between risk, operating conditions and the sizing of a process. This favors the formulation of mathematical models that allow to find the conditions of a process that guarantee a minimum risk. Currently, the concept of sustainability requires simultaneously considering the environmental, economic and social aspects. The social aspect can be evaluated through risk, if it is quantified according to the damage to people. Including a risk function that allows a safe design, represents a complicated task because it is generally necessary to couple the degrees of freedom involved in the objective economic and environmental function in the safety. Obtaining an expression that allows to optimize the decision variables from the point

of view of safety. Generally, the risk is an objective that is opposed to the economic factor, because the solutions contemplate values that represent safer operating conditions (pressures and low temperatures), which does not represent adequate values for the economic function since it is translated into low yields or efficiencies. In some cases, safety does not contradict the economic and environmental objective. That is, the most economical designs correspond to the safest ones. In order to illustrate the aforementioned, two papers are presented that show the effect of the incorporation of safety in the design. The first job consists of the selection of the most appropriate technology for the production of syngas, in this, the safety aspect was considered as a post-optimization analysis, where the optimal conditions that provide better qualities of syngas at the lowest cost were evaluated. On the other hand, in the second work a multiobjective approach is considered, for the selection of the best working fluid in a rankine cycle, with application to geothermal energy. The importance of involving safety in the selection of the working fluid lies in the nature of the candidate fluids, which present dangerous characteristics capable of causing damage. Both works are described in detail in chapters 1 and 2.

1.5 Objective of this Thesis

The general objective of this Thesis is to develop strategies to account for the safety issue since the first stage in the chemical process design. Particularly, the following specific objectives have been considered:

- A new method for the accounting safety as objective of design in the processing of shale gas for syngas production must be development.
- Safety is going to be accounted for in the optimal design of geothermal facilities for the selection of working fluids.

1.6 Hypothesis.

Involving safety since the first stage in the optimal design of chemical processes will produce new sustainable processes, since the obtained design must account for economic, environmental and social aspects, decreasing this way the potential damages (economic, environmental and social) for the consequence of an accident.

CHAPTER 2

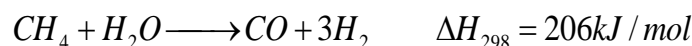
Optimization of the Production of Syngas from Shale Gas with Economic and Safety Considerations

Reforming is an essential technology for the monetization of shale gas through the production of syngas. Steam reforming, partial oxidation, dry reforming, or combined reforming may be used. Traditionally, $H_2:CO$ ratio, yield or economic criteria have been used to select the type of reforming technology. The operating conditions, the nature of the reactions and compounds produced in the reforming technologies create the necessity to know the level of risk presented by these technologies. Thus, this paper introduces an approach for the optimal selection and design of reforming technologies incorporating economic aspects. A quantitative risk analysis is applied to the obtained solutions for evaluating the risk. The approach optimally selects the technology or set of technologies and operating conditions required to comply with a specific quality of syngas, maximizing the net profit. The optimization model was solved using genetic algorithms in the MATLAB® platform coupled with the ASPEN Plus® software for process and thermodynamic modeling. The results show that the steam reforming is the best technology to reach the highest quality of syngas with the lowest risk for the simulated conditions.

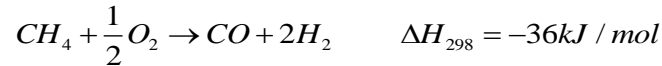
2.1 Introduction

Recently, shale gas production has drastically increased from an average growth of 2.7% per year from 1995-2000 to 47.9% per year from 2005-2011 (EIA, 2013). With the continued growth, shale gas is estimated to provide up to 50% of the production of natural gas for 2040 (EIA, 2015). This tendency is expected to continue because of the increasing demands for energy and feedstocks for chemical manufacturing (Lozano-Maya, 2013). Specifically, the interest in shale gas is attributed to technical, environmental, and economic benefits compared with other forms of fossil fuels (Choi et al., 2014). Since shale gas can be converted into a multitude of value-added chemicals, it is anticipated to reshape the process industries in the US and around the world (Sirola, 2014), hydrogen production from shale gas is a clear example (Noureldin and El-Halwagi, 2015). Other examples include the production of syngas (Julian-Duran, 2014), ethylene (Thiruvankataswamy et al., 2016), ethylene using flue gases (Dinh et al., 2014), propylene (Jasper and El-Halwagi, 2015), methanol and gas to liquid processes (Bao et al., 2010), transportation fuels (Gabriel et al., 2014), Fischer Tropsh products (Martinez., et al 2013) and other petrochemicals (Bamufleh et al., 2016). In all of these monetization pathways, reforming of shale gas into synthesis gas (syngas) is a central chemical pathway. The selection of type and operating variables for reforming is essential in the optimal design of the process, and this impacts the technical, economic, environmental and safety attributes of the process (Noureldin et al., 2014).

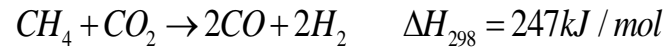
There are four primary types of reforming that can be used to transform shale/natural gas into syngas. The alternatives are steam reforming (SR), partial oxidation (POX), dry reforming (DR) and combined reforming (CR). These reforming approaches require different reactants (oxygen, steam, carbon dioxide), external utilities (heating and cooling) and operating conditions (pressure and temperature) to produce syngas with different $H_2:CO$ ratios, costs of production and levels of security due to the material inventories and operating conditions. In SR, shale/natural gas reacts with steam in the presence of a catalyst (Angeli et al., 2016) as follows:



The reforming reaction is highly endothermic and requires a large amount of energy (Zhu et al., 2015). It is particularly attractive for the production of hydrogen or the production of syngas with a high H₂:CO ratio. Partial oxidation is an exothermic reaction, using oxygen as an oxidizing agent. It has advantages for usage for production of hydrogen and syngas at small and medium capacities (Al-Musa et al., 2015) and H₂:CO ratios around 2 (Ding et al., 2015) through the following reaction:



Dry reforming is a catalytic endothermic reaction that converts methane and carbon dioxide into syngas. It is particularly attractive in managing greenhouse gas emissions through CO₂ to produce syngas at low H₂: CO ratios (around 1), which is suitable for several applications (Noureldin et al., 2015) or may be combined with other reforming technologies (Ay and Uner, 2015):



Other methodologies proposed for the production of syngas are based on the use of biomass as raw material (Richardson et al., 2015), these have focused on the improvement and modification of existing processes to improve the quality of syngas (Haro et al., 2016). Purification of syngas obtained from biomass using magnesite as bed material has been studied (Siedlecki and Jong, 2011). Traditionally, natural gas is the main raw material and the most used technologies have been steam reforming (SR), partial oxidation (POX) and dry reforming (DR). Nowadays, research for the production of syngas is directed to the use of new raw materials, purification as well as the development of new technologies (for example SMR membrane (Shahhosseini et al., 2016)).

Although several efforts have been made to improve these reforming technologies from different perspectives, the selection and optimization of the appropriate option for a particular application is not a trivial task because it depends on several intertwined factors.

In previously reported works for the selection and design of reforming technologies such as the one reported by Noureldin et al. (2014), the optimization step has been performed with simplified thermodynamic models and design equations.

In addition, the conventional approaches have focused on economic and environmental issues. It is important to assess the safety of the processes, especially given the potential for fire and explosion. Thus, in this work a systematic procedure for the selection of reforming technologies and operating conditions for specific syngas ratios is carried out, then a risk assessment is performed to determine the level of risk of the proposed approaches.

2.2 Problem Statement

Fig. 2.1 shows the key aspects of the problem statement. Shale gas is extracted from a set of wells, then it is mixed (M1) to yield a total flowrate of shale gas ($F^{Total-inlet-SG}$) with an average composition ($F^{Total-inlet-SG}$). Then, this stream can be divided and fed to one or more of the candidate reforming technologies: SR, POX, DR, and CR (which represents a combination of at least two of the available technologies) to produce syngas. Each technology has different requirements in addition to methane, such as steam for SR, oxygen for POX and CO₂ is required for DR, external utilities: heating for SR and DR or cooling for the exothermic reaction of POX, operating pressure and temperature. Each technology produces different qualities of syngas, while SR is characterized by producing high quality, POX and DR produce lower quality. The quality of syngas is an important factor that should be considered in the formulation of the problem, due to the fact that syngas is the main raw material for other processes such as Fischer-Tropsch, Methanol, ammonia, etc.; these processes require very specific quality of syngas. The quality of the syngas depends on the operating variables (pressure and temperature), feed ratio of shale gas/feedstock and catalyst, in addition to the selection of the optimal technology.

Thus, the objective is to select the optimal technology or combination of technologies that maximize the net profit, the methodology can also find the optimal values of pressure, temperature and shale gas-feedstock ratio, for the selected technology. After the optimization procedure, a QRA is applied to the obtained solutions, with the purpose of evaluating the level of risk for these solutions; this way, allowing the decision makers to consider this factor in the design process.

The proposed strategy for solving the problem is to use a hybrid platform involving Matlab® - Visual Basic® - ASPEN Plus®. The simulation parameters are generated using genetic algorithms in Matlab®, these variables are sent via Visual Basic® to the simulation platform in ASPEN Plus® to perform rigorous thermodynamic and design calculations, and the response variables are returned to Matlab® to evaluate the objective function. Finally, the risk assessment is evaluated using the software SCRI®, which are reported in a proper way to the decision makers.

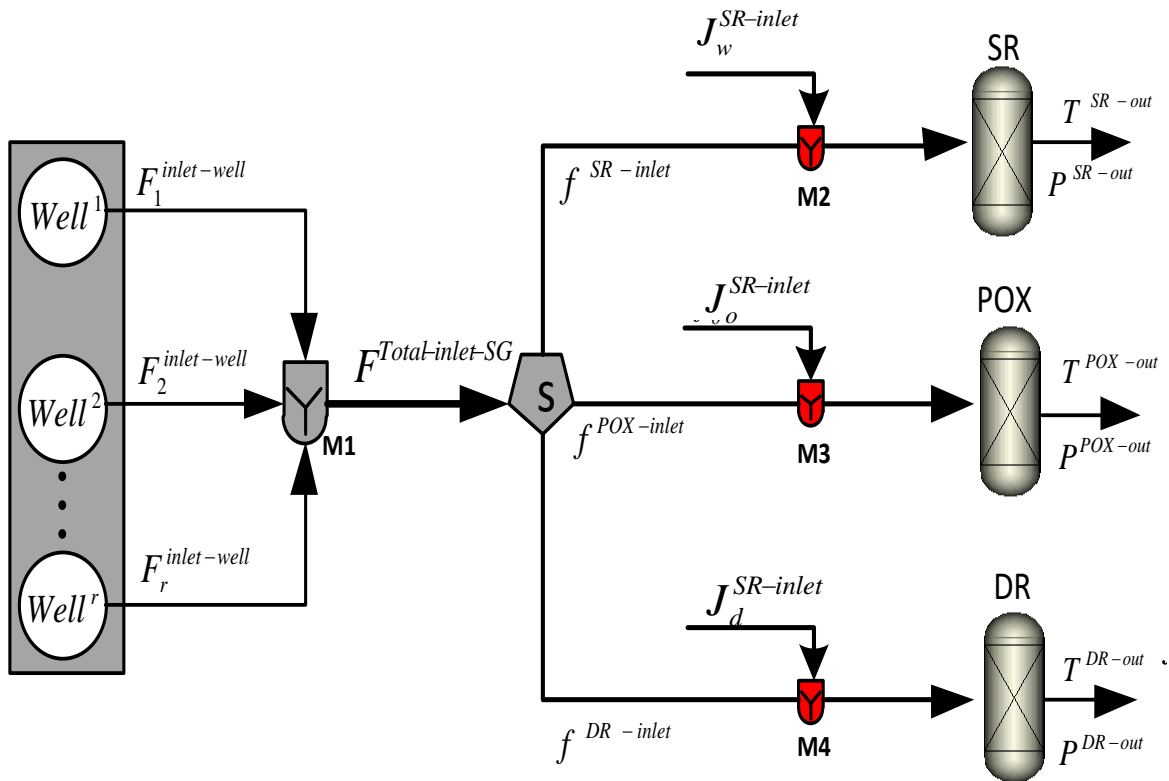


Fig. 2.1. Superstructure associated with the selection of syngas production technologies.

2.3 Model Formulation

The objective is to find the optimal technology or combination of technologies and operating conditions (Pressure and Temperature), which maximize the net profit (Netprofit) that considers the revenues from the sales of syngas (*Annual Sale Revenue*), minus the costs of raw materials (*Raw Material Costs*), external utilities (*Utilities Costs*), and annualized fixed cost (*Technology Cost*). Hence:

$$NETPROFIT = Annual\ Sale\ Revenue - Raw\ Material\ Costs - Utilities\ Costs - Technology\ Cost \quad (2.1)$$

The following is a discussion of the terms contributing to the net profit function.

Annual Sale Revenue

The economic value of syngas depends on its quality and quantity. This way, the annual revenue is obtained considering the quality of the product. The following model (obtained from reported data (Noureldin et al., 2014)) has been proposed to relate the price of syngas (*PriceSyngas*) with the ratio of the produced amounts of H₂ and CO ($f_{H_2}^{out}, f_{CO}^{out}$) as follows:

$$PriceSyngas(\$ / kg) = 0.0761 \left(\frac{f_{H_2}^{out}}{f_{CO}^{out}} \right) - 0.0009 \quad (2.2)$$

This assumption simplifies the optimization procedure, however uncertainty in the selling price of products and purchase cost of raw materials should be considered. Therefore, the revenues are given as follows:

$$Annual\ Sale\ Revenue = Annual\ Sale\ Revenue^{SR} + Annual\ Sale\ Revenue^{POX} + Annual\ Sale\ Revenue^{DR} \quad (2.3)$$

$$Annual\ Sale\ Revenue^{DR} = (f_{H_2}^{DR-out} + f_{CO}^{DR-out}) (PriceSyngas) \quad (2.4)$$

$$Annual\ Sale\ Revenue^{POX} = (f_{H_2}^{POX-out} + f_{CO}^{POX-out}) (PriceSyngas) \quad (2.5)$$

$$Annual\ Sale\ Revenue^{DR} = (f_{H_2}^{DR-out} + f_{CO}^{DR-out}) (PriceSyngas) \quad (2.6)$$

Raw Material Costs

Each technology requires different reactants (steam, carbon dioxide and oxygen) to produce syngas. The following expressions are used to evaluate the raw material costs:

$$Raw\ Material\ Costs = H (Raw\ Material\ Costs^{SR} + Raw\ Material\ Costs^{POX} + Raw\ Material\ Costs^{DR}) \quad (2.7)$$

where H corresponds to the working hours in a year.

$$Raw\ Material\ Costs^{SR} = J_w^{SR-inlet} (S) + f^{SR-inlet} (G) \quad (2.8)$$

$$Raw\ Material\ Costs^{POX} = J_o^{POX-inlet} (O) + f^{POX-inlet} (G) \quad (2.9)$$

$$Raw\ Material\ Costs^{DR} = J_d^{DR-inlet} (D) + f^{DR-inlet} (G) \quad (2.10)$$

where $J_w^{SR-inlet}$, $J_o^{SR-inlet}$, $J_d^{SR-inlet}$ are the input streams of reactants (S, O and D) to each technology and $f^{SR-inlet}$, $f^{POX-inlet}$, $f^{DR-inlet}$ are the input streams from G to each technology, respectively.

Utilities Costs

The utility cost is calculated as follows

$$Utilities\ Costs = H (Utility\ Cost^{SR} + Utility\ Cost^{POX} + Utility\ Cost^{DR}) \quad (2.11)$$

$$Utility\ Cost^{SR} = (EP)Q^{SR} \quad (2.12)$$

$$Utility\ Cost^{POX} = (EP)Q^{POX} \quad (2.13)$$

$$Utility\ Cost^{DR} = (EP)Q^{DR} \quad (2.14)$$

Technology Costs

The cost for each technology is composed of a variable cost (VC) and a fixed cost (FC), the variable part is a function of the capacity. Thus, the cost for each technology can be expressed as follows:

$$Equipment\ Cost^{SR} = k_f \left(FC + VC(f^{SR-inlet} + J_w^{SR-inlet}) \right)^\gamma \quad (2.15)$$

$$Equipment\ Cost^{POX} = k_f \left(FC + VC(f^{POX-inlet} + J_o^{POX-inlet}) \right)^\gamma \quad (2.16)$$

$$Equipment\ Cost^{POX} = k_f \left(FC + VC(f^{DR-inlet} + J_d^{DR-inlet}) \right)^\gamma \quad (2.17)$$

Flow Distribution Constraint

The model allows selecting the optimal technology or set of technologies for the production of syngas to a specific quality. The total shale gas flowrate (F_{Total}^{NG-in}) must be sent to one or more of the available technologies, this is modeled as follows:

$$F^{Total-inlet-SG} = f^{SR-inlet} + f^{POX-inlet} + f^{DR-inlet} \quad (2.18)$$

where, $f^{SR-inlet}$, $f^{POX-inlet}$ and $f^{DR-inlet}$ are inputs for each technology and $F^{Total-inlet-SG}$ is the total inlet flowrate.

2.4 Risk Assessment

The choice of a particular quality of syngas ($H_2:CO$ ratio) has a direct impact on the selection of the technology to be used. It also impacts the risk level due to the different requirements of raw materials and operating conditions of each technology. Consequently, it is important to carry out a quantitative risk analysis to include safety in the decision making for the selection of a specific process. **Fig. 2.2** shows the calculation algorithm to perform the risk assessment. The first step involves the identification of the incident(s) that can occur in the reaction units. An incident refers to the release of mass or energy. Methods such as HAZOP may be used to generate these scenarios. An event tree approach is often used to identify the possible incidents and their evolution under certain circumstances.

According to the characteristics of the incident, the nature of the released material, and the environmental conditions, the incident may evolve to an accident such as a boiling liquid expanding vapor explosion (BLEVE), a vapor cloud explosion (VCE), a flash fire or a jet fire.



Fig. 2.2. The steps for quantifying risk.

The consequences are determined based on the characteristics and conditions of each accident. It is necessary to quantify the damage that such consequences may cause to personnel and facilities. Vulnerability models are used, one of the most used is the Probit approach, which is a statistical method that represents the relationship between a probability function and a particular load to exposure of a risk. It is based on the probabilistic quantification of the vulnerability of people and facilities to physical effects of a certain magnitude that is assumed to be known. The method consists in applying statistical correlations in order to estimate the consequences associated with the magnitude of a physical variable (radiation and overpressure) caused by an accident (BLEVE, VCE and Flash Fire). This methodology allows determining the proportion of the population or facilities that would be affected due to the accident at a certain location. This way, it is associated with the likelihood of damage to a Probit value. The Probit value is determined by equation (2.19), where V represents the physical variable of the accident and $K1$ and $K2$ are constants.

$$Y = K1 + K2 \ln(V) \quad (1.19)$$

To quantify the damage, Probit functions are used to evaluate different types of consequences caused by the physical variables of accidents.

The following is an example of a Probit function associated with deaths from the effects of radiation exposure:

$$Y = -39.83 + 3.0186 \ln(tI^{4/3}) \quad (2.20)$$

Another Probit function estimates the deaths caused by overpressure as follows:

$$Y = -77.1 + 6.911 \ln(p) \quad (2.21)$$

Overpressure and radiation profiles may be obtained using computer-aided tools (e.g., software SCRI®). The Probit value can be transformed into a probability percentage of damage through the following relationship:

$$P = 50(1 + \frac{Y - 5}{(|Y - 5|)} \operatorname{erf}(\frac{(|Y - 5|)}{\sqrt{2}}) \quad (2.22)$$

The frequency of each accident depends on the initial frequency associated with the occurrence of the incident and the associated probabilities that the latter results in an immediate or delayed ignition. The frequency of incidents can be calculated from databases for each technology.

The risk quantification is done in terms of individual risks. The individual risk is the risk that a person has based on location. This involves a damage of a certain magnitude and with certain frequency due to the effects of physical variables caused by the occurrence of an accident. As given by the following expression, the individual risk (IR) is determined by multiplying the probability of damage caused by an accident ($P_{x,y,i}$) and the frequency of the accident (f_i):

$$IR_{x,y} = \sum_{i=1}^n f_i P_{x,y,i} \quad (2.23)$$

2.5 Solution Strategy

The model was formulated and solved using ASPEN Plus®, Matlab® and Visual Basic®, the risk was assessed using the software SCRI (SCRI, 2015). **Fig. 2.3** shows the implemented solution algorithm. For a given amount of inlet shale gas $F^{Total-inlet-SG}$, it is necessary to know the optimal technology or set of technologies, in which the greatest benefit is achieved.

The calculation sequence begins in Matlab®, which generates, through genetic algorithms (a stochastic optimization technique that mimics the process of natural selection (Wang et al., 2015)), a data set, which corresponds to values of the process variables; these data are: the temperature of each technology U (T_U^{inlet}), operating pressure of technology U (P_U^{inlet}), shale gas (SG) flowrate sent to each technology U ($f_{SG,U}^{inlet}$) and reactants flowrate R ($f_{R,U}^{inlet}$) necessary to react with methane in technology U. These data are sent to Visual Basic®, which works as an interface, storing the generated data vector from Matlab®. Visual Basic® sends the same data set that Matlab® generates without modifying (see **Fig. 2.3**). ASPEN Plus® receives the data set and solves the mass and energy balances with rigorous thermodynamic calculations and design equation. The data obtained from ASPEN Plus® are: product flowrate P (hydrogen and carbon monoxide) produced in technology U ($f_{P,U}^{out}$), heat added to or removed (\dot{Q}_U^{out}) and costs related to the amount of reactants used in the technology U ($\dot{C}_{R,U}^{out}$). The data collected from ASPEN Plus® are returned to Visual Basic®, it reads the data set and evaluates the *Annual Sale Revenue*, *Raw Material Costs*, *Utilities Costs* and *Technology Cost*. The result is sent to Matlab®, where the objective function is evaluated (through Equation (1.1)). The process is iterative; this way, Matlab® generates another data set and the process is repeated. When the problem converges, Matlab® provides the resulting *NETPROFIT* value as well as the optimal values of temperature ($T_U^{optimal}$), pressure ($P_U^{optimal}$) and reactant flowrates ($f_{R,U}^{optimal}$). The final step of the algorithm is the application of a QRA to the obtained solutions, where the SCRI® software is used for the QRA. The individual risk is the result of the application of QRA, which then is reported in a proper way for the decision makers.

It should be noticed that prior to the optimization, it is necessary to perform the simulation, where ASPEN Plus® equilibrium-based reforming models are used for the simulation of the three reaction systems. Given the nature of the substances that take part of the reaction systems, the thermodynamic model used was SRK.

The manipulated variables were pressure and temperature of each reactor, the supply flow rate of steam (SR), oxygen (POX) and carbon dioxide (DR) and the flow rate of methane feed to each technology. The upper and lower bounds for these variables are for SR: 673-1173K and 0.01 MPa-4 MPa, for POX: 1,523-1,673 K and 2 MPa-4MPa, for DR: 773-1273 K and 0.01 MPa-2 MPa.

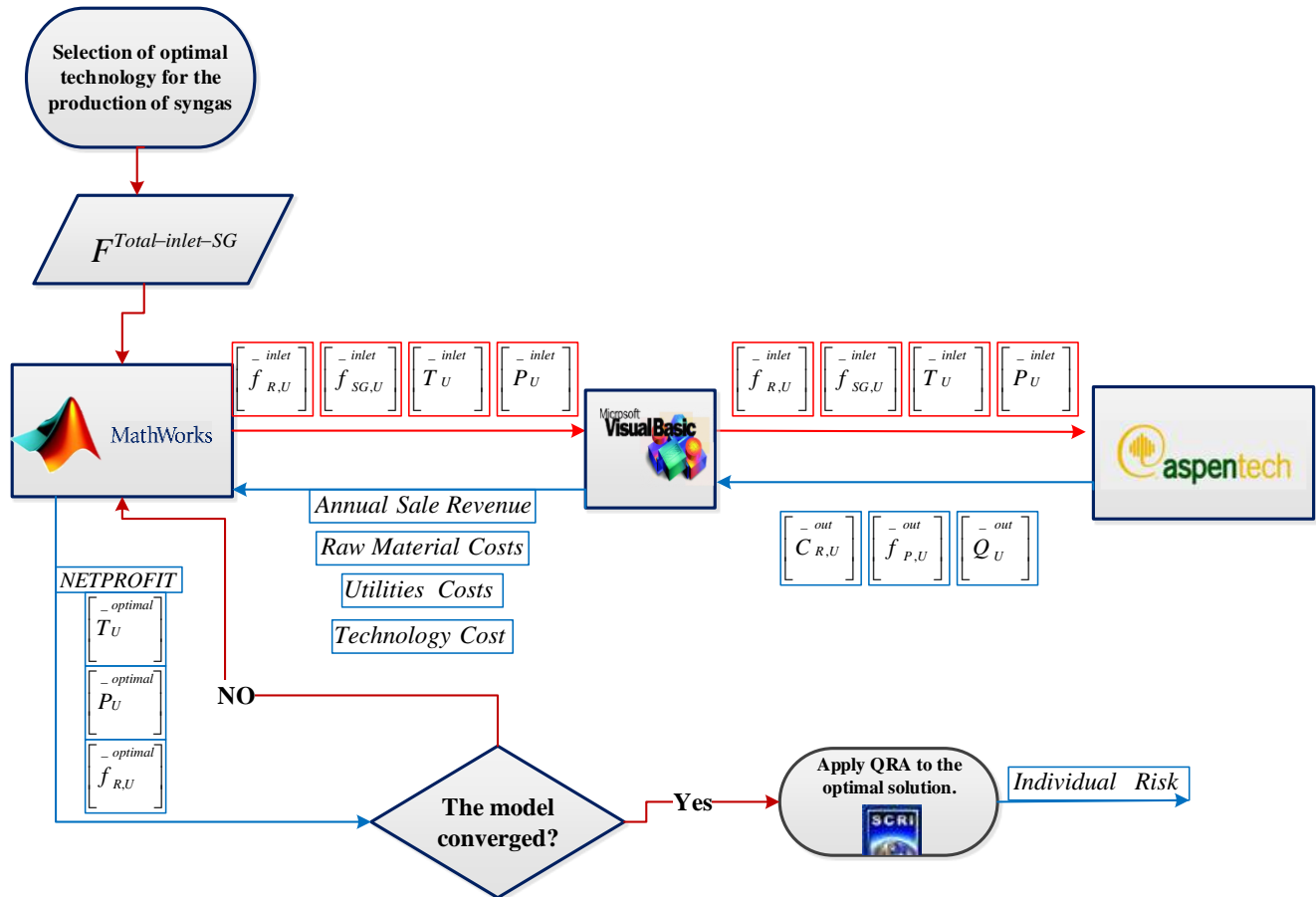


Fig. 2.3. Model solution algorithm.

The mass and energy balances were made based on the composition of shale gas (see **Table 2.1**) reported by Nouredin et al. (2015). This composition is used (without loss of generality in the formulation) to demonstrate the applicability of the proposed approach. The model can be easily revised to handle any available feedstock composition. In evaluating the risk, the wind speed was set as 1.5 m/s and an atmospheric stability type F was selected.

The maximum distances were determined to reach a value of 0, 50 and 100 probability of death. Additionally, the individual risk for a distance of 10 m was determined. It should be noticed that the sale price of syngas is a function of the H₂:CO ratio because the applications of the syngas depend on this ratio.

Table 2.1. Shale gas composition for the case study.

Component	Mole Fraction
Methane	0.81
Ethane	0.06
Propane	0.02
Carbon Dioxide	0.03
Nitrogen	0.08

2.6 Results

The model was solved for different ratios of syngas. The obtained results are shown in **Fig. 2.4** and **Table 2.2**. The curve shows the behavior between H₂:CO ratio and Netprofit. The maximum profit is achieved at a ratio of 2.9 obtained using steam reforming with the following operating conditions (see **Table 2.3**): temperature of 1120.75 K, Pressure: 0.11 MPa, and steam input: 399.7 kmol/hr (see **Fig. 2.5**). The net profit for this configuration is \$4.36x10⁷ year⁻¹. Furthermore, this solution is the safest within the examined options. For a ratio of 1, the selected technology is dry reforming. The main incentive to consider this option would be the conversion of two greenhouse gases (CH₄ and CO₂) into value-added products. This particular ratio is preferred for the production of dimethyl ether (Aasberg-Petersen et al., 2011). If safety is used as the only criterion, the lowest risk corresponds to a minimum ratio of 0.16. Nonetheless, this option is not economically attractive and the aforementioned ratio is not suitable for commercial applications.

The QRA results are shown in **Tables 2.4** and **2.5**. For a distance of 10 m, dry reforming is associated with the greatest risk which may be attributed to the operating conditions (e.g., high pressure) which increase the area impacted by dispersion.

Another important aspect to consider is that high temperatures and low pressures promote hydrogen yield, which enhances the value of syngas. Higher pressures lead to larger areas of impact through dispersion. For instance, for steam reforming operated at 0.19 MPa, the risk increases by 28% compared to an operating pressure of 0.11 MPa. This trend can also be seen in **Table 2.5**, when the pressure is increased, the toxic release accident increases its damaged area. Whereas, for the rest of the accidents, the effect of the pressure and temperature (within the explored range 0.10-0.30 MPa and 873.15-1120.15 K) do not have a significant impact.

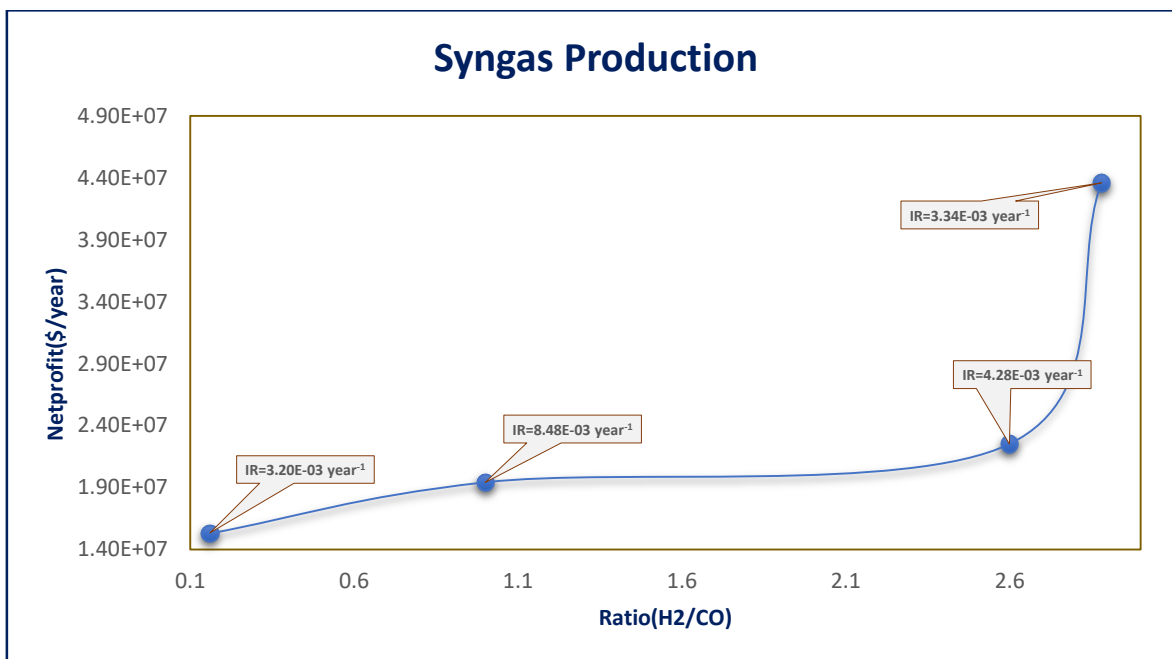


Fig. 2.4. Curve for the net profit versus H2:CO ratio (IR is individual risk).

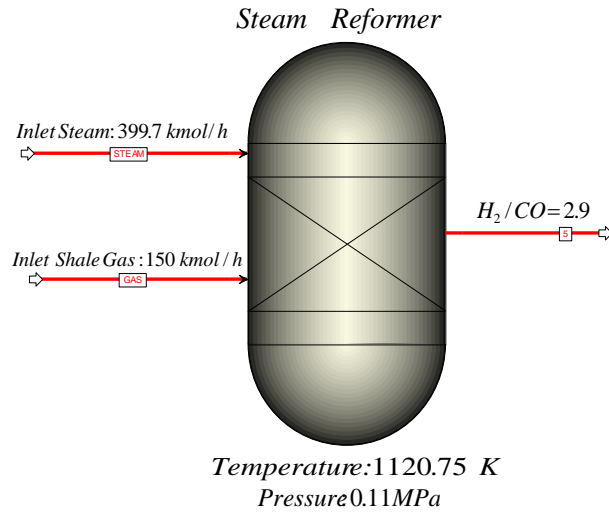


Fig. 2.5. Optimal solution for a ratio $H_2:CO = 2.9$.

Table 2.2. Optimal solutions for different qualities of syngas.

Ratio(H_2/CO)	Net profit(MM\$/year)	Technology
2.90	43.60	SR
2.60	22.50	SR
1.00	19.40	DR
0.16	15.30	SR+DR

Table 2.3. Operating conditions for different ratios.

Ratio	Technology	Pressure (MPa)	Temperature (K)
2.90	SR	0.11	1,121.15
2.60	SR	0.19	1,090.15
1.00	DR	0.30	1,074.15
0.16	SR	0.11	1,023.15
	DR	0.10	873.15

Table 2.4. Individual risk (IR) for a distance of 10 m.

Total individual risk for 10 m				
Ratio	Technology	Instantaneous release IR	Continuous release IR	Total IR
2.90	SR	1.54E-06	1.80E-06	3.34E-06
2.60	SR	1.40E-06	2.88E-06	4.28E-06
1.00	DR	3.08E-06	5.40E-06	8.48E-06
0.16	SR+DR	1.40E-06	1.80E-06	3.20E-06

Table 2.5. Maximum distance for a probability of damage of 0, 50 and 100%.

Maximum distance for a probability of damage 0%, 50%, 100 % (m)					
Ratio	Technology	Outcome accidents	0%	50%	100%
2.90	SR	BLEVE	282.73	144.96	98.43
		VCE	49.57	34.25	28.49
		Toxic Release	3.65	2.12	1.61
2.60	SR	BLEVE	279.18	143.16	97.21
		VCE	49.09	33.92	28.21
		Toxic Release	10.13	8.61	1.84
1.00	DR	BLEVE	238.15	122.31	83.09
		VCE	43.43	30.01	24.96
		Toxic Release	15.41	13.05	11.35
0.16	SR+DR	BLEVE	136.56	70.51	47.97
		VCE	28.27	19.54	16.25
		Toxic Release	3.82	2.13	1.78

2.7 Conclusions

This chapter has presented an optimization-based approach for incorporating economic and safety considerations in the selection of reforming technology for the production of syngas from shale gas. A coordinated integration of process simulation and QRA was used to model the process under various conditions and to quantify the associated risks. The results show that for the selected shale gas composition and the selected criteria, SR is the optimal technology to produce syngas, representing the option with the highest profit and lowest risk. The reduction in risk is attributed to the more favorable operating conditions, which reduce the impacted area by dispersion. The results also show that for a $H_2:CO$ ratio of 1, dry reforming should be selected. Nonetheless, the risk at this ratio is higher than that evaluated for a ratio of 2.9. Combined reforming was not selected in any of the examined scenarios. The case study also evaluated the hazard in various forms such as BLEVE, VCE, and toxic release. It is worth noting that the general approach proposed in this paper can be used to solve other case studies with different input data. The results are expected to vary based on the inputs.

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CHAPTER 3

A Multi-objective optimization approach for the selection of working fluids of geothermal facilities: Economic, environmental and social aspects

The selection of the working fluid for Organic Rankine Cycles has traditionally been approached from systematic heuristic methods, which perform a characterization and prior selection considering mainly one objective, thus avoiding a selection considering simultaneously the objectives related to sustainability and safety. The objective of this work is to propose a methodology for the optimal selection of the working fluid for Organic Rankine Cycles. The model is presented as a multi-objective approach, which simultaneously considers the economic, environmental and safety aspects. The economic objective function considers the profit obtained by selling the energy produced. Safety was evaluated in terms of individual risk for each of the components of the Organic Rankine Cycles and it was formulated as a function of the operating conditions and hazardous properties of each working fluid. The environmental function is based on carbon dioxide emissions, this considers carbon dioxide mitigation, emission due to the use of cooling water as well emissions due lost to release of material. The methodology was applied to the case of geothermal facilities to select the optimal working fluid although it can be extended to waste heat recovery. The results show that the hydrocarbons represent better solutions, thus among a list of 24 working fluids, toluene is selected as the best fluid.

3.1 Introduction

The use of renewable resources for energy production has been presented as a clean alternative to the use of fossil-based resources. Intensifying the use of natural resources has as main advantage the reduction of the environmental impact (Gunther and Hellman, 2017), by reducing or mitigating the emission of pollutants (Wolf et al., 2016). Nowadays, the most used renewable resources are: Hydroelectric, wind, solar, bioenergy and geothermal. Of these, geothermal energy produces less than 1% of the world's energy consumed, despite its wide availability, which is of 43×10^6 EJ (World Energy Council, 2016). In the American continent, countries like USA and Mexico have potential reserves that have not yet been widely exploited (Gutierrez-Negrín and Lippmann, 2016). In Asia, Indonesia has a high reserve potential representing 40% of world reserves (Nasruddin et al., 2016), meanwhile China has been a pioneer in the use of its resources and today presents an installed capacity of 27.78 MWe (Zhu et al., 2015). The technologies used for the conversion of geothermal to electrical energy depend on the type of source. For sources of high enthalpy ($>180^\circ\text{C}$), steam is used directly to produce power (direct-steam, Phair, 2016). If the temperature is between $101-180^\circ\text{C}$, the reservoir is called as medium enthalpy and in this case a binary cycle is used (Spadacini et al., 2016). The Organic Rankine Cycle (ORC) technology is often used as an interface in energy conversion from medium enthalpy sources to allow for an economic exploitation of these resources. However, the efficiency of the ORC is currently still low and improving it depends mainly on the proper selection of the working fluid (Hung et al., 1997). The selection of the working fluid is a complicated task, because the list of candidates is large. Each fluid has different thermodynamic properties, which have a direct impact on the overall efficiency of the cycle, such is the case of molecular structure, which has a direct effect on efficiency, because high efficiencies are favored by compounds with double bonds or cyclic (Zhai et al., 2014). In addition, the critical temperature is not significant in the thermal efficiency of each working fluid (Liu et al., 2004). The study of ORCs has focused on the selection of the working fluid and the design of the cycle, based on the use of methodologies focused on the search of the fluid that provides the best energy efficiency. In this regard, Roy and Misra (2012) proposed a parametric optimization for the selection of the working fluid considering only the efficiency. Borsukiewicz-Gozdur and Nowak (2007)

presented a thermodynamic analysis, applied to natural and synthetic refrigerants and mixtures, to select the working fluid that shows the highest efficiency. Drescher and Brüggemann (2007) concluded that alkylbenzenes provide the highest efficiencies in biomass power and heat plants. Saleh et al. (2007) proposed an approach for the selection of the working fluid based solely on the thermodynamic aspect. However, the fluid selection should not only be based on the cycle economy, safety and environmental impact should also be taken into account simultaneously. The working fluids used for producing energy from geothermal sources belong to two chemical groups, hydrocarbons and refrigerants. The chemical nature of these working fluids requires that the selection and design of the cycle take into consideration sustainability and safety issues. Each group presents advantages and disadvantages. On the one hand, refrigerants show significant effects on the environment, presenting high values for ozone depletion potential (ODP) and global warming potential (GWP) (Saleh et al., 2007), the first related to the damage to the ozone layer and the second with global warming, since most of these belong to the family of freons. On the other hand, hydrocarbons have higher values of risk, due to the explosive and flammable nature. In this sense, several strategies have been proposed that consider the selection of working fluid considering thermodynamic efficiency, indicators related to environmental damage and safety. Some of these works consider formulations applied to the selection of the working fluid in an ORC for solar energy conversion. In these formulations, safety is shown as a relative (qualitative) measure between each compound (Tchanche et al., 2009). Other studies consider the calculation of the safety issues through the use of indexes referring to the toxicity and flammability of working fluids (Papadopoulos et al., 2010). In refrigeration, where an ORC is also frequently used, multi-objective optimization approaches have been presented to consider economic, environmental and safety issues for the optimization of the cycle. The developed model is used to decide between two working fluids. In that work, the risk is based on the quantitative risk analysis (QRA), which is performed prior to optimization and it is obtained in economic terms (Eini et al., 2016). The importance of the study of ORC technology lies on its wide use. It can be used for the production of power from renewable sources (solar power plants) but it can also be used for recovering energy from waste heat sources (Quoilin et al., 2013). The growing use and widespread availability of renewable resources require improved energy conversion processes, thus generating methodologies to

ensure the optimum selection for the working fluid and operation of the ORC is necessary. The main novelty of the present work consists in presenting a multi-objective approach for selecting the working fluid in geothermal power plants, and the proposed approach is the first one that considers simultaneously economic, environmental and safety objectives. It should be noticed that previously reported approaches have not simultaneously considered these three aspects. The three metrics are function of the operating conditions and the characteristics of the working fluids, in this work the social aspect was considered in terms of risk. The above implies the solution of a conventional Rankine cycle, so the problem is addressed to the optimum selection of the working fluid and to the solution of the cycle. **Fig. 3.1** shows a simplified scheme of a binary cycle used in the conversion of geothermal energy from medium enthalpy reservoirs into power. It corresponds to a basic flow diagram for ORC's that are reported elsewhere (see for example DiPippo, 2016). The cycle consists of a condenser, a pump, a turbine and a heat exchanger which operates between the working fluid and the water from the geothermal reservoir. The operating conditions of each of the components of the cycle are determined by the working fluid, in such a way that the efficiency of the cycle depends on an appropriate selection. Traditionally, hydrocarbons and refrigerants have been used, selecting the one that provides a better energy efficiency. Under these selection criteria, it may be easy to select from an extensive list of hydrocarbons and refrigerants the most appropriate one. However, the concept of sustainability indicates that there are two other selection criteria that must also be considered. If the concept of sustainability is incorporated into the selection of the working fluid, it will be observed that the task is not simple, due to the properties and characteristics of each candidate fluid. On the environmental side, hydrocarbons are more environmentally friendly with respect to refrigerants, which are linked to the damage of the ozone layer. For the social part related to risk, hydrocarbons are more hazardous than refrigerants because they are explosive and flammable (Troynikov et al, 2016). Even choosing between one compound and another from the same group is complicated, due to the difference in the properties of one with respect to another. In this way, the problem to be solved is to find the optimum working fluid considering simultaneously economic, environmental and safety objectives. Next section describes the problem addressed. It is important to mention that, even though the methodology presented is general to any ORC, the correlations obtained are specific for the

typical operating conditions of the various fluids, including the heat source. For different applications, the range of operating conditions may differ and the correlations may also be different.

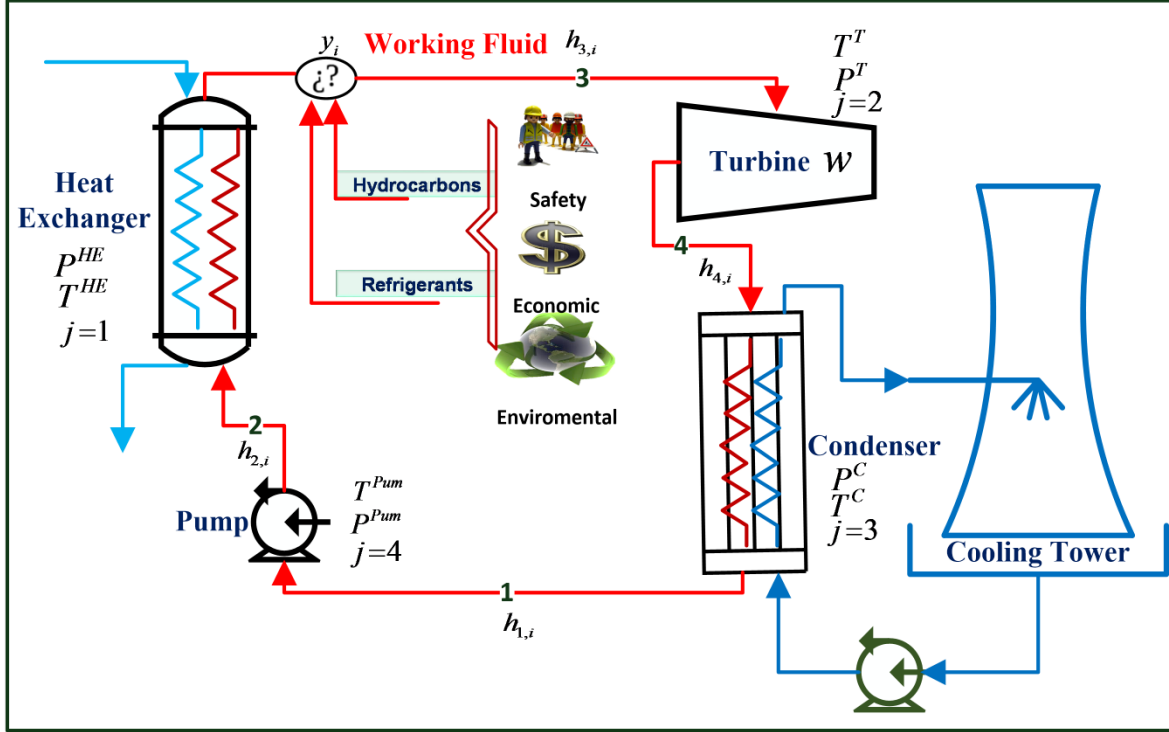


Fig. 3.1. Optimum selection of working fluid.

3.2 Methods

In order to simultaneously consider the economic, environmental and safety aspects, a metric has been developed to quantitatively account for the three pillars. The flowchart shown in **Fig. 3.1** is used as the basis for the development of an equation that describes each metric. For a better understanding, we define the sets as follows. J corresponds to the set of equipment that integrates the binary power cycle, I is the set of working fluids which is comprised of hydrocarbons and refrigerants. This section describes in detail the development of each term of the metric. We divide the section into four topics. The first three show the formulation of the terms corresponding to each of the three objectives, safety, economic and environmental ones, and the fourth one presents the solution strategy used to solve the multi-objective optimization problem.

3.2.1 Safety Objective Function

Traditionally the social aspect of a project or process is measured in terms of benefits to society, such is the case of jobs creation. Protection to workers as well as to populations that are settled in the surroundings of a chemical process can also be a criterion to account for the social issues of a particular process. Individual risk is the metric used to assess risk. This metric represents the risk that a person may be exposed to in a certain position. The main idea is to select a working fluid, which causes the lowest risk to the workers or the population close to the process in case that an incident occurs. Thus, in this study, the risk was considered as a social objective function.

The binary cycle is composed of four elements, see **Fig. 3.2**. Each of the units may generate different accidents related to fire and explosion. The risk function expressed by Equation (3.1) represents the total risk of the cycle (*TotalRisk*) and it corresponds to the sum of the risk due to each component of the cycle. Each of the elements j of the cycle may have two types of incidents, a continuous and/or an instantaneous release, for instance an incident is the loss of matter. These two types of incidents can occur in all elements of the cycle. Continuous release is the emission of a substance through a hole while instantaneous release refers to the total release of the stored substance. The risk of each element, $RCRisk_j$, is computed by adding the risk due to a continuous ($CRRISK_j$) and an instantaneous release ($IRRisk_j$) of matter (see Equation (3.2)). Each substance has a different behavior in the way it is emitted into the atmosphere, due to the difference in their properties. Thus, each element j will have a specific risk for each working fluid, according to the type of emission and can be computed by Equations (3.3) and (3.4).

$$TotalRisk = \sum_{j \in J} RCRisk_j \quad (3.1)$$

$$RCRisk_j = CRRISK_j + IRRisk_j \quad \forall j \in J \quad (3.2)$$

$$CRRISK_j = \sum_{i \in I} IR_{i,j,d}^{CRRISK} \quad \forall j \in J \quad (3.3)$$

$$IRRisk_j = \sum_{i \in I} IR_{i,j,d}^{IRRisk} \quad \forall j \in J \quad (3.4)$$

Each incident may evolve into a set of accidents (h), which vary according to the chemical nature of each working fluid. In this way, the risk of each type of emission is given by Equations (3.5) and (3.6), which consider the sum of the individual risks of all possible accidents that may occur.

$$IR_{i,j,d}^{CCRRISK} = \sum_{h \in H} IR_{i,j,d,h}^{CCRRISK} \quad \forall i \in I, \forall j \in J, \forall d \in D \quad (3.5)$$

$$IR_{i,j,d}^{IRRisk} = \sum_{h \in H} IR_{i,j,d,h}^{IRRisk} \quad \forall i \in I, \forall j \in J, \forall d \in D \quad (3.6)$$

The individual risk refers to the frequency and magnitude of damage that a person may suffer in a position d due to exposure to a physical variable caused by an accident. The risk has units of year^{-1} and it is obtained by the product between the frequency of occurrence ($f_{i,j,h}$) of accident h for the element j and $p_{i,j,d,h}$, which represents the probability of affectation due to the effect of the exposure to the physical variable caused by the accident in the position d . For a continuous and instantaneous release, the individual risk is obtained by Equations (3.7) and (3.8), respectively.

$$IR_{i,j,d,h}^{CCRRISK} = f_{i,j,h} p_{i,j,d,h}^{CCRRISK} \quad \forall i \in I, \forall j \in J, \forall d \in D, \forall h \in H \quad (3.7)$$

$$IR_{i,j,d,h}^{IRRisk} = f_{i,j,h} p_{i,j,d,h}^{IRRisk} \quad \forall i \in I, \forall j \in J, \forall d \in D, \forall h \in H \quad (3.8)$$

In Equations (3.8) and (3.7), $p_{i,j,d,h}$ and $f_{i,j,h}$ are values obtained through the quantitative risk analysis (QRA) (CCPS, 2000), where $f_{i,j,h}$ is a known parameter evaluated by a frequency analysis.

Incidents Identification

Incident identification is often performed using qualitative risk analysis methods, HAZOP is an example of these type of methods (Kletz, 1999). If the cycle components are analyzed, it is possible to determine if the instantaneous release can occur in the heat exchanger and condenser while the release continues on all components.

Consequence Estimation

The consequence is assessed based on the physical variables that cause the accidents. It depends on the operating conditions of a process and the characteristics of the substances (toxicity, flammability and explosiveness). Therefore, it is convenient to express the consequence as a function of the operating variables of each component of the cycle and of the properties of each working fluid. The first step in assessing the consequence of an accident consists of determining the rate of emission of an incident. The emission of a substance to the environment depends on the phase, the storage and operating conditions as well as the physical properties of the substance (density, molecular weight, etc.). In this work, we have developed correlations to quantify the consequence of an accident for each of the working fluids, considering a liquid phase and gas phase emission. Equation (3.9) shows the form of the correlation obtained for a liquid phase emission, which is a function of the operating pressure of each component of the cycle. On the other hand, the gas phase emission is a function of the operating temperature and pressure according to Equation (3.10).

$$QL_{i,j} = a_i + P_j b_i \quad \forall i \in I, \forall j \in J \quad (3.9)$$

$$QG_{i,j} = U_i + Z_i P_j - N_i T_j \quad \forall i \in I, \forall j \in J \quad (3.10)$$

Where a_i, b_i, U_i, Z_i and N_i are constants that depend on each working fluid. P_j and T_j are the operating pressure (Pa) and temperature (K). $QL_{i,j}$ is the mass flow rate of liquid phase for each working fluid and process unit in kg/s and $QG_{i,j}$ represents the gas phase mass flow. In the appendix A, identified as **Tables S1** and **S2**, we present the values of the coefficients for Equations (3.9) and (3.10) for each of the 24 fluids evaluated.

Having determined the mass flow rate of emission of each working fluid in different phases, it is possible to assess the reach and magnitude of the accidents according to the type of working fluid and operating conditions. Based on the type of incident and the characteristics of the released substance, different accidents may occur (h). Each working fluid has different hazard properties, some are flammable and explosive (hydrocarbons) and others are toxic. Accidents related to a continuous gas phase release that may occur if the substance is flammable, explosive and toxic are: Jet Fire, UVCE (unconfined vapor cloud explosions) and toxic release.

If the emission occurs in liquid phase, Pool Fire will occur instead. Every accident produces one or more physical variables, such as an UVCE, which produces an overpressure wave and fireball. If the substance is not flammable or explosive but toxic, the concentration is the physical variable considered for the evaluation of the consequence. In this paper, for a continuous release in gas phase, the following accidents were considered: Jet Fire, UVCE and Toxic Release. For a liquid phase release: Pool Fire, UVCE and Toxic Release. For Pool Fire and Jet Fire, the calculated physical variable was radiation dose, for UVCE overpressure and finally for toxicity the concentration. It should be noted that only the hydrocarbons have flammable properties, so the calculations of the physical variables of radiation and overpressure for the Jet Fire, Pool Fire and VCE accidents were only obtained for these. The calculation of these physical variables is explained below, it is worth mentioning that these correlations were obtained using the SCRI software by fitting the values reported by the software as a function of the variables of operation. For continuous emission calculations an orifice diameter of 10 mm with a duration of 20 minutes as well as a discharge coefficient of 0.65 was considered. From these data and using the SCRI software, correlations (9) and (10) were obtained. For the dispersion calculation, the Pasquill Gifford model was used, in addition it was considered the worst scenario defined as calm conditions, atmospheric stability type F, wind speed of 1.5 m/s (Haag and Ale, 2005).

Radiation Dose

Jet Fire. This accident occurs in gas phase release and its reach depends significantly on the pressure. For this accident, a correlation is developed for the radiation dose ($DRJF_{i,j}$) as a function of the gas phase emission flow rate $QG_{i,j}$ and the distance d , for each of the working fluids. The correlation obtained is shown in Equation (11), where $DRJF_{i,j}$ is a radiation dose for fluid i and unit j in kW/m², $K6_i, K7_i, K8_i$ are specific constants, and d is the distance or position at which individual risk assessment is required (see **Table S3**).

$$DRJF_{i,j} = K6_i - K7_i d + K8_i QG_{i,j} \quad \forall i \in I, \forall j \in J \quad (3.11)$$

Pool Fire. It occurs in liquid phase emissions of flammable fluids. The physical variable calculated is radiation dose. A correlation was obtained for computing the radiation dose of fluid i at unit j $DRPF_{i,j}$ as a function of the emission flow in liquid phase $QL_{i,j}$ and the distance d . The correlation obtained is shown in Equation (3.12), where $K11_i, s_i$ and w_i are constants for each fluid i and the values of these are shown in the supplementary material (see **Table S4**).

$$DRPF_{i,j} = K11_i - s_i d + w_i QL_{i,j} \quad \forall i \in I, \forall j \in J \quad (3.12)$$

Overpressure

UVCE. If the substance is flammable and explosive, this accident can occur in an instantaneous and/or continuous release. For an UVCE, the objective is to find the overpressure profile for a cloud mass. Here a time (t) for the duration of the emission of 20 minutes is assumed based on literature (Haag and Ale, 2005). If the gas or liquid phase emission flow rate and the duration of the leak are known from statistical data, it is possible to calculate the amount of mass involved in the explosion. Consequently, it is possible to establish a ratio that allows the calculation of the overpressure value ($OVCE_{i,j}$) as a function of the emission flow $QG_{i,j}$ and the distance d (see Equation (3.13)). x_i, j_i and q_i are fitting parameters (see supplementary material **Table S5**).

$$OVCE_{i,j} = x_i - j_i d + q_i QG_{i,j} t \quad \forall i \in I, \forall j \in J \quad (3.13)$$

Concentration

Toxicity. LC50 is an indicator of acute toxicity. It refers to the concentration in ppm that can kill 50% of a population. Concentration is the key variable for assessing the toxic effects of a substance, thus establishing a correlation between emission flow, distance and concentration $CTR_{i,j}$. Equation (3.14) shows the correlation that relates these variables, where $CTR_{i,j}$ is the concentration in ppm at the distance d for working fluid i , and $K10_i, HH_i$ and V_i are constants, whose values were obtained for each of the 24 fluids and are shown in the **Table S6**.

$$CTR_{i,j} = K10_i - HH_i d + V_i QG_{i,j} \quad \forall i \in I, \forall j \in J \quad (3.14)$$

Probability of damage

The result of the accidents in terms of damage on people can be measured using vulnerability models. In this case we use the Probit model (Crowl and Louvar, 2011). The Probit functions used are referred to fatal effects on people. For radiation, we considered the Probit function related to death by third degree burns (Equation (3.15)), which applies to radiation by Jet Fire ($DRJF$) and Pool Fire ($DRPF$). With regards to pressure, Equation (3.16), it is associated with deaths from pulmonary hemorrhage due to exposure to shockwave (Crowl and Louvar, 2011). The effects of toxicity were measured through the LC50.

$$YDR_{i,j} = -39.83 + 3.0186 \ln(t(DRJF_{i,j} \text{ or } DRPF_{i,j})^{4/3}) \quad \forall i \in I, \forall j \in J \quad (3.15)$$

$$YOVC_{i,j} = -77.1 + 6.91 \ln(OVC_{i,j}) \quad \forall i \in I, \forall j \in J \quad (3.16)$$

Subsequently, the Probit values obtained from Equations (3.15) and (3.16) are converted to probability of damage by Equation (3.17), which allows calculating the probability value $p_{i,j,d,h}$ of any physical variable, from the Probit value of this, at a distance d . On the right hand side of Equation (3.17), it can be seen that the parameter 1.005 is multiplied by the binary variable Y_i , which is associated with the existence of the working fluid, if it does not exist then it takes the value of zero.

$$p_{i,j,d,h} \left(1 + e^{\left(\frac{5.004 - (YDR_{i,j} \text{ or } YOVC_{i,j})}{0.612} \right)} \right) \leq 1.005 Y_i \quad \forall i \in I, \forall j \in J, \forall d \in D, \forall h \in H \quad (3.17)$$

In the case of toxicity, a linear relationship is established based on the value of its LC50, thus according to the Equation (3.18), for a given value of concentration is possible to know directly the value of the probability of affectation. The LC50 values for each of the 24 fluids are shown in **Table S7** (AHRINET, 2000).

$$\frac{LC_{50i} p_{i,j,d,h}}{CTR_{i,j}} \leq 0.5 Y_i \quad \forall i \in I, \forall j \in J, \forall d \in D, \forall h \in H \quad (3.18)$$

It should be noted that if the pressure and temperature of the cycle are fixed, it is possible to know, prior to optimization, Probit values associated with radiation and overpressure ($YDR_{i,j}, YOVC_{i,j}$) as well as concentration $CTR_{i,j}$.

In this way, in Equations (3.19) and (3.20), the only variable is the probability $p_{i,j,d,h}$. In this sense, if the binary variable takes the value of zero in these equations, it means that the probability will be zero, so the fluid with that probability will not be selected.

Additionally, a constraint is required to ensure that only one working fluid is to be selected (see Equation (3.19)).

$$\sum_{i \in I} Y_i = 1 \quad \forall i \in I \quad (3.19)$$

Frequency Analysis

The frequency analysis was performed using the event tree, the initial frequencies were obtained from the “Purple Book” (see Haag and Ale, 2005) for each of the components of the cycle. It should be mentioned that the frequency value is associated with the type of incident and accident that can occur for the component j of this mode. When this variable takes the value of 0, it indicates that the accident h does not occur in that equipment. In **Fig. 3.2**, an event tree is observed for a continuous release in the pump. It is possible to appreciate the evolution of an incident to a set of accidents. It is also possible to observe the calculation of the frequency for each of the equipment that integrate the binary cycle. This analysis was performed for the entire cycle and the results are shown in **Table 3.1**.

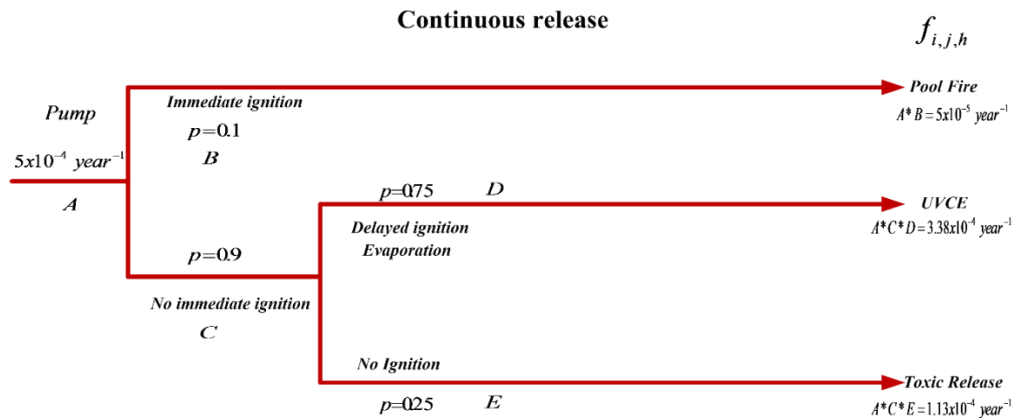


Fig. 3.2. Event tree for continuous release in the Pump.

Table 3.1. Frequency analysis.

Equipment	Outcome Frequency due to Continuous Release (f_j year)	Outcome Frequency due to Pool Fire (year)	Outcome Frequency due to UVCE (year)	Outcome Frequency due to Jet Fire (year)	Outcome Frequency due to Toxic Release ($f_{i,j,h}$ year)
Pump	$5 \cdot 10^{-4}$	$5 \cdot 10^{-5}$	$3.38 \cdot 10^{-4}$	0	$1.13 \cdot 10^{-4}$
Turbine	$1.9 \cdot 10^{-4}$	0	$1.28 \cdot 10^{-4}$	$1.9 \cdot 10^{-5}$	$4.28 \cdot 10^{-5}$
Heat Exchanger	$5 \cdot 10^{-5}$	0	$3.38 \cdot 10^{-5}$	$5 \cdot 10^{-6}$	$1.13 \cdot 10^{-5}$
Condenser	$6 \cdot 10^{-5}$	$6 \cdot 10^{-6}$	$4.05 \cdot 10^{-5}$	0	$1.35 \cdot 10^{-5}$

Fig. 3.3 shows a summary of the calculation of individual risk for each element j (i.e., a heat exchanger). It is possible to appreciate that in each of these elements a sustained release material instantaneous liquid phase or gas phase can occur. According to these two types of incidents, a certain number of accidents can occur, from which a correlation was obtained depending on the emission flow and the distance d of interest to which the risk value is desired, finally for each of the accidents at a distance a probability value is obtained $p_{i,j,d,h}$, which multiplied by the frequency value results in the individual risk. The individual risk was calculated at a distance of 50 m for all fluids. This distance was used as a criterion for comparing the risk for work fluids, for all accidents.

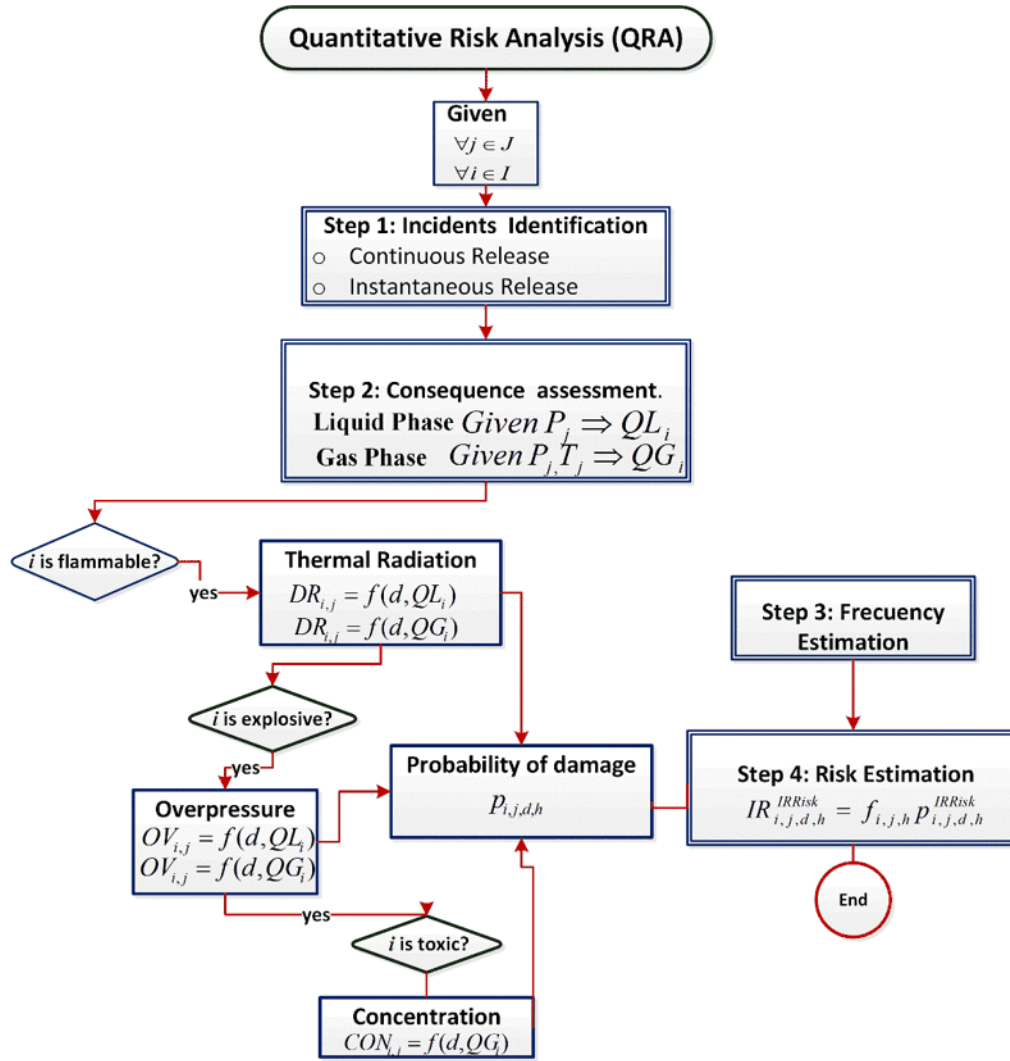


Fig. 3.3. Algorithm for calculating individual risk

3.2.2 Economic objective function

The economic objective is presented as the profit obtained by selling the power produced. In **Figs. 3.3** and **3.4** it is possible to identify the four thermodynamic states, which are described below:

- 1-2: Adiabatic compression of the liquid to a certain pressure (isentropic process), stage that will be realized through a pump.
- 2-3: Heating and vaporization of the liquid in a heat exchanger (isobaric process). This stage can be used to obtain saturated steam or superheated steam, depending on the type of Rankine cycle. In this case, only until obtaining saturated steam, using for this purpose a single heat exchanger.
- 3-4: Adiabatic expansion of the saturated steam, using a turbine, which will be connected to a generator to produce power.
- 4-1: Condensation of the steam leaving the turbine, until obtaining saturated liquid.

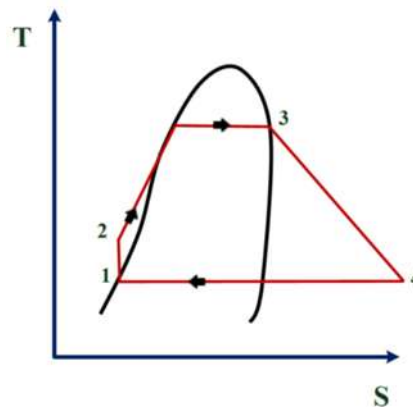


Fig. 3.4. T-S diagram of the basic Rankine cycle.

The considerations made for the resolution of the cycle are explained in detail below.

The deviations of ideality in the processes that occur within the turbine and the pump were not considered, and the heat exchangers were also considered to operate adiabatically. As it can be seen in **Fig. 3.4**, the cycle is determined by two temperature limits.

The lower temperature limit is fixed as a function of the temperature of the water available as refrigerant in the condenser. In this case, a temperature of 10°C was taken as the reference, which corresponds to the average temperature of the Gallego river located in Spain, considering the installation of the cycle in Spain (Government of Aragon, 2007), the condensation temperature for all fluids was 23°C, to avoid temperature cross. Regarding to the maximum temperature or upper limit of the cycle, several criteria have been established to fix this limit, both of which depend on the geothermal fluid or brine input to the heat exchanger (DiPppo, 2016), and on the saturation properties of each working fluid in particular:

- For any of the working fluids it is satisfied that the maximum temperature at which the heat exchanger can operate is one that at the maximum ensures that during the expansion in the turbine no drops of liquid are formed inside it. Since all fluids that have been considered are dry type or in the case of a refrigerant, isentropic type, the lower temperature limit can be determined at the point of maximum entropy searched within the steam saturation curve.
- If the maximum temperature which can operate some fluid exceeds the temperature at which the brine reaches the exchanger (167.75°C); then, for these the temperature at which maximum amount may be 162°C, temperature that fixed in such a way that the utilization of the heat yielded by the brine is good and that a thermal shock does not occur inside the heat exchanger.

Table S8 shows the thermodynamic states for the 24 fluids. Once the cycle states for all fluids are determined, the heat added to the heat exchanger is calculated, for the purpose of calculating the amount of fluid flow required (FM_i), for the cycle. This heat is given by the brine and is adjusted to the following expression:

$$Q_c = m_{brine} (h_{inject} - h_{production}) \quad (3.20)$$

Where h_{inject} is the enthalpy of the brine at the inlet of the heat exchanger, and $h_{production}$ is the enthalpy of the brine at the outlet of the heat exchanger.

For the computation of these enthalpies, the pressure drop is considered negligible, the outlet pressure of the evaporator is considered to remain unchanged, while to determine the outlet temperature of the exchanger brine a number of factors must be taken into account, because this temperature will be the temperature at which the brine is reinjected back to the reservoir. The temperature and pressure at which the brine is reinjected can give rise to problems such as the cooling of the reservoir, expulsion of the brine from the injection well due to excessive pressure preventing it from flowing into the reservoir, induction of seismic problems, etc. (see DATA.GOV, 2015). This is why it was decided to fix the outlet temperature of the exchanger at 70°C by placing the injection well beyond the influence of the reservoir, thus avoiding the generation of the problems above mentioned. Using Q_c , calculated as above, it is possible to determine the mass flow for the working fluid (FM_i), which is required in the exchanger (and therefore throughout the cycle), taking as an adiabatic operation, so the heat transferred will be the same as the absorbed:

$$Qa_i = Qc_i = FM_i(h_{3,i} - h_{2,i}) \quad \forall i \in I \quad (3.21)$$

Where $h_{3,i}$ is the enthalpy exchanger outlet, and $h_{2,i}$ the enthalpy exchanger inlet. **Table S9** shows the mass flows of the 24 working fluids.

Thus, Equation (3.22) represents the product of the selling price (PV) in € / MW and the power generated annually by the cycle in MW / year for each working fluid i .

$$GVP = \sum_{i \in I} W_i PV \quad (3.22)$$

$$W_i = \sum_{i \in I} \frac{(h_{3,i} - h_{4,i}) - (h_{2,i} - h_{1,i})}{PM_i FM_i} Y_i \quad \forall i \in I \quad (3.23)$$

The power was calculated by solving the cycle for each of the 24 fluids by Equation (23) (see **Table 3.2** for the features of the cycle in terms of entropy, enthalpy and operating temperatures). In this equation, FM_i corresponds to the working fluid flow in kg/s, PM_i is the molecular weight of each fluid and $h_{3,i}$, $h_{4,i}$, $h_{2,i}$ and $h_{1,i}$ are the enthalpy values corresponding to the four thermodynamic states of the cycle.

Table 3.2. Power produced from each fluid.

<i>Working Fluid</i>	<i>W_i(MW)</i>	<i>Working Fluid</i>	<i>W_i(MW)</i>
Benzene	13.42	R113	12.04
Butane	9.97	R114	9.43
Cyclohexane	12.75	R115	3.75
Decane	11.70	R123	11.58
Heptane	11.72	R124	7.20
Hexane	11.74	R218	4.08
Isobutane	8.80	R227ea	6.50
Isohexane	11.49	R236ea	7.83
Isopentane	11.44	R245ca	10.99
Nonane	11.71	R245fa	10.03
Octane	11.72	RC318	7.45
Pentane	11.66	Toluene	13.32

3.2.3 Environmental objective function

The environmental objective considers the impact of each of the fluids in terms of CO₂ emissions. The environmental objective function, represented by Equation (3.23), is comprised of three terms. The first corresponds to the Total Equivalent Warming Impact, *TEWI*. It considers the direct impact in terms of CO₂ emissions of a working fluid due to its leakage. For the purpose of comparison, the Global Warming Potential (GWP) indicator was used, which is a relative measure of how much heat can be trapped by a particular greenhouse gas compared to a gas reference, usually carbon dioxide. The second term refers to the emissions of CO₂ due to the use of water in the condenser (*EW*). Finally, the third term of the environmental objective function represents the mitigation of CO₂ due to the energy generated by the use of geothermal resources.

$$Environmental = TEWI + EW - MCO_2 \quad (3.24)$$

TEWI

In the coal plant CO₂ emission is inevitable, but in the rankine cycle this emission is subject to the occurrence of a leak. This is considered in the model by TEWI which represents the amount of CO₂ emissions equivalent to the working fluid emitted due to leaks.

This contribution is obtained by Equation (3.25), which consists of three terms that, multiplied by the GWP_i , provide the amount of direct CO₂ emissions. GWP_i is a conversion factor whose units are kg CO₂ per kg of working fluid i . The first two terms of the equation are associated with direct emissions due to leakage, thus $QL_{i,j}$ and $QG_{i,j}$ correspond to the liquid and gas phase flows that can occur in each element of the cycle. f_j^l and f_j^g are the frequencies of occurrence of a continuous release, specific for each element of the cycle, taken from the risk analysis (see **Table 3.2**). δ is the operating lifetime of the cycle in years. The third term of the equation is related to the emissions due to the recovery or recycling of the working fluid, thus multiplying the load of the working fluid (FM_i) by the recovery factor ξ , it is possible to know the amount of CO₂ emitted due to losses in the fluid recovery. It is necessary to mention that for the calculation of the TEWI, in this work we only consider the continuous release for all elements of the cycle. Emission in liquid phase is considered in the pump and the condenser, while in the turbine and the heat exchanger we assume that the emissions are in gas phase. The lifetime of the cycle is considered to be 30 years and the GWP_i data were taken from (AHRINET, 2000). The desirable GWP must be a value lower or equal to zero, so the goal is to make this value as low as possible. It should be noticed that refrigerants have high GWP values (see **Table S10**).

$$TEWI = \sum_{i \in I} \sum_{j \in J} Y_i GWP_i \left[\delta f_j^l QL_{i,j} + \delta f_j^g QG_{i,j} + FM_i \xi \right] \quad (3.25)$$

CO₂ emitted due evaporation losses (EW)

Each working fluid needs cooling water in the condenser to be condensed. By using the flow rate of the working fluid and the enthalpies ($h_{4,i}$ and $h_{1,i}$) at the inlet and outlet of the condenser, we can compute the flow of cooling water required. The cooling water is within a cooling cycle involving a cooling tower.

The losses of water represent the consumption of water and with it, we can compute the amount of CO₂ equivalent due to water consumption in Equation (3.26) (Perry and Green, 1998), where EW is the amount of CO₂ emitted in kg/year, ΔT_w is the temperature gradient which has a value of 8°C and $C_p W$ is heat capacity. 0.3 is a factor that indicates the amount of kg of CO₂ emitted per kg of evaporated water (Water UK, 2007). This is to ensure that the selected fluid generates low CO₂ emissions.

$$EW = 0.3 \sum_{i \in I} Y_i \Delta T_E 0.00085 \frac{(h_{4,i} - h_{1,i}) FM_i}{PM_w C_{p_w} \Delta T_w} \quad \forall i \in I \quad (3.26)$$

CO₂ mitigation (MCO₂)

Mitigation by substitution of current sources of CO₂ such as power production using fossil fuels has been presented as an attractive solution to the growing CO₂ emissions (Pomponi and Moncanter, 2016). The power produced from geothermal sources contribute mitigate CO₂ emissions. Energy production using natural gas generates 236 g CO₂ / kWhr. However, the use of coal yields higher CO₂ emissions (812 g CO₂/kWhr, GEOELEC, 2013). Using these data and the power efficiency of each of the fluids it is possible to compute the amount of CO₂ that each one can mitigate. In this way, Equation (3.27) calculates the amount of kg of CO₂ mitigated per year for each of the working fluids. EPEC is the amount of gr CO₂/kWhr produced by the combustion of coal.

$$MCO_2 = \sum_{i \in I} W_i EPEC \quad \forall i \in I \quad (3.27)$$

It should be noticed that other environmental objective functions can be considered in future works. The reason for considering the emissions as the environmental assessment was because there is a huge impact associated to the emissions of CO₂ for the use of the considered fluids. On the other hand, in this paper was not considered a term related to water pollution, this is because there is a closed cycle, where the working fluid does not have a direct contact with water.

2.3 Solution strategy

The problem was formulated as a multi-objective problem, where the goal is to maximize profits from energy sales (GVP), minimize risk ($TotalRisk$) and minimize environmental impact which is linked to CO_2 emissions (see Equation (3.28)).

$$OFF = [MinTotalRisk, Max GVP, Min Enviromental] \quad (3.28)$$

The strategy used to solve this multi-objective problem is the maximization of a normalized objective function (see Marler and Arora, 2004). This alternative is selected to avoid using weighting-based methods, so that the model lends the same importance to all the considered objectives. In order to normalize each of the objectives, we first optimize each one separately to obtain the best GVP_{MAX} , $ENVIRONMENTAL_{MAX}$ and $TotalRisk_{MAX}$. Equation (3.29) shows the terms that integrate this normalized function. The first term is related to the economic factor which relates the revenues due to sales, so the economic term in the equation is positive, which results in the selection of fluids that provide high efficiencies, the second term represents the environmental contribution which accounts for the CO_2 emissions due to leaks, emissions due to the use of cooling water and CO_2 emissions mitigated due to the production of electricity using geothermal energy. In the environmental objective function, it is desirable that the first two terms of Equation (3.27) have the smallest possible values (obtaining high values in the mitigation of CO_2), so if we minimize Equation (3.27), the maximum CO_2 value can be mitigated, which is desirable. If Equation (3.27) is observed again, it is possible to notice that the term for mitigating CO_2 is negative, which is reflected in Equation (3.29), which seeks to maximize the environmental term. The third term corresponds to risk, which must be maximized, the way the risk term is presented in the normalized objective function is related to risk values, which may be small, thus avoiding the importance of the decision to this objective. The third term involves minimizing the value of $TotalRisk$ by maximizing the third term.

$$NF = \left[\frac{GVP}{GVP_{MAX}} \right] + \left[\frac{ENVIROMENTAL}{ENVIROMENTAL_{MAX}} \right] + \left[\frac{TotalRisk_{MAX} - TotalRisk}{TotalRisk_{MAX}} \right] \quad (3.29)$$

The problem was coded in the software GAMS and it consists of 24 binary variables, 1,819 constraints and 71 equations. Noticed that other multi-objective optimization techniques can be used for solving the proposed model.

3.4 Results and Discussion

Table 3.3 shows the results obtained by solving the model for different scenarios. We first solve each of the objectives separately. If we solve the problem minimizing the risk, the solution focuses on the group of refrigerants. In this case, the formulation chooses refrigerant R115, which has a total risk of $2.38 \cdot 10^{-9}$ year⁻¹. While this solution represents the best value for the risk, the value of the environmental objective function is high and positive $4.78 \cdot 10^{10}$ t CO₂/year. The positive value implies that although CO₂ mitigation exists, in case of a leak in any of the elements of the cycle, the CO₂ emissions will be high, this is due to the high GWP value of the refrigerants compared to the hydrocarbons, which is equal to 0. Another reason why minimizing the risk the solution tends to refrigerants and not to hydrocarbons, is because they do not present dangerous characteristics that cause accidents related to fire and explosion, being only toxic. On the other hand, this solution represents as another disadvantage, the low efficiencies, as it can be seen in the value of the GPV.

When targeting the minimum environmental impact, the solution favors hydrocarbons, thus the working fluid selected under this scenario is benzene, presenting a negative value of emissions, which is desirable because it means that the value of CO₂ mitigated is greater than emissions due to leakage or the use of condensation water. This solution shows that the risk and environmental factor are opposite objectives, because higher values of CO₂ mitigation are presented by hydrocarbons, which have high levels of risk due to these as well as being toxic, flammable and explosive. The third scenario consists on maximizing the GPV, it is possible to see that the result in this last case is equal with the previous case. This is due to the fact that both, the economic and the emission terms, are highly influenced by the efficiency of the cycle since mitigation of CO₂ emissions are an important contribution of the environmental term.

The solution of the above cases provided the optimum values for each of the objectives. We use those values so as to normalize the objectives within the multi-objective formulation, see Equation (2.31). The solution of the normalized function gave preference to the hydrocarbons, as it can be seen in **Table 3.3**, selecting toluene as the best option. The environmental value obtained for toluene is interesting because it mitigates -9.473,000 Ton CO₂/year, likewise the value of GWP is high 6,731,400 €/year. If a second best working fluid is selected, benzene would be the second option. It presents better values of GWP and environmental function compared to toluene, because, if we observe **Table 3.2**, benzene is the fluid that generates the most power. However, the risk associated to benzene is the factor that put this fluid as second best behind toluene. The reason is mostly due to the higher operating pressure and temperature. For example, the operating pressure at the condenser is 11,575 Pa for benzene, while the pressure in the condenser for toluene is 3,484 Pa. Needless to say that high operating pressures cause a greater risk, because they provide a higher rate of emissions of a substance increasing the radius of impact if an accident occurs. So, although benzene presents the best values on two objectives, it is not the best option due to the associated risk. Cyclohexane is the third working fluid selected by the methodology, which presents a lower risk of $4.94 \cdot 10^{-4} \text{ year}^{-1}$ compared with benzene, but higher than toluene. In addition, the values associated with GWP and the environmental factor are lower than those shown for the other two fluids. As a fourth fluid, isohexane was found which has a higher, but very close, toluene risk $4.74 \cdot 10^{-4} \text{ year}^{-1}$ but with a lower GWP value. The solutions found are consistent with the objective functions proposed as well as with the data associated to each working fluid. One of the reasons why the solutions were linked to the hydrocarbons is due to two factors, the first one is referred to the economic and environmental objectives, which do not contradict each other as it happens with the risk objective. On the other hand, the refrigerants present high values of GWP, which translates into high and positive values in the environmental function. In this way, the solution tends to the hydrocarbons, which besides have high efficiencies and very low values or equal to zero of GWP. The reason for having high risk values is due to two main factors, the first is related to the distance of risk assessment, which is a short distance for accidents such as VCE.

On the other hand it is due to the amount of material involved in the accidents, where the main parameters that defined that amount are related to the leakage orifice diameter, leakage time and above all by the operating conditions of each of the equipment of the cycle, which are different for each fluid. The above is reflected in the difference in risk values in the solutions shown in **Table 3.3**.

Table 3.3. Results.

Solution	Selected Working Fluid	Total Risk (year ⁻¹)	Environmental (Ton CO ₂ /year)	GVP (€/year)
Min Total Risk	R115	$2.38 \cdot 10^{-9}$	4,78E+10	1,897,000
Min Environmental	Benzene	$5.09 \cdot 10^{-4}$	-9,544,100	6,782,100
Max GVP	Benzene	$5.09 \cdot 10^{-4}$	-9,544,100	6,782,100
Max NF 1	Toluene	$4.76 \cdot 10^{-4}$	-9,473,000	6,731,400
2	Benzene	$5.09 \cdot 10^{-4}$	-9,544,100	6,782,100
3	Cyclohexane	$4.94 \cdot 10^{-4}$	-9,068,000	6,443,800
4	Isohexane	$4.74 \cdot 10^{-4}$	-8,176,000	5,809,900

3.5 Conclusions

This paper has presented a multi-objective optimization approach for selecting the optimum fluid for converting geothermal energy into power involving simultaneously economic, environmental and safety aspects. The proposed approach has shown that it is possible to select, from a set of working fluid candidates, the fluid that has the best properties to ensure an efficient, safe and less impact to the environment operation. Cycle efficiency, CO₂ emissions and QRA analysis are used to formulate the objective function to account simultaneously for the three terms. Hydrocarbons provide the best solutions, because most refrigerants are associated with strong impact to the ozone layer. The developed model represents a proper tool for decision makers, because it considers the three key pillars in the sustainability and it is able to provide the best solution. The model presented in this work was formulated specifically for ORC's and in particular for geothermal applications; however, the proposed approach can be extended and generalized for the application to other processes related to the selection of a working fluid accounting for sustainability criteria. In addition to the selection of the working fluid, the developed metrics allow the design of the process, which was not considered in this work and can be considered in future works.

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Overall Discussion on “Involving Safety in the Optimal Design of Chemical Processes”

The methodologies proposed in this work are related to the design of safe processes, these have shown the impact that safety has on the synthesis of a process. Generally, safety is a goal that is opposite with economic factors, that is, a safe design can be very expensive and opposite, the goal should always be to find balanced solutions among the set of criteria considered in the design. When we involve safety as a factor in the design we can conclude that it is necessary to take into account the following main points.

Approach: Nowadays there are four main approaches as strategies for reducing or eliminating the risk of a process (Active, Passive, Inherent and Procedural). Each of these strategies acting in different stages of evolution of an accident (initiation, propagation and termination). The ideal is to attack the problem in the initiation stage, so the approach used should mitigate the problem in the early stage of the accident (initiation). On the other hand, an approach should be considered to minimize or eliminate (passive and inherent), and not control the risk (active and procedural). The inherent approach is the most recommended, the most robust because it meets the above qualities.

Metrics: A large number of metrics are currently available for risk assessment. These metrics can be of quantitative and qualitative nature. Indices are often widely used, however, these are based on fixed parameters of the substances, being useful in providing information regarding the risk of a process, but these limit the selection of the appropriate conditions of operation of this. The most appropriate metrics to represent the risk, must be based on the physical properties of the substances, in order to formulate an objective function that allows to optimize the operating conditions. The individual risk and social risk are the metrics used in these works, these two are based on the QRA, which consists of a methodology that considers the physical properties of the substance, allowing the optimization of the operating conditions of the process. Moreover, it is necessary to mention a very important aspect in relation to the metrics used to measure risk, this has to do with the way in which the risk arises, it can be presented in economic terms or in terms of fatalities.

The main disadvantage of presenting the risk in economic terms is that it avoids the generation of multiobjective models of optimization besides that it is complicated to put price to any human losses. Thus it is more convenient to present the risk in terms of fatalities (social risk) or in terms of frequency (individual risk).

The points mentioned above were the main conclusions of the experience generated in the development of these works. Thus, in addition to develop these methodologies to serve as a tool and guide to a decision taken, the development of this work also allowed to generate criteria that will involve more adequately the safety concept design process.

Appendix A. Supplementary Material

Table S1. Continuous release liquid-phase.

<i>Working Fluid i</i>	<i>a_i</i>	<i>b</i>
Benzene	8.96	9.34E-07
Toluene	8.19	9.34E-07
Butene	9.83	9.34E-07
Isobutene	10.00	9.34E-07
Pentane	9.64	9.34E-07
Isopentane	9.71	9.34E-07
Hexane	9.42	9.34E-07
Isohexane	9.74	9.34E-07
Cyclohexane	8.64	9.34E-07
Heptane	9.22	9.34E-07
Octane	9.09	9.34E-07
Nonane	9.00	9.34E-07
Decane	8.92	9.34E-06
R113	6.21	9.34E-06
R114	6.19	9.34E-06
R115	6.13	9.34E-06
R123	6.31	9.34E-07
R124	6.22	9.34E-07
R218	6.02	9.34E-07
R227ea	6.31	9.34E-07
R236fa	6.25	9.34E-07
R245ca	6.12	9.34E-07
R245fa	6.32	9.34E-07
RC318	5.96	9.34E-07

Table S2. Continuous release gas-phase.

<i>Working Fluid i</i>	U_i	Z_i	N_i
Benzene	3.44	0.000005	0.000047
Toluene	3.67	0.000005	0.000051
Butene	3.12	0.000004	0.000041
Isobutene	3.12	0.000004	0.000041
Pentane	3.36	0.000005	0.000045
Isopentane	3.36	0.000005	0.000045
Hexane	3.55	0.000005	0.000049
Isohexane	3.55	0.000005	0.000049
Cyclohexane	2.81	0.000005	0.000038
Heptane	3.75	0.000005	0.000053
Octane	3.93	0.000006	0.000056
Nonane	4.05	0.000006	0.000057
Decane	4.46	0.000007	0.000066
R113	4.00	0.000006	0.000056
R114	3.81	0.000006	0.000054
R115	4.46	0.000007	0.000067
R123	4.54	0.000007	0.000068
R124	3.95	0.000006	0.000057
R218	4.97	0.000008	0.000076
R227ea	4.76	0.000007	0.000072
R236fa	4.22	0.000007	0.000071
R245ca	4.21	0.000007	0.000073
R245fa	4.72	0.000007	0.000074
RC318	5.07	0.000008	0.000078

Table S3. Jet Fire correlation.

<i>Working Fluid i</i>	$K6_i$	$K7_i$	$K8_i$
Benzene	3.01	0.040	0.104
Toluene	2.83	0.038	0.096
Butane	3.20	0.043	0.108
Isobutene	3.19	0.042	0.108
Pentane	3.14	0.042	0.107
Isopentane	3.14	0.042	0.106
Hexane	3.15	0.042	0.105
Isohexane	2.69	0.036	0.091
Cyclohexane	3.03	0.040	0.102
Heptane	3.12	0.042	0.105
Octane	3.35	0.045	0.114
Nonane	3.34	0.045	0.113
Decane	3.34	0.044	0.113

Table S4. Pool Fire correlation.

<i>Working Fluid i</i>	$K11_i$	s_i	w_i
Benzene	3.07	0.040	100.85
Toluene	3.70	0.048	124.26
Butene	3.26	0.043	110.25
Isobutene	2.99	0.039	100.74
Pentane	3.00	0.039	99.43
Isopentane	3.74	0.049	125.37
Hexane	3.19	0.042	108.03
Isohexane	3.25	0.043	109.25
Cyclohexane	3.56	0.047	119.90
Heptane	3.27	0.043	110.01
Octane	4.06	0.053	137.09
Nonane	4.04	0.053	135.91
Decane	4.08	0.054	137.51

Table S5. VCE correlation.

Working Fluid i	x_i	j_i	q_i
Benzene	342	4.491	0.004990
Toluene	316	4.152	0.004639
Butane	348	4.564	0.005082
Isobutene	346	4.553	0.005071
Pentane	347	4.455	0.005841
Isopentane	342	4.848	0.004513
Hexane	341	4.558	0.005126
Isohexane	349	4.957	0.004952
Cyclohexane	335	4.399	0.004849
Heptane	341	4.479	0.004990
Octane	360	4.744	0.005293
Nonane	360	4.737	0.005263
Decane	360	4.737	0.005263

Table S6. Concentration correlation.

<i>Working Fluid i</i>	<i>KI0_i</i>	<i>HH_i</i>	<i>V_i</i>
Benzene	38.335	564	3.892
Toluene	32.493	478	3.299
Butane	59.211	951	5.721
Isobutene	59.211	951	5.721
Pentane	41.474	610	4.213
Isopentane	41.474	610	4.213
Hexane	34.738	511	3.527
Isohexane	34.738	511	3.527
Cyclohexane	35.558	523	3.612
Heptane	29.313	431	3.068
Octane	26.182	385	2.661
Nonane	23.327	343	2.371
Decane	21.016	309	2.136
R113	15986	235	1.625
R114	17.486	257	1.778
R115	19.376	285	1.966
R123	19.579	288	1.988
R124	21.904	322	2.227
R218	15.911	234	1.617
R227ea	17.608	259	1.788
R236fa	19.702	289	00
R245ca	22.311	328	2.268
R245fa	22.311	328	2.268
RC318	14.958	220	1.520

Table S7. Acute Toxicity (LC₅₀) (AHRINET, 2000)

Working Fluid	LC50(ppm)
Benzene	44,700
Toluene	7,585
Butane	280,000
Isobutene	368,000
Pentane	6,106
Isopentane	51,000
Hexane	38,500
Isohexane	3,125
Cyclohexane	9,558
Heptane	48,000
Octane	25,250
Nonane	3,200
Decane	12,413
R113	52,500
R114	255,000
R115	800,000
R123	32,000
R124	262,500
R218	400,000
R227ea	788,696
R236fa	457,000
R245ca	84,900
R245fa	203,000
RC318	800,000

Table S8. Thermodynamic parameters.

Isobutene					Butane				
<i>State</i>	<i>h</i> (kJ/mol)	<i>T</i> (°C)	<i>s</i> (J/mol·K)	<i>W_i</i> (MW)	<i>State</i>	<i>h</i> (kJ/mol)	<i>T</i> (°C)	<i>s</i> (J/mol·K)	<i>W_i</i> (MW)
1	14.770	23.00	69.112	8.798	1	14.797	23.00	69.225	9.968
2	14.978	23.98	69.112		2	15.022	23.94	69.225	
3	39.689	108.40	138.260		3	43.290	126.14	146.120	
4	35.274	35.07	138.260		4	37.613	39.06	146.120	
Pentane					Isopentane				
<i>State</i>	<i>h</i> (kJ/mol)	<i>T</i> (°C)	<i>s</i> (J/mol·K)	<i>W_i</i> (MW)	<i>State</i>	<i>h</i> (kJ/mol)	<i>T</i> (°C)	<i>s</i> (J/mol·K)	<i>W</i> (MW)
1	-2.204	23.00	-7.269	11.659	1	-0.793	23.00	-2.649	11.442
2	-1.986	23.61	-7.269		2	-0.537	23.75	-2.649	
3	39.569	162.00	100.086		3	38.944	162.00	99.813	
4	29.976	66.97	100.086		4	29.947	67.43	99.813	
Hexane					Isohexane				
<i>State</i>	<i>h</i> (kJ/mol)	<i>T</i> (°C)	<i>s</i> (J/mol·K)	<i>W_i</i> (MW)	<i>State</i>	<i>h</i> (kJ/mol)	<i>T</i> (°C)	<i>s</i> (J/mol·K)	<i>W_i</i> (MW)
1	-9.244	23.00	-28.962	11.737	1	-7.436	23.00	-23.602	11.494
2	-9.123	23.26	-28.962		2	-7.291	23.31	-23.602	
3	42.870	162.00	104.248		3	42.999	162.00	105.698	
4	30.940	78.92	104.248		4	31.669	81.58	105.698	
Cyclohexane					Heptane				
<i>State</i>	<i>h</i> (kJ/mol)	<i>T</i> (°C)	<i>s</i> (J/mol·K)	<i>W_i</i> (MW)	<i>State</i>	<i>h</i> (kJ/mol)	<i>T</i> (°C)	<i>s</i> (J/mol·K)	<i>W_i</i> (MW)
1	-9.648	23.00	-29.656	12.748	1	-18.053	23.00	-54.123	11.722
2	-9.574	23.18	-29.656		2	-17.982	23.11	-54.123	
3	40.345	162.00	96.371		3	43.781	162.00	103.619	
4	27.957	62.38	96.371		4	29.701	84.89	103.619	
Octane					Nonane				
<i>State</i>	<i>h</i> (kJ/mol)	<i>T</i> (°C)	<i>s</i> (J/mol·K)	<i>W_i</i> (MW)	<i>State</i>	<i>h</i> (kJ/mol)	<i>T</i> (°C)	<i>s</i> (J/mol·K)	<i>W_i</i> (MW)
1	-28.434	23.00	-82.024	11.719	1	-40.281	23.00	-112.292	11.705
2	-28.393	23.06	-82.024		2	-40.257	23.02	-112.292	
3	42.819	162.00	99.477		3	40.018	162.00	92.068	
4	26.630	88.27	99.477		4	21.812	90.52	92.068	
Decane					R113				
<i>State</i>	<i>h</i> (kJ/mol)	<i>T</i> (°C)	<i>s</i> (J/mol·K)	<i>W_i</i> (MW)	<i>State</i>	<i>h</i> (kJ/mol)	<i>T</i> (°C)	<i>s</i> (J/mol·K)	<i>W_i</i> (MW)

1	-53.559	23.00	-144.799	11.697	1	41.380	23.00	201.088	12.035
2	-53.542	23.02	-144.799		2	41.554	23.45	201.088	
3	35.613	162.00	82.009		3	84.986	162.00	312.603	
4	15.417	91.76	82.009		4	74.697	61.40	312.603	
R114					R115				
State	<i>h</i> (kJ/mol)	<i>T</i> (°C)	<i>s</i> (J/mol·K)	<i>W_i</i> (MW)	State	<i>h</i> (kJ/mol)	<i>T</i> (°C)	<i>s</i> (J/mol·K)	<i>W_i</i> (MW)
1	38.015	23.00	184.342	9.432	1	34.634	23.00	167.439	3.754
2	38.247	23.85	184.342		2	34.731	23.69	167.439	
3	68.393	122.37	267.250		3	50.994	50.24	218.360	
4	62.659	44.30	267.250		4	49.716	25.24	218.360	
R123					R124				
State	<i>h</i> (kJ/mol)	<i>T</i> (°C)	<i>s</i> (J/mol·K)	<i>W_i</i> (MW)	State	<i>h</i> (kJ/mol)	<i>T</i> (°C)	<i>s</i> (J/mol·K)	<i>W_i</i> (MW)
1	34.119	23.00	165.331	11.580	1	30.772	23.00	148.625	7.200
2	34.331	23.70	165.331		2	30.909	23.67	148.625	
3	70.534	150.62	260,020		3	54.864	84.57	218.230	
4	62.210	39.42	260,020		4	51.389	27.15	218.230	
R218					R227ea				
State	<i>h</i> (kJ/mol)	<i>T</i> (°C)	<i>s</i> (J/mol·K)	<i>W_i</i> (MW)	State	<i>h</i> (kJ/mol)	<i>T</i> (°C)	<i>s</i> (J/mol·K)	<i>W_i</i> (MW)
1	42.419	23.00	204.742	4.085	1	38.482	23.00	185.659	6.496
2	42.561	23.86	204.742		2	38.667	23.81	185.659	
3	59.508	55.82	257.410		3	62.678	82.24	256.420	
4	58.027	29.06	257.410		4	59.475	35.35	256.420	
R236ea					R236fa				
State	<i>h</i> (kJ/mol)	<i>T</i> (°C)	<i>s</i> (J/mol·K)	<i>W_i</i> (MW)	State	<i>h</i> (kJ/mol)	<i>T</i> (°C)	<i>s</i> (J/mol·K)	<i>W_i</i> (MW)
1	34.712	23.00	167.121	9.303	1	34.725	23.00	167.151	7.826
2	34.956	23.84	167.121		2	34.900	23.66	167.151	
3	67.637	122.81	257.260		3	63.486	97.44	248.910	
4	61.510	44.66	257.260		4	58.982	37.12	248.910	
R245ca					R245fa				
State	<i>h</i> (kJ/mol)	<i>T</i> (°C)	<i>s</i> (J/mol·K)	<i>W_i</i> (MW)	State	<i>h</i> (kJ/mol)	<i>T</i> (°C)	<i>s</i> (J/mol·K)	<i>W_i</i> (MW)
1	30.829	23.00	148.152	10.994	1	30.858	23.00	148.247	10.033
2	31.056	23.67	148.152		2	31.075	23.72	148.247	
3	69.447	147.68	249.790		3	65.821	129.40	242.560	
4	61.053	47.77	249.790		4	58.858	41.46	242.560	
RC318					Benzene				

<i>State</i>	<i>h</i> (kJ/mol)	<i>T</i> (°C)	<i>s</i> (J/mol·K)	<i>W_i</i> (MW)	<i>State</i>	<i>h</i> (kJ/mol)	<i>T</i> (°C)	<i>s</i> (J/mol·K)	<i>W_i</i> (MW)
1	44.987	23.00	217.464	7.445	1	-7.968	23.00	-24.539	13.416
2	45.226	23.84	217.464		2	-7.904	23.17	-24.539	
3	74.584	100.83	301.760		3	38.566	162.00	91.621	
4	70.115	47.72	301.760		4	26.437	28.85	91.621	
Toluene									
<i>State</i>	<i>h</i> (kJ/mol)	<i>T</i> (°C)	<i>s</i> (J/mol·K)	<i>W_i</i> (MW)					
1	-14.893	23.00	-43.863	13.317					
2	-14.855	23.08	-43.863						
3	39.811	162.00	92.859						
4	25.686	45.62	92.859						

Table S9. Mass flow required for the ORC.

<i>Working Fluid i</i>	<i>PM_i</i> <i>(kg/kmol)</i>	<i>FM_i</i> <i>(kg/s)</i>
Benzene	78.11	86.87
Toluene	92.14	87.10
Butane	58.12	106.26
Isobutane	58.12	121.55
Pentane	72.15	89.73
Isopentane	72.15	94.44
Hexane	86.18	85.66
Isohexane	86.18	88.56
Cyclohexane	84.16	87.13
Heptane	100.20	83.84
Octane	114.23	82.90
Nonane	128.26	82.57
Decane	142.28	82.47
R245ca	134.05	180.45
R245fa	134.05	199.37
R123	152.93	218.31
R113	187.38	222.96
R236ea	152.04	240.42
R236fa	152.04	274.87
R114	170.92	293.01
R124	136.48	294.43
RC318	200.03	352.12
R227ea	170.03	365.96
R115	154.47	490.86
R218	188.02	573.38

Table S10. GWP_i values (AHRINET, 2000)

Compound	GWP_i(kgCO₂/kgi)
Butane	4
Isobutane	3
Pentane	5
Isopentane	5
R113	6,000
R114	9,800
R115	10,300
R123	120
R124	620
R218	8,600
R227ea	3,800
R236fa	9,400
R245ca	720
R245fa	760
RC318	11,200

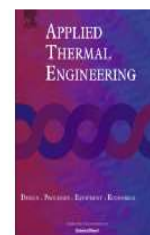
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Research Paper

Optimization of the production of syngas from shale gas with economic and safety considerations



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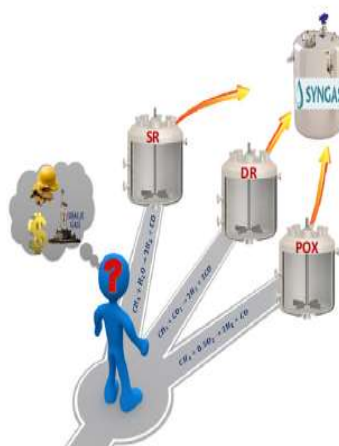
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HIGHLIGHTS

- An optimization approach is presented for the production of syngas from shale gas.
- Economic and safety issues are considered.
- A solution approach that links ASPEN PLUS, MATLAB and SCRI has been implemented.
- A case study is presented to show the applicability of the proposed approach.

GRAPHICAL ABSTRACT





Research article

A multi-objective optimization approach for the selection of working fluids of geothermal facilities: Economic, environmental and social aspects



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ABSTRACT

The selection of the working fluid for Organic Rankine Cycles has traditionally been addressed from systematic heuristic methods, which perform a characterization and prior selection considering mainly one objective, thus avoiding a selection considering simultaneously the objectives related to sustainability and safety. The objective of this work is to propose a methodology for the optimal selection of the working fluid for Organic Rankine Cycles. The model is presented as a multi-objective approach, which simultaneously considers the economic, environmental and safety aspects. The economic objective function considers the profit obtained by selling the energy produced. Safety was evaluated in terms of individual risk for each of the components of the Organic Rankine Cycles and it was formulated as a function of the operating conditions and hazardous properties of each working fluid. The environmental function is based on carbon dioxide emissions, considering carbon dioxide mitigation, emission due to the use of cooling water as well emissions due material release. The methodology was applied to the case of geothermal facilities to select the optimal working fluid although it can be extended to waste heat recovery. The results show that the hydrocarbons represent better solutions, thus among a list of 24 working fluids, toluene is selected as the best fluid.

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