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## **Theoretical Model for the Transportation of Stranded Gases As Hydrates**

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### **Abstract**

In the oil and gas industry, safe, on-time delivery and cost-effective ways of transporting oil and gas is required. Natural gas hydrates (NGH) technology (which involves production, transportation and regasification) can be used to transport natural gas and or stranded gas or gas that will be flared or re-injected, in bulk carriers.

In the previous work on NGH Technology, the constraint had been on how hydrate with natural gas can be sustained to delivery. This work introduces a favourable theoretical thermodynamic model of heat loss reduction with reference to various insulating membrane diameter and aids in the transportation of the hydrated stranded gases to delivery at a stated duration without the need for time consuming re-gasification. Mathematical models including Fourier's law of heat transfer, fourrier's law of mass transfer, Peng Robinson equation of state and break even analysis for economics were employed in validation of feasibility of this new technology, HYGAS. Also, HYGAS software from the platform of Microsoft Visual Basic. Net is developed for modelling and designing of hydration of gas for economic transportation.

**Keywords:** Natural Gas Hydrate · Transportation · HyGas

### **Introduction**

The natural gas hydrates technology includes-production, transportation and the process of re-gasifying natural gas hydrates. Natural gas hydrate production works with the principle of using standard reactor, pumps, separators and heat exchangers in process operation.

The origin of this research dated back to the works of Gudmundsson and Borrehaug (1996) who discovered that hydrate production process could be technically feasible. This led to Gudmundsson suggestion that a process by which natural gas with the addition of water are made to have contact in a stirred tank reactors at typically 65 bar and 10°C.

Natural gas hydrate contains up to 182 SCF of gas per volume of hydrate. Gudmundsson, Parlaktuna and Khokhar (1992, 1994) concluded that produced hydrates can be transported and stored at atmospheric pressure and temperatures below 0°C, typically at-15°C, without significant loss of gas. The storage capacity and the stability of hydrates at atmospheric pressure, make NGH technology, a safe and economical method for handling natural gas. Two concepts, the dry hydrate concept and the hydrate slurry

concept were being development at NTNU. In the dry hydrate concept natural gas hydrates are produced in stirred tank reactors and with reactors water. After being produced, the hydrates are separated from the water, and simultaneously frozen and depressurized to low temperature and atmospheric pressure. Hydrate crystals are then available for transport by bulk carriers to the market. In the hydrate slurry concept, the gas first produced in a water continuous phase and then in an oil continuous phase. The final product is a hydrate-oil slurry with free water, in pipelines to shore or transportable in shuttle tankers (Gudmundsson et al, 1998). In both concepts, gas hydrates are produced by contacting water with natural gas in a chain of stirred tank reactors.

The hydrate formation process has some special features. A hydrate reactor is a three-phase slurry reactor as the production water is slightly denser than the hydrate. The kinetics of hydrate formation is poorly understood, and mass and heat transfer effects are believed to be important for the overall rate of hydrate formation. Most of the reported studies of hydrate formation have been carried out in small scale batch or semi-batch reactors and not in continuous stirred tank reactor (CSTRs) as needed in a commercial process. Models based on reactor experiments are seen to be system specific.

By studying the hydrate formation process in this type of reactor, established knowledge can provide valuable information in understanding the process. Hydrate formation is an exothermic process by producing in a water continuous system such as a stirred tank reactor, the water phase as a heat sink for the heat of hydrate formation, so that the temperature in the reactor can be controlled. The upper temperature in hydrate production is restricted by be equilibrium temperature for the existence of hydrates.

The production of hydrates and its transportation, which is the primary focus of this study, seeks to obtain a deeper knowledge of the processes that occurs in hydrate formation using theoretical modeling, such understanding is vital for an effective operation of a hydrate production design, commercial transportation initially for the scale-up from laboratory to pilot plant size.

## Literature Review

Stranded gases could be defined as any hydrocarbon-based gas which is not economical to be produced or transported to the market. Examples are associated gas, flared/vented gas, and gases that are been re-injected into the reservoir to comply with regulatory bodies of hydrocarbon exploration other than its use for maintaining reservoir-pressure.

As there tends to be a growing demand for gas consumption in Nigeria and in the world; there may be a requirement for improved synthetic hydrate formation processes which can provide new and economic storage, transportation, safe and processing capabilities. The major problem here is when these gases are transported as hydrate the delivery time is of great concern as such even in the humid region, Ice and Promoters are added to boost delivery time without untimely re-gasification while on transit.

## Hydrate Equilibrium Conditions

At hydrate equilibrium conditions, solid hydrate may exist in equilibrium with liquid water or ice, gas and some additive. Such temperature and pressure conditions are defined by the hydrate equilibrium curve for a given gas and water composition. Hydrates can only form at temperatures lower than the equilibrium temperature and simultaneously at pressures higher than the equilibrium pressure. The distance from the equilibrium conditions is the driving force for hydrate formation hence; the hydrate equilibrium curve represents the pressure and temperature condition where the hydrates dissociate.

Hydrate equilibrium curve can be predicted from statistical thermodynamics using the van der Waals and Platteeuw model with some modifications, which is thoroughly explained by Sloan (1998). Also other simpler methods based on hand calculation and phase diagrams exist (Sloan, 1998). Available computer programs based on statistical thermodynamic models, such as CSMhyd (1998) or PVTsim (2001) can predict hydrate equilibrium conditions.

## Mechanisms of Gas Hydrate Formation

The thermodynamic behavior of hydrate system forms the basis for understanding the mechanisms of hydrate formation. The time-dependent phenomenon of hydrate formation kinetics is described by applying crystallization theories including nucleation, growth, agglomeration and breakage. So far, the most studied phenomena of gas hydrate formation are the nucleation and growth processes.

Nucleation is a microscopic stochastic phenomenon where gas-water clusters (nuclei) grow and disperse until some nuclei have grown to a critical size. Nucleation may occur spontaneously (homogeneous nucleation), or it may be induced around impurities (heterogeneous nucleation). In contrast to primary nucleation, where nucleation commences without crystals present, secondary nucleation occurs in the vicinity of already growing crystals in the system.

The time from the first gas-liquid contact to the first detection of a hydrate phase is called the induction time. In macroscopic studies, the induction time has been used as a measure of the nucleation period (Skovborg et al., 1993, Monfort and Nzihou, 1993, Yousif, 1994, Natarajan, Bishnoi and Kalogerakis, 1994). These studies indicate that the induction time increases dramatically when the driving force for hydrate formation approaches zero.

The rates at which hydrates are formed have been measured by many researchers after nucleation, (which is the hydrate growth stage). The rate of formation of hydrates is been expressed in terms of the rate of gas consumption. One of the very important works done on this subject was that of Vysniauskas and Bishnoi (1983) who started a research to measure the rate of hydrate formation in a semi-batch reactor .the results from this work gave rise to the theory that the rate of hydrate formation depends on the gas-liquid pressure, interfacial area, temperature and subcooling. Ostergaard et al (2000) measured, in a rocking cell, the hydrate formation rate from gas dissolved in a North Sea black oil to investigate the possibilities of separating gas from oil by producing hydrates. They found that the memory effect of water and the hydrodynamic conditions greatly influence the formation rate. Also, they pointed out that better design of the reactor will significantly improve the rate, and thus, reduce the required volume of the reactor.

## Gas Hydrate Formation Models

Several hydrate formation models have been published on the basis of experimental results from batch or semi-batch reactors. All the models required fitting of experimental data to obtain empirical constants. Rasmussen (1994) develop a more easilier model which considered the gas consumption rate alone to depend on the gas from the gas transport phase to that of the liquid bulk phase as expressed in the following equation

$$\frac{dn}{dt} = K_L A (g-1) C_{wo} (x_{int} - x_b) \quad (1)$$

The rate of consumption from [equation \(1\)](#) above is a function of the mass transfer coefficient of the gas-liquid, the gas-liquid interfacial area and also the mole fraction driving force.

That the rate of hydrate formation may be mass transport-limited does not imply that measurements of particle size distributions are redundant. Hem et al (1999) pointed out that information about the particle size distribution is not accessible with measurements of the gas consumption rate only.

Lekvam and Ruoff (1993) develop a reaction kinetic model for methane hydrate formation using a method referred to as the pseudo-elementary reaction steps (Lekvam and Ruoff 1993.) The initial reactants were liquid water and gaseous methane and obtained the product as hydrate. Dissolved methane and some hydrate precursor species were used as reaction intermediates. The gas dissolution in water phase, the buildup of the precursor and also the growth of methane hydrate using an autocatalytic process were used as the dynamic elements. The rate constants were determined for each pseudo-elementary reaction with one gas phase for different reaction at various times. Gaillard, Monfort and Peytavy (1996) modeled

nucleation, growth and agglomeration in their hydrate loop (with liquid hydrocarbons) applying crystallization theory and methane gas consumption measurements. They proposed a population balance for the hydrate crystals in the system and expressed the nucleation, growth and agglomeration rates by empirical correlations. Experiment obtained by Gaillard *et al* (1999) who worked on nucleation and agglomeration growth in their hydrate loop observed no induction time.

## The Hydrate/Liquid Interface for THF Interfacial Measurements

The determination of the formation kinetics of non-stoichiometric compound is difficult due to the fact that its mass and porosity has not been determined. Although an explicit mechanism by which hydrates are found has not been established. Zhang *et al*, (1996) suggested that an addition of SDS on the THF interface is capable of reducing the induction time a considerable consistent time. Zhang placed the THF hydrates in a Malvern Nanosizer ZS at a temperature of 3.2°C. With a 10-wt THF solution THF hydrates usually dissociate at a temperature of 4°C.

However, using various concentrations of SDS, the surfactant concentrations on the hydrate particles were measured by Zeta potential and fluorescence. This marked the first discovery of the effects of SDS on the hydrate/liquid interface at the microscopic level. To further confirm a hydrophobic layer to have been formed on the hydrate/liquid interface fluorescence measurements were carried out. (Zhang *et al.*, 1996).

## Methodology

**HyGas** software is developed for the modeling and design of hydration of gas for economic transportation. This is an emerging technology in the oil and gas industry. **HyGas** was developed from the platform of Microsoft Visual Basic. Net. It uses the basis of Visual Basic (VB) Programming Language. Visual Basic is an object oriented Programming Language (OOP). **HyGas** uses a number of Objects and classes for building functions that are deployed for this analysis. Although **HyGas** is intended to be used for academic purposes but it could be customized for specific operations and for field use. It has the advantage of easy to use and very simple analysis. It can be applied by engineers in the oil and gas industry and those in other industry outside oil and gas. It can easily be upgraded, updated and has the flexibility of being re-designed for special operations should a customized operation been required.

## The Working Principle of Hygas Software

**HyGas** simply means “Hydrated Gas”. The software was built primarily for data analysis purposes. **HyGas** works on the principle of Input – output logic and utilize a number of well known models such as the Fourier’s law, Exponential law, Peng Robison Correlation and Cash Flow Analysis for economic evaluation. Data are feed into the software via input boxes and simply click on the command buttons to compute the required information. The Splash screen and welcome graphics user interface (GUI) home page of **HyGas** is as shown in [figure 1](#).

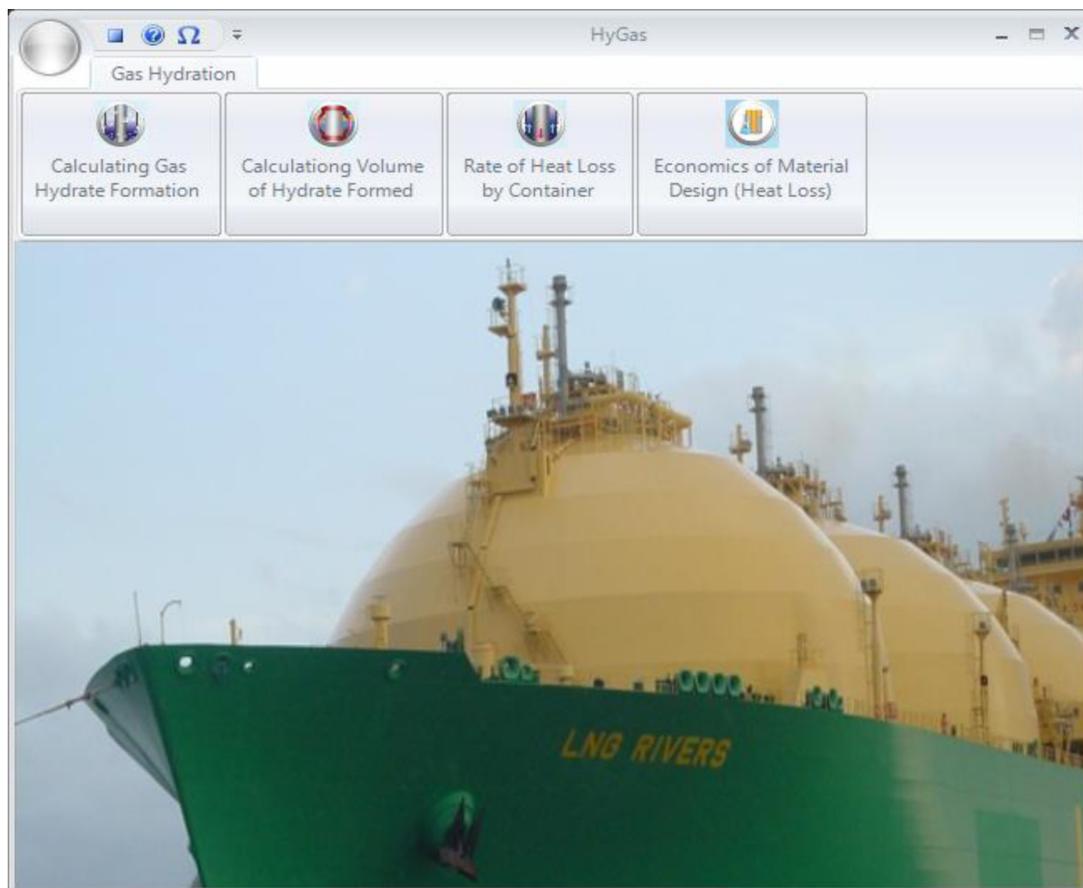


Figure 1—Shows HyGas Software Default Home Windows

## Data Presentation and Analysis

Analysis is carried out with the help of newly developed software called “HyGas”. The software has the capacity of modeling the formation rate of hydrate under certain conditions of temperature and pressure, calculate the volume of gas that can be stored in the hydrate, modeling the rate of heat loss in the hydrate due to long distance of transportation and also can also analyze the economic implication of such models.

## Calculating and Analyzing Rate of Heat Loss

From Fourier’s law, the rate of heat loss by a body is exponentially related to the time or duration of exposure for a given material thickness. [Figure 2](#) shows the effects of time and varying insulation thickness on heat loss.

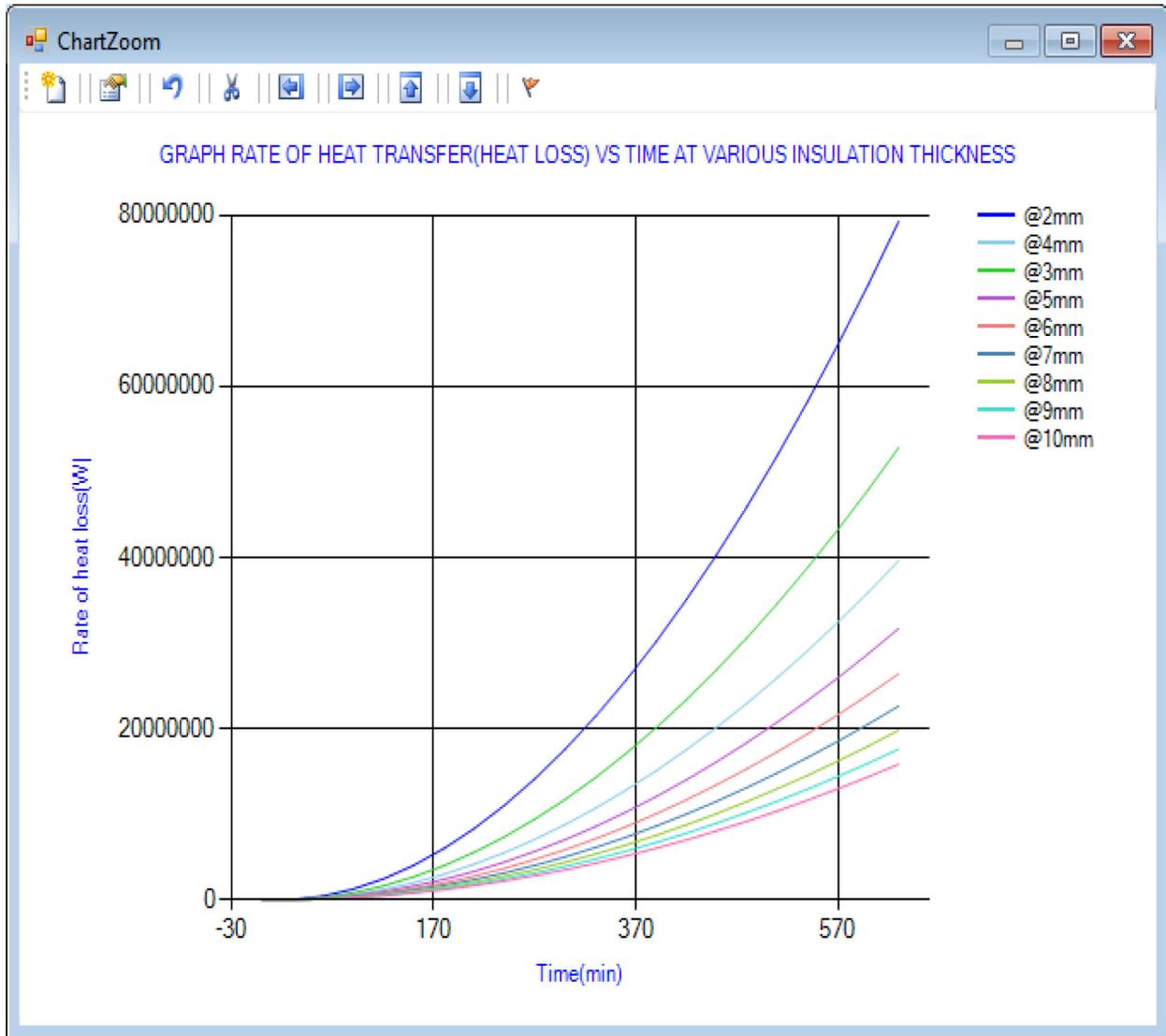


Figure 2—Shows Effects of Heat loss on Varying Insulation thickness

The Tables below are Input data for heat loss on varying insulation thickness.

Table 1—Vessel Insulation Input Variables

Input data	Parameter unit	Values
Insulation Radius (R)	Mm	4.0
Insulation thickness (S)	Mm	2.0
Insulation thermal conductivity (K)	1/Mk	230
Insulation thermal gradient (G)	1/T	0.152

Table 2—Transport Fluid Input Variables

Input data	Parameter unit	Values
Average fluid velocity (V)	m/s	300
Fluid density ( $\varphi$ )	lbm/ft <sup>3</sup>	42
Fluid heat capacity (CP)	Kg/k	220

**Table 3—Temperature and other Input Parameters**

Input data	Parameter unit	Values
Outer medium temperature ( $T_0$ )	°C	28
Inner Medium temperature (T)	°C	26
Fluid temperature ( $T_s$ )	°C	26
Vessel orientation angel ( $\Phi$ )	Degree	0

**Table 4—Vessel input variables**

Input data	Parameter unit	Values
Start time ( $t_0$ )	minute	0
End time ( $t_n$ )	Minute	620
Increment (integer)	no unit	30
Vessel area (A)	M <sup>2</sup>	4

From [Figure 2](#) above, the rate of heat loss reduces gradually as the insulation thickness increases and reach its peak at 7mm thickness. From there on any further increase in the insulation thickness does not bring significant reduction in rate of heat loss. Thus the optimum range of operation of the insulation thickness is between 4mm and 7mm for the given material and design used in this project. [Figure 3](#) shows the full interface of varying insulation thickness and its results.

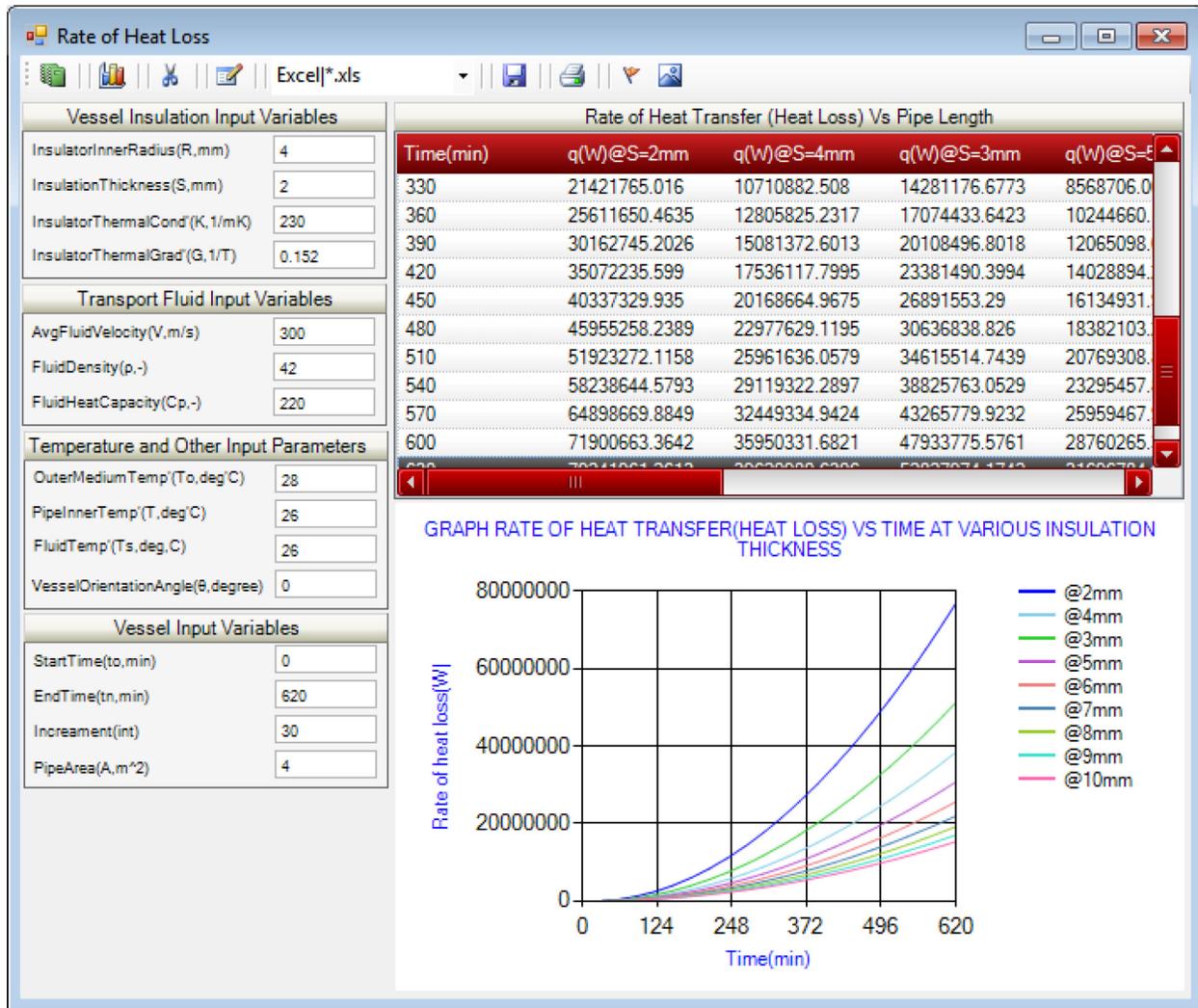


Figure 3—Shows Effects of Heat loss on Varying Insulation thickness

## Conclusion

It has been observed theoretically that Fourier’s law of mass transfer can be modeled and program drawn so that at a glance using given mass, volume of hydrate formed can be determined. A quick observation of Fourier’s law on rate of mass transfer modeled with Peng Robinson equation of state converted to surface condition reveals exponential growth of hydrate rate and thus, volume.

Hydrate observed at the sub-surface (in the well), when brought to the surface can be converted to surface condition, stored and transported.

The heat transfer with respect to time is the most important factor considered of the hydrate equilibrium and transportation conditions to be sustained to delivery if good vessel insulation and lagging design is done with respect to insulation thickness, heat loss can be controlled and hydrate equilibrium condition attained to delivery.

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