Methane Hydrate Gas Storage Systems for Automobiles

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Abstract- Methane is the best fuel in the carbon family and is source of renewable energy having large potential. Although the methane exist in the form of methane hydrates, it is also possible to easily produce in the form of biogas. This study is an attempt to develop the methane storage system for automobiles to reduce cost of fuel. The direct use of methane hydrate in automobiles is proposed. Solar energy is proposed for the dissociation of methane hydrate for fuel economy. Economical analysis of the proposed system is done by comparing use of solar energy, microwave and burning of methane for hydrate dissociation. The existing fuel supply chain is modified for the cost reduction of methane. It is proposed that cost of natural gas can be reduced by modifying the natural gas supply chain. The need of regasification of natural gas hydrates at the dock is eliminated with the proposed modifications in the supply chain.

Keywords Natural gas hydrates, compressed natural gas, Liquefied natural gas, Regasification, Dissociation, self preservation effect.

1. Introduction

In the year 2008 deposits of methane hydrates were discovered in deep sea, although the hydrates were first documented in 1810. According to estimates the amount of methane is double more than the deposits of fossil fuels. Methane is best fuel among the fuels of carbon family. Guowei Hu et. al demonstrated the use of dry water as efficient medium for hydrate formation with increased formation rate and storage capacity formation rate was improved by pressure temperature conditions [1]. Dissociation of methane hydrate for regasification was investigated by Song He. Hydrate was heated with 2.45 GHz microwave. Regasification time reduced with increase in power. High temperatures are found advantageous but are avoided by considering safety [3]. The effect of methane hydrate dissociation at different temperature on stability of porous sediments was investigated by Yongchen song et. al. A verity of methods have been proposed for the recovery of natural gas from gas hydrates such as pressurization, thermal injection, usage of inhibitors and CO_2 replacement. Gas recovery using thermal injection has been the important choice of the gas recovery [2]. The amount of methane sequestered in the gas hydrates around the Indian coastal area is around 1900 trillion cubic meters. The hydrates were also discovered in the basins of Indian rivers [11, 12]. The volume of gas is 1500 times of current natural gas reserve of India. 10% recovery from the huge cache of energy can meet the energy requirement of India for century [13]. The combined use of natural gas hydrate regasification with liquefied natural gas receiving terminal was focused by Seolin shin et.al. The chain proposed, demonstrated save upto 10.6% of the total chain cost. It was also concluded that risk of proposed chain reduced with increase in shipping distance [4]. Gas supply chain using natural gas hydrate was proposed by Guoshua shi et. al. Gas production, transportation and regasification of natural gas hydrate was compared with liquefied natural gas.

The cost of proposed natural gas hydrate chain was found 80% of liquefied natural gas chain [5]. Chuang ji et. al. showed that gas production rate is a sensitive function of well pressure, reservoir temperature [7]. Energy balance studies were carried out and the simulation of hydrate dissociation was studied by G. A. Ramdass et. al. The study was based on the Indian scenario [10]. The effect of ultrasonic power, temperature and pressure on induction time was investigated by SUN Shicai [9]. The technical advantages and the economic efficiency of natural gas hydrate suggested the natural gas hydrate as alternative for liquefied natural gas. From the observation of the existing gas supply chain and automotive fuel system, it is required reduce the cost of hydrate storage and transport system and modify the automotive fuel system. Methane is also obtained from biogas. It is best source of renewable energy. There is scope for the improvement of production, storage and transportation of methane. The current work is an attempt to develop the automotive fuel storage system and to use the methane hydrate as a source of methane for the engine operation. With the implementation of this work on site it is possible to replace compressed natural gas and liquefied natural gas technologies.

2. Kinetics Of Methane Hydrate Formation

Methane hydrate formation can be expressed as gas consumed with respect to time. When the temperature of water is reduced to its freezing point, it exhibits particular structure. Voids are created in the molecular structure of ice, these voids are filled with gas molecules during hydrate formation. There are three phases of methane hydrate formation dissolution, Induction and growth. The driving force is required for the formation of methane hydrate. There are different views of researchers regarding the driving forces such as temperature difference, concentration difference, difference of fugacity are some of the forces formation methane is dissolved in the water, Agitation is provided to increase the rate of dissolution. Increase in considered for hydrate formation. In first stage of hydrate pressure also has proportional effect on the formation of hydrate. After the dissolution of gas, hydrate nuclei are evolved as the temperature drops. The period from the start to the generation of first nuclei is called dissolution period. The formation of hydrate nuclei starts at two different interfaces, one at the gas-water interface and other at the molecule of dissolved gas in the water. Nuclei are evolved within the entire water and the hydrates can be detected at this time, this period is marked by the turbidity. After this point nuclei grow rapidly and hydrates are formed. Period after the dissolution and before the turbidity is called induction period and the period after turbidity to the full growth of hydrate is called growth period. The rate of dissolution increases with pressure increase and agitation.

3. Comparison With Compressed Natural Gas And Liquefied Natural Gas

The Comparison of hydrate technology with liquefied natural gas and compressed natural gas given by Guoshua shi et. al is shown in Table 1 [5].

Table 1. Comparison among liquefied natural gas, compressed natural gas and natural gas hydrate Technologies.

Technological Characteristics	Technologies		
	liquefied natural gas	compressed natural gas	natural gas hydrate
Natural gas purification requirement before production.	High	High	Low
Storage Pressure (MPa)	Atmospheric Pressure	20	Atmospheric Pressure
Storage temperature (°C).	-162.2	25	-15
Gas storage Capacity per m^3 production	620sm^3	220sm^3	152-180sm^3
Storage tank	Cryogenic storage tank using double layer metal structure.	Seamless pressure storage tank	Common adiabatic atmospheric storage tank.
Security	Lowest	Lower	High

The formation of compressed natural gas requires the expensive multistage compression and the pressure is 20Mpa and the liquefied natural gas formation requires the cryogenic refrigeration Process. The formation temperature of liquefied natural gas is -162°C. The purification requirement of natural gas is not strictly required for the formation of hydrates, inversely it stabilizes structure of methane hydrate. In case of liquefied natural gas, the presence of water and acid can cause blockage of the pipes and corrosion of equipment's respectively. Heavy hydrocarbon molecules acid gas components and water vapours are removed before the liquefaction. The natural gas hydrate refrigerated to -15°C can be stored at atmospheric pressure. Natural Gas Hydrate is in equilibrium state at around 193 K under atmospheric pressure and natural gas hydrate is expected to be stowed and transported at higher temperature due to its special property so-called "Self Preservation Effect" [8]. Simple adiabatic atmospheric storage tanks can be used to store natural gas hydrate. The methane molecules forms compound with water molecules. Therefore, for removal of methane melting of crystal structure is required. The latent heat of thaw of hydrate is 500-600kJ/kg at 0-20°C [5]. The decomposition requires very high thermal energy which provides betters safety. The heating and decompression are mature technologies of regasification. Sometimes, methanol is used to shift dew point of dissociation of hydrates. There is little difference between density of hydrates and water, which makes it difficult to separate water from hydrates by conventional gravity separator during production of natural gas hydrate.

4. Storage And Transportation Of Methane Hydrate

The conventional technologies used for storage of methane are compressed natural gas and Liquefied natural gas. Methane is fuel with lower density. It is stored in the compressed form. Although the compressed gas, liquefied natural gas technologies are available for the storage and transportation, there is need for cost effective method of storage and transportation. Under certain temperature and pressure, a stable water crystalline ice-like substance can be formed in the presence of natural gas and liquid water. If methane hydrate is either warmed or depressurized, it will revert back to water and natural gas. Artificial gas hydrates can be manufactured easily with moderate production conditions. The conventional gas transport system is shown in Fig. 1.

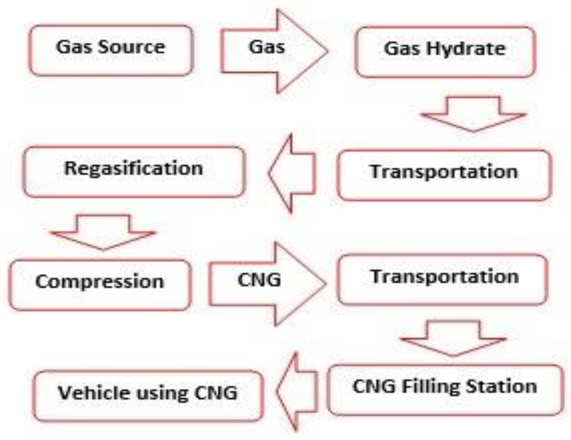

Fig. 1. Conventional gas transport system.

For the reduction of per unit cost of methane the system is proposed as shown in Fig. 2.

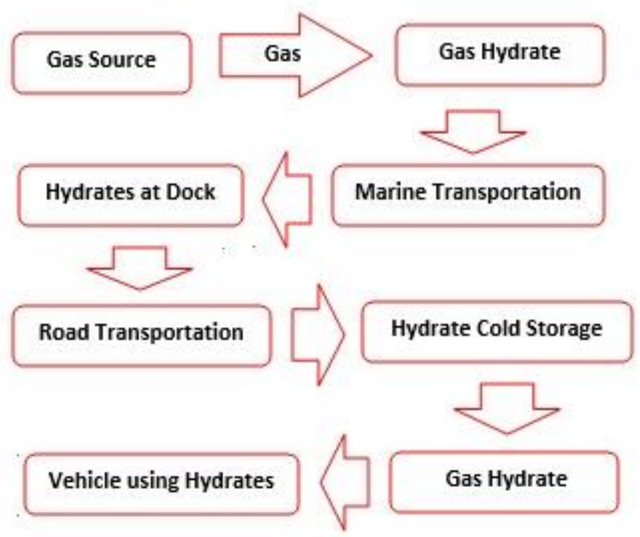

Fig. 2. Proposed gas transport system.

The pressure and temperature required for producing hydrate is 20-60 bars and 0-200°C respectively and the storage temperature is -150°C. And the density of hydrate is 900kg/m^3. Currently this technology is not well established in India this is used by some of the countries such as China, Japan and USA. End users of natural gas are 3000 to 5000 km away from deposits of hydrates. Due to low production and transportation cost, hydrate is the best solution for distances of this range [4]. The cost of regasification of hydrate is higher than liquefied natural gas but the transportation cost is less and transportation becomes more economical as the distance of transportation increases. Compressed natural gas is uneconomical for such large distances because of the large size and also the multistage compression required. The cost per unit mass of chains are compared by Seolin shin et.al are shown in Table 2 [4].

Table 2. Cost per unit mass for the chains.

Annualized Cost	Conventional liquefied natural gas	Proposed Chain (Hydrate + liquefied natural gas)
Formation		
Capital Cost	92.69	83.22
Operating	17.58	21.69
Regasification		
Capital cost	3.68	6.44
Operating	0.68	2.57
All cost in ($/ton).		

Costs associated with road transport of methane hydrate and its use in vehicles are shown in Table 3.

Table 3. Costs associated with road transport of methane hydrate and its use in vehicles.

Chain using compressed	Chain using Hydrates
Cost of natural gas hydrate unloading(at dock)	Cost of natural gas hydrate unloading(at dock)
Cost of natural gas hydrate regasification (after receiving hydrate at dock)	Nil
Cost of gas compression to compressed natural gas	
Cost of cylinders	Cost of adiabatic storage tank
Cost of loading	Cost of loading
Cost of transportation	Cost of transportation
	Cost of Refrigeration
Cost of compressed natural gas filling station	Cost of cold storage house
Cost of vehicle using compressed natural gas	Cost of vehicle using Hydrate

Conventionally compressed natural gas is used for transportation of natural gas over small distances. The cost of methane hydrate transport from hydrate deposits to the dock is less as compared to the liquefied natural gas is already been demonstrated. For the further transport there are two kind of chains, one using compressed natural gas and another proposed chain using hydrate. The costs associated with these chins are shown in Table 2 and Table 3. The weight of natural gas hydrate is 7.46 times the weight of natural gas and space required is 1.4 times for same amount of gas. The empty compressed natural gas cylinders used in India for compressed natural gas transport weights 48kg with volume 0.05m^3. The weight of the compressed natural gas cylinder (200bar) is 5.8 times the weight of natural gas. The weight of natural gas hydrate is 1.28 times the weight of compressed natural gas cylinder. The length and diameter of cylinder 835mm and 316mm. The total space occupied by cylinder is 0.65m^3. The gas stored per m^3 of the compressed natural gas cylinder, considering the total space occupied by cylinder is 169.2 sm^3 per m^3 or less if we consider the inter cylinder spacing. For hydrate it is 150 to 180sm^3 per m^3. The values are of energy requirement and equivalent mass of methane required are compared using bar charts as shown in Fig. 3 and Fig. 4 respectively.

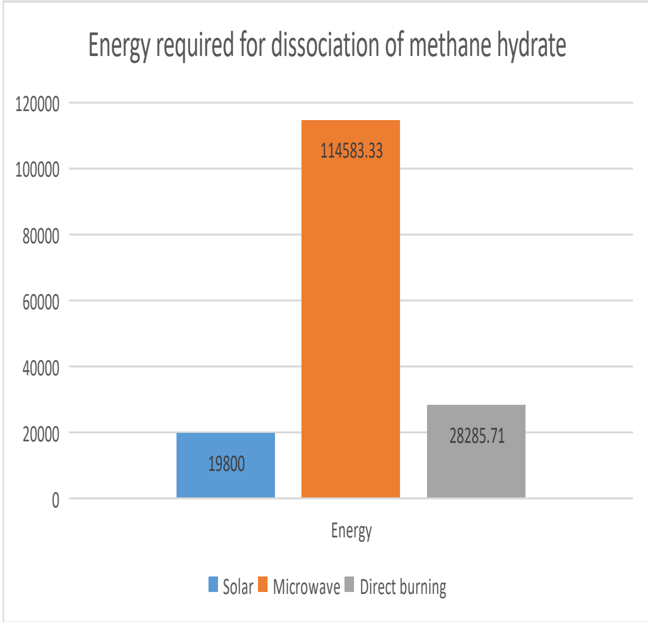

Fig. 3. Comparison of energy required for dissociation of methane hydrates.

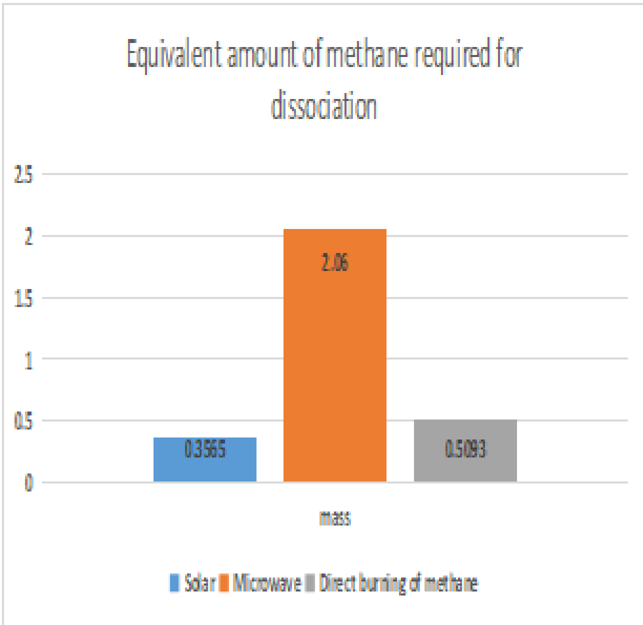

Fig. 4. Comparison of equivalent amount of methane required for dissociation.

This shows that the cost of hydrate transportation is almost same as cost of compressed natural gas transportation. The cost of refrigeration is always less than the cost of natural gas hydrate regasification and gas compression using cascaded system. The proposed chain is more economical than the conventional chain in India. The excess of water need to be removed before the compression due to high content of water in hydrates. This is achieved by the process of flash separation. Because of its ineffectiveness further dehydration is required. The water content increases exponentially with temperature and pressure so, additional dehydration is required. After the first flash separator the temperature is decreased to reduce the duty of dehydration. There are other methods such as enhanced dew point shifts adsorption, absorption are considered for dehydration after the rough water removal. Adsorption using a molecular sieve could reduce the water contents to less than 0.1 ppm but absorbent media are highly expensive. Furthermore, this method is energy intensive and causes pressure drop which makes it difficult to meet the regasification pressure of 70 bar. Second, natural gas hydrate can be dehydrated by absorption process where an absorbent such as tri-ethyl glycol is used to set to the water content to about 30ppm. This is economically unfavourable because large amount of absorbent is required for large scale process. The method of enhanced dew point shift is composed of compression where the dew point temperature of natural gas hydrate water mixture is increased cooling process where the enhanced mixture is condensed and flash separation where the mixture undergoes vapour-liquid phase separation as a result both compression and dehydration can be obtained whereas the performance of this method just remains at 100 ppm of water. Energy required for hydrate dissociation using microwave and direct burning is 114583.33kJ and 28285.71kJ respectively, but the use of solar energy is only 19800kJ and is free of cost. The equivalent amount of methane required for regasification using solar energy, microwave and direct burning is 0.3565kg, 2.06kg, 0.5093kg respectively.

5. Method Suitable For Automobiles

There are several ways of regasification of hydrates such as steam heating, depressurization and thermal injection. Hydrates can be regasified using microwave for small scale regasification, thermal injection is used for dissociation of hydrates in hydrate deposits. This method has been used widely over the years. By considering the bulkiness of depressurization, thermal injection the use of microwave is suitable for automobiles. The method using solar energy for dissociation of hydrates is also proposed and the calculation of daily run after the dissociation of methane hydrate using solar energy is done. The energy required for the dissociation of hydrate using solar, microwave and direct burning of methane are calculated in Table 4, Table 5, Table 6.

Table 4. Calculation of vehicle run after daily dissociation of methane hydrate.

Use of solar energy for regasification.	
Area exposed to sunlight	$1m^2$.
Average Solar density(India)	5.5kWh daily.
Enthalpy of dissociation of methane hydrate	431.15kJ/kg.
Average hydrate melt daily	45.923kg.
Average content of methane in hydrate	13.4% by mass.
Mileage of car running on CNG(Considered)	18km/kg.
Distance travelled using 6.153kg of gas	110.754km

Table 5. Calculation of energy required for microwave and equivalent methane.

Use of microwave for regasification.	
Energy required to melt 45.923 kg hydrate	19800kJ
Efficiency of microwave(Considered)	60%
Energy required for microwave to melt	33000kJ
Power required for microwave	763kW.
Engine efficiency(Considered)	32%
Efficiency of alternator(Considered)	90%
Energy supplied to engine for melting	114583.33kJ
Amount of methane require for producing 114583.33kJ	2.06kg

Table 6. Calculation of methane required for dissociation using direct methane burning.

Use of heat produced by burning methane for regasification	
Calorific value of methane	55530kJ/kg
The amount of energy required for melting 45.923kg of hydrate. (Efficiency of heating considered 70%)	28285.71kJ
The amount of methane required for producing 28285kJ	0.5093kg.

Hydrates can be regasified easily using microwave and power source required for microwave is available within the automobile. The mileage of car running on compressed natural gas is considered as 18km/kg and the hydrate dissociation is calculated using the average energy density in India. The amount of hydrate melt daily using solar energy is 45.923kg. The average content of methane in hydrate 13.4% by mass. It is calculated that the amount of gas released after the dissociation of 45.923kg of hydrate is 6.153kg. With the above considered mileage car can travel 110.754km daily. The equivalent amount of energy required for dissociation using the microwave and direct burning of methane considering the efficiency of the system are also calculated along with the equivalent mass of methane required for dissociation. The efficiency of engine, alternator and microwave considered are 32%, 90% and 60% respectively.

6. Modification In Existing Fuel System

The existing fuel system can be replaced with the proposed system shown in Fig. 5. In proposed system hydrates are taken into vehicle fuel storage system where it is heated using the microwave. The enthalpy of dissociation of hydrate is 431 kJ/kg [6].

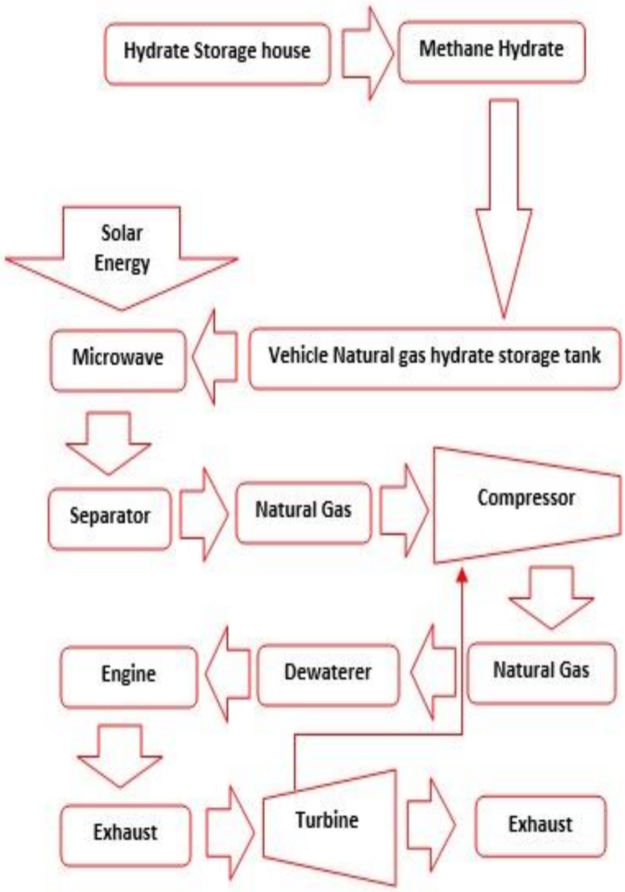

Fig. 5. The proposed fuel system for automobiles to use hydrates in automobiles.

It is economically unfeasible to heat hydrate using microwave, so the assistance of solar energy is taken. The average density of solar energy in India is 4-7 kWh/m^2. In certain areas it is 6-7kWh/m^2. Considering average solar density of 5.5kWh/m^2. Mass of hydrate dissociated daily considering area of $1m^2$. The fuel tank is converted into heating chamber of microwave and the glass is provided at the upper side for the absorption of solar energy.

=19800/431.5 =45.923kg.

Considering mass of gas /kg of hydrate13.4%. Gas released due to solar energy /day =6.153kg. If tanks are provided the gas released can be used on the next day. In the proposed system natural gas hydrates are directly used in the natural gas hydrate storage system of vehicle which can dissociate hydrate using solar or microwave. The released gas is sent to the separator to remove water vapour from the gas. The methane is then compressed using the turbocharger. The water vapours are again removed before it is sent to the engine. The developed system is entirely new except the turbocharger.

7. Future Scope

The present work focus on the anticipated global fuel crises by considering the anticipated conditions. It is required to focus on use of non-renewable energy sources such as biogas, solar energy. Despite of good production sources available the problem in transportation, fuel storage has been the problem of prime importance. It is possible to emphasis on the recent hydrate technology as a main source of storage and transportation. The intrinsic kinetics of clathrate hydrate formation was studied using experimental and theoretical approach however, the optimization of hydrate reactor for artificial methane hydrate formation was not focused. It is possible to reduce time and to save energy and cost by optimizing the reactor. There is scope for development of system for formation of biogas hydrates. It is also possible to improve biogas production rate by using stirred biogas plant with controlled conditions. The combination of biogas with proposed fuel system for automobile will help in development of smart cities or energy independent cities. There is scope to optimize proposed system. Production of biogas is biological process. The production of biogas depends on the environmental conditions available for the growth of bacteria. The fermenter used for production of curd in hotel maintains the environmental conditions which enables the formation of curd within few minutes. The fermenters with higher capacity specially designed for production of biogas can be used to improve biogas production. This can be implemented after checking the economical feasibility. The retention period of biogas production is very high.

It is possible to reduce the retention period by controlling the environmental conditions of biogas production. The agitation required for the production of biogas can be archived by using stirrer and motor.

7.1The concept of smart fuel independent city.

The biogas is efficient and easily producible fuel for rural areas. For the use of biogas as alternative fuel in the vehicle, it is required to compress the gas. The production of bio compressed natural gas require cascading of the compressor so the system becomes economically unfeasible. If the cost of production, storage and transportation is reduced the bio compressed natural gas will be easily available as alternative fuel. The storage and transportation cost of biogas can be reduced by storing biogas in the form of hydrates. The refrigeration system is also required for the formation of hydrate. The pressure and temperature conditions are easily achievable using compressor and refrigeration system. The pressure required is 20 bar instead of 200 bar required for compressed natural gas. It is possible to construct artificial methane hydrate reactor with low capital investment than cascaded system. The operating cost will be comparable with the cascaded system used for compressed natural gas. The hydrate crystals can be stored at atmospheric pressure and at temperature of -15ºC. The hydrates produced within city can be used as a source of gas for the proposed automotive fuel system. Capital investment cost of cascaded system is Rs. 500,000 and the estimated capital investment cost of the proposed system is Rs. 200,000. Regasification cost can be neglected if we use solar energy.

8. Conclusion

1. It is concluded that the fuel system was successfully developed for the direct use of hydrate as a source of fuel for automotive engines. The use of solar energy in the developed system reduces the cost per kg of methane. Gas hydrates can be directly used in automotive fuel system by eliminating regasification cost.

2. From the comparison of dissociation methods it is concluded that solar energy is the effective method of hydrate dissociation for automobiles. The proposed system using the solar assisted regasification process reduces the regasification cost.

3.The amount of hydrate dissociated daily using the solar energy is 45.923 kg which releases the 6.153 kg of methane.

4.The proposed system save the 0.509 kg equivalent amount of methane required for dissociation of hydrate. With the use of solar energy for regasification vehicle can travel 110 km daily.

5. The modification in the conventional gas transport system eliminates the cost of regasification and compression. The use of methane extracted from biogas in the proposed system can develop the energy independent cities. The proposed will reduce the cost of methane and will assist in utilization of renewable energy. Optimization of production, transportation and mainly regasification increases the economical feasibility of usage of hydrate in automobiles.

Acknowledgements

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