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## Effects of combustion products composition models on the exergetic analysis of spark-ignition engine fuelled with ethanol

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**Abstract** The engine simulations have become an integral part of engine design and development. They are based on approximations and assumptions. The precision of the results depends on the accuracy of these hypotheses. The simplified models of frozen composition, chemical equilibrium and chemical kinetics provide the compositions of combustion products for engine cycle simulations. This paper evaluates the effects of different operating conditions and hypotheses on the exergetic analysis of a spark-ignition engine. The Brazilian automotive market has the highest number of flex-fuel vehicles. Therefore, a flex-fuel engine is considered for simulations in order to demonstrate the effects of these different hypotheses. The stroke length and bore diameter have the same value of 80 mm. The in-cylinder irreversibility is calculated for each case at the closed part of the engine cycle. A comparative analysis of these hypotheses provides a comprehensive evaluation of their effects on exergetic analysis. Higher values of accumulated irreversibility are observed for the oversimplified hypothesis.

**Keywords:** Engine simulations; Combustion products; Spark-ignition engines; Ethanol; Irreversibility

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## Nomenclature

$A$	–	area
$C_k$	–	molar concentration of the $k$ th species
$c_p$	–	specific heat at constant pressure
$c_v$	–	specific heat at constant volume
$Ex$	–	total extensive exergy
$Ex^{Ch}$	–	chemical exergy
$ex^{Ch}$	–	specific chemical exergy
$ex^{Ch}$	–	specific chemical exergy on molar basis
$h^{HT}$	–	coefficient of heat transfer
$I$	–	irreversibility
$K_C$	–	molar concentration equilibrium constant
$k_b$	–	backward rate constant
$k_f$	–	forward rate constant
$L$	–	maximum number of chemical reactions
$M$	–	molar weight
$m$	–	mass
$P$	–	pressure
$Q$	–	heat transfer
$R$	–	constant of a mixture of gases
$r_c$	–	compression ratio
$S$	–	entropy
$T$	–	temperature
$t$	–	time
$U$	–	internal energy
$V$	–	volume
$x$	–	mass fraction

## Greek symbols

$\lambda$	–	relative air-fuel ratio
$\eta$	–	efficiency
$\nu''$	–	stoichiometric coefficient of a product of a elementary reaction
$\nu'$	–	stoichiometric coefficient of a reactant of a elementary reaction
$\nu_{k,l}$	–	difference between stoichiometric coefficients
$\theta$	–	crank position
$\omega$	–	angular velocity of the engine

## Subscripts

0	–	ambient conditions
II	–	second law
b	–	combustion

$i$	–	zone
$j$	–	iteration
$k$	–	component of a mixture
$l$	–	chemical reaction
$p$	–	products of combustion
$r$	–	reactants
$SOC$	–	start of combustion
$w$	–	cylinder wall

## 1 Introduction

Engine modeling has evolved with the ability to understand physical and chemical processes. Moreover, increasing computational capacity has also contributed to the engine modeling and simulation. These models help to understand physical and chemical phenomena and predict operating characteristics of internal combustion engines. Thermodynamic properties of working fluids can be determined by using algorithms in order to solve a set of differential equations, including conservation of mass and energy for engine cycle simulations. Heywood described this procedure in detail [5]. The working fluids inside cylinders may refer to air-fuel mixture and combustion products. Mathematical models are used to describe the in-cylinder phenomena. These models are based on hypotheses and assumptions and the reliability of these models depends on the accuracy of assumptions and approximations [10].

Engine simulations can be performed to carry out exergy analysis. Irreversibilities are quantified by carrying out exergy analysis [11]. Most of the exergy destruction can be attributed to the combustion process in internal combustion engines. Internal heat transfer is chiefly responsible for entropy production during combustion [2]. The accuracy of estimated exergy destruction depends on the realization of all the chemical reactions occurring during combustion [3,4]. Caton investigated the effects of different parameters on exergy losses during combustion [1]. Pollutant formation is directly associated with combustion. Composition of combustion gases can be estimated by different models.

Thus, frozen, chemical equilibrium and chemical kinetics hypotheses are considered for the compositions of combustion gases in this paper. The effects of engine operating conditions are evaluated for the aforementioned hypotheses. The accumulated irreversibility and second law efficiencies are also estimated for different cases and hypotheses. The detailed comparative analysis of these assumptions and their effects is presented.

## 2 Materials and methods

A comparison of exergetic analyses was carried out by considering frozen, chemical equilibrium and chemical kinetics compositions for reacting-gas mixtures in the engine. A flex-fuel spark-ignition engine fuelled with Brazilian commercial gasohol and hydrous ethanol was selected for these analyses. A computer code was developed for in-cylinder simulations by using Matlab [14], a high-level language and interactive environment for numerical computation, visualization, and programming.

### 2.1 Frozen composition

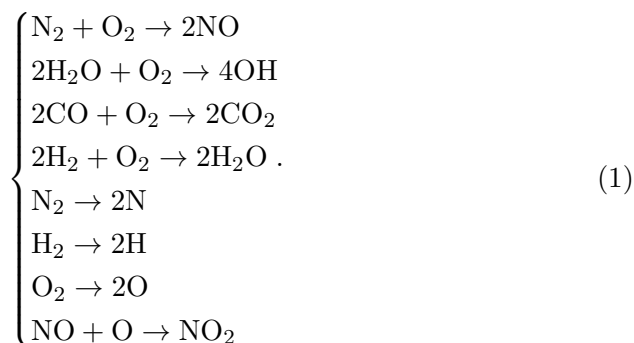
This hypothesis considers burned and unburned mixtures of fixed compositions. These compositions are given for stoichiometric, lean and rich burned mixtures in Tab. 1.

Table 1: Compositions for stoichiometric, lean and rich burned mixtures.

Burned mixtures	Combustion species
Stoichiometric	Argon (Ar) Nitrogen (N <sub>2</sub> ) Carbon dioxide (CO <sub>2</sub> ) Water (H <sub>2</sub> O)
Lean	Argon (Ar) Nitrogen (N <sub>2</sub> ) Oxygen (O <sub>2</sub> ) Carbon dioxide (CO <sub>2</sub> ) Water (H <sub>2</sub> O)
Rich	Argon (Ar) Nitrogen (N <sub>2</sub> ) Carbon dioxide (CO <sub>2</sub> ) Carbon monoxide (CO) Hydrogen (H <sub>2</sub> ) Water (H <sub>2</sub> O)

## 2.2 Chemical equilibrium composition

The chemical equilibrium model considers thirteen combustion products. These chemical species are argon (Ar), carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), atomic hydrogen (H), hydrogen (H<sub>2</sub>), water vapor (H<sub>2</sub>O), hydroxyl (OH), atomic oxygen (O), oxygen (O<sub>2</sub>), atomic nitrogen (N), nitrogen (N<sub>2</sub>), nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>). The following chemical reactions are considered for this hypothesis:



The details of the model are provided by Lima and Gallo [8] and Way [13].

## 2.3 Chemical kinetics composition

The chemical kinetics model considers twelve chemical species for combustion products, which are argon (Ar), carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), atomic hydrogen (H), hydrogen (H<sub>2</sub>), water vapor (H<sub>2</sub>O), hydroxyl (OH), atomic oxygen (O), oxygen (O<sub>2</sub>), atomic nitrogen (N), nitrogen (N<sub>2</sub>) and nitric oxide (NO). The mass-action law is applied in order to obtain the differential equations for each specie [12]

$$\frac{dC_k}{dt} = \sum_{i=1}^L \nu_{k,i} q_i, \quad (2)$$

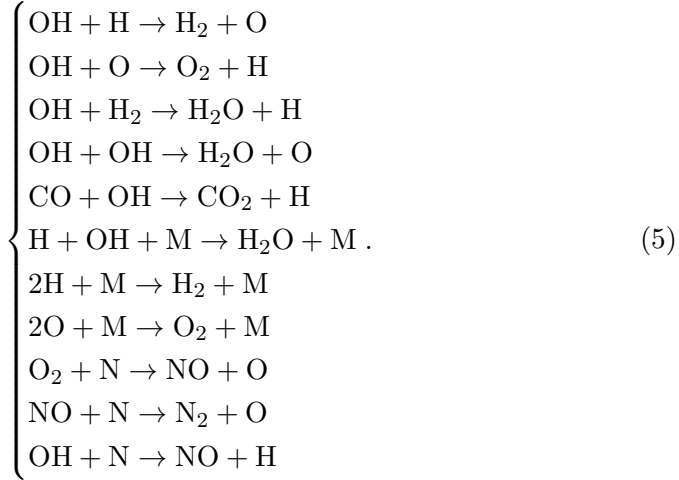
where  $q_l$  represents the reaction rate of a chemical reaction

$$q_l = k_{f,l} \prod_{k=1}^N C_k^{\nu'_{k,l}} - k_{b,l} \prod_{k=1}^N C_k^{\nu''_{k,l}}. \quad (3)$$

The forward ( $k_f$ ) and backward ( $k_b$ ) constants are related to the equilibrium constant

$$K_C(T) = \frac{k_f(T)}{k_b(T)}. \quad (4)$$

The implicit trapezoidal method, adopted by Lima and Gallo [9], is applied in order to carry out the simulations. They presented a chemical kinetic model by considering the following chemical reactions:



## 2.4 Engine simulations and exergy analysis

Mathematical models help to provide good approximations of real thermodynamic cycles of engines at different operating conditions. However, reliability of these models depends on the veracity of assumptions and approximations [10]. Specific heat, entropy and enthalpy are temperature-dependent thermodynamic properties, which are calculated for the each content of in-cylinder mixture according to the assumptions of each chemical composition model. A two-zone thermodynamic model was developed in order to carry out engine cycle simulations:

$$\frac{dT_r}{d\theta} = \frac{\delta Q_r + V_r \frac{dP}{d\theta}}{m_r c_p}, \quad (6)$$

$$\frac{dT_p}{d\theta} = \frac{\delta Q_p + V_p \frac{dP}{d\theta} + c_p(T_r - T_p) \frac{dm_p}{d\theta}}{m_p c_p}, \quad (7)$$

$$m_p = m \left\{ 1 - \exp \left[ -6.908 \left( \frac{\theta - \theta_{SOC}}{\Delta\theta_b} \right)^3 \right] \right\}. \quad (8)$$

Temperatures of reactants and products are given by Eqs. (6) and (7), respectively. Equation (8) provides the mass of products, represented by

$m_p$ , given by Wiebe function while keeping combustion duration ( $\Delta\theta_b = 50^\circ$ ) as constant. In-cylinder pressure is given by relation

$$\frac{dP}{d\theta} = \frac{P \frac{dV}{d\theta} + (R_r T_r - R_p T_p) \frac{dm_p}{d\theta} - \frac{R_r}{c_p} \delta Q_r - \frac{R_p}{c_p} \left[ \delta Q_p + c_p (T_r - T_p) \frac{dm_p}{d\theta} \right]}{\frac{V_r R_r}{c_p} + \frac{V_p R_p}{c_p} - V}. \quad (9)$$

These differential equations were solved by using a 5th order Runge-Kutta method. Irreversibilities were quantified by carrying out the exergetic analysis [11]. Change in irreversibility with respect to the crank angle is given by

$$\Delta I = \left(1 - \frac{T_0}{T_w}\right) (\delta Q_r + \delta Q_p) \delta\theta - P \delta V - \Delta Ex. \quad (10)$$

The reference temperature is denoted by  $T_0$  and the temperature of cylinder wall is denoted by  $T_w$ . Rate of heat transfer for each zone can be determined by

$$\delta Q_i = \frac{h_i^{HT} A_i (T_i - T_w)}{\omega}, \quad (11)$$

wherein the instantaneous area of each zone is represented by  $A_i$ . The heat transfer coefficient  $h_i^{HT}$  is calculated by the model described by Hohenberg [6].

The sum of changes in exergies of reactants and products provides the total change in exergy as presented by

$$\Delta Ex = \Delta Ex_r + \Delta Ex_p. \quad (12)$$

The terms of the equations are:

$$\Delta Ex_i = \Delta U_i - T_0 \Delta S_i + \Delta Ex_i^{Ch}, \quad (13)$$

$$\Delta U_i = m_i c_v \Delta T, \quad (14)$$

$$\Delta S_1 = m \left[ c_p \ln \left( \frac{T_i^j}{T_i^{j-1}} \right) - R \ln \left( \frac{P^j}{P^{j-1}} \right) \right], \quad (15)$$

$$\Delta Ex_i^{Ch} = (m_i ex_i^{Ch})^j - (m_i ex_i^{Ch})^{j-1}. \quad (16)$$

Second law efficiency can be derived from the ratio between the desired effect, which is the indicated power of the engine ( $\dot{W}$ ) and the exergetic content of the fuel ( $E\dot{x}_{fuel}$ ) [7]

$$\eta_{II} = \frac{\dot{W}}{E\dot{x}_{fuel}}. \quad (17)$$

### 3 Results

Simulation results are obtained for different engine operating conditions. A base case is considered in order to carry out comparative analysis for engine simulations. The operating conditions for each case are presented in Tab. 2. The evaluated parameters are engine speed, compression ratio ( $r_c$ ), relative air-fuel ratio ( $\lambda$ ) and fuel. Brazilian gasohol E27 (gasoline with 27% v/v of ethanol) and hydrous ethanol E95h (hydrous ethanol with 5% v/v of water) are considered as fuels for simulations.

Table 2: Engine operating conditions for different cases.

Case	Engine speed, rpm	$r_c$	$\lambda$	Fuel
Base	2000	12:1	1	E95h
1	2000	12:1	0.92	E95h
2	2000	12:1	1.12	E95h
3	1000	12:1	1	E95h
4	5000	12:1	1	E95h
5	2000	12:1	1	E27
6	2000	8:1	1	E95h
7	2000	14:1	1	E95h

The accumulated irreversibility for each hypothesis is presented in Fig. 1. Lower accumulated irreversibility can be observed for the chemical kinetics hypothesis during the combustion phase. The main reason is due to the formation of carbon monoxide (CO) and other intermediate chemical species in the combustion products, which have higher chemical exergetic content compared to that of final products. Soon after the start of combustion, exergy destruction remains low due to the formation of CO.

The comparative analysis is carried out comparing the concentrations of carbon monoxide (CO) and nitric oxide (NO) as functions of crank angle for stoichiometric, lean and rich conditions. The results for the concentration of carbon monoxide are shown in Figs. 2, 3, and 4. Frozen composition presents a non-zero value only for rich conditions due to the assumption of complete combustion. The rich condition presents the highest concentration of carbon monoxide for frozen, chemical equilibrium and chemical kinetics hypotheses. Lower concentration of CO can be observed for higher air-fuel (A/F) ratios. Carbon monoxide participates in reactions to form



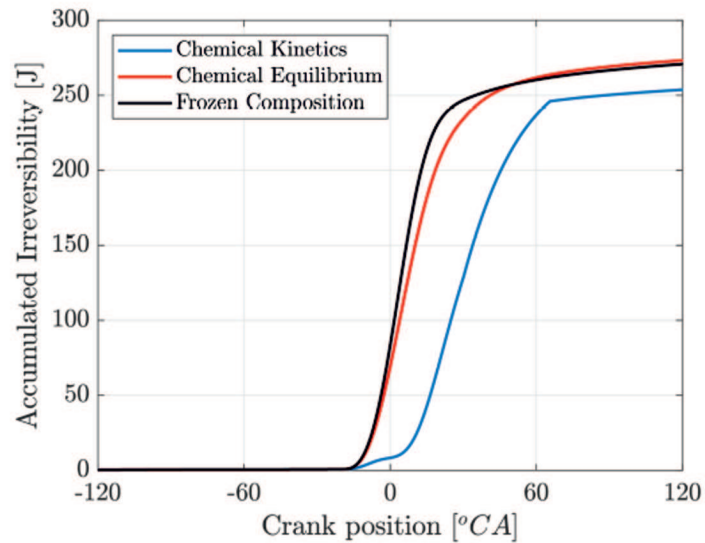


Figure 1: Effects of crank angle and chemical composition hypothesis on accumulated irreversibility.

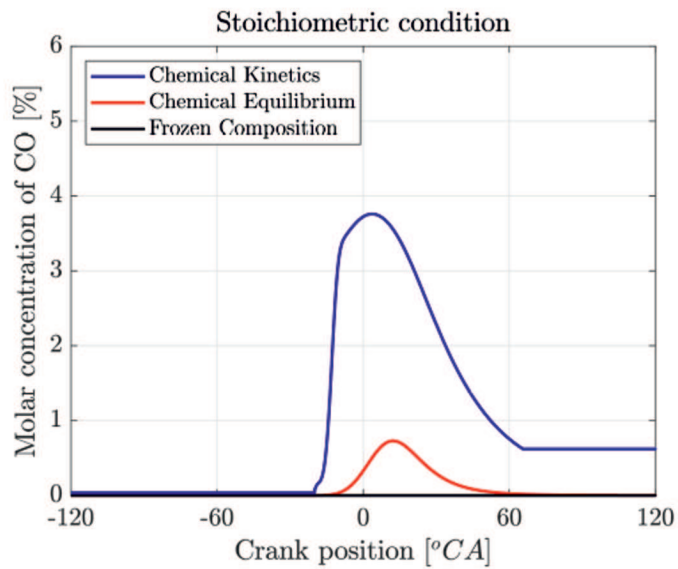


Figure 2: Concentration of carbon monoxide as a function of crank angle for stoichiometric condition.

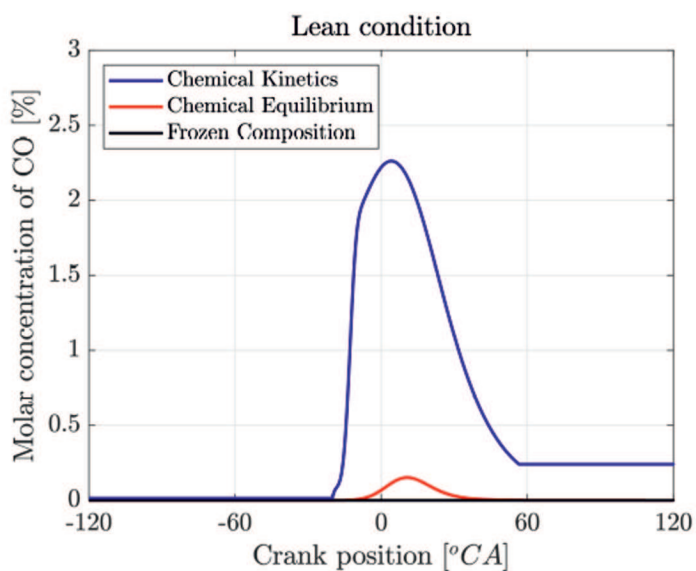


Figure 3: Concentration of carbon monoxide as a function of crank angle for lean condition.

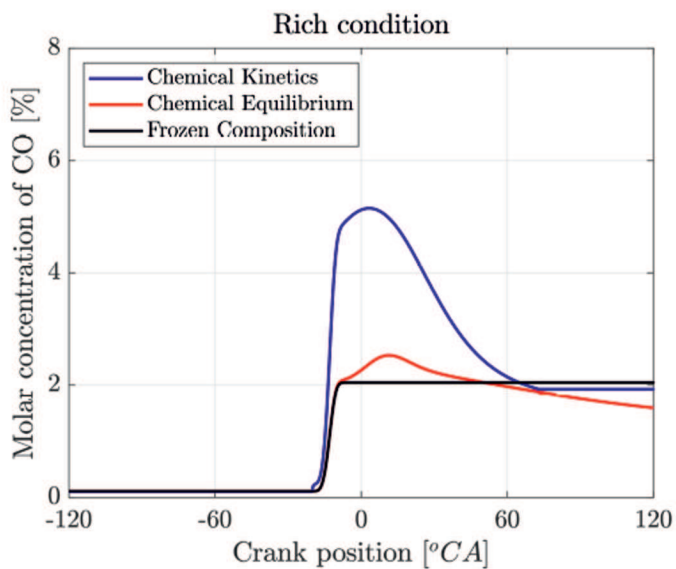


Figure 4: Concentration of carbon monoxide as a function of crank angle for rich condition.

carbon dioxide after combustion for chemical equilibrium hypothesis, therefore a lower concentration of carbon monoxide can be observed. However, it does not represent the real phenomenon. Since the reaction rate for carbon dioxide formation is slower, the concentration of carbon monoxide is conserved for chemical kinetics hypothesis. Consequently, the exergy destruction is lower for chemical kinetics hypothesis.

The nitric oxide concentration as function of crank angle for stoichiometric, lean and rich conditions are presented in Figs. 5, 6, and 7, respectively. Frozen hypothesis does not consider NO formation. The concentration of nitric oxide decreases after combustion for chemical equilibrium hypothesis. The final concentrations for stoichiometric, lean and rich conditions present a consistent behavior for chemical kinetics hypothesis. Since the molar concentration of nitric oxide is lower than that of carbon monoxide and its formation proceeds through endothermic reactions, therefore it does not affect the exergy destruction considerably.

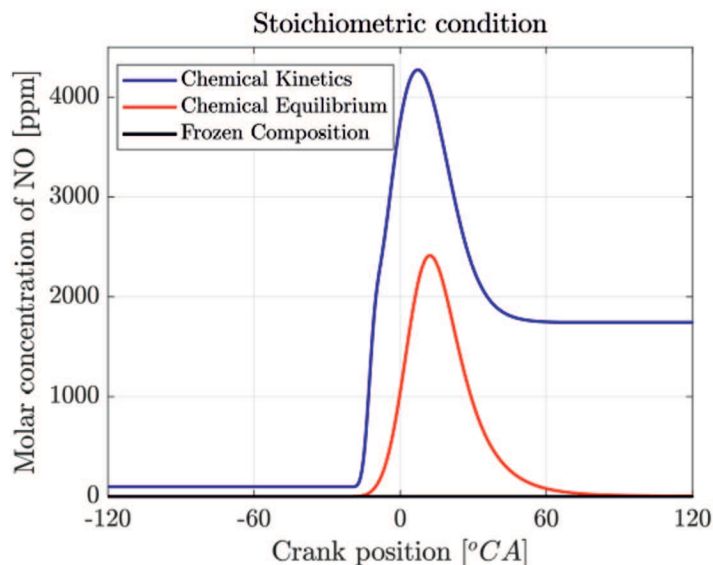


Figure 5: Concentration of nitric oxide as a function of crank angle for stoichiometric condition.

The accumulated irreversibility as a function of different operating conditions for a flex-fuel spark-ignition engine is shown in Fig. 8. All conditions, except for case 1, present similar trend while comparing composition hypotheses. Irreversibility for chemical equilibrium hypothesis is the highest

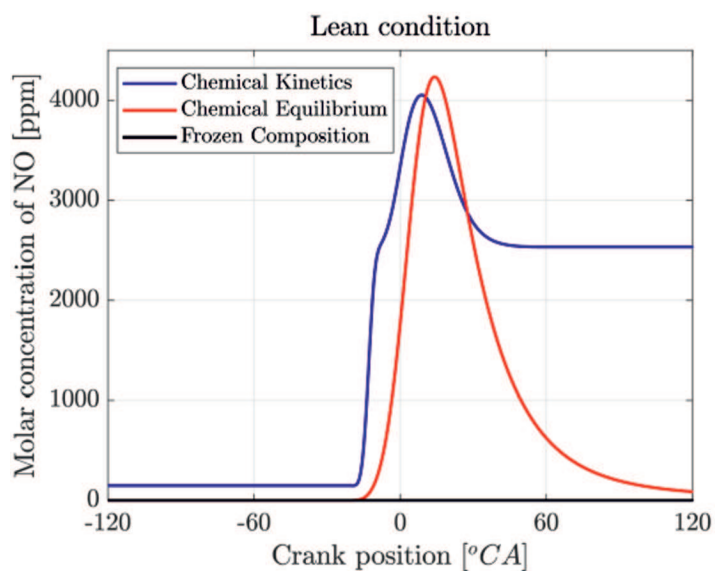


Figure 6: Concentration of nitric oxide as a function of crank angle for lean condition.

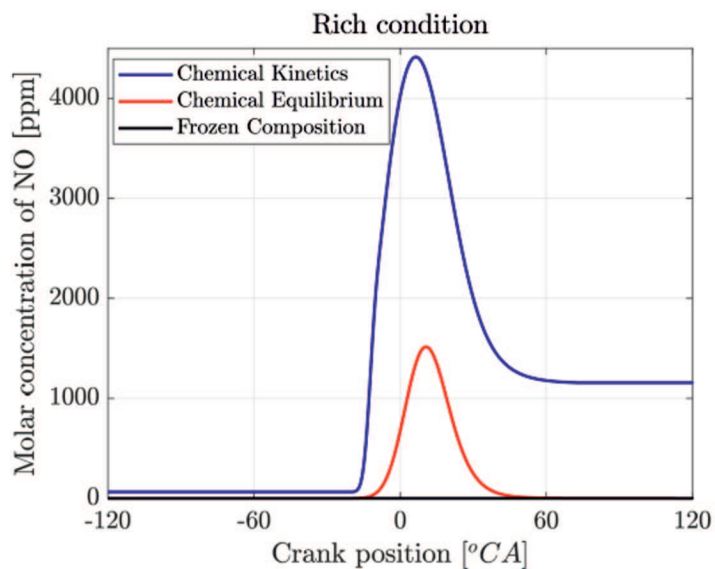


Figure 7: Concentration of nitric oxide as a function of crank angle for rich condition.

for those conditions, while irreversibility for chemical kinetics is lowest.

Chemical equilibrium hypothesis is based on the criteria of Gibbs free energy minimization. Chemical exergy is dependant on Gibbs free energy. Hence the highest irreversibility is observed for chemical equilibrium hypothesis.

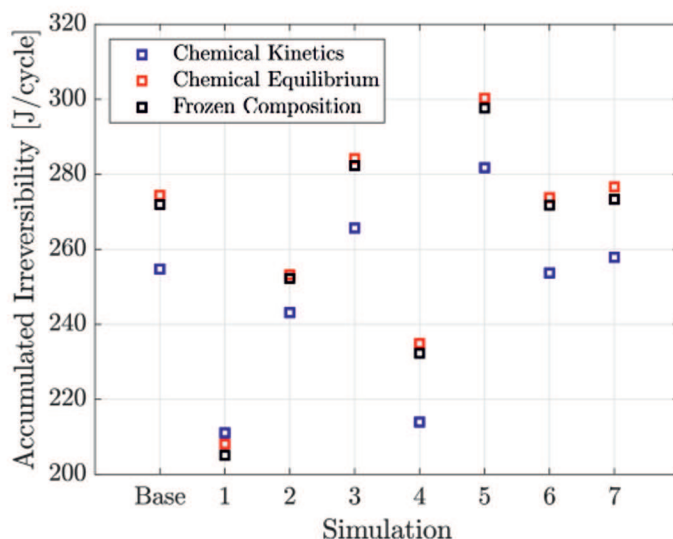


Figure 8: Effects of different engine operating conditions on accumulated irreversibility for chemical composition hypotheses.

Chemical kinetics hypothesis presents the highest accumulated irreversibility for case 1. This outcome is unexpected, which reveals the dependency of the first law analysis on lower heating value (LHV) of fuel. One possible explanation could be the fact that LHV is calculated based on complete combustion. The combustion is incomplete for rich conditions, therefore part of fuel energy is still present in combustion products.

Table 3 presents a comparison between the accumulated irreversibility of frozen, chemical equilibrium and chemical kinetics hypotheses while assuming the chemical kinetics hypothesis as comparatively accurate.

Second law efficiency for different hypotheses and cases is presented in Fig. 9. Chemical kinetics hypothesis presented the highest 2nd law efficiency for all cases. Additionally, lower values of combustion irreversibilities are observed for hydrous ethanol compared to that of gasohol fuel (case 5). Consequently, gasohol exhibits lower values of second law efficiency for all hypotheses. The cases with medium engine speeds exhibit higher values of

Table 3: Relative deviations of accumulated irreversibility for chemical equilibrium and frozen composition hypotheses.

Case	Relative deviation, %	
	Chemical equilibrium	Frozen composition
Base	7.72	6.76
1	-1.40	2.84
2	4.15	3.75
3	6.97	6.25
4	9.77	8.57
5	6.57	5.63
6	7.90	7.10
7	7.29	5.99

second law efficiency. The lower values of efficiencies for lower and higher engine speeds are due to higher heat losses and lower volumetric efficiency respectively. The engines with higher compression ratios have higher thermal efficiencies. Accordingly, the second law efficiency is also higher for a higher compression ratio.

## 4 Conclusions

Effects of engine operating parameters and chemical composition hypotheses on accumulated irreversibility and second law efficiency were evaluated for ethanol fuelled spark-ignition engine. Accumulated irreversibility is higher for chemical equilibrium and frozen compositions for all engine operating conditions excluding fuel rich conditions. The inappropriate consideration of energy released by combustion is responsible for higher accumulated irreversibility of chemical kinetics hypothesis. Chemical kinetics hypothesis exhibits higher values of second law efficiency for all engine operating conditions. Gasohol fuel has higher values of accumulated irreversibility and second law efficiency. Different hypotheses for the compositions of combustion products and engine operating conditions have a significant effect on accumulated irreversibility and second law efficiency, which are affirmed by the relative deviations of accumulated irreversibility provided by engine simulations.

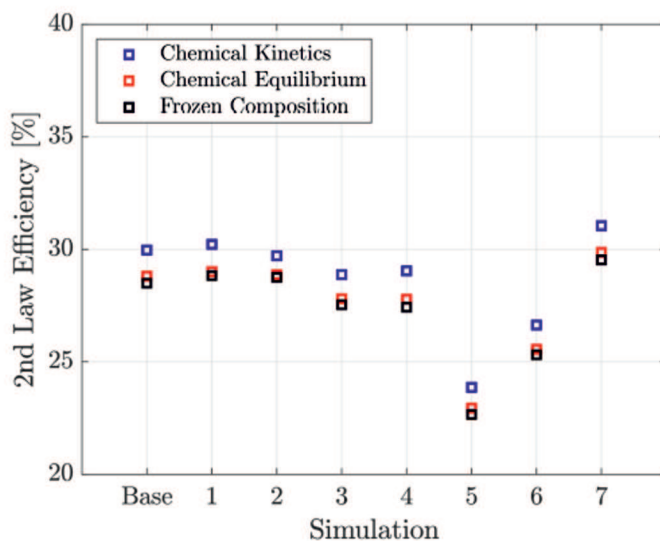


Figure 9: Effects of different engine operating conditions on second law efficiency for chemical composition hypotheses.

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