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Feasibility of LOHC as hydrogen storage option for maritime industry

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FEASIBILITY OF LOHC AS HYDROGEN STORAGE OPTION FOR MARITIME INDUSTRY

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A dissertation submitted to the World Maritime University in partial fulfilment of the requirements for the award of the degree of Master of Science in Maritime Affairs

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Declaration

I certify that all the material in this dissertation that is not my own work has been identified, and that no material is included for which a degree has previously been conferred on me.

The contents of this dissertation reflect my own personal views, and are not necessarily endorsed by the University.

(Signature):

(Date): 25th September 2023

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Abstract

Title of Dissertation: **Feasibility of LOHC as Hydrogen storage option for maritime industry.**

Degree: **Master of Science**

The study mainly focused on the option of using Hydrogen onboard through liquid organic hydrogen carrier. To combat global warming and to become decarbonize as per the set target of IMO around 2050, alternative fuel option need investigation and the study tried to contributed on the decarbonization journey of maritime industry.

Among the existing possible alternative fuels, hydrogen due to its high energy density and possibility to be produced from renewable energy sources getting interest though storage challenge is making it difficult to be used onboard. One option of carrying hydrogen in ambient condition is carrying through LOHC. H2 can be carried and dehydrogenated whenever required through onboard dehydrogenation reactor. The simulation using DWSim showed the possibility of producing hydrogen onboard with satisfactory purity percentage using gas-liquid separator. The combustion simulation with Cantera provided understanding that, this H2 can be combustible in an ICE which enables to proceed further for checking options with LOHC.

The analysis reveals, the LOHC's possibility is not satisfactory in consideration of bunker storage capacity but in specific route base option it can be implemented. For transportation of hydrogen LOHC can be a solution for hydrogen storage with option to be used for propulsion.

KEYWORDS: LOHC, Dehydrogenation, Hydrogen, Simulation, IC engine

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List of Abbreviations

CO2	Carbon di Oxide
DBT	Dibenzyl toluene
DMCP1	1-1, Di-methyl-cyclopentane
DMCP2	1-2, Di-methyl-cyclopentanes
DMCP3	1-3, Di-methyl-cyclopentane
DME	Di-methyl-either
ECP	Ethyl-cyclopentane
H2	Hydrogen
H2ICE	Hydrogen fueled Internal Combustion Engine
ICE	Internal Combustion Engine
IEA	International Energy Agency
IMO	International Maritime Organization
LNG	Liquified Natural Gas
LOHC	Liquid organic hydrogen carrier
MCH	Methylcyclohexane
MeOH	Methanol
MEPC	Marine Environment Protection Committee
MTH	Methylcyclohexane–toluene-hydrogen
MXN	3-methylhexane
NECZ	N-ethyl-carbazole
NH3	Ammonia
NOx	Nitric Oxide and Nitrogen Oxide
PDBT	Per hydro dibenzyl toluene
PSA	Pressure swing adsorption
TOL	Toluene
UNCTAD	United Nation Conference on Trade and Development

Nomenclature

k_A	Rate constant of Dehydrogenation
K_A	Equilibrium constant of Dehydrogenation
k_T	Rate constant of Hydrogenation
K_T	Equilibrium constant of Hydrogenation
n_A	Order of Dehydrogenation Reaction
n_T	Order of Hydrogenation Reaction
P_A	Partial pressure of Methylcyclohexane
P_{D1}	Partial Pressure of 1-1, di-methyl-cyclopentane
P_{D2}	Partial Pressure of 1-2, di-methyl-cyclopentanes
P_{D3}	Partial Pressure of 1-3, di-methyl-cyclopentanes
P_E	Partial Pressure of ethyl-cyclopentane
P_H	Partial Pressure of Hydrogen
P_M	Partial Pressure of 3-Methylhexane
P_T	Partial Pressure of Toluene
r_A	Rate of Dehydrogenation
r_T	Rate of Hydrogenation
T	Temperature

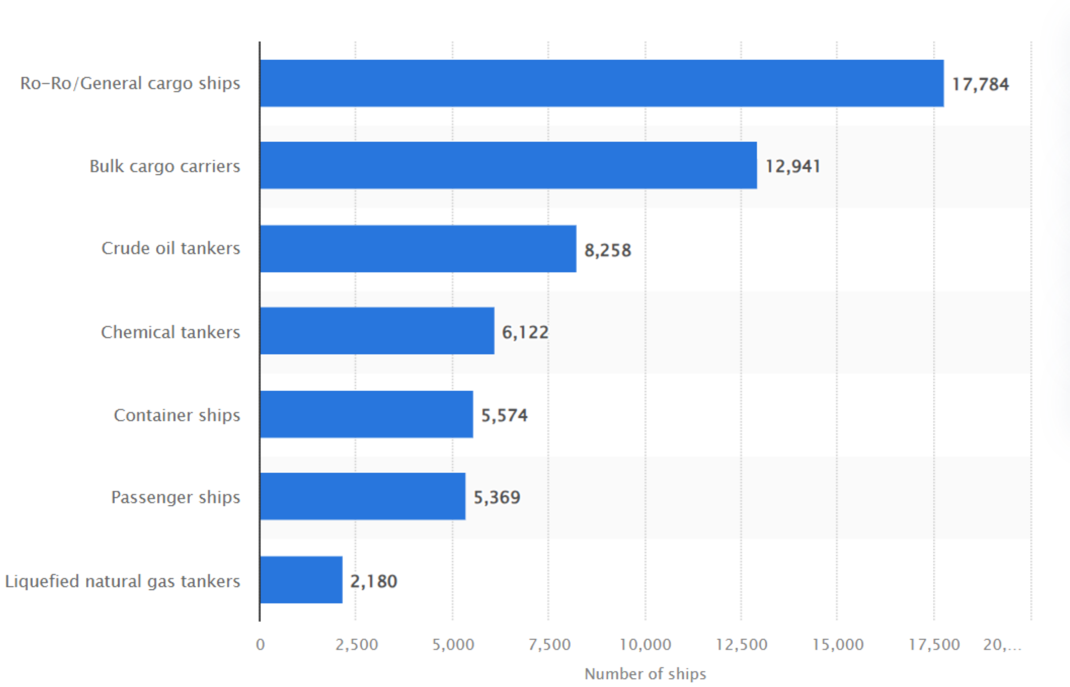
Introduction

With the gradual decrease in fossil energy reserve and drastic global warming issues, clean energy sources are getting priorities to become future energy sources for saving nature. In line with Paris agreement international shipping industry is set to become net zero close to 2050 as agreed on IMO MEPC 80 by the member states. The revised IMO GHG strategy strives the maritime sector to achieve both technological and economic advancement for the strategy set out with definite targets. In 2022, the estimated CO2 emission from shipping industry is about 2% (IEA,2023). To reduce the emission and achieve the target set at MEPC 80 in line with Paris agreement to combat global warming, maritime industry is shifting towards decarbonization. Industry is seeking solution to find fuels that has less impact on environment with characteristics of less emission and trying to find suitable technologies in support of decarbonization for the merchant vessels. Amongst the clean energy sources, hydrogen can be a potential race winner for its possibility to be produced from green and time-bound renewable energy sources for producing continuous energy.

1.1.Current Status vessel worldwide using Fossil Fuel

As per Statista report (2023) around 58,000 merchant ships trading internationally. These vessels mostly run on fossil energy. To accomplish the transition towards greener shipping industry the existing vessel need to be transformed and restructured to use the renewable and green energy sources.

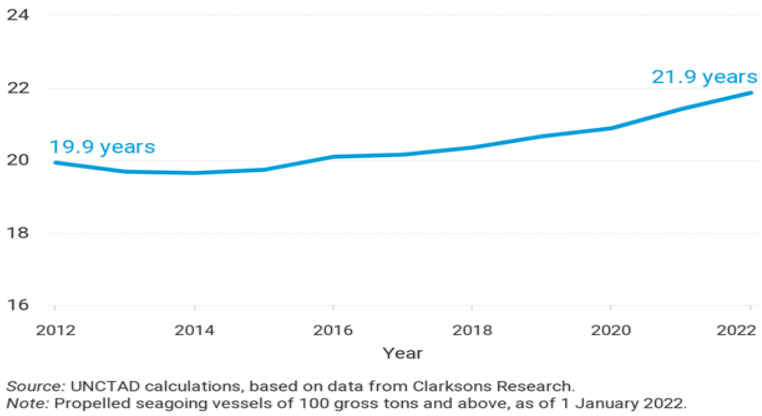
Figure 1 Merchant Vessels numbers as of January 1, 2022, by type



Source: Statista (2023)

But world's merchant fleet average age is nearly 22 as per report from UNCTAD. The average age depicts that, these huge number of ships will be at their end of life by 5-15 years mostly depending on the ship type. The age factor restricts investment on restructure and shipping companies are trying to use the existing vessel intact without much of the investment on structure or new energy conversion equipment such as wind sail, solar or fuel cells.

Figure 2 Merchant fleet average age,2012-2022



1.2. Possible solutions for ships

The maritime industry requires to support the existing vessel to run smoothly without much of alteration and find best suited intermediate transition solution for ageing vessels. Existing alternatives like biofuels, ammonia or hydrogen show better emission reduction potential (Bougas, 2022). The carbon reduction potential of these alternatives arguably better (Kim et al., 2020). Some ship owners prefer methanol and LNG as a transitional fuel. But considering the carbon emission, hydrogen has good potential to become next generation fuel. Electrolysis is a possible way to produce hydrogen using electricity from renewable sources which involves no CO2. There is no generation of carbon emission either in the combustion process. More research required in consideration of hydrogen to be transitional fuel to establish the required infrastructure and overcome the existing challenges.

1.3. Challenges of Hydrogen energy

Hydrogen is an alternative fuel that is attracting increased interest due to its low carbon emissions. To become a mature energy source, Hydrogen energy need to be explored and investigated in certain sub topic areas. The production of hydrogen can be mostly electrochemical. It can also be produced photochemical or photoelectrochemical process involving catalytic actions in some of the methods. Most of the process requires external energies through electricity. Involvement of electricity can be easily incorporated through green energy solution making hydrogen production efficient and carbon free. The production process of hydrogen is becoming a good investigating point to find the best suitable production method.

Some other vital areas to be researched are storage of hydrogen and safe transportation. In sub topic categories, chemical properties of storage materials, safety measures, hazardous scenario analysis, market analysis for H2 can be included. Combustion of hydrogen is another interesting area to be investigated. Though the combustion in theory doesn't produce CO2 reduces Sox emission but the NOx emission cannot be ignored (White et al., 2006). The combustion and also fuel cell mechanism and involving emission with these processes requires proper answers before hydrogen's mass use as fuel.

For maritime sector, efficient storage as well as safe transportation are the biggest hurdles need to overcome regarding H2. The storage mechanism considering safety, state of hydrogen whether gaseous or liquid or chemically induced, and also materials composition and transportation (Başhan and Üst, 2022) all these questions need to be comprehensively investigated for the efficient hydrogen uses in maritime industry. The main barriers to the mass application of hydrogen energy involves safe condition and adequate capacity of storage with proper technological measures for maintaining transportable condition. Drawbacks of hydrogen storage system includes complex thermal management, condition for operating pressure and temperature, high prices of the catalyst, chemical kinetics of reactions and safety conditions (Etienne & Michel, 2019).

1.4. Scope of the research

Based on the challenges mentioned, the storage of hydrogen is crucial and proper conditions to be achieved in line with production of hydrogen, transportation, end-use either combustion or in fuel-cell technology. To become future generation, fuel the infrastructure and procedure need to be started early. For that reason, existing merchant fleet need to investigate the possibility of using hydrogen as an intermediate fuel which will facilitate future infrastructure to be in advancement. One step to the process can be the use of bunker tank on an existing commercial ocean-going vessel as a hydrogen storage tank deserves investigation.

1.5. Aims and Objectives

The aim of this research is to investigate the possible storage option using LOHC for hydrogen in to be used maritime industry. These include systemic literature review of storage options focusing on liquid organic hydrogen carrier (LOHC), dehydrogenation process through chemical kinetics and combustion scenario for hydrogen regenerated from LOHC. In consideration of hydrogen as a next generation fuel following research question peeps through which the study formatted.

The questions guiding the study are

1 What are the technologies to store hydrogen?

2. What procedure can be used for the safe transportation of green hydrogen?

3. How existing vessel can store hydrogen without changing much of the condition with existing facilities?

4. How onboard hydrogen can be utilized for the extraction of energy?

The research questions formatted the objectives of the study. The objective includes

1.Possibility of LOHC to be a solution for hydrogen storage on board ship for carrying hydrogen.

2.Onboard dehydrogenation feasibility from LOHC to be used for combustion or for fuel cell.

3.Combustion scenario analysis using hydrogen and possible LOHC chemical mechanism.

1.6. Contribution

It is expected that this work will provide an insight into possibility of using LOHC to carry hydrogen as an intermediate fuel for the existing vessels using the existing tank condition and also understanding of hydrogen transportation solution as like LNG carriers. In particular, the study reveals intermediate use of hydrogen through LOHC and pathway to become future generation zero carbon fuel for maritime industry.

1.7. Organization of Thesis

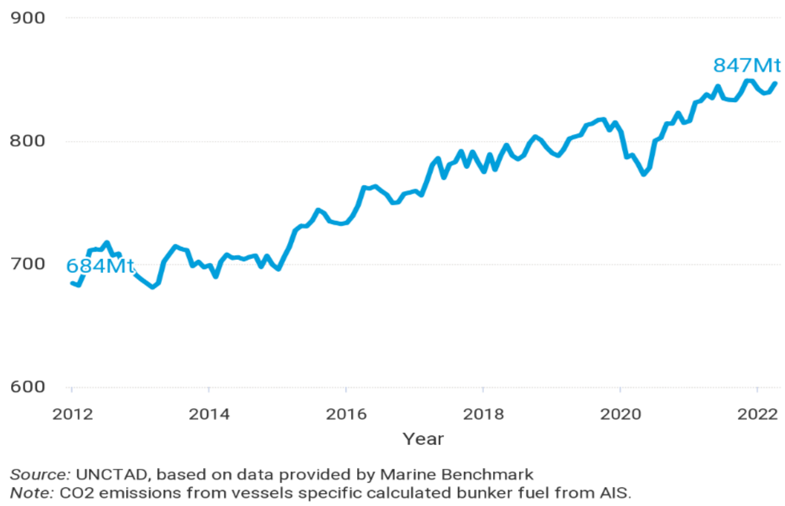
The study commenced through the summarization of related works and identification of knowledge gap in chapter 2. The consequent chapter 3 represents the objective and methodology. In Chapters 4 and 5 with result and a case study, the objective of the study analyzed. The concluding chapters 6 and 7 organized with discussion, conclusion, limitation and future scope of work.

Literature Review

2.1. IMO Decarbonization Strategy

To combat global climate vulnerability, shipping industry seeking technological solution for cleaner energy sources. IMO adopted revised strategy in 2023 with specific targets and goals. IMO set out checkpoints to reduce the total annual GHG emissions from international shipping by at least 20%, striving for 30%, by 2030 and at least 70%, striving for 80%, by 2040, compared to 2008. The ultimate target is set to reach net-zero GHG emissions by or around 2050. The strategy indicates uptake of zero or near-zero GHG emission technologies, fuels and/or energy sources to represent at least 5%, striving for 10%, of the energy used by international shipping by 2030 (IMO MEPC 80). Current Status of Fuel and vessel worldwide using Fossil Fuel shows it is remarkably.

Figure 3 CO2 emission by vessel from 2012 to 2022



Increasing and need to adopt low or zero emission technology to reach to the targets set by IMO member states.

Different low emission fuels already getting exposure to be used on board in view of decarbonizing the international shipping. Ammonia, methanol, bio-fuels, hydrogen are some of the considerable next generation fuels for shipping. The emission reduction potential for using alternatives like ammonia, biofuels or methanol is considerably higher (Bougas, 2022). The carbon reduction potential is argued to be highest (Kim et al., 2020). Considering the life-cycle carbon emission hydrogen production methods is likely achievable using renewably generated electricity (Breiki & Bicer, 2020). The main barrier while using hydrogen is regarding transportation and storage.

2.2. Hydrogen as possible fuel

Hydrogen is a highly combustible gas. It is generally colourless non-toxic gas with wide flammable range. Form electrolysis of water hydrogen can be found. It can also be produced from coal, natural gas but CO2 will be produced as by-products (Bougas, 2022). Hydrogen generation through electrolysis involves no emission of CO2 (IEA, 2021). The energy content of hydrogen is quite high than other fuels. It possesses some special characteristics which are the high heating value of combustion, clean as there's zero carbon content, wider range of flammability, it's low ignition energy requirement, production possibility from renewables, most abundant in the universe (Jain et al., 2009) make it qualified to become future energy source. The energy density of hydrogen is approximately 120.2MJ/kg which is almost 3 times of diesel(42.7MJ/kg) and 6 times of alcohols (Pattrick, 2019). For the high energy density, it can reduce fuel consumption in comparison. But the volumetric energy density is lower compare to other fuels. Estimated requirement of spaces for liquified hydrogen is 4 times that of MGO and about 2 times of natural gas for equivalent energy content (ABS, 2021).

Table 1 *Properties of Hydrogen*

Properties	Unit	Hydrogen compressed	Hydrogen Liquid
Boiling Point	^oC (@ 1 atm)	-252.9	-33.3
Density	kg/m3	23(350 bar)	71
Specific energy LHV	MJ/kg	120.1	120.1
Specific energy LHV	kWh/kg	33.3	33.3
Energy density	MJ/m3	5040	8500
Energy density	kWh/m3	1400	2357.7
Storage Temp	^oC	25	-252.9
Storage Pressure	bar	350–700	1
Flammability range	In air (by volume)	4-75%	14.8-33.5%

(Source: Erdemir et al., 2021)

Table 1 shows the properties for hydrogen in different states. The temperature and pressure requirement are the challenging condition to be maintained and one of the major challenges in transportation and storage of hydrogen. These states concern the safety issues while using vastly as well maintain cryogenic state is quite expensive in comparison to options in ambient conditions. Other than the gas or liquid state, hydrogen can be carried with liquid organic carriers which can be stored without the pressure and temperature adjustment.

2.3. Production of hydrogen from Renewable Energy

The current renewable energy sources like solar, wind, ocean, hydro power have one major drawback of suppling continuous electricity and require storage like battery to be installed for the conservation of energy and continuous use. Mostly lithium-ion batteries are used for the storage of energy for renewables. It requires lithium to be extracted for the production of batteries. One better solution to store the energy is in the form of hydrogen which can be produced through the electrolysis of water using renewable energy sources to get continuous energy supply. The suitable hydrogen storage option and possibility of using H2 gas in ICE will enhance the use of hydrogen for storing energy produced from renewable energy sources.

2.4. Different hydrogen storage Options

Hydrogen is naturally a gas. It is the lightest element with atomic number 1. The main storage option for hydrogen as can be understand from the Table 1 properties. The options are either gas under high pressure or liquid with very low temperature.

To store hydrogen in gaseous state very high-pressure pressure compression is required. In almost 350-700 bar pressurized tanks hydrogen is compressed and stored. Now-a day's steel tanks with carbon fiber wrapping is used to store hydrogen in high pressure (CMB-tech, 2023).

Liquified hydrogen storage require temperature below -253C to store hydrogen in cryogenic state. The tanks need to be highly engineered to avoid leaking and changes in temperature. Changes in temperature though very negligible can result in greater inner wall pressure change which may lead to disastrous situation.

In liquid state, organic hydrides, ammonia, formic acid or methanol are good options to store Hydrogen. In the mentioned chemicals, no involvement of CO_2 release in hydrides or ammonia. Methanol involves potential CO_2 release if recycled through hydrogenation of CO_2 (Chen et al., 2021). High volumetric and gravimetric density of ammonia respectively 108 kgH_2/m^3 NH_3 at 20 ◦C and 8.6 bar and 17.8 wt% makes is possible candidate to become an energy carrier (Klerke et al., 2008). This ammonia can be cracked into CO_2 free hydrogen (Lamb et al., 2019) to be used in fuel cell or combustion engines or gas turbines for power generation. But in case of ammonia the synthesis path needs to be green otherwise it cannot be considered as an alternative hydrogen carrier.

Methanol and Di-methyl-either (DME) can be good storage option for H_2. Methanol has a volumetric density of 99.7kg H_2 per m^3 and gravimetric density of 12.6wt%. On the hand the volumetric and gravimetric densities of liquified DME are 88.9 kgH_2 m^{-3} and 13.1 wt% (Bobbo et al., 2005) which make both MeOH and DME a considerable hydrogen storage option. The H_2 storage is done through catalytic conversion of air-captured CO_2. Through catalytic reactor steam reformation is done to regenerate the H_2/CO_2 and via pressure swing adsorption (PSA), membrane, or solvent-based carbon capture the removal of H_2 is done (Takeshi & Suzuki, 2004). Both the cases are suitable for hydrogen storage but as both can be used as alternative fuel but produce carbon emission and also using those as hydrogen carrier will enhance the emission further hence these are less suitable carriers to be used in marine industry.

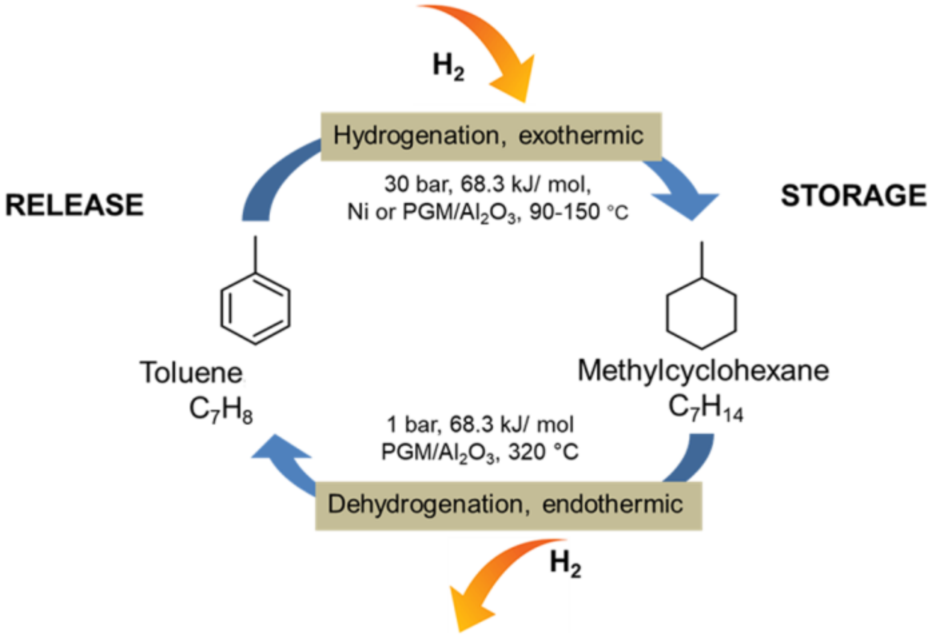
The suitable option to carry hydrogen is reversible hydrogeneration and dehydrogenation of liquid organic hydrogen carriers. The mechanism involves introduction of hydrogen through catalytic action to hydrogenate unsaturated organic molecules (Preuster et al., 2016). Some of the LOHCs are methylcyclohexane (MCH), perhydro-dibenzyl toluene (H18-DBT), and N-ethyl carbazole. Hydrogen transportation using LOHC is getting research attraction as it can avoid cryogenic state of hydrogen and safely transport using vessels.

2.5. Liquid Organic Hydrogen Carrier

LOHCs are chemicals consists of homocyclic or heterocyclic aromatic rings and possesses hydrogen storage density between 5 and 7.2 wt%, comprising between 50 to 60 g of hydrogen per liter (Laurens et al., 2021). LOHC can be defined as ‘‘Liquids or low melting solids that can be reversibly hydrogenated and dehydrogenated at elevated temperatures in the presence of a catalyst.’’ (Aakko-Saksa et al., 2018). Though the volumetric density is very slightly lower but the option to store at room temperature make it advantageous comparing to the liquid hydrogen.

The overall process of all LOHC is mostly similar. The storage is done through hydrogeneration and the hydrogen is released in the reverse process. The reaction steps are combination of two different thermal conditions. One is the exothermic hydrogenation reaction, and the other is endothermic dehydrogenation to release hydrogen. Figure (4) shows the general overview of toluene-MCH conversion schematic. In the hydrogenation, toluene with converted to MCH through exothermic process. On the reverse condition, with presence of suitable catalyst in a favorable condition, MCH release hydrogen and transformed to toluene. The dehydrogenation process is endothermic and require around 68.5KJ/mol energy.

Figure 4 Hydrogenation and dehydrogenation



Source (Phillimon et al., 2019)

2.5.1. Hydrogenation

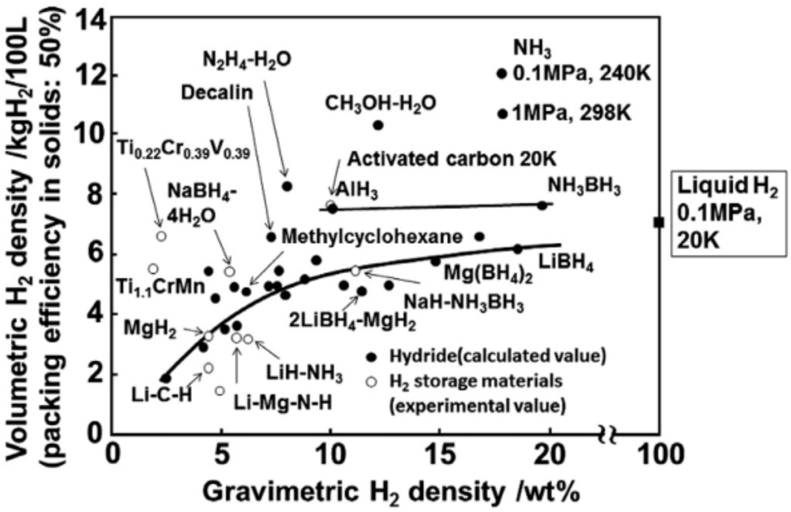
In process of hydrogenation, H2 gas in its forward reaction under suitable condition with the LOHC compound forms a hydrogenated compound containing hydrogen. This process requires suitable conditions to be meet under catalyst. The hydrogenation process mostly exothermic and reaction involves production of saturated carriers.

2.5.2. Dehydrogenation

To release hydrogen from the hydrogenated compound, in appropriate heating or catalytic processes LOHC material through the reverse dehydrogenation reaction release the hydrogen. In the cyclic process, as the reaction is reversible, heat management is critical. Proper LOHC selection with proper catalyst can lead to better storage ability for hydrogen. The process requires only heat which leads to another dimension to possible use of waste heat recovery system to become more efficient.

LOHC property those to be considered for its use are the storage density, low reaction enthalpy, availability, low environmental hazards. Studies carried out on the comparison based on availability, cost, toxicity. As hydrogen can be transported at ambient temperature, it is one of the suitable ways for transportation. Some of the Common LOHCs are, are N-ethycarbalzole (NECZ) -perhydro-N-ethyl- carbazole, methylcyclohexane (MCH)-toluene, dibenzylto- luene (DBT) -per hydro dibenzyl toluene (PDBT) (Bourane et al., 2016).

Figure 5 Hydrogen Density in different carriers



Source (Kojima, 2017)

Yoshitsugu Kojima in his work regarding ammonia economy presented the Hydrogen densities in hydrogen carriers (Kojima, 2017). Form the graph it is evident that, ammonia or methanol have good gravimetric and volumetric densities of hydrogen but options like MCH have a moderate position in the graph. MCH compare to the other two, can become a better option considering its less toxic and zero emission dehydrogenation characteristics.

2.6. Comparative studies on LOHC candidates

Studies carried out on potentials of LOHC and comparison of different LOHC. The organic carriers are getting exposure to different utilization in wide range of application. Japan as investing more on hydrogen technology also investing options for using LOHC as carrier for hydrogen and already started different projects like hydrogen import from Brunei to Japan using MCH as carrier to establish a hydrogen supply chain (Nature, 2022). H18-DBT is used by German Hydrogenious as their motto suggests carrying H2 as fuel through organic carriers on a higher scale (Hydrogeneous, 2022). The approach to use LOHC enables the opportunity of using the existing infrastructure of chemicals for transportation of H2 in the context of utilization as fuel.

Different LOHC provides different property advantage as per requirement of uses. In case of purity of hydrogen in the dehydrogenation process, liquid hydrogen or ammonia shows better suited while Methylcyclohexane is considered suitable for combustion due to its lower purity of hydrogen. (Aziz et al., 2018). Research has been carried out on different LOHC candidates considering the molar weight, gravimetric and volumetric density of hydrogen, enthalpy change and more other characteristics. Based on studies of Taube et al. (1983), Zhang et al. (2011), Shukla et al. (2012), Alhumaidan et al. (2011), Usman et al. (2012), Rao et al. (2022) the below comparative table has been demonstrated to get the better understanding of different LOHC and other type of hydrogen carriers characteristics.

Table 2 *Different LOHC and other type of hydrogen carriers' characteristics.*

Characteristics	Liquid hydrogen	Ammonia	Methanol +H20	Toluene -MCH	N-ethyl Carbazole	Dibenzyl Toluene
Molecular weight	2.016	7.03	50.05710	98.19	195.254	272.384
Density (kg m-3)	706	682 (0.1 MPa)	976	769	543	663
Boiling Point(°C)	-252.9	-33.34	64.7	101	348.3±15.0	397.6
Hydrogen density (wt%)	100	17.8	12.5	6.16	5.8	6.2
Hydrogen release temp. (°C)	-252.9	350–900	300-500	200-400	180-270	250-320
Regeneration temp. (°C)	-	400–600	150-350	100-200	130-170	150-200
Enthalpy change (kJ/mol)	0.899	30.6	43.6	68.3	55	65.3

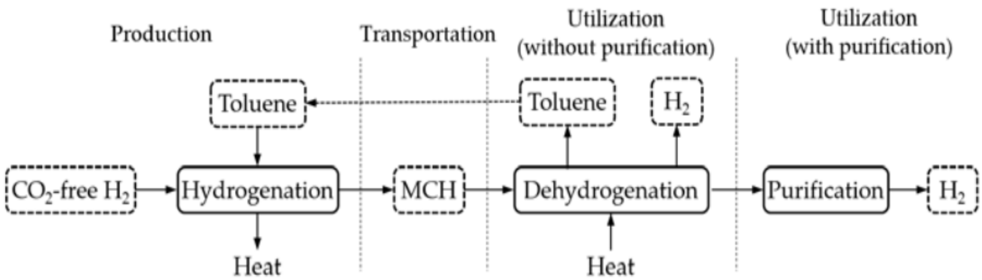
Form Table 2 it is evident that, the cryogenic state liquid hydrogen makes it difficult to meet the conditions to store hydrogen. To attain certain temperature or 350 bar pressure is not possible for existing merchant vessels. Ammonia and methanol though both can be used as good hydrogen carrier, but they already have their own status as future alternative fuels. Ammonia, due to its toxicity will not be a good option considering the safety and health of seafarers. But the emission reduction will not be achievable in both the cases if production is not emission free. In the case of Liquid organic carries, MCH depicts advantage as the availability of toluene is quite good and due to its already existing production and transportation infrastructure. Table 1 suggests hydrogen release temperature of MCH which is 200-400^{o}C is quite reachable and the hydrogen density(%wt) 6.16% which is higher than United States Department of Energy mandate of 5.5%. (McQueen et al. 2020). To carry hydrogen as an intermediate option until proper technology invention, MTH system is quite attractive option for hydrogen storage and transportation.

2.6.1. MCH as possible carrier for onboard Hydrogen

MCH outlines some advantages to become an option for onboard storage and dehydrogenation for further use. The advantages can be the states of MCH and products of dehydrogenation is noncarcinogen. This enables the possibility to use existing infrastructure to be applied for storage, transportation and distribution for the operation and delivery. The hydrogen density of 6.16% or 47.4 g H2/L MCH is considered to be a satisfactory amount of hydrogen is contained in a molecule of methylcyclohexane (Usman, 2010). The reaction for conversion from MCH-toluene-hydrogen can be activated in mild condition which makes MCH adventurous.

In reversible reaction, MCH is dehydrogenated to toluene and again in the forward path converted to MCH through hydrogenation of toluene. The overall process is called MTH system. It is an important reaction for the formation of naphtha and hydrogen storage application. The methylcyclohexane–toluene-hydrogen (MTH) system schematic has been demonstrated in the figure (6).

Figure 6 MCH-Toluene conversion schematic



Source (Aziz et al, 2018)

The schematic in figure (6) shows the MTH overall system. It needs to be anticipated that, the H2 need to be produced in a CO2 free process, considerably through electrolysis using renewable energy sources. The produced H2 in the production of MCH goes through the exothermic process with toluene and converted to MCH which is liquid in ambient temperature and pressure. For the extraction of H2 in the utilization site, the dehydrogenation process frees H2 and converts MCH to toluene again making it ready for further use as hydrogen carrier through the cyclic process. The H2 required to be purified in case of suing for combustion or to be used in fuel cell mechanism. As the dehydrogenation process is endothermic, possibility of utilizing waste heat can be examined for H2 direct combustion use in ICE. All these supports the analysis to be concise on MCH for further analysis and research.

2.7. Different Simulation studies of LOHC dehydrogenation

Research on LOHC in different aspect considering conversion rate, mechanism of different catalyst, reactor requirement, temperature and pressure dependency have been reported in different studies. The simulation of dehydrogenation of LOHC's like DBT-PDBT, MCH-toluene, NECZ-PNEC (N ethylcarbazol- Perhydro-Nethyl Carbazol) using tools like Aspen-plus, Simulink-Matlab, Simusolv, DWSim has been carried out to investigate different characteristics of dehydrogenation process of

LOHC. Hamayun et al. (2020) investigated the operational condition of MCH-toluene conversion using Aspen-HYSYS. The catalyst considered in the study is 1 wt. % Pt/γ-Al2O3. It considered the operating dehydrogenation temperature between 300-500oC. Plug flow reactor with power law model has been demonstrated in the study. Hydrogen addition in the feed has been done in this study for the enhancement of catalyst's stability but it reduced the conversion rate of MCH. Power generation system from H2 storage in MCH has been reported in the study by Juangsa et al(2018). An integrated system using dehydrogenation and a power generation process modelled in the study by covering the endothermic dehydrogenation reaction through air-fuel combustion of H2 generated heat (Juangsa et al 2018). In this study also platinum on alumina considered as catalyst with temperature around 500oC. The system observed sensitivity through adjusting main parameters like pressure, inlet temperature, condenser pressure to analyze the sensitivity over other system. The result showed significant influence of the parameter and outlined that, variation in parameters is sensitive to the system performance and scope of improvement was revealed. Mizsey et al (1999) modelled fixed bed reactor for catalytic dehydrogenation to be used in storage option. Kinetic and transport parameters are measured and the study used interstage membranes for hydrogen separation to improve efficiency (Mizsey et al 1999). The conversion reported in the investigation was 98%. Works considering other LOHC mostly DBT-PDBT using simulation tools like Aspen plus has been reported in the studies by Peters (2019), Haupt (2017), Naseem (2020). Mostly platinum on alumina catalyst with operating temperature between 300-450 have been demonstrated in the studies.

2.8. Combustion of Hydrogen from LOHC in internal Combustion

As mentioned in table 1, the energy density of hydrogen is approximately 120.2MJ/kg which makes it favorable to be used as a fuel replacing conventional fossil fuels. With barrier of storage option, another comprehensive finding required in support of the combustion of H2 in ICE. Literature on H2ICE has been carried out for long. Reviews on H2ICE back from 1980 can be found on the works by Escher. H2 combustion studies carried out in different sub area as it is vast and require analysis of number of issues to become concrete. Serrano's (2021) study modelled dual combustion in 2T engine considering different supply strategies for H2 in the engine. Water injection also considered to reduce NOx emission which also results in removing the possibility of self-ignition and combustion knocking. The model reports an efficiency of 53% and also shows corresponding matching with diesel mode performance. White et al (2005) provided a comprehensive technical review on the H2ICE with focus on earlier studies on related matters. The study concluded providing positive prospects on higher efficiency, high power density, multimode operation but doubts on long term future due to unpredictable future of hydrogen economy.

Mostly for transport and light engines, the studies are focused. Heavy duty engines for marine propulsion correspondingly have fewer studies. Issues regarding storage hinder the attraction of H2 study for maritime industry. With the consideration of LOHC, new window opened in the field. Some basic new study can be circulated around the feed of H2 from dehydrogenation of LOHC. Potential uses for LOHC in mostly for fuel cell technologies has grown interest. But very few studies demonstrated the potential uses for combustion modeling on board dehydrogenation reactor. Several projects ongoing like Hystra between Japan and Australia for carrying CO2 free hydrogen. The storage possibility and combustion objectives are focused in the study to get better understanding of using LOHC onboard both for transportation, dehydrogenation and combustion.

Methodology

The methodology of the study is guided by the research questions mentioned in introductory chapter. The focus of the study is to get an intermediate solution for vessels to use hydrogen. A mixed methodology is applied cumulating systemic literature review with simulation of chemical kinetics for the suitable LOHC. Further study done on the combustion behaviour of hydrogen to understand the utilization onboard vessel.

3.1. Tools of the research

The tools used to carry out the kinetics simulation is DWSim which is an open-source platform for chemical process simulation. The MCH dehydrogenation is simulated using DWSim to understand the kinetics. The platform offers process modelling by using its own data repository and also from other sources. Python program can be incorporated for kinetics and other calculations.

For the combustion behaviour understanding, python embedded Cantera is used. Python version 3.11 and Cantera version 3.0 were the versions used for the study. The powerful tool Cantera provides satisfactory behaviour analysis with the chemical mechanism of the desired fuel.

3.2. Chemical Kinetics of the study

3.2.1. Chemical Kinetics

Chemical kinetics govern the transformation of species (Kee et al., 2018) in proceeding of a chemical reaction. Chemical kinetics provide an insight to any chemical reactions including every sub step with infused components. It focuses on understanding of how reactants transformed into products with influence of factors of the components which determines the rate of reactions.

3.2.2. Basic Reaction of MCH-toluene Hydrogenation and Dehydrogenation

The basic reaction involves the forward dehydrogenation reaction in which MCH converts into toluene and generates hydrogen. In the reverse dehydrogenation, toluene with hydrogen produces carrier MCH. The overall dehydrogenation and hydrogenation of MCH-Toluene is an important system called MTH (methylcyclohexane–toluene-hydrogen) in hydrogen storage applications.

Forward Reaction: $\underset{\text{MCH}}{C_7H_{14}} \rightarrow \underset{\text{Toluene}}{C_7H_8} + 3H_2$ ……………. (i)

Reverse Reaction: $\underset{\text{Toluene}}{C_7H_8 + 3H_2} \rightarrow \underset{\text{MCH}}{C_7H_{14}}$ ……………...(ii)

This basic reaction is reversible and the forward MCH-toluene is endothermic which cools the reactor bed. On the other hand, the reverse Toluene-MCH reaction is exothermic. In case of onboard dehydrogenation, for the hydrogen to be freed, it requires heat for the reaction to be activated.

3.2.3. Kinetics Model for the MCH dehydrogenation

Research has been carried on different catalyst for the dehydrogenation of MCH. Most researchers done the research on platinum containing alumina supported catalyst. Some of the research also done study on the kinetics modelling based on Pt/Zeolite catalyst. The simulation considered the kinetic model presented by Usman et al (2015). The study carried out the modelling based on 1.0 wt% Pt/zeolite beta catalyst. Though other studies use alumina, the zeolite with low acidity and relatively large surface area such as zeolite beta (Usman et al., 2015) exhibits better support in cracking and isomerization reactions.

The overall forward dehydrogenation reaction based on Pt/zeolite beta catalyst with by-products is:

$$6MCH \leftrightarrow TOL + DMCP1 + DMCP\ 2 + DMCP\ 3 + ECP + MXN + 2H_2 \text{ ……(iii)}$$

The overall reverse hydrogenation is:

$$6TOL + 19\ H_2 \leftrightarrow MCH + DMCP + DMCP + DMCP + ECP + MXN \text{ ………. (iv)}$$

Usman et al (2015) defined rate equation for dehydrogenation based on the overall equation:

$$(-r_A) = k_A \cdot \left(P_A \cdot - \frac{(P_T \cdot P_{D1} \cdot P_{D2} \cdot P_{D3} \cdot P_E \cdot P_M \, P_{H_2}^2)^{1/6}}{K_A} \right)^{n_A} \text{................(v)}$$

Again, the hydrogenation reaction was defined as below:

$$(-r_T) = k_T \cdot \left(P_T \cdot P_{H_2}^{19/6} - \frac{(P_A \cdot P_{D1} \cdot P_{D2} \cdot P_{D3} \cdot P_E \cdot P_M)^{1/6}}{K_T} \right)^{n_T} \text{............. (vi)}$$

Stull et al. (1969) described values for Gibbs energy formation for each components formed the below two equations for the equilibrium constant.

$$lnK_A = -5.3515 * \frac{1000}{T} + 9.2364 \text{..............(vii)}$$

$$lnK_T = 24.72 * \frac{1000}{T} - 46.49 \text{...................(viii)}$$

These equations and obtained basic parameter values from Usman et al (2015) were used for the simulation to understand the MCH-toluene-Hydrogen or MTH process.

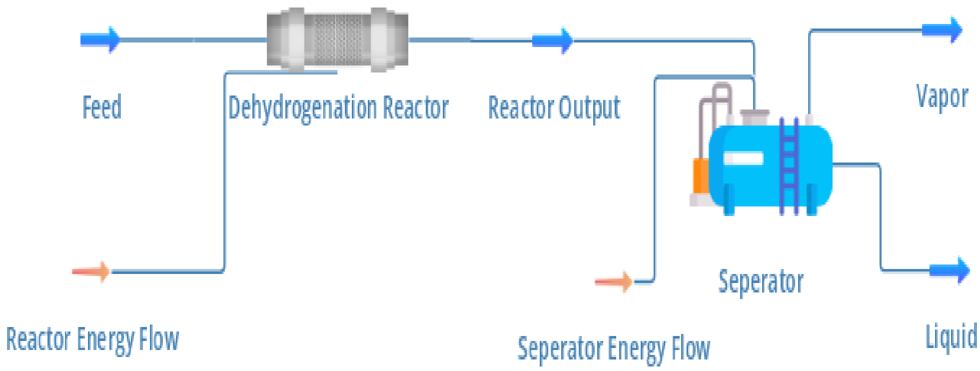
3.2.4. Reactor Modelling of MCH-Toluene-Hydrogen Reactor

The reactor assumed to be one dimensional plug flow reactor. The wall temperature considered constant throughout the reactor length. Very negligible pressure drop is assumed. Axial direction heat transfer considered to be taken place between wall and fluid. Peng Robinson thermodynamic package is used which is a cubic equation state relating temperature, pressure and molar volume of a pure component mixture at equilibrium (Rao et al, 2022).

3.2.5. Schematic of Simulation

In figure (7) the schematic of the MTH conversion has been shown. The basic two part of the simulation is setting up the reactor and the gas-liquid separator. The feed is the input which in this case MCH. The reactor used is plug flow reactor. The output of the reactor then feed into the separator for separation of gas and liquid. The separator setting allowed to condense out cyclopentanes from the vapor and provide mostly H2 gas in the gas output.

Figure 7 Schematic of MCH Dehydrogenation Simulation



3.3. Combustion Simulation
3.3.1. Combustion scenario analysis

Python embedded Cantera platform used for the combustion scenario analysis. Simulation parameters set similar of a (gaseous) Diesel-type internal combustion engine. The simulation uses H2 and Cyclopentanes as fuel, which is injected close to top dead centre. numerous simplifying assumptions are made to understand the behaviour of the combine fuel nature.

In the combustion simulation, both the air and fuel compositions are used. The air composition O2 and N2 were combined as intake of air in the chamber. For the purpose of the study, hydrogen with cyclopentanes, the by-products in the earlier chemical simulation of dehydrogenation were combined to analyse the behaviour and combustion scenario. The self-ignition temperature of hydrogen is quite high which prohibits the direct use of hydrogen in compression ignition engine. The most favourable way to burn H2 by suing diesel as ignition as ignition source or spark plugs. Some other issues with H2 are high NOx emission and knocking (Kumar, 2018). These options require further studies for H2 to become the efficient fuel.

3.3.2. Reaction Mechanism

Reaction mechanism defines the step-by-step chemical reactions (Marjorie, 1965) in a chemical process. For any combustion to take place the reaction process needs to be defined to proceed with each sub-chemical process for the final outcome. During reaction, intermediate species are formed which is consumed ultimately in the consecutive steps are defined in the mechanism. The rate laws of reaction are also provided in kinetic modelling which describes the overall dependencies of the rate of reaction on the reactants. It is actually detailed and comprehensive description of any chemical process that explains how rate of reaction depends on temperature, pressure, catalyst, concentrations and different other conditions.

For understanding the behaviour of MTH to be used as H2 storage on board vessel the ultimate goal is to use the H2 in the ICE. The reaction mechanism for MCH defines the nature of combustion of H2 with cyclopentanes as impurities. The reaction mechanism for MCH(Methylcyclohexane) and its dehydrogenated by-products cyclopentanes is used for the ICE combustion simulation. The mechanism used in the simulation which is updated with new reaction pathways is validated over .5 to 1.5 temperature range and 15 to 50 bar pressure range is done by Weber et al (2014). Also, validation was done for equivalence ratio range of 680 to 900K with air-like compositions.

3.3.3. Different Parameters used for the combustion process

For the simulation 3000rpm engine is assumed. The piston diameter is 0.083m with compression ratio of 20. The displacement volume is considered to be 500cm3. The turbochargers inlet pressure and temperatures are defined with inlet air composition of O2 and N2 in a ration approximately of 1:3. The fuel properties as mentioned earlier mainly defined with the reaction mechanism. Here H2 with MCH and its by-products mainly cyclopentanes are used for simulation with changing ratios to understand the combustion behaviour using H2 through dehydrogenation from LOHC materials.

Result and Analysis

4.1. MCH conversion Simulation

The basic MTH simulation has been done based on the inlet condition of 1.01325 bar and setting the temperature to 300°C. The Reactor length set to 1m and volume set to $1m^3$. The reaction considered to be in mixed phase and both vapor and liquid phases were noted in the outlet.

Table 3 *Inlet condition for MTH simulation*

Properties	
Temperature	300 C
Pressure	1.01325 bar
Mass Flow	3600 kg/h
Molar Flow of MCH	36.6651 kmol/h
Volumetric Flow	1728.06 m3/h
Mixture Molar Fraction	
Methylcyclohexane	1
Cis-1,2-dimethylcyclopentane	0
1,1-dimethylcyclopentane	0
Cis-1,3-dimethylcyclopentane	0
3-methylhexane	0
Ethylcyclopentane	0
Hydrogen	0
Toluene	0

The reaction residence time was 0.00055183h and there was very negligible pressure Drop of 4.0417E-08 bar. The result showed 99.7249 % conversion of MCH which is similar to theoretical value of 99% conversion. The reaction heat is 72.552 KW. The reactor outlet is transmitted to the separator to condense out other by-products and separate gas and liquid phases. Between the two phases, the percentage of H2 in vapor is high and about 97.9989% which is quite satisfactory and separation from the reactor is easier as most of the vapor is containing hydrogen. The other chemicals in the vapor are cyclopentanes and toluene. The density of vapor is 1.99 kg/m3 with molecular weight of 98.1861 kg/mol.

Table 4 *Molar fraction in vapor*

Molar Fraction (Vapor)	
Methylcyclohexane	5.02E-05
Cis-1,2-dimethylcyclopentane	0.00285475
1,1-dimethylcyclopentane	0.00463144
Cis-1,3-dimethylcyclopentane	0.00399354
3-methylhexane	0.00414893
Ethylcyclopentane	0.0024767
Hydrogen	0.979989
Toluene	0.00185502

In the liquid phase, the molar fraction of hydrogen is 0.00079. This indicates most of the H2 produced is in the vapor and the liquid contains the other bi-products of the reaction. In the liquid, the toluene percentage is slightly higher with cyclopentanes.

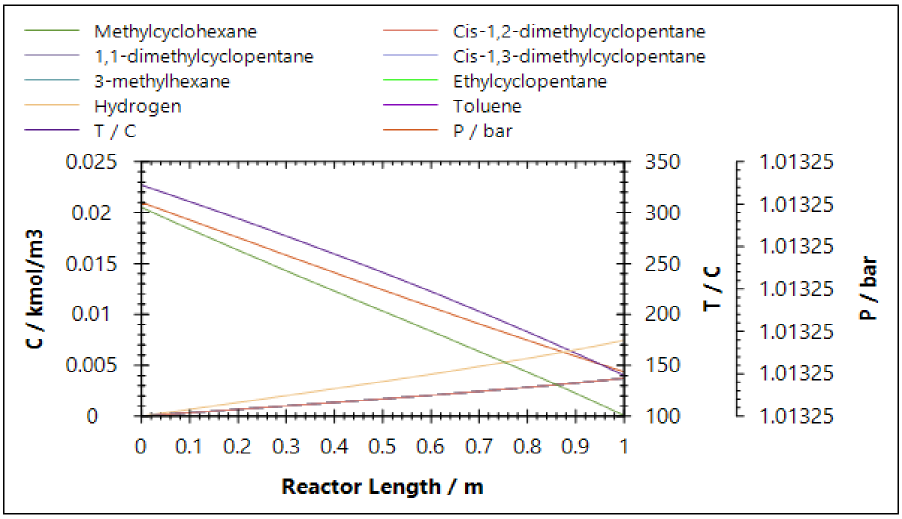
Table 5 *Molar Fraction (Overall Liquid)*

Molar Fraction (Overall Liquid)	
Methylcyclohexane	0.00275093
Cis-1,2-dimethylcyclopentane	0.166237
1,1-dimethylcyclopentane	0.165632
Cis-1,3-dimethylcyclopentane	0.165849
3-methylhexane	0.165797
Ethyl cyclopentane	0.166366
Hydrogen	0.000790264
Toluene	0.166577

In both the states, molar fraction of MCH is very less which support the conversion percentage and in the vapor state the percentage of H2 is very high which provide insights of using MCH as hydrogen carrier.

The concentration profile is shown below. It shows the concentration of MCH over the reactor length. In X axis the concentration has been shown in C/kmol/m^3. T/C refers to temperature and P/Bar refers to pressure of the reactor. The pressure drop is not so significant over time. The concentration of MCH over the reactor length decreases smoothly with no sharp turns. The concentration of H2 shows an exponential increase with reactor length.

Figure 8 MCH conversion; Inlet Temperature 300°C



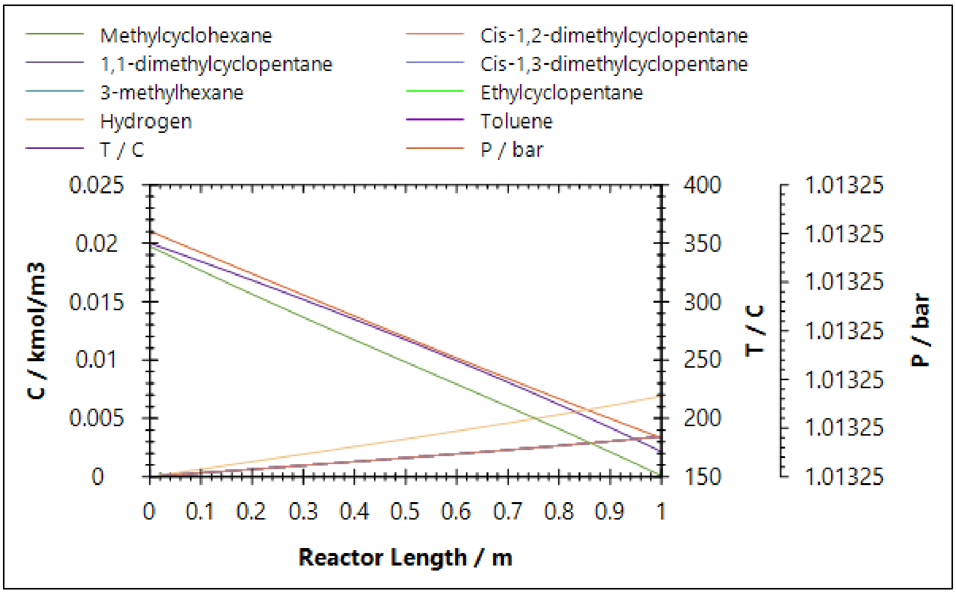
The simulation has shown different results depending on the conditions. Considering the variation in temperature, pressure, and reactor length and volume different conditions and conversion rate has been measured. Three situations have been analysed for the purpose of the study.

1. Changing the inlet temperature
2. Regulating the inlet pressure
3. Sensitivity with regulating mass flow

4.1.1. Inlet temperature

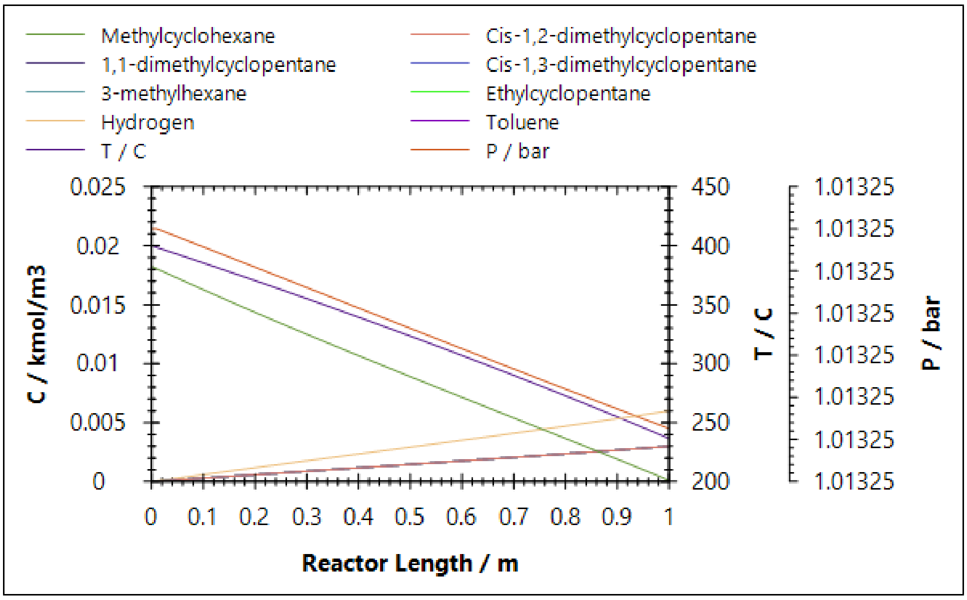
The concentration profile with changing inlet temperature to 350 degrees has been shown below. The Concentration of MCH over reactor length is still smooth and no sharp changes has been recorded. The pressure drop is not also significant. The temperature also shows very similar pattern as of the basic simulation and decreasing over the length not so significantly. The conversion rate for MCH recorded as 99.5962%. the hydrogen molar fraction in the vapor found to be 98.02% which has a increase then the basic simulation with 300° C.

Figure 9 MCH conversion; Inlet Temperature 350°C



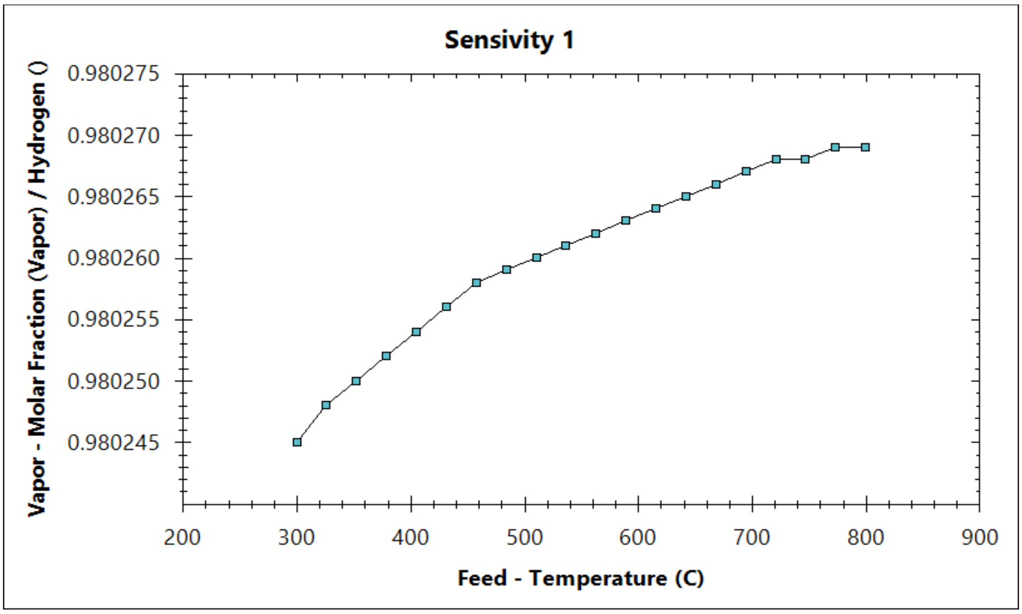
At 400 degrees both the conversion and H2 concentration in vapor reduced to respectively 99.3642%, and 98.02%.

Figure 10 MCH conversion with inlet temperature 400°C



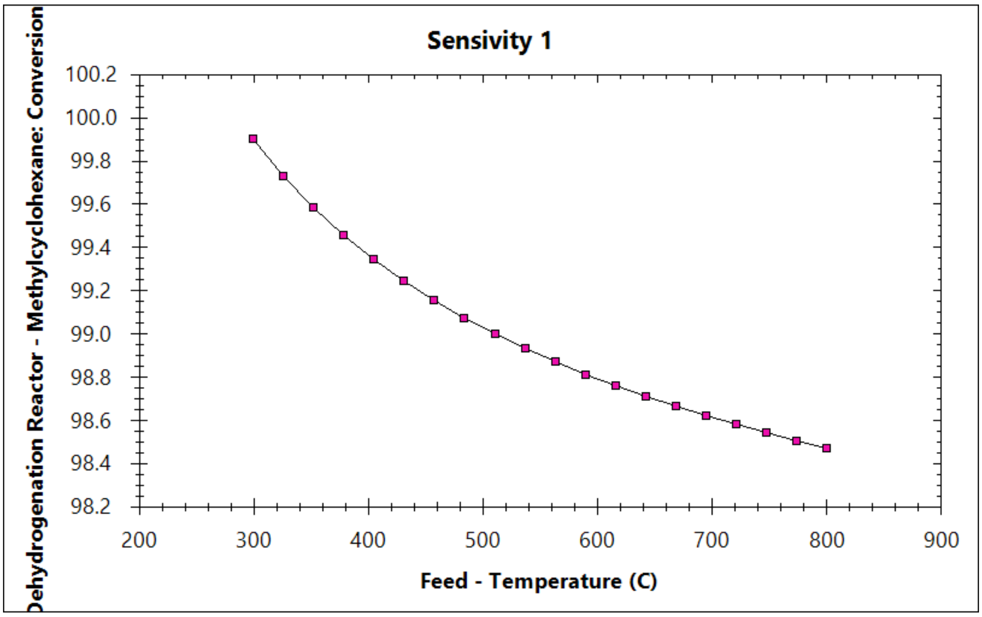
Sensitivity analysis of Hydrogen molar fraction in vapor has been done considering change in temperature from 300 to 800°C. Temperature is considered to be independent variable with upper limit of 800 and lower limit of 300 with step of 20. The sensitivity also checked the conversion rate of MCH.

Figure 11 Sensitivity of Temperature: Molar Fraction Hydrogen in Vapor



It shows the hydrogen molar fraction in vapor in the outlet negligible increases with increase in temperature. With variation in temperature the hydrogen molar fraction is quite on the satisfactory range. The conversion of MCH remains in the range of around 98-99% almost over the range of temperature but shows a declining nature with increase of temperature. This indicates the conversion of MCH decreases over temperature increase.

Figure 12 Sensitivity of temperature change: Conversion rate of MCH



4.1.2. Regulating the inlet pressure

The second sensitivity checked the reaction behaviour through regulating the pressure. The pressure variation set in between 1to 20 bar with a step of 10. With increase in pressure, molar fraction of H2 increased. The graph shows that, with increase in pressure from 1-5 the curve is more stepper but after 5 bar with every increase the smoother nature has been demonstrated.

With increasing pressure, though the conversion rate is over 99% but shows a decrease over the incremental pressure. It seems increasing pressure effects the conversion rate inversely.

Figure 13 Concentration of H2 with increased pressure

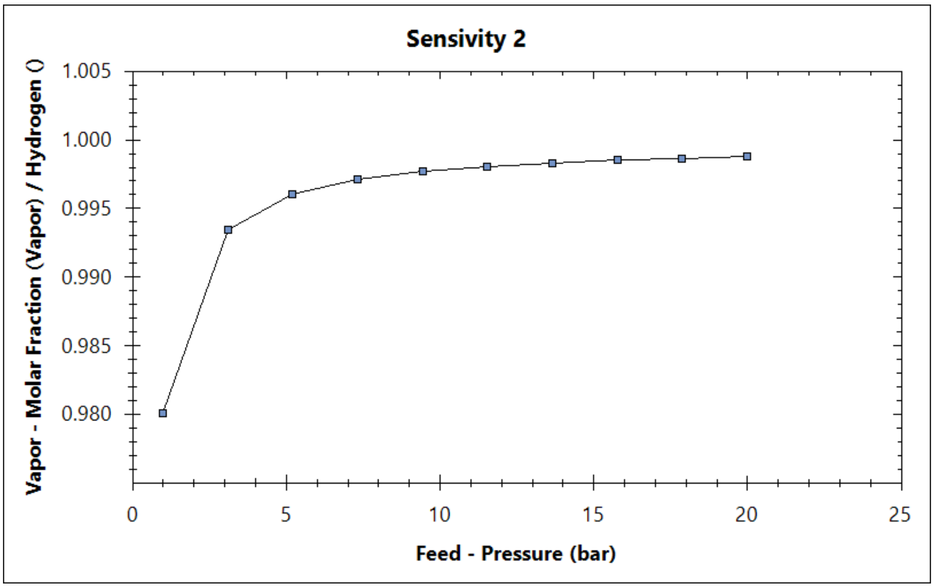
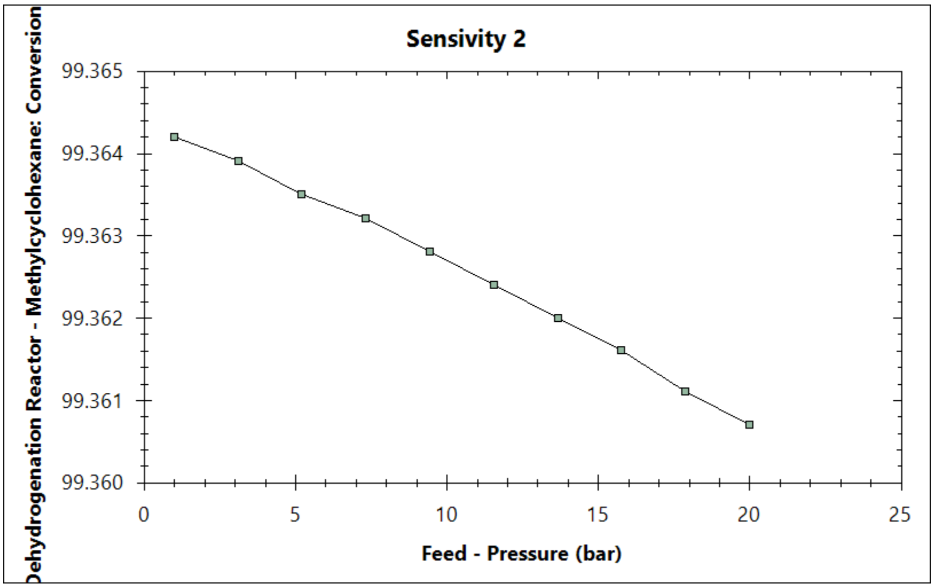


Figure 14 MCH conversion rate with regulating pressure



To get optimum condition of temperature and pressure for conversion rate of MCH and molar fraction of H2, third sensitivity analysis considers variation in both temperature and pressure. The temperature and pressure considered to be independent variable with temperature range from 300 to 800°C and pressure from 1 bar to 20 bar. The result shows the increase in pressure increases the Hydrogen molar fraction in the vapor. Hence, maintaining the temperature at standard value increasing pressure would result in satisfactory hydrogen molar fraction.

Figure 15 H2 concentration in vapor with sensitivity of pressure and temperature

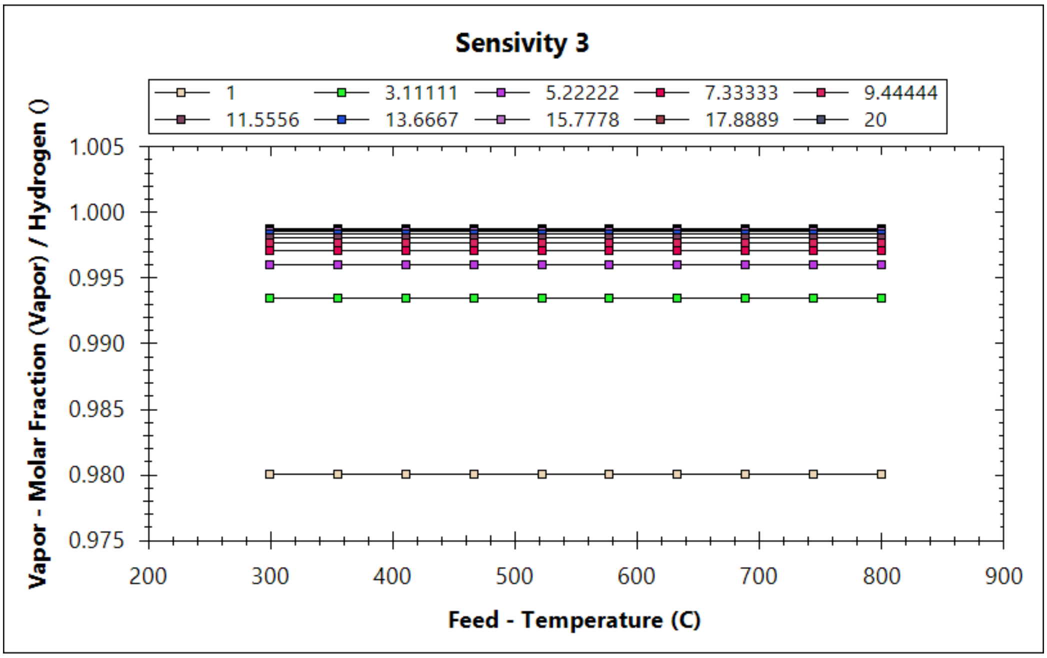
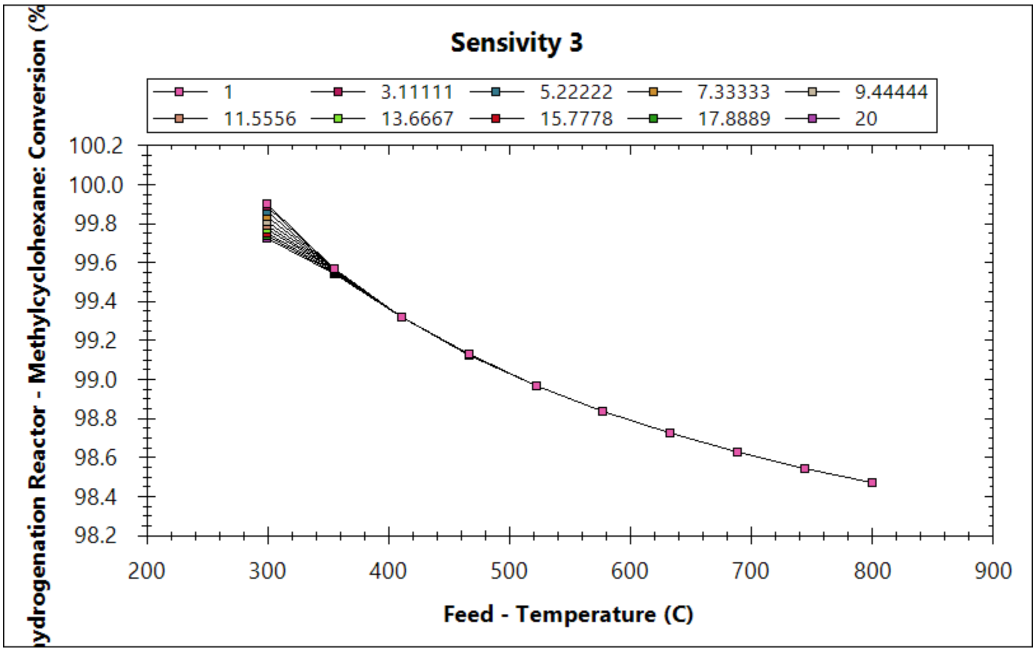


Figure 16 MCH conversion with sensitivity of temperature and pressure.



In case of MCH conversion, it is on the range of over 99% as like the previous sensitivity analysis. But decline noted after going further with temperature increase beyond 400°C. For pressure increase also, the decrease of conversion rate is noticeable. Its summaries that, around 400°C with pressure in between 1-10 bar can be considered as a favourable set up condition to get better conversion rate of MCH and molar concentration of H2.

4.1.3. Sensitivity analysis regulating mass flow

The mass flow shows the conversion rate of MCH decreases after certain range. For analysis the mass flow is set between 1000kg/h to 5000kg/h. There are no significant changes in the molar fraction of hydrogen and the conversion rate of MCH. Both the parameter exhibits fractional fluctuation but over the basic conversion rate and molar fraction mentioned in 4.1.

Figure 17 Sensitivity of MCH conversion rate with regulating mass flow

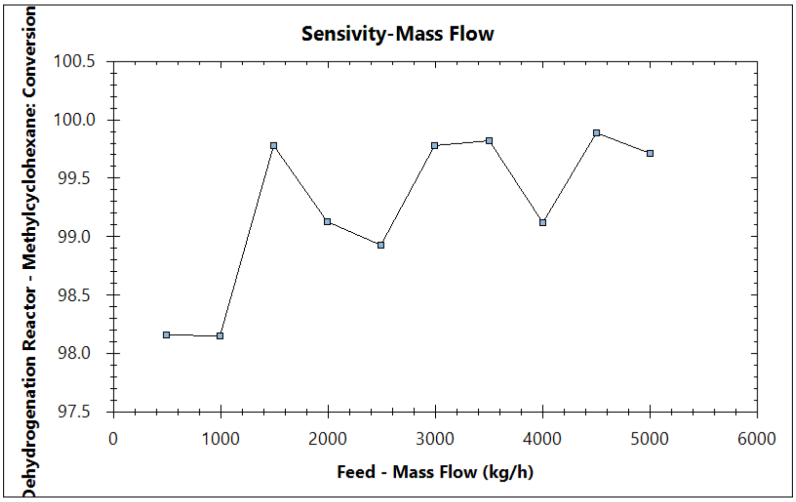
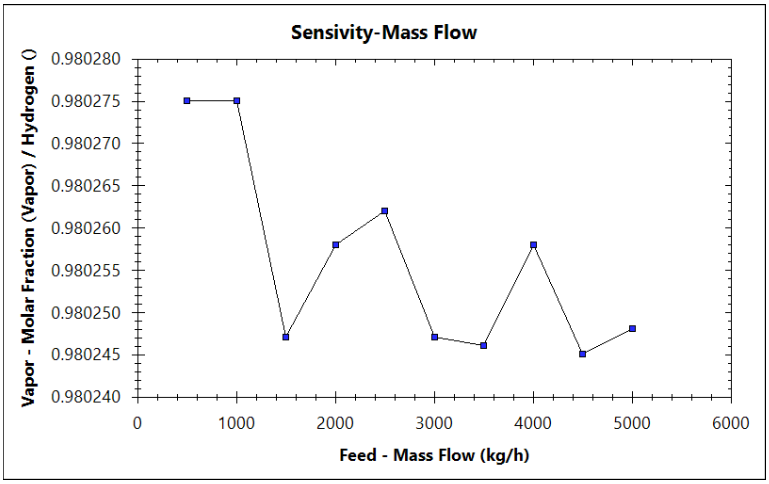


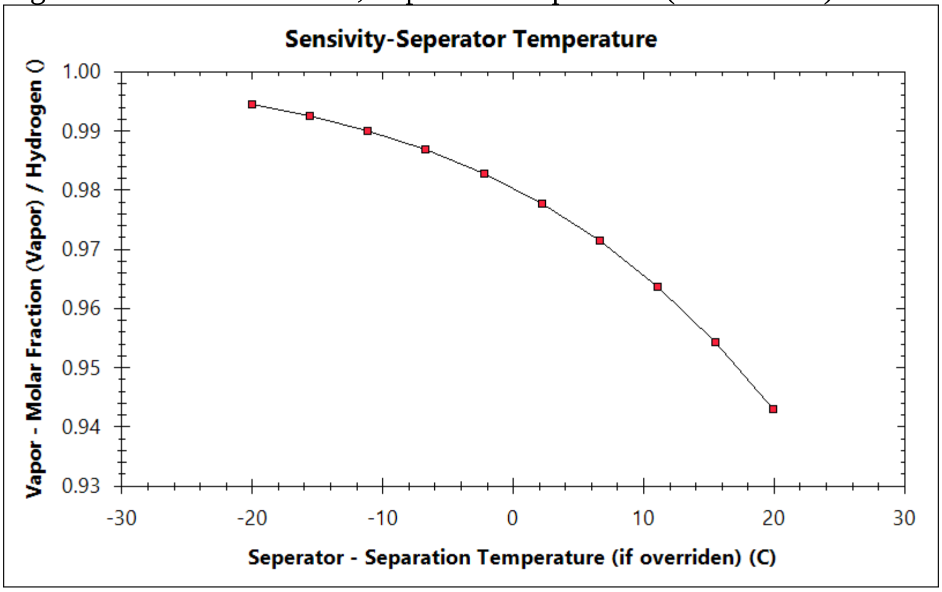
Figure 18 Sensitivity of MCH conversion rate with regulating mass flow



4.2. Separation of H2

Separator is inserted to condense out the bi-products in the MTH conversion process. The separator temperature maintained in a way considering the boiling points of DMCP of about 87.5^{O}C and that of toluene which is 110.6^{o}C. The H2 produced through dehydrogenation of MCH to be used in combustion need to be separated from DMCP's and toluene's which are produced in the conversion reaction. To understand the separator action and H2 molar fraction in the separated vapor, analysis performed setting the temperature range from -20 to 20^{o}C.

Figure 19 H2 concentration; Separator temperature (-20 to 20°C)



The sensitivity of H2 molar fraction with respect to separator temperature shows expected result as the concentration increases with decrease in temperature and vice versa. This will enable the separated H2 to be used for analysing the combustion behaviour in IC engine.

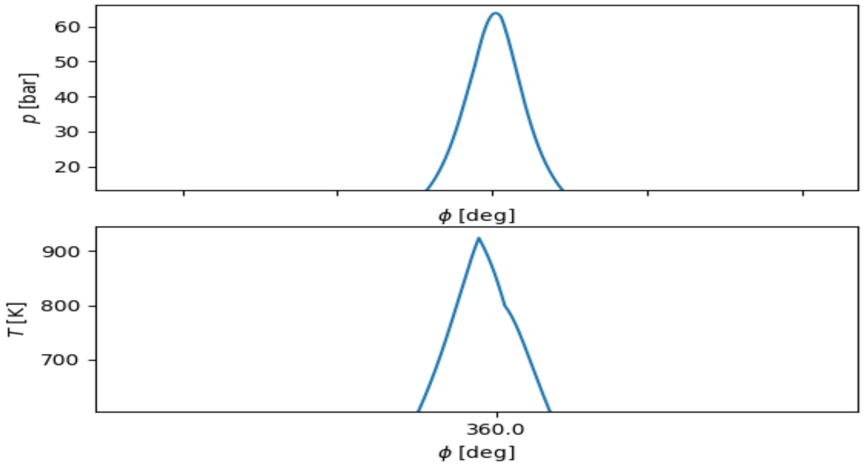
4.3 Simulation of H2 combustion

To understand the behaviour of combustion assumption made on flowing the separator gas output to engine. The simulation objective is to observe the combustion behavior of fuel that is combined with hydrogen and the byproducts of MCH combustion. The assumption is feeding the vapor to engine for combustion. The air composition considered a mixture of oxygen and nitrogen in a ratio of 1:3.76. Three fuel combination has been considered to get the ratio between H2 and bi-products of MCH for the combustion in ICE.

4.3.1. Fuel Composition H2: DMCP=0.97:0.03

The basic simulation considers 97% H2 and 3% of dimethyl cyclopentanes as the molar fraction of cyclopentanes are higher after H2 in the vapor phase of MCH conversion.

Figure 20 Pressure and Temperature Diagram (H=0.97, C7H14=0.03)

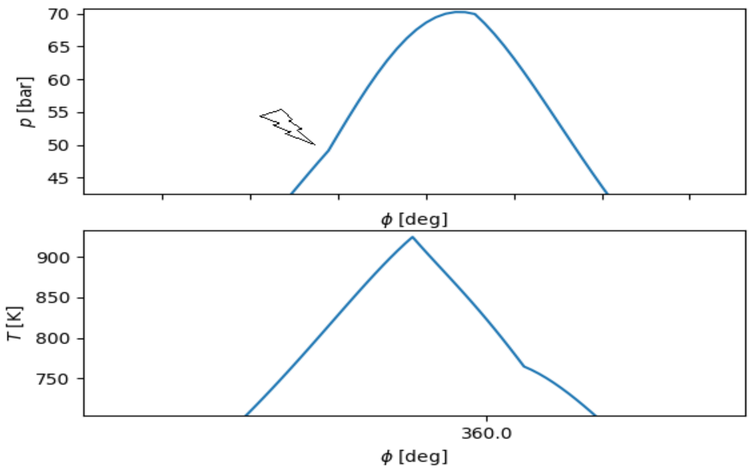


The composition of fuel exhibits no combustion which indicates to reduce the concentration of DMCP from the fuel composition.

4.3.2. Fuel Composition H2: DMCP= 0.99:0.01

The second simulation have been performed changing the fuel composition. The concentration of H2 increased to 99% and DMCP to 1%. This combination has shown some prospects of combustion. This provides the idea to reduce the DMCP from the fuel mixture more to get better combustion using H2.

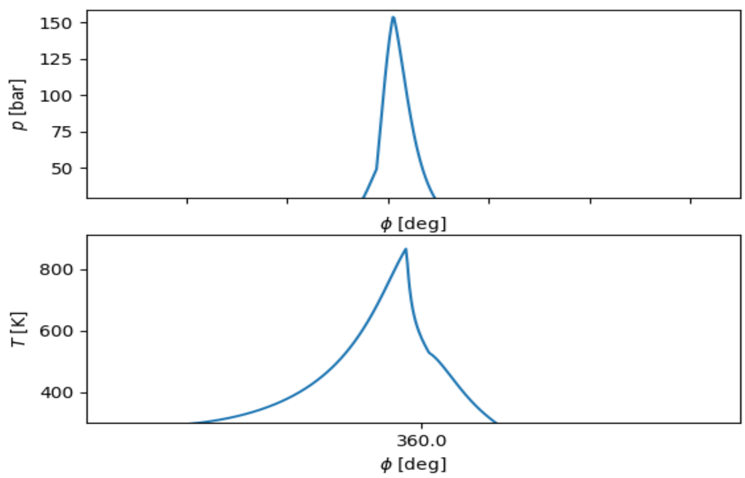
Figure 21 Pressure and Temperature Diagram (H=0.99, DMCP=0.01)



4.3.3. Fuel Composition H2: DMCP=0.99:0.001

The third simulation have been performed reducing DMCP concentration to 0.001 keeping H2 to 0.99. In this case, some combustion behaviour has been observed and it depicts with presence of small amount of Cyclopentanes with H2 is combustible in ICE.

Figure 22 Pressure and Temperature Diagram (H=0.99, DMCP=0.001)



The fuel composition of H2 and DMCP indicates that, the separator needs to be designed in a way to reduce the DMCP percentage more to get higher concentration of H2. The sensitivity of temperature in the separator shows that, below -10^{O} the concentration of H2 is higher and these can be feed to engine to get better output.

Case Study

To determine the requirement of MCH in comparison with diesel for vessel, a handy size vessel's fuel consumption and storage capacity are used in the study. The particulars used for the case study are as below

Table 6 *Ship Particular of Oil-Chemical tanker*

Capacity	Summer DWT	38867mt
Engine Power	ME	6780 KW @ 108 rpm
	AE	970KW @ 720 rpm
Storage Capacity	Cargo	40246.469 m3
	HFO Bunker tank	1160 mt
	MGO Bunker tank	251 mt
Consumption per day	HFO	25ton/day
	MGO	4ton/day

From the vessel particular, it is found that, the per day requirement of the vessel is 4mt or 4000kg of diesel and 25mt or 25000kg of HFO. Here the equivalence from Diesel to H2 is studied.

From literature review it is known that, the energy density of Hydrogen is 120.2MJ/KG and the energy density of Diesel is 42.7MJ/KG. As there is 4 ton or 4000kg of Deisel requirement per day,

The per day hydrogen requirement to replace diesel will be = (4000*42.7)/120.2kg
= 1420.97kg

Table shows the equivalent consumption of H2 compare to Diesel and HFO per day.

Table 7 *Equivalent consumption of Hydrogen*

Energy Density	Diesel	42.7*	MJ/kg
	HFO	40.3*	MJ/kg
	Hydrogen	120.2	MJ/kg
Consumption	Diesel	4000	Kg
	HFO	25000	Kg
Equivalent Consumption	H2 to Diesel	1420.97	Kg
	H2 to HFO	8381.86	Kg

*Source (Aronietis et al, 2016)

5.1 Consideration with the balanced equation (iii)

The kinetic model of MCH used represents the below balanced equation:

$$6MCH \leftrightarrow TOL + DMCP1 + DMCP\,2 + DMCP\,3 + ECP + MXN + 2H_2$$

Where, The molar mass of H2 = 2.016g/mol

The molar mass of MCH = 98.189g/mol

The ratio for the extraction of H2 from MCH as per the balance equation(iii) will be

= (2*2.016)/(6*98.189)

If we consider to replace the diesel with H2 and need the H2 to be dehydrogenated from MCH onboard,

The requirement of MCH is $= \frac{6*98.189}{2*2.016}$ *1400kg

= 207622.97kg

~207 ton of MCH

The percentage increased equivalent to diesel requirement is = (207/4) *100%

~51%.

The percentage increase for both HFO and diesel has shown below

Table 8 *Percentage increase of storage for MCH to Diesel & HFO considering equation(iii)*

Molar mass of MCH	µMCH	98.189	
Molar Mass of H2	µH2	2.016	
Balance Equation (iii)	MCH:H2=6*μ_{MCH} :2*μ_{H2}	146.115	
Equivalent MCH to diesel		207623.7	kg
Percentage increase	%	51.90593	
Equivalent MCH to HFO		1224713	Kg
Percentage increase	%	**48.9885**	

5.2 Consideration with balance equation (i)

$$C_7H_{14} \rightarrow C_7H_8 + 3H_2$$

The ratio for the extraction of H2 from MCH as per the balance equation will be

= (3*2.016)/ (1*98.189)

The requirement of MCH is $= \frac{98.189}{3*2.016} *1420.96kg$

$= 23069.3Kg$

~23.069ton

The percentage increased equivalent to diesel requirement is = (23.069/4) *100%

~5.767%.

The percentage increase for both HFO and diesel has shown below in table (9)

Table 9 *Percentage increase of storage for MCH to Diesel & HFO considering equation (i)*

Balance Equation (i)	MCH:H2=1*μ_{MCH} :3*μ_{H2}	16.235	-
Equivalent MCH to diesel		23069.3	kg
Percentage increase	%	**5.767325**	**%**
Equivalent MCH to HFO		136079.2	kg
Percentage increase	%	**5.443167**	**%**

5.3 Consideration regarding total bunker tank capacity

The MGO tank capacity from table (6) is 251 mt. We found per day requirement of MCH for hydrogen to produce equivalent energy of diesel is 207 ton.

Hence the day manages by MCH with considering storage of 251 will be (251/207) day or 1.2 days. Which means, storing MCH for dehydrogenation in the diesel tank, will enable the ship to operate for 1.2 days replacing diesel with H2. The day of operation data calculated for HFO and for both balance equation (i) and (ii) and presented in table (10)

Table 10 *Day of operation while storing MCH for H2*

	HFO storage	1160	ton
	Diesel Storage	251	ton
Equation(iii)	Per day MCH to HFO	1224.712502	ton
	Per day MCH to Diesel	207.6237174	Ton
	Day manages with MCH to HFO	0.947161067	Day

	Day manages with MCH to Diesel	1.208917763	Day
Equation (i)	Per day MCH to HFO	136.0791669	Ton
	Per day MCH to Diesel	23.06930194	Ton
	Day manages with MCH to HFO	8.524449604	Day
	Day manages with MCH to Diesel	10.88025987	Day

Based on above calculation, it shows that, the model with bi-products like DMCP will not be viable to consider an option for replacing diesel but with the basic formula (i) it shows prospects as the requirement of storage only increased by below 6%. Though the managed days with the total bunker storage will be 8.5 and 10.88 days respectively for HFO and diesel which indicates frequent bunkering will be required. It summarizes that, selection of proper catalyst to get the satisfactory conversion reducing bi-products in the dehydrogenation process can be considered as an option to use MCH to carry hydrogen to replace gasoline for specific route base approach.

Discussion

The result on different condition shows the sensitivity of conversion rate of MCH and molar fraction of H2, which are considered for the purpose of the study. The MCH conversion rate with changing temperature shows steady change though it is over 99% in the preset conditions. The dehydrogenation varies with the increase in temperature and shows a linear decline with increase of inlet temperature over 300 degrees. The H2 molar fraction shows negligible increase with the change of temperature.

The other sensitivity study by varying pressure shows different characteristics and increase in the H2 molar fraction. The MCH conversion rate fluctuation is not so significant with the pressure variation as it is above 99%. It indicates that, pressure increase will increase the H2 molar fraction in the vapor therefore, maintaining the temperature at standard value while increasing pressure can lead to satisfactory point of the dehydrogenation process.

The mass flow also has effects on the conversion rate of MCH though there is little effect on H2 molar fraction in vapor. The increased mass flow increases the conversion rate.

Through the combustion, the finding shows that, presence of DMCP will hinder the combustion of H2 in IC engine. To get combustible hydrogen, the bi-products of MCH conversion in the vapor need to be separated. As the boiling point of DMCP is lower approximately 80^oC which can be condense through a condenser to get hydrogen without other substances.
The sensitivity of the separator over setting the temperature from -20^oC to 20^oC showed that, below temperature -10^oC the H2 concentration is over 0.99 and most of the DMCP condensed out. This can be applied to get hydrogen without any mixture of bi-products of the MCH conversion.

From the case study, broader understanding regarding LOHC to be used as hydrogen carrier has been achieved. For the purpose of using hydrogen as an alternative fuel instead of Diesel/HFO through MCH, the storage space requirement will be higher and also bunkering frequency will be increased to a greater extend which makes it difficult to use organic carriers as hydrogen storage option. But for specific route base operation, there is possibility to use LOHC as an option considering availability of bunkering facility.

The study outcome led to some findings and understandings as below:

1. LOHC can be an option for hydrogen storage and transportation for both maritime and energy sector. It reduces the requirement for cryogenic state which enables already existing chemical tankers to be used as a hydrogen carrier. Depending on the delivery terminal, either with dehydrogenation reactor or without reactor both type of transportation mode can be established. Furthermore, the LOHC specially toluene has already a good production infrastructure and transportation facilities established which will make it easier for future expansion. As hydrogen has good opportunities to be produced using renewables and less carbon emission potential, it is getting investment in several parts of the world for green hydrogen production which requires transportation facility all over the world. In that case, LOHC and specifically MCH can be a good option due to toluene availability and easier dehydrogenation of MCH.

2. Using LOHC to carry hydrogen to be used as bunker for existing vessel is not quite satisfactory as the hydrogen carrying capacity is in between 5-7%wt. The large requirement of bunker will be challenging. Based on routes and short passage though it can be satisfactory but for long voyage it requires more research to be carried out based on specific route and type of vessel. One best option is to use H2 mixing with diesel which will enable new path to use hydrogen as an intermediate fuel focusing on future of hydrogen. This concept of using mixture of hydrogen and HFO will be a good option and LOHC like MCH with production facility and dehydrogenation percentage

can be utilized for the supply of fractional H2 onboard. Only modification need to be done is to set up the reactor for dehydrogenation to get the H2 flow.

3. The best possible outcome of using LOHC will be in carriage of H2 as a product in H2 driven vessel. In this case, concept similar to LNG carrier can be applied, where the LNG transported is used for fuelling the vessel. H2 can be carried through LOHC and with inclusion of dehydrogenation reactor, H2 can be extracted on board for IC engine. In this case, the H2 with diesel mix concept can be used. The diesel will be carried in the bunker tanks and H2 will come from the storage tanks through dehydrogenation reactor. For future energy sector new era of H2 carrier like that of LNG carrier will be started thorough the materialization of this concept.

Conclusion & Future Scope

6.1. Conclusion

The prospect of LOHC as hydrogen carrier is getting enhanced research due to its good hydrogen carrying capacity. The study shows the possibility of carrying hydrogen without much of the requirement of changing pressure and temperature. The onboard dehydrogenation can be easily achieved through installing reactor for extracting out the hydrogen from LOHC. The combustion process shows the possibility of using hydrogen in IC engine. Hydrogen for its high thermal efficiency and less carbon emission can be a good option to replace fossil fuel, and options like LOHC can solve the storage problem encountered regarding storage for using hydrogen for energy sector. The renewable sources can be easily used for hydrogen production and cheap LOHC like toluene-MCH will enable new dimension of H2 storage and transportation option. To be used as in intermediate fuel, LOHC exhibits storage capacity issues, as compare to Diesel/HFO the storage requirement is quite high. But options to support existing vessels in carrying and using H2 with HFO/diesel need further investigation to meet the IMO GHG target of 2030 and accelerate the infrastructure of hydrogen for the days to come.

6.2. Limitation

The study focused on MCH dehydrogenation considering kinetics mechanism using Pt/Zeolite catalyst. The simulation usually considers the pre-set condition and does not fully replicate practical experimental environments. In the combustion simulation, only behavior of H2 combustion is depicted. It only checks the combustion behavior of H2 and DMCP to understand the fuel composition nature in an IC engine.

6.3. Future scope of work

Different dimension of future studies can be done for LOHC both for storage option and maritime industry. As not much of studies done on the cost and production of different LOHC, hence cost benefit analysis between LOHC carrier and hydrogen carrier in cryogenic state will give better understanding of using LOHC. Also, the analysis can lead to the prospects of comparing with other alternative fuel options for energy sector.

In relation to maritime field, ship specific studies to use LOHC both as hydrogen storage for transportation and as fuel can be investigated. The reactor design for onboard dehydrogenation requires further studies. Furthermore, bunkering possibility of hydrogen using LOHC through hydrogenation reactor can be a good research option as this will be challenging for any kind of alternative fuel. These studies can also be done through comparing with other available alternatives to find out best suited option for maritime industry.

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MEPC 80/WP.12 Annex 1, page 1 I:\MEPC\80\WP\MEPC 80-WP.12.docx ANNEX 1 DRAFT RESOLUTION Adopted on [7 July 2023] 2023 IMO STRATEGY ON REDUCTION OF GHG EMISSIONS FROM SHIPS

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Appendix A Kinetic model parameter used for DWSim Dehydrogenation Simulation

	Dehydrogenation			Hydrogenation		
	Parameter	Value	Unit	Parameter	Value	Unit
Rate Constant	k_{rA}	1.143×10 −5	mol s−1 g-cat−1 bar−nA	k_{rT}	0.5252×10 −5	mol s−1 g-cat−1 bar−nT
Arrhenius Number	B_A	6.424	-	B_T	−29.24	-
Activation Energy	(E_A)	6	kJ mol−1	(E_T)	−129.14	kJ mol-1
Order of reaction	n_A	0.074	-	n_T	0.3088	-

Source Usman et al(2015)