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Fuel constituent effects on fuel reforming properties for fuel cell applications

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ABSTRACT

The effect of different types of compounds commonly found in diesel fuel (e.g., paraffins, naphthenes, and aromatics), as well as their chemical structure (e.g., branched versus linear paraffins) on fuel reforming has been investigated. Diesel reforming is very complicated because diesel is a complex mixture of hundreds of compounds with greatly different reactivities. The syngas production rates at the same conditions were observed in this order: paraffins > naphthenes ≫ aromatics. Additionally, the type of reforming performed (OSR, CPOX, or SR) as well as the process parameters (space velocity and reaction temperature) significantly affected the syngas production rates as well as carbon formation. The reactivity of one fuel component can affect the conversion pattern of others, e.g., overall yields from the reforming of a fuel mixture are not additive of yields from individual fuel components, rather the more reactive component is consumed first. Furthermore, the type of substituent in aromatics and naphthenes, the carbon chain length in *n*-paraffins, branching in paraffins, and degree of aromatic saturation affect the overall hydrocarbon conversion, syngas selectivity, and carbon formation. The presence of sulfur compounds in the fuel caused significant drops in H_2 yields compared to CO yields.

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1. Introduction

The idling of heavy diesel trucks used in military and commercial applications has been identified as an economic and environmental concern. Although some idling cannot be prevented, i.e. after start-up or in traffic, engines are often idled to provide supplementary power to accessories and climate control devices [1,2]. Van Den Berg [3] assessed the total electrical demands of a parked commercial truck to be around 4.2 kW. Such power requirements at the current time can only be met by idling, as the power requirements cannot be met by the batteries alone. At idle, the engine operates around 4–11% efficiency [4], compared to ~40% during normal operation [1,5]. Also, incomplete combustion of the fuel leads to increased amounts of particulate matter as well as NO_x and SO_x. Several studies [4,6] have documented that the engine emissions are greater during idling than under a full load.

Fuel cells are being investigated as auxiliary power units (APUs) for diesel vehicles because their high efficiency and low emissions can reduce the problems associated with discretionary idling. The solid oxide fuel cell (SOFC) and proton exchange membrane fuel cell (PEMFC) have emerged as possible APU devices. SOFC-based APUs offer a more practical approach than PEMFCs. The high temperature operation of the SOFC makes it less susceptible to contaminants like sulfur, and further simplifies the fuel processing system by eliminating the need for a CO clean-up step as is necessary for PEM-based fuel cells. In addition, the SOFC also has the additional ability of processing a significant fraction of methane directly in the incoming fuel. This is actually beneficial because the cell cooling provided by excess cathode air can be minimized due to the endothermic reforming of the methane on the anode and has the net effect of increasing system efficiency by removing heat and reducing parasitic pump requirements for the cathode air.

Although SOFCs run more efficiently on H_2 as fuel [7], current H_2 distribution networks and on-board storage technology are not advanced enough to handle extensive transportation demands [8]. Therefore, in the near term, the on-board catalytic reforming of the liquid fuel from the vehicle into a H_2-rich gas offers an attractive solution. Transportation fuels such as diesel have an existing, wide-spread distribution infrastructure [9], and can be easily converted into a H_2-rich gas. Diesel fuel reforming is also critical to the development of fuel cells for military applications [10].

The three general approaches to the catalytic reforming of diesel, steam reforming (SR), catalytic partial oxidation (CPOX), and oxidative steam reforming (OSR), are described below for a diesel fuel designated C_nH_m [11];

$$\text{SR}: \ C_nH_m + H_2O \rightarrow CO_x + H_2 \quad \Delta H_r > 0 \tag{1}$$

$$\text{CPOX}: \ C_nH_m + O_2 \rightarrow CO_x + H_2(+H_2O) \quad \Delta H_r < 0 \tag{2}$$

$$\text{OSR}: \ C_nH_m + O_2 + H_2O \rightarrow CO_x + H_2 \quad \Delta H_r \sim 0 \tag{3}$$

(where $n \sim 10$–20 and $x = 1$ or 2).

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Ahmed and Krumpelt [8] showed that for a number of fuels, OSR is slightly more thermodynamically efficient than SR or CPOX, though their analysis did not include diesel fuel. A similar conclusion can be drawn from a recent paper by Lutz et al. [12], who used *n*-heptane as a model fuel. The presence of steam in the reactant mixture for OSR reduces carbon deposition compared to CPOX [13] and results in a slightly higher hydrogen content in the product gas [14]. While it is recognized that exhaust gas recirculation-assisted reforming is possible [15,16], air-fed CPOX reforming is the simplest from a cost, complexity, and operational standpoint in cases where water is not readily available or desired.

In diesel fuel, the constituents can have carbon numbers ranging from 6 to 24. Lower hydrocarbons will react differently than higher hydrocarbons even within the same class of hydrocarbons; e.g., *n*-octane behaves differently in reforming than *n*-tetradecane. Also, the number of isomers increases as the carbon number increases in a hydrocarbon chain, e.g., tetradecane, $C_{14}H_{30}$, may have 1858 isomers [17]. Having such a complex composition makes reforming diesel a very complicated process because each component can undergo several different reactions, e.g., oxidation, steam/CO_2 reforming, etc. Some organic structures of diesel constituents are more favorable for certain reactions and, therefore, react differently. This suggests that a better understanding of the reforming reactions as a function of fuel composition, catalyst formulation, oxygen-to-carbon ratio, steam-to-carbon ratio, and temperature is required to ensure dynamic operation of fuel reformer during transients and during the long-term operations. It also helps in understanding how the chemical structure of diesel fuel components affects the overall reforming reaction rate, carbon formation, and the deactivation by sulfur poisoning. Furthermore, an understanding of how various classes of fuel compounds react, and interact, will assist in formulating an optimal catalyst for the fuel reforming process.

In the present work, the effects of the type of fuel constituent, chemical structure (e.g., paraffin branching), and sulfur poisoning on the overall hydrocarbon conversion, syngas selectivity, and carbon formation were studied for three different reforming modes (oxidative steam reforming, partial oxidation, and steam reforming). Due to very similar trends observed and significant amount of data generated from each of the three reforming modes, figures from only oxidative steam reforming will be presented in this paper. However, we point-out any significant differences among these three reforming modes.

2. Experimental

2.1. Diesel fuel composition analysis

Compositional analysis of the diesel fuels was performed by Triton Analysis Corporation using its NOISE™ (Nitric Oxide Ionization Spectrometry Evaluation) technique. In the NOISE analysis, diesel fuel components are first separated based on boiling point. In addition, gas chromatography separates sulfur-containing compounds from aromatics of the same molecular weight. Boiling point fractions are then bombarded with "soft" NO^+ ions. Mass spectrometry identifies each component, and reports by boiling region and degree of saturation. NOISE analysis gives percentages by boiling point and by *Z*-number (for C_nH_{2n+z}) where *Z* distinguishes between paraffins, cycloparaffins, mono-, di-, and tri-aromatics [18].

2.2. Reactor system and reaction conditions

The experimental system used for this study as well as its detailed description is documented elsewhere [19]. Briefly, these runs were carried out in a fixed bed continuous-flow reactor. The catalyst was diluted with quartz sand (5/1 by weight) to avoid channeling and to minimize temperature gradients. The bed was placed in a tubular reactor (8 mm i.d.) with a coaxially centered thermocouple at the center of the bed. Nitrogen and air were delivered by mass flow controllers and the liquid feeds were delivered by a high accuracy HPLC dual pump.

A summary of experimental conditions used in this study is given in Table 1. Individual model compounds representing each homologous series in diesel were subject of oxidative steam reforming (OSR), catalytic partial oxidation (CPOX), and steam reforming (SR) at temperature and space velocity ranges given in Table 1. Binary as well as tertiary compound mixture studies were also conducted to understand the interaction effects of feed components. Experiments were designed according to an on face centered central composite design for surface mapping the reforming. Temperature and space velocity were taken as design factors and the yields of H_2, CO, and CO_2 were used as responses for response surface plots. A total of ten experiments were conducted for each surface map; four corner points, four axial points, and one central point (replicated). The data from the experiment results were fitted to a quadratic equation. The fit of the data to the equation was checked by regression coefficient (R^2).

n-Tetradecane (TD), decalin (decahydronaphthalene; DHN), and 1-methylnaphthalene (MN) were identified as model compounds to represent paraffins, naphthenes, and aromatics, respectively, found in diesel. Also, additional model compounds that are structurally different than original model compounds were evaluated for their reforming properties. Compounds studied were *n*-hexadecane (HD; *n*-cetane), isocetane (2,2,4,4,6,8,8-heptamethylnonane), tetralin (tetrahydronaphthalene; THN), *n*-butylcyclohexane (NBCH), *t*-butylcyclohexane (TBCH), *n*-butylbenzene (NBB), *iso*-butylbenzene (IBB), *t*-butylbenzene (TBB), and *p*-isopropyltoluene (*p*-cymene; PC). Dibenzothiophene (DBT) was used as a sulfur-containing surrogate. DBT (50 ppm) was mixed in TD to mimic the sulfur concentration present in commercially available diesel.

0.61 wt% Pt/γ-Alumina (Alfa Aesar) catalyst (surface area 103 m^2/g and metal dispersion 60%) was used in this study as a base catalyst. Temperature programmed oxidation (TPO) of the spent catalyst was used to determine the amount of carbon deposited during the reforming reaction. An on-line mass spectrometer was used to monitor the CO_2 concentrations continuously during TPO. The total carbon accumulated on the catalysts was determined from the area under the TPO curve.

2.3. Product analysis

The gases (N_2, O_2, CO, CO_2, and H_2) were analyzed using a Thermo Onix mass spectrometer (Model No. Prima δb, a 200 a.m.u. scanning magnetic sector mass spectrometer). The gaseous hydrocarbon products (C_1–C_6 paraffins, C_2–C_6 olefins, and benzene) were analyzed using a HP5890 gas chromatograph equipped with a flame ionization detector. Oxygen conversion was always complete during these experiments. Although, water was produced in the reaction, it was not quantitatively analyzed. Overall carbon balances were typically 100 ± 5%.

Table 1
Experimental conditions.

	OSR	SR	CPOX
O/C^a	0.6	0.0	1.0 or 1.2
H_2O/C	1.5	3.0	0.0
T (°C)	750–900	750–900	750–900
GHSV (h^{-1})	21,500–143,000	21,500–143,000	21,500–143,000

[a] Molar ratio, calculated based only on molecular diatomic oxygen in the inlet air.