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Power Generation Using SOFC and VOC treatment

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Abstract

VOC (Volatile Organic Compounds) are organic compounds that can easily evaporate at room temperatures. Many VOCs are hazardous to human health and environment. The primary operation of an oil shuttle tanker is the loading and unloading of oil cargo at ports. During this process, a large quantity of lighter components evaporates from the oil. These oil vapours are technically called Volatile Organic Compounds (VOC), which are explosive in nature. VOC is also generated when the oil inside the tanks splashes while the ship is at sea. Here we propose the idea where rather than using these VOCs directly, we concentrate the VOC and steam reforms them which produce carbon monoxide, carbon dioxide and hydrogen. These products are then fed into Solid Oxide Fuel Cells (SOFCs) which uses these products to produce electrical energy for the ships. These SOFCs produce electrical energy with zero emissions and produce water and heat as by product which cause zero harm to the environment and reduce the pollution in the environment that the VOC would have caused. The power generated by Solid Oxide Fuel Cells is used for the electrical requirements on the ship which otherwise would have led to emissions which would have harmed the environment. The energy from the SOFC is produced with zero harmful emissions and caters to the requirements of the vessel.

Keywords: Volatile Organic Compound, Solid Oxide Fuel Cell, Power Generation, Steam Reforming

1. Introduction (Volatile organic compound)

Volatile Organic Compounds (VOCs) are any organic compounds that have an initial boiling point less than or equal to 250°C (482°F) when measured at a standard atmospheric pressure of 101.3 kPa. VOCs are a mixture of light end hydrocarbons (such as methane, ethane, propane or butane) that evaporate within the range of normal atmospheric conditions. VOCs are generated when cargo flashes in the piping system from the source to the cargo tanks, and from evaporation from the oil surface inside the cargo oil tanks during and after loading. During loading of crude oil tankers and the subsequent vessel transit, VOCs may be released to the atmosphere together with the inert gas. VOCs include a variety of chemicals, some of which may have short- and long-term adverse health effects. The emission of these pollutants has led to a large decline in air quality in numerous

regions around the world, which has ultimately led to concerns regarding their impact on human health and general well-being.[1-5].

1.1 Generation of Volatile Organic Compounds

VOCs are generated due to the positive pressure generated in cargo tankers while loading, the loaded voyage to discharge port and the from discharge port to the next port. During loading of tankers, the inert gas atmosphere has to be displaced. During the loading process or in the transit stages, the amount of VOCs that have evolved into the inert gas tank atmosphere is linked to the oil's volatility. Volatility is the tendency of a substance to vaporise.

1.2 IMO Regulation-15

There are two aspects of VOC control within this regulation. In the first, regulations 15.1 – 15.5 and 15.7, control on VOC emitted to the

atmosphere in respect of certain ports or terminals is achieved by a requirement to utilize a vapour emission control system (VECS). Where so required, both the shipboard and shore arrangements are to be in accordance with MSC/Circ.585 "Standards for vapour emission control systems". A Party may choose to apply such controls only to particular ports or terminals under its jurisdiction and only to certain sizes of tankers or cargo types. Where such controls are required at particular ports or terminals, tankers not so fitted may be accepted for a period of up to 3 years from the implementation date. The second aspect of this regulation, regulation 15.6, requires that all tankers carrying crude oil have an approved and effectively implemented ship specific VOC Management Plan covering at least the points given in the regulation. [6-10].

1.3 Environmental Impact of Volatile Organic Compounds

VOCs can broadly be classified into 2 groups that are methane and non-methane. The methane VOCs leads to greenhouse effect and contribute to global warming while the non-methane VOCs can lead to low level of petrochemical oxidants which can be detrimental to human health. VOCs can also be toxic, carcinogenic and teratogenic. During tanker loading operations, there is a higher flow of inert gas/VOC emissions exiting the cargo tanks through the mast riser into the atmosphere. The high flow rate can result in higher than normal VOC generation and can trap oil in the inert gas/VOC flow, which can then spill on the vessel deck. [8-12].

Table.1. Vapour Pressure of Common High VOC at 15°C

compound	Vapour pressure (kPa)	Emission Factor (kg/te)
acetone	19.6	0.13
benzene	7.84	0.071
cumene	0.166	0.0023
cyclohexane	8.13	0.079
ethanol	4.32	0.023
ethyl acetate	7.82	0.080
ethylbenzene	0.71	0.0088
ethylene glycol	0.00718	0.000052
MEK	7.82	0.065
methanol	9.84	0.037
m-xylene	0.602	0.0074
o-xylene	0.474	0.0058
p-xylene	0.638	0.0078
styrene	0	0.0053
toluene	2.21	0.024
pentane	46.5	0.39
hexane	12.8	0.13
cyclohexanone	3.70×10^{-5}	4.2×10^{-7}
cyclohexanol	7.58×10^{-6}	8.7×10^{-8}

The above table indicates the emission factor of various VOCs which together combine to form a mixture and get released in the atmosphere. Calculations:

$$E = S \frac{M_w p_v m_l}{10^3 R T \rho_l}$$

where E is the emission in tonnes, M_w is the molecular weight of the vapour, p_v is the vapour pressure of the cargo in Pa, m_l is the mass of liquid loaded in tonnes, R is the gas constant in J/(mol.K), T is the absolute temperature in K and ρ_l is the density of the liquid in kg/m³. S is an experimentally determined dimensionless constant that the USEPA calls a "saturation factor".

2. Solid Oxide Fuel Cells (SOFCs)

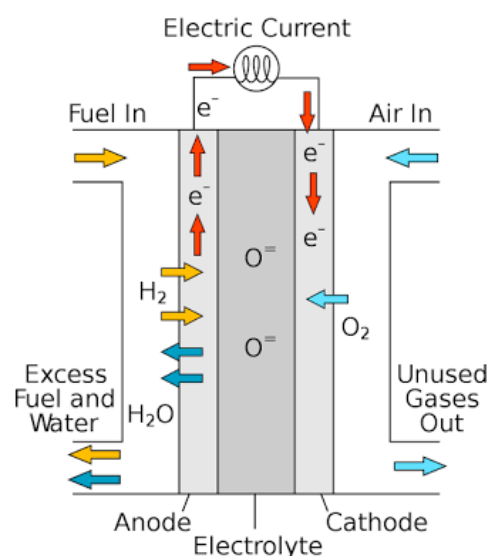


Fig.1. Solid Oxide Fuel Cell

Today world needs highly efficient system that can fulfil the growing demand for energy. One of the best solutions is the fuel cell, SOFC is considered by many developed countries as an alternative solution of energy in near future. Rising fuel prices and at the same time increase in the consumption of electricity it is necessary to implement much more efficient system for its production. SOFC is an electrochemical conversion device that produces electricity directly from oxidizing a fuel without combustion and no emission of pollutants. It utilizes solid oxide material as an electrolyte that conducts negative oxygen ions from the cathode to the anode. Hydrogen, carbon monoxide or other organic compound electrochemical oxidation by oxygen ions occurs on the side of the anode. In this reaction, for each oxygen ion, water is released by

product with heat as well as two electrons. Where they do the job, these electrons pass into an external circuit. When these electrons come back to the cathode material again, this cycle repeats. It consists of a catalyst for setting the rate of reaction and mobilizing the ions from one electrode to another.

2.1 Construction of SOFC

The SOFC comprises of different components like electrode, electrolyte, material for sealing, interconnects and distribution of fuel.

2.1.1 Cathode

The reduction of oxygen in SOFC takes place at cathode. The cathode must have high electronic and oxygen ion conductivity, matching thermal expansion coefficient with electrolyte chemical stability at operating temperature sufficient porosity and better catalyst for reduction reaction.

2.1.2 Anode

The primary objective of anode is the oxidation of fuel and to provide a path to electrons produced in oxidation reaction so they can reach at current collector. The SOFC anode should have properties like good electronic conductivity, sufficient permeability, good electro-catalytic activity, phase relevance with current collector and electrolyte, good microstructural strength to operate at SOFC working and a relating comparable thermal expansion coefficient with electrolyte.

2.1.3 Electrolyte

An electrolyte is a component in a solid oxide fuel cell used for the ion transportation between electrodes. High oxygen conductivity over a wide range of oxygen partial pressure is needed by electrolyte. A material can be a good electrolyte if it meets multifaceted property criteria. The electrolyte must be fully dense with no open porosity in order to avoid any cross diffusion of fuel and oxidant constituent.

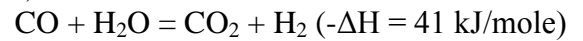
3. Steam Reforming of Volatile Organic Compounds

The principal process for converting hydrocarbons into hydrogen is steam reforming. It is reversible and strongly endothermic, and according to the principle of le Chatelier it must be carried out at high temperature. These involve following reactions:-

- First step of the steam reforming process involve organic compound reacting with steam at 600°C to 700°C to produce a synthesis gas

(syngas), a mixture which is made up of hydrogen and carbon monoxide (CO).

- $CH_4 + H_2O = CO + 3H_2$ ($-\Delta H = -206$ kJ/mole)
- The carbon monoxide formed in the first reaction is reacted with steam with a catalyst to form hydrogen and carbon dioxide, the second step known as the water gas shift (WGS) reaction. This process also occurs in two phases consisting of high temperature shift (HTS) at 35 ° C and low temperature shift (LTS) at 190 ° C.



As we can see steam reforming is endothermic reaction which requires heat and this need is fulfilled by supply of heat from SOFC.

- Third step which is called pressure swing adsorption, which is used to adsorb Carbon dioxide from the gas stream, leaving eventually hydrogen. Adsorbent materials are zeolite, activated carbon etc. It utilizes the fact that under high pressure gases like carbon dioxide are attracted towards these solid surfaces.

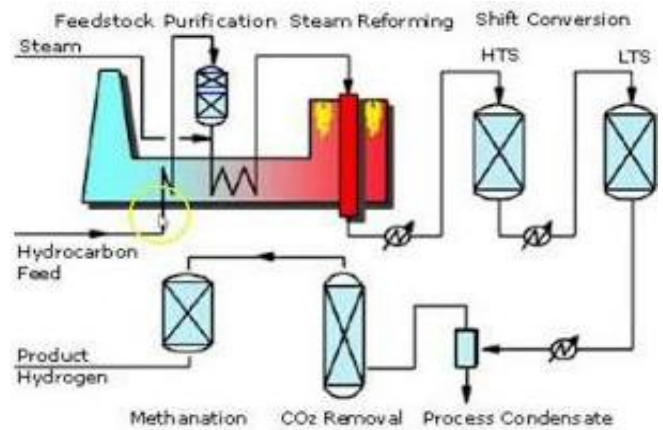


Fig.2. Steam Reforming of VOC
4. Methodology

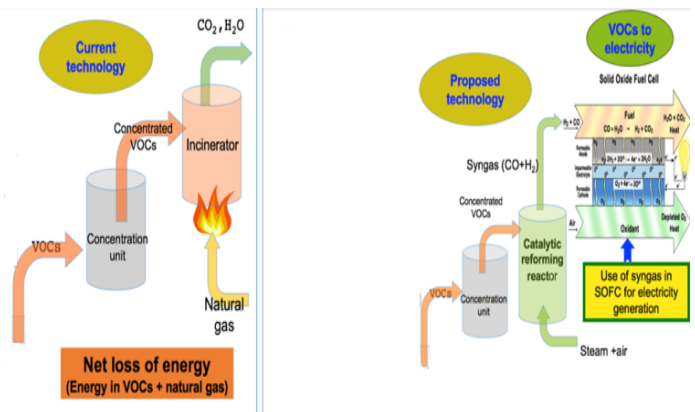


Fig.3. Proposed Methodology

The outline of the process that we suggest goes on with the process of trapping and condensing the VOCs which is generally released due to the displacement of the inert gas atmosphere at the time of loading or unloading in oil tankers. These VOCs are trapped and condensed in the concentration unit. This VOC then further is steam reformed in the catalytic reforming reactor which results in the formation of syngas that comprises of carbon monoxide (CO) and hydrogen gas (H₂) which act as the supply for the Solid Oxide Fuel Cells (SOFC) which produces electrical energy using the same and give out heat (exothermic reaction), water and electrical energy. The electrical energy is used to cater the electrical needs on the ship whereas the heat is used during the reforming process. The heat radiated is used for the steam reforming process of the VOC. As we go into the details, the VOC which otherwise would have been wasted and caused harm to the environment is now trapped and condensed and is sent for steam reformation which gives out syngas i.e. a combination of hydrogen gas and carbon monoxide which are further passed onto the solid oxide fuel cells for the further process. In the SOFC, various reactions occur at the cathode and the anode which results in the formation of water, heat and 2 electrons. The water and heat are used in various parts of this process to make this system self-sustainable, whereas the electrons flow in the circuit which leads to the generation of current in the circuit i.e. electrical power is generated. Further moving, CO₂ removal chambers are also there which consists of particles like activated charcoals or newly invented polymers like polyethylenimine which can capture the CO₂. In this manner the proposed technology can help in tackling a lot of issues and has great advantages.

5. Advantages of the Proposed System

- It is easy to manufacture and requires less components and parts. It is a solid state device.
- The by-products of the steam reforming process can be fed directly to the device that is **hydrogen**.
- The heat produced in the cell can be used as heat source/supplementary for other processes, here for steam reforming process.
- The steam produced can be used to run auxiliary steam turbine to produce more electricity.

- The fuel cell is more tolerant towards impurities than other fuel cells which in turn require less maintenance.
- The VOC which otherwise would have harmed the environment are now used to produce electrical energy.
- The required product for production of electrical energy is the substance that would have got wasted and caused harm to the environment.

6. Financial Factor

Fuel cell systems will compete with battery powered systems, internal combustion engine systems, and simply engine idling for application on long haul trucks. Fuel cell APU's offer a number of advantages over conventional technologies including fuel cost savings, reduced maintenance, and environmental benefits. However, fuel cell systems continue to have a higher first cost than conventional alternatives.

Table.2. Cost Comparison

	Fuel Cell	ICE Genset	Idling Truck Engine
Retail Cost of Power System	\$10,541	\$7,500	-
Power Source	5 kW SOFC Stack	15hp Diesel Engine	400hp Diesel Engine
Hours of Operation per Year (Hrs)	2,000	2,000	2,000
Energy Efficiency	30%	25%	3-4%
Fuel Consumption per Hour (gal/hr)	0.22	0.30	0.72 ⁴⁰
Maintenance Cost (per hour)	\$0.05	\$0.07	\$0.15
Fuel Cost (per hour)	\$0.77	\$1.05	\$3.50
Heater and Air Conditioner	\$1,800	-	\$1,800
Installation Cost	\$1,500	\$1,500	-
O & M Cost over 3 Years	\$300	\$420	\$900
Fuel Cost over 3 Years	\$4,620	\$6,300	\$15,120
Total Cost over 3 Years	\$18,761	\$15,720	\$17,820

Here the point to focus on is that the recurring cost for maintenance, fuel, fuel consumption are lower for the fuel cell and the efficiency is higher than that of the available technology, thereby making it an efficient and long term usable technology.

Moving further these fuel cells have less moving parts than that in the I.C. Engines and other systems therefore making it an easy to maintain system and also decreasing the physical maintenance cost. With advancements it was tested that 1cm*1cm SOFC was successful in producing 0.13 W of energy at 350°C, which makes it capable to produce 130kW of energy by a 10m*10m system.

7. Utilization of the electrical energy

The electrical energy that is produced can be used for both DC and AC work by the following arrangement on the vessel:

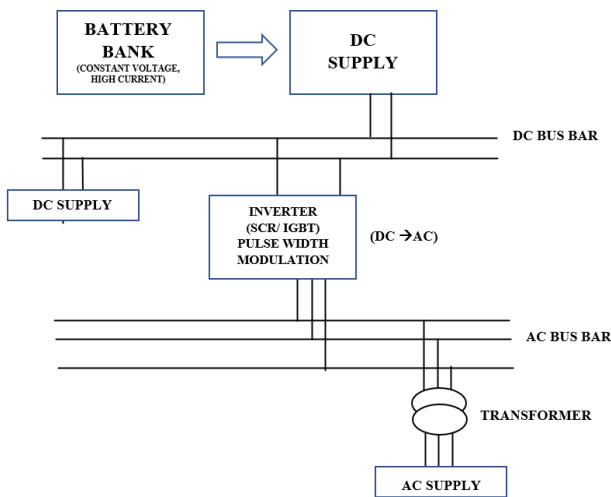


Fig.4.Utilization of the electrical energy

Conclusion

Keeping in mind the harm that VOC causes to the environment and the IMO Regulation 15 to look after the same, we suggest the steam reforming of the VOC to produce the intake substances for SOFC which produces electrical energy in a cost efficient manner. In this manner, we use the otherwise harmful substance to produce electrical power for the vessel.

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