

Computational optimization of autothermal reactor based on chemical kinetic modeling of NATO F-76 for naval fuel cell system

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Abstract

Fuel cells provide great potential for electric power generation on-board surface ships. Autothermal reformer (ATR) is the core of the fuel processing system. Today naval ships use F-76 marine diesel fuel. In this study, ATR in NATO F-76 diesel fuelled solid oxide fuel cell system was optimized based on chemical kinetic modeling. Our analysis determined reactor or catalyst volume based on chemical kinetic modeling of NATO F-76 for naval fuel cells. The thermodynamic calculations were made with a commercial calculation tool (Comsol Reaction Engineering Lab.) using $C_{14}H_{30}$ as model fuel and an enhanced set of considered species and thermodynamic data.

Keywords: Autothermal reforming, NATO F-76, Fuel cell, Kinetic Modeling, Optimization

1. Introduction

Fuel cell based auxiliary power units (FC APU) are a promising alternative to conventional motor/generator based technologies. Hydrogen is the 'natural' fuel for most types of fuel cells. There are two main ways to produce hydrogen: one is by the electrolysis of water, the other is by reforming of fossil fuels, such as natural gas, gasoline and diesel. It has been suggested that fuel reforming is the more practical method due to its high-energy efficiency [1].

The diesel oil composition is not constant, as it is a function of starting crude oil source: it consists of numerous components and no single compound predominates [2]. In this study, NATO F-76 was chosen as a fuel. Because it has very high volumetric hydrogen density [1] and gravimetric density (min.12.5% H_2) [3]

and power systems for the navies of NATO countries operate on NATO F-76 marine diesel fuel that contains up to 1% by weight sulfur [3,4]. By 2008, maximum sulfur content is 0.5 % wt [3]. There is a need for the conversion of logistic NATO F-76 marine diesel fuel to a hydrogen rich gas, suitable for fuel cells.

Therefore, for the sake of simplicity in the search of chemical and physical properties, tetradecane ($C_{14}H_{30}$) was assumed in this work as the compound representative of the diesel fuel oil. Tetradecane is a good choice to be used as a surrogate for NATO F-76 fuel for the development of fuel processing systems since it is a heavy hydrocarbon liquid. Fuel properties is given Table 1 [5].

Table 1
Fuel Properties

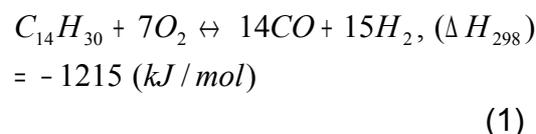
Fuel	Molecular Formula	Mole Weight
NATO F-76	$C_{14.8}H_{26.9}$ (avg)	205
Tetradecane	$C_{14}H_{30}$	198.39

Basically, reactor sizing is a process of accounting for changes in the masses of reactant and product species and of energy in each differential volume element of the reactor [6]. For individual reactors, the analyses have indicated that size and weight are very important. The optimize processor design will maximize the power density (kW/kg) and the specific power (kW/l).

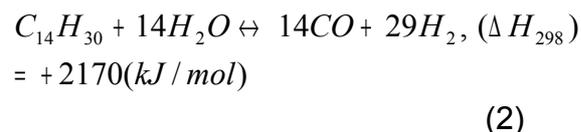
There has been no investigation into the mechanisms that are dominant in ATR of liquid fuels, it is widely accepted hydrogen is generated through two reactions that occur somewhat simultaneously, partial oxidation and steam reforming, which are described by the following reactions [7]:

Global reactions:

Partial Oxidation (POx):



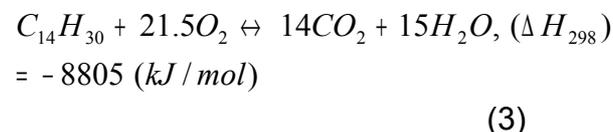
Steam reforming (SR):



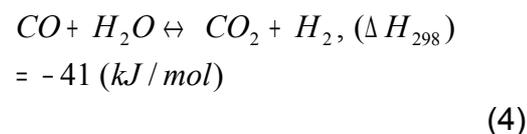
It has also been postulated that complete fuel oxidation and the water gas shift reactions play a significant role in overall mechanism for diesel ATR due to the presence of significant

amounts of CO_2 in the product stream [7].

Oxidation (Ox):



Water gas shift reaction (WGS):



2. Model development

Onboard surface warship, SOFC system providing 120 kW power has been designed. General system properties and ATR inlet gas composition are listed in the Tables 2, 3, and 4 [8], respectively. System runs in atmospheric pressure and its pressure drop is 0.1 bar.

Table 2
General System Properties

Type of fuel cell	SOFC
Net power	120 kW
Fuel type	NATO F-76
Type of reformer	ATR
Steam/carbon ratio	3.5
O ₂ /C	0.3
Pressure	Atmospheric pressure +0.1 bar
Fuel storage	Liquid diesel tank

Table 3
ATR inlet gas composition

Substance	mol/mol diesel	kg/h	m ³ /h	mol/h
NATO F-76	1	30	12	146
O ₂	3.80	17.79	45	554
N ₂	14.290	58.55	169	2086

H ₂ O	45.3148	119.36	542	6615
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The parameters obtained at atmospheric pressure via HSC Chemistry software described in Table 5.

Table 4
ATR exit gas composition (Inlet of fuel cell)

Reformate gas	mol/mol diesel	mol/m ³
H ₂	26.086	3.75
CO	4.3922	0.64
N ₂	14.290	2.26
H ₂ O	31.413	4.58
CO ₂	8.5549	1.24

In addition to the concentration dependence, we can include the temperature dependence of reaction rates by using the predefined Arrhenius expressions for the rate constants:

$$k = AT^n \exp\left(-\frac{E}{R_g T}\right) \quad (5)$$

In the Arrhenius parameters area, A denotes the frequency factor, n the temperature exponent, E the activation energy (J/mol) and R_g the gas constant, 8.314 J/(mol·K). The pre-exponential factor, including the frequency factor A and the temperature factor Tⁿ, is given the units (m³ mol⁻¹)^{α-1}/s, where α is the order of the reaction (with respect to the concentrations).

The entire mechanism contains 58 reactions and 30 species. The experimental reactor was comprised of a platinum catalyst supported on particulate alumina. While the catalyst serves to initiate the reaction mechanism, a mixture of gas phase

and surface reactions occur throughout the reactor. Table 6 summarizes the reaction mechanism and associated kinetic parameters [7].

A kinetic model of the mechanism was constructed using the standard procedures for developing reduced chemical kinetic models and was processed using The COMSOL Reaction Engineering Lab simulation software. The model includes initial reaction temperature, initial species concentration simulation duration, feed temperature, feed concentrations, and reactor space velocity. Kinetic parameters, thermodynamic and transport properties of gases were taken from literature [9, 10].

In this study, reactor types are the Continuous Stirred Tank Reactor (CSTR) with constant volume and the plug flow reactor (PFR) [11]. Reacting fluids in the gas phase are assumed to behave as ideal gases. CSTR is given in Fig.1 and PFR is given in Fig.2.

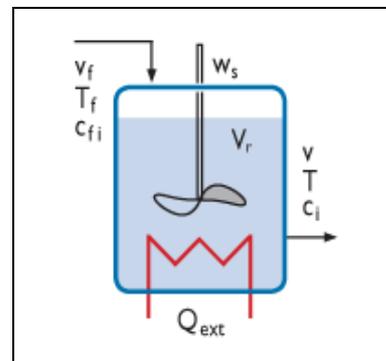


Fig.1. Continuous stirred tank reactor

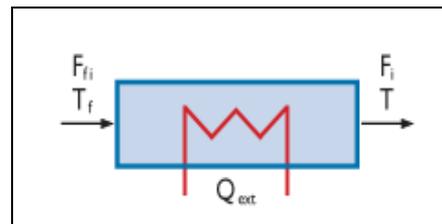


Fig.2. The Plug-flow reactor

Table 5
Tetradecane auto thermal reforming reaction mechanism
(provided by Lucas Dorazio, Marco J. Castaldi)

ID	Reaction	A (s ⁻¹)	n	E (J/mol)
1	$C_{14}H_{30} + 7O_2 \rightleftharpoons 15H_2 + 14CO$	5.0E+46	0.0	0
2	$C_{14}H_{30} + 21.5O_2 \rightleftharpoons 15H_2O + 14CO_2$	4.9E+15	0.0	0
3	$C_{14}H_{30} \rightleftharpoons C_7H_{16} + C_7H_{14}$	8.5E+05	0.0	82149.2
4	$C_{14}H_{30} + 14H_2O \rightleftharpoons 29H_2 + 14CO$	9.6E+56	0.0	2171706
5	$C_7H_{16} + 7H_2O \rightleftharpoons 15H_2 + 7CO$	3.5E+31	0.0	1107664
6	$C_7H_{14} + 7H_2O \rightleftharpoons 14H_2 + 7CO$	3.8E+36	0.0	919722.7
7	$C_2H_4 + 2H_2O \rightleftharpoons 4H_2 + 2CO$	5.0E+09	0.0	210462.1
8	$C_3H_6 + 3H_2O \rightleftharpoons 6H_2 + 3CO$	3.3E+13	0.0	373738.9
9	$CH_4 + H_2O \rightleftharpoons 3H_2 + CO$	7.6E+07	0.0	206266.9
10	$CO + H_2O \rightleftharpoons CO_2 + H_2$	1.0E+11	0.0	0
11	$C_7H_{14} + 3.5O_2 \rightleftharpoons 7H_2 + 7CO$	1.3E+30	0.0	0
12	$C_7H_{14} + 10.5O_2 \rightleftharpoons 7H_2O + 7CO_2$	9.2E+14	0.0	0
13	$C_7H_{16} + 3.5O_2 \rightleftharpoons 8H_2 + 7CO$	1.8E+25	0.0	0
14	$C_7H_{16} + 11O_2 \rightleftharpoons 8H_2O + 7CO_2$	2.4E+09	0.0	0
15	$C_7H_{16} \rightleftharpoons C_4H_9 + C_3H_7$	1.0E+40	-4.2	132855.5
16	$C_7H_{14} + H \rightleftharpoons C_7H_{13} + H_2$	2.5E+05	0.7	26293.1
17	$C_7H_{13} \rightleftharpoons C_4H_7 + C_3H_6$	7.2E+06	0.0	188406
18	$C_4H_7 \rightleftharpoons C_2H_4 + C_2H_3$	4.3E+05	0.0	154911.6
19	$C_4H_9 \rightleftharpoons C_3H_6 + CH_3$	1.4E+09	-0.3	30249.63
20	$C_4H_9 \rightleftharpoons C_2H_5 + C_2H_4$	1.4E+09	-0.3	29600.68
21	$C_4H_9 \rightleftharpoons C_4H_8 + H$	5.4E+08	-0.3	159768.3
22	$C_4H_8 \rightleftharpoons C_2H_3 + C_2H_5$	5.3E+09	-0.2	405156.6
23	$C_3H_7 \rightleftharpoons CH_3 + C_2H_4$	2.2E+07	-0.1	118905.1
24	$C_3H_7 \rightleftharpoons H + C_3H_6$	7.9E+07	-0.2	154158
25	$C_3H_7 + O_2 \rightleftharpoons C_3H_6 + HO_2$	7.5E+05	0.0	12560.4
26	$CH_3 + H_2 \rightleftharpoons CH_4 + H$	2.8E+01	0.7	7749.767
27	$C_2H_5 + H \rightleftharpoons 2CH_3$	8.7E+06	0.0	0
28	$CH_3 + H_2O \rightleftharpoons CH_4 + OH$	3.1E+05	0.7	0
29	$CH_3 + C_2H_5 \rightleftharpoons CH_4 + C_2H_4$	4.0E+13	-0.1	0
30	$CH_3 + H_2 \rightleftharpoons CH_4 + H$	5.9E+05	0.7	0
31	$CH_3 + HCO \rightleftharpoons C_2H_4 + O$	2.9E+03	0.3	133014.6
32	$O + H_2 \rightleftharpoons H + OH$	2.6E+02	0.6	26343.35

ID	Reaction	A (s ⁻¹)	n	E (J/mol)
33	$CH_3 + OH \rightleftharpoons CH_4 + O$	2.1E+02	0.5	16412.26
34	$CH_3 + O \rightleftharpoons CH_2O + H$	1.3E+07	0.0	0
35	$CH_2O + H_2 \rightleftharpoons CH_3 + OH$	3.9E+07	0.0	318322.4
36	$CH_2O + OH \rightleftharpoons HCO + H_2O$	7.6E+04	0.3	0
37	$HCO + OH \rightleftharpoons CO + H_2O$	1.5E+07	0.0	0
38	$HCO + H \rightleftharpoons CO + H_2$	1.2E+07	0.0	0
39	$HCO + CH_3 \rightleftharpoons CH_4 + CO$	1.6E+07	0.0	0
40	$HCO + O \rightleftharpoons CO_2 + H$	7.9E+06	0.0	0
41	$C_2H_3 + H_2O \rightleftharpoons C_2H_4 + OH$	2.1E+05	0.0	84657.1
42	$HO_2 + H \rightleftharpoons OH + OH$	1.2E+07	0.0	1235.106
43	$HO_2 + O \rightleftharpoons OH + O_2$	8.2E+06	0.0	0
44	$CH_3 + HO_2 \rightleftharpoons CH_4 + O_2$	4.4E+09	0.0	0
45	$H_2 \rightleftharpoons H + H$	1.2E+10	-0.3	418680
46	$C_2H_4 + H \rightleftharpoons CH + CH_4$	8.3E+11	-0.1	185826.9
47	$C_2H_4 + OH \rightleftharpoons C_2H_3 + H_2O$	7.9E+10	0.0	19945.92
48	$C_2H_4 + CH_3 \rightleftharpoons C_3H_6 + H$	2.1E+27	-1.4	105909.3
49	$C_2H_4 + O_2 \rightleftharpoons C_2H_3 + HO_2$	1.4E+11	0.0	194937.4
50	$C_2H_4 + H \rightleftharpoons C_2H_3 + H_2$	2.0E-02	1.1	8649.929
51	$C_2H_4 \rightleftharpoons C_2H_2 + H_2$	7.2E+10	0.0	254557.4
52	$C_2H_4 + HO_2 \rightleftharpoons C_2H_5 + O_2$	4.5E+24	-1.3	74726.01
53	$C_2H_4 \rightleftharpoons C_2H_3 + H$	3.0E+12	0.0	358725
54	$C_2H_4 + OH \rightleftharpoons C_2H_4OH$	6.7E+09	0.0	0
55	$C_2H_4 + C_2H_3 \rightleftharpoons C_4H_7$	5.8E+08	0.0	23446.08
56	$C_2H_4 + H_2 \rightleftharpoons 2CH_3$	2.0E+10	0.2	283731.1
57	$C_2H_4 + H \rightleftharpoons CH_2(S) + CH_3$	4.3E+12	0.0	230575.4
58	$C_2H_4 + CO \rightleftharpoons CH_2(S) + CH_2CO$	6.7E+12	0.0	353700.9

For a perfectly mixed reactor with a predefined constant temperature, we do not need the reacting system's energy balance in order to describe the system behavior. The behavior is defined as the composition and the production or consumption of species over time.

The reactions run under isothermal conditions, and the temperature is kept at 973.15 K throughout. The simulation takes place in CSTR and PFR. The purpose of the

modeling is to study the composition in the reactor over time and determine how long it takes the system to reach steady state, where it is possible to

determine the reaction's equilibrium constant.

The COMSOL Reaction Engineering Lab was used to create models of reacting systems. The CSTR has reacting species entering and leaving the reactor by means of feed and outlet streams. The reactor is once again assumed to be perfectly mixed,

so that the species concentrations of the exit stream are the same as the concentrations in the reactor volume.

For CSTR,

The species mass balances are given by:

$$\frac{d(c_i V_r)}{dt} = v_{f,i} c_{f,i} - v_{ci} + R_i V_r \quad (7)$$

Where v is the volumetric flow rate (m^3/s) of the outlet stream. Assuming constant reactor volume:

$$\frac{dV_r}{dt} = 0 \quad (8)$$

and setting the volumetric flow rate to:

$$v = \sum v_{f,i} + v_p \quad (9)$$

The term v_p denotes the volumetric production rate due to reaction (m^3/s):

$$v_p = \frac{R_g T}{p} \sum_j \sum_i v_{ij} r_j V_r \quad (10)$$

where v_{ij} is the stoichiometric coefficient of species i in reaction j , M_i denotes the species molecular weight (kg/mol), ρ_i the species density (kg/m^3), and r_j is the reaction rate ($\text{mol}/(\text{s} \cdot \text{m}^3)$) of reaction j .

For an ideal gas, the species molar volume (m^3/mol) is the same for all species:

$$\frac{M_i}{\rho_i} = \frac{R_g T}{p} \quad (11)$$

Equation can be rewritten as:

$$V_r \frac{dc_i}{dt} = v_{f,i} c_{f,i} - \left(\sum v_{f,i} + v_p \right) c_i + R_i V_r \quad (12)$$

The energy balance for an ideal reacting gas is:

$$V_r \sum_i c_i C_{p,i} \frac{dT}{dt} = w_s + Q + Q_{ext} + V_r \frac{dp}{dt} + \sum_i v_{f,i} c_{f,i} (h_{f,i} - h_i) \quad (13)$$

For an incompressible and ideally mixed reacting liquid, the energy balance is:

$$V_r \sum_i c_i C_{p,i} \frac{dT}{dt} = w_s + Q + Q_{ext} + \sum_i v_{f,i} c_{f,i} (h_{f,i} - h_i) \quad (14)$$

For PFR,

The species mass balances are given by:

$$\frac{dF_i}{dV} = R_i \quad (15)$$

where F_i is the species molar flow (mol/s), V is the reactor volume (m^3) and R_i denotes the species rate expression ($\text{mol}/(\text{m}^3 \cdot \text{s})$).

$$c_i = \frac{F_i}{v} \quad (16)$$

where v is the volumetric flow rate (m^3/s). For ideal gases:

$$v = \frac{R_g T}{p} \sum_i F_i \quad (17)$$

so that

$$c_i = \frac{p}{R_g T} \frac{F_i}{\sum_i F_i} \quad (18)$$

Another important parameter in reforming is the space velocity (SV) and residence time. SV is defined as

the proportion between the standard volumetric flow rate and the reactor volume, where u_o is the volumetric flow rate and V_{cat} is reactor or catalyst volume. Hourly space velocities for gases and liquids are typically denoted by GHSV and LHSV. Residence time is the actual time spent by an element of fluid in the reactor. In terms of volumetric flow and catalyst volume it is [6]

$$SV = \frac{v_o}{V_{cat}} \quad (19)$$

3. Results and discussion

Autothermal reforming is a combination of partial oxidation and steam reforming. The fuel is mixed with steam and substoichiometric amounts of oxygen or air where the ratios of oxygen to carbon (O: C) and steam to carbon (S: C) are properly adjusted so that the partial combustion supplies the necessary heat for endothermic steam reforming. Max. H_2 concentration and residence time is given Table 6. Concentration of max. H_2 plot as a function of GHSV is given in Fig.2.

Table 6
Optimization of ATR

Volume of ATR (l)	GHSV (h^{-1})	Concentration, H_2 (mol/m^3)	Residence time, t (s)
15	51,200	3.699	1.00
14	54,857	3.714	0.50
13	59,076	3.700	0.45
12	64,000	3.690	0.40
11	69,818	3.689	0.35
10	76,800	3.617	0.30

Figure 2 shows the effect of space velocity on the yields of H_2 from the autothermal reforming of n-tetradecane at 700 °C.

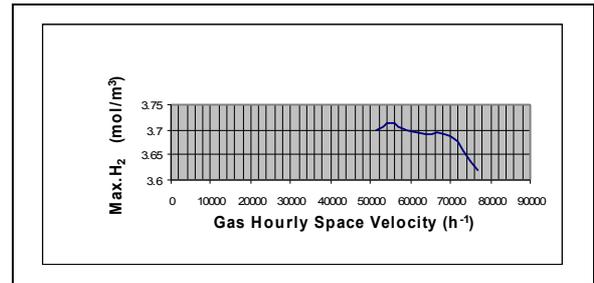


Fig.2. Concentration of max. H_2 plot as a function of GHSV

The diesel autothermal reformer (ATR) simulation setup consists of a diesel as a fuel input system and reformat analytical train. The ATR process regarded as a combination of two separate reactions: partial oxidation (POX) and steam reforming (SR). The ideal POX reaction is to convert diesel to H_2 and CO_2 . Similarly the ideal SR reaction also convert diesel to H_2 and CO_2 .

Under the idealized ATR reaction, the hydrogen is stoichiometrically converted to H_2 and CO_2 . However, this idealized chemistry is not attained because of the coexistence of other chemical reactions (the reverse water-gas shift reaction, methanation, and incomplete conversion).

The concentration profile generated by the model for major reactants and products for the 700 °C at different SV conditions is plotted in Fig. 3-7.

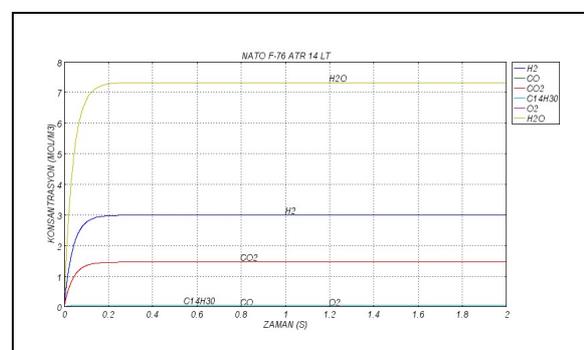


Fig.3. Reactant and major product concentration (reactor volume:14 l)

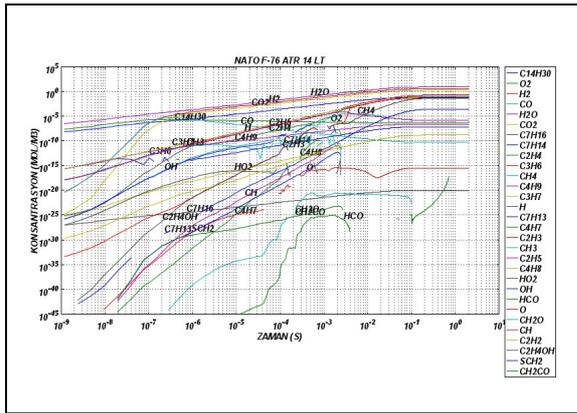


Fig.4. All the substances concentration plot as a function of residence time (reactor volume:14 l)

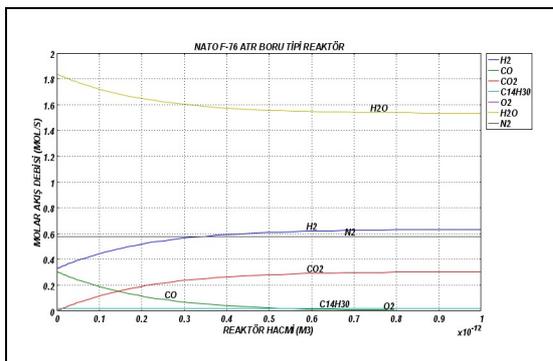


Fig.5. All the substances concentration plot as a function of residence time (reactor volume:1 l)

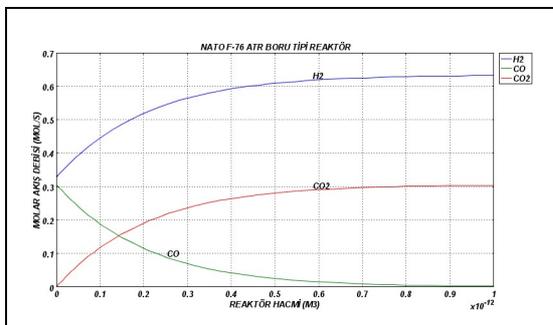


Fig.6. All the substances concentration plot as a function of residence time (reactor volume:1 l)

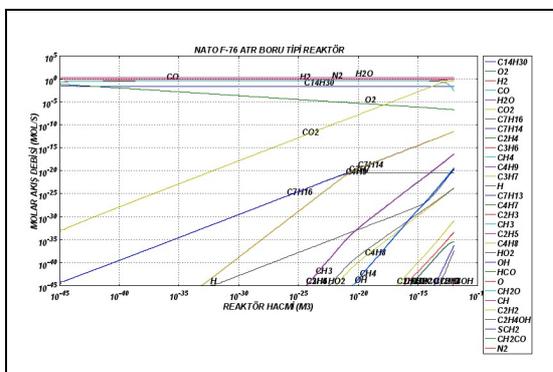


Fig.7. All the substances concentration plot as a function of residence time (reactor volume:1 l)

4. Conclusions

Computational ATR optimization based on a kinetic model describing the auto thermal reforming of NATO F-76 has been developed. This model accurately predicts the reaction products at a range of space velocities and temperatures. The steam to carbon and oxygen to carbon ratios chosen during operation impacts the reactor sizes.

Our simulation determined optimum volume of ATR. In CSTR, The ATR volume for power production of 120 kW in NATO F-76 diesel fuelled SOFC system was 14 liter and max. concentration of H₂ at exit of ATR was 3.711 mol/m³. In PFR, it was 1 liter. Generally, the yields of H₂ and CO increased with increasing reaction temperature and decreasing space velocity.

The studies have shown that it is basically possible to convert NATO F-76 diesel fuel into hydrogen-rich gas suitable to be used in fuel cells. Further developments in the next years are needed to bring this technology to commercialization and to meet all requirements of today's energy generation onboard naval ships.

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