

TECHNOLOGICAL PATHWAYS AND ECONOMICS OF DME-PRODUCTION FROM “DRY” BIOMASS

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ABSTRACT: Two different concepts for large-scale production of dimethyl ether (DME) from wood were developed. These concepts are based around wood gasifiers and single-pass DME synthesis reactor. The main differences between the two concepts are the two gasifiers adopted. Specifically one uses a steam blown atmospheric circulating fluidised bed (CFB) gasifier in comparison to a pressurised (CFB) gasifier utilising a mixture of steam and oxygen as gasifying agents used in the other. Results of the simulations showed, that 600 kg/h or 1 040 kg/h DME could be produced from concept 1 and concept 2, respectively. But however, electricity generation from gas and steam turbines is higher for concept 1, for which reason total efficiency concerning DME and electricity production is nearly equal for both concepts. Finally, economics of these two concepts were investigated. The investment cost for concept 2 were considerably higher than for concept 1, which can be accounted to higher cost of pressurised gasification. This disadvantage of concept 2 ultimately leads to better overall profitability of concept 1. From analysis of both concepts the DME synthesis step is identified as major bottle neck. Therefore, Fraunhofer UMSICHT installs a flexible test plant for the future investigation of this reaction.

Keywords: biofuel, biomass to liquid (BtL), polygeneration, economics, dimethyl ether

1 INTRODUCTION

1.1 General Introduction

Biomass-derived dimethyl ether (DME) is a promising 2nd generation biofuel. Via gasification for example, biomass feedstock can be converted into synthesis gas, which then can be used for synthesis of DME [1]. Synthesis can be performed in two steps, where methanol is produced first and then dehydrated to DME, or in one step, where methanol production and dehydration step simultaneously occur in one reactor [2,3]. However, the complete process chain for the production of DME via one-step synthesis from synthesis gas obtained by wood gasification has not been investigated sufficiently, especially at a large scale. To evaluate possibilities of DME in the future biofuels market, it is necessary to tackle this knowledge gap. This is the aim of the presented modeling work.

1.2 Properties & Use of DME

At ambient conditions, DME appears in its gaseous form, being colour- and odourless. But since DME has a low vapour pressure at 20°C (see Table I), it can be liquefied without problems for easier transport and storage. For various fields of applications, DME is classified into three different qualities: high-purity, technical and fuel quality [4]. Depending on these groups, impurities like water, methanol or sulphur components can vary from negligibly low concentrations (less than 10 mg/kg Methanol in high purity DME) up to a share of 10 wt% for methanol and water in fuel quality DME [5].

Most commonly, DME is used as an aerosol propellant. Another possible application, now and in the future, is the substitution of diesel or LPG. For diesel replacement, DME is attractive due to its high cetane number (see Table 1) and low emissions of NO_x, carbon monoxide and hydrocarbons. Modifications to fuel storage and fuel delivery systems, but not to the engine itself, are necessary due to different fuel properties. However, a significant drawback is the energy density, which is lower for DME than for diesel. Therefore, to achieve the same driving range, the fuel storage capacity

for DME has to be twice as big as for diesel [2]. The same problem is revealed in transport applications of LPG, where DME can be used as a substitute. But since the difference in energy density between DME and LPG is smaller than for DME and Diesel, this problem is of minor importance. Due to similar properties of DME and LPG, substitution can be accomplished easily. In some devices technical modifications are necessary, like for example in domestic cooking stoves, where the nozzle diameter has to be enhanced in order to achieve stable combustion [7,8].

Table I: Properties of DME [4,6]

Quality	Value	Unit
Molecular Weight	46.07	g/mol
Normal Boiling Point	-24.8	°C
Melting Point	-151.0	°C
Liquid Density (20 °C)	668.3	kg/m ³
Vapor Pressure (-20 °C)	1.2	bar
Vapor Pressure (+20 °C)	5.1	bar
Lower Heating Value	28.9	MJ/kg
Self Ignition Temperature	235	°C
Cetane Number	55 – 60	-

To sum up, it can be concluded, that DME is a suitable substitution for diesel and especially LPG, where only minor technical modifications are necessary. Although DME has a lower energy density compared to diesel, truck manufacturer like Volvo already use it for fleet tests [20].

2 PRODUCTION CONCEPTS FOR DME FROM WOODEN BIOMASS

2.1 General approach

Production of DME from synthesis gas obtained by wood gasification has not been realised in a large scale yet. To gather more information about a process like this, two different production concepts were developed. For these concepts, the main reactors and instruments were included in a model and, based upon this model, all necessary data like temperature, pressure, throughput,

DME production and finally, electricity and heat generation were calculated. Subsequently, with all these information, economics of DME production were investigated.

2.2 Gasifier

The main differences between the two concepts are the two gasifiers adopted. For concept 1, an atmospheric circulating fluidised bed gasifier was used, where the gasifier concept was developed by Taylor Biomass Energy. The concept comprises two reactors, one as the actual gasifier and the other one as a combustion reactor. In the combustion reactor, unreacted residues from the gasifier like char are oxidised with air. Heat released in this process is transferred to the gasifier with help of circulating bed material to supply the endothermic steam blown gasification process with heat. The gasifier of concept 2 not only uses steam as gasifying agent, but a mixture of oxygen and steam. Therefore it does not need an external heat source, but electricity is necessary to produce pure oxygen. The gasifier, also of circulating fluidised bed type, is the so called Värnamo-Gasifier, but already incorporating all modifications planned by the Chrisgas-Project. Since it operates under a pressure of 30 bar, compression effort of the product gas for further processing is less than for the other gasifier concept, which is of atmospheric type.

The H_2/CO -Ratio of the produced was about 2,5 for concept 1 and nearly 1 for concept 2 (see Table II). However, the specific quantity of gas produced was seen for the Chrisgas-Gasifier as being greater due to the different gasification technique employed. Both gasifiers produce synthesis gas undiluted by nitrogen, what is necessary for subsequent fuel synthesis. To obtain comparable and reasonable results for a large scale concept, a capacity of 60 MW fuel input was set for both concepts, whereas wood chips were used as fuel.

Table II: Gas composition after gasifier exit

	Concept 1 [19] [Vol.-%]	Concept 2 [18] [Vol.-%]
CO	10.2	11.9
H ₂	27.1	11.8
CO ₂	11.0	27.9
H ₂ O	43.2	37.7
CH ₄	6.7	8.1
C ₂ H ₄	1.2	1.5
C ₂ H ₆	0.3	0.1
Tar	-	0.3
N ₂	0.4	0.6
Total	100	100
Total Gas Flow [Nm ³ /h]	17,480	20,070

2.2 Gas cleaning

Synthesis gas derived from wood gasification generally contains several impurities. Most important for the subsequent process is the removal of tar to prevent plugging and other related problems. For concept 1, this step is already incorporated in the gasifier (Taylor Biomass Energy), where a gas conditioning is installed after the gasifier reactor. Here, tars in the product gas stream are reformed to carbon monoxide and hydrogen by hot, catalytic active bed material exiting the combustion reactor. In contrast to this, an additional tar reforming unit has to be installed for the gasifier of

concept 2. In this reactor, tar is reformed on Nickel-Catalysts above a temperature of 850°C [9]. Both reforming methods reduce tar content in the synthesis gas to negligibly small concentrations.

As a next step, small particles, which have not been caught in the cyclone, are removed by a metallic filter. For improvement of particle separation, calcium oxide is injected to build up a filter cake, where also hydrogen chloride and alkali metals can be adsorbed. After particle removal, sulphur components like hydrogen sulphide or carbonyl sulphide are the only harmful impurities remaining in the gas stream. To clean the synthesis gas from these, a zinc oxide guard bed is installed. At an operating temperature of 165°C exit concentrations of hydrogen sulphide can be theoretically reduced to 10⁻⁴ ppm.

Since a large content of carbon dioxide reduces carbon conversion during synthesis, carbon dioxide should also be removed from the synthesis gas to some extent. For this purpose, an amine scrubber is employed. Specifically, methyl diethanolamine is used as a solvent, where CO₂ is absorbed at 50°C and stripped of at 110°C. For concept 1, most of the carbon dioxide can be separated in one scrubbing step. However, since the gasifier of concept 2 uses an oxygen / steam mixture instead of pure steam, carbon dioxide content in this product gas was seen as being greater as for concept 1. Therefore, scrubbing process has to be designed in two steps in order to obtain reasonably low exit concentrations of CO₂.

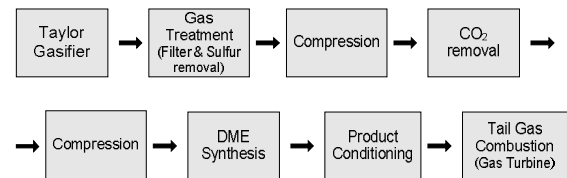


Figure 1: Production concept 1 (Taylor process)

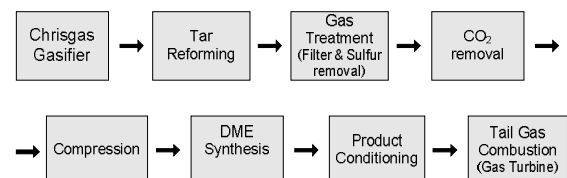


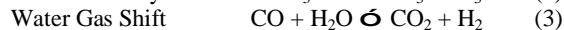
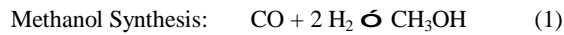
Figure 2: Production concept 2 (Chrisgas process)

To attain the required synthesis pressure of 50 bar, both gas streams have to be compressed. Since concept 2 incorporates a gasifier operating under pressure, the gas can be compressed in one step from 30 bar to 50 bar directly before synthesis (see Figure 2). But for concept 1, where the gasifier is of atmospheric type, compression has to be conducted in two steps. Here, the first step (1 – 25 bar) is already placed before the CO₂- removal unit, since higher pressure enhances absorption rates significantly. Second compression up to synthesis pressure of 50 bar is also accomplished before entering the synthesis reactor (see Figure 1).

Although composition of synthesis gas leaving both gasifiers is quite different, the process chain for gas conversion to DME and utilization of remaining gas components is pretty much the same starting at the CO₂-scrubbing step.

2.3 DME synthesis

Conventional production of DME from natural gas is accomplished via a two step process, where at first methanol is produced from the synthesis gas and then methanol is dehydrated to DME in a subsequent reactor. But this process is not necessarily advantageous, since equilibrium boundaries are very strict for methanol synthesis step. This problem can be overcome by merging the two steps in one reactor, where combination of the synthesis reactions (Equation 1-3) mitigates the restrictions given by thermodynamic equilibrium of the system.



So, by employing a one step process, not only higher conversion efficiency can be reached due to synergetic effects, but also economics can be improved, since only one reactor is necessary for DME-Synthesis. Research effort has been concentrated on this topic and therefore technical applications are seen to be feasible [6,10,11].

One-step process is employed in this work, since it is more advantageous than conventional two-step production. Specifically, the reactor is modelled as a slurry reactor where synthesis gas is processed to DME in once-through mode under a synthesis pressure of 50 bar and a temperature of 250 °C. Due to possible high conversion efficiencies, recycling of the synthesis gas is not necessary [12]. For modelling work, CO conversion is set at 50% of the conversion in thermodynamic equilibrium (according to [10]). Results are shown in Table III, where it can be seen that DME production is significantly higher for concept 2, specifically its energy equivalent is 8.6 MW whereas for concept 1 only 4.8 MW DME are produced.

Table III: DME production

	Concept 1 [kg/h]	Concept 2 [kg/h]
Synthesis Gas Input	4,041	6,574
DME Production	608	1,037
Unconverted Gas	3,277	5,428

2.4 Product recovery

Separation of DME from unconverted synthesis gas can be done in many ways, for example by cooling the reactor effluent down to -40 °C in order to condensate DME [13]. Additionally, the gas is refluxed with liquid DME to absorb CO₂, which can be harmful for subsequent recycling to the synthesis reactor.

However, the process adopted in this work is based on a work of Air Products and Chemicals [14], where a product recovery without recycling of unconverted gas is investigated. At first, the pressurised gas is cooled to separate high boiling components like water and methanol. Also some DME and CO₂ absorbed in the liquids are withdrawn. Cooling and separation is repeated to condense all residual methanol and DME from the gas. All liquid streams are then distilled in order to remove dissolved CO₂ from the stream, and in a second distillation column, methanol and DME are finally separated.

2.5 Tail gas utilization

After product recovery, the remaining synthesis gas still has a considerable heating value. For energetic utilization the gas can be burned in an internal combustion engine or a gas turbine. Here, a gas turbine can be employed, since synthesis gas is still pressurised (19 bar) and this energy can additionally be used in the turbine. To assure combustion with tolerable high temperatures (max. 1 100 °C) a hyperstoichiometric amount of air has to be added to the process (equivalence ratio: 4.5 – 5), which also has to be compressed up to a pressure of 13 barg. With an electrical efficiency of the gas turbine of 31 %, an electricity production of 9.4 MW for concept 1 (Taylor process) and 10 MW for concept 2 (Chrisgas process), respectively, is calculated.

2.6 Heat integration

In the DME production process, much surplus heat can be used to generate steam, which, for efficiency purposes, can be fed to a steam turbine. To provide optimal use of the heat and maximise steam production, the heat integration network can be designed by a pinch analysis [15]. Results of this analysis showed that most steam can be produced by the hot synthesis gas after the gasifier and gas turbine exhaust gases. By these and several other minor heat supplying streams a total amount of 37,5 t/h steam (34 bar, 450°C) can be raised in concept 1 and 30 t/h for concept 2, respectively. By feeding this to a steam turbine, an additional electricity output of 14.1 MW for concept 1 and 11.4 MW for concept 2 can be generated. Heat, which has to be extracted during the condensation of steam after the turbine, is used for district heating.

2.7 Process efficiency

Even if production of DME or electricity as well as heat for district heating is different for both concepts, overall efficiency is similar (see Figure 3). In total, concept 1 can convert 76.5 % of power content of the wood into product energy content, whereas for concept 2 an efficiency of 73.8 % can be achieved.

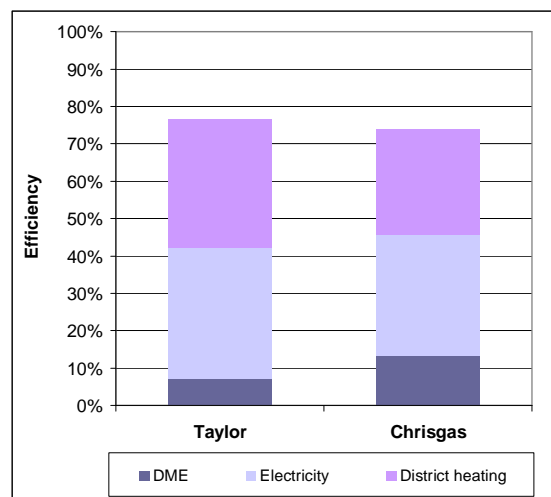


Figure 3: Process efficiencies

3 PLANT ECONOMICS

3.1 Capital cost

All analysis are based on German economic conditions of the year 2008. The first step for economic analysis was the determination of capital cost for the two production concepts. The complete capital costs comprise costs for machines and reactors, planning and construction, piping, electrical installation, process measuring and control technology as well as miscellaneous items. The main difference in the costs of the two concepts is the gasifier adopted and the oxygen supply by air separation for the Chrisgas concept. Specifically, the fuel feed into the pressurized gasifier in the Chrisgas concept is much more expensive than the fuel feed into the atmospheric gasifier of the Taylor concept. To a certain extent, this difference between the concepts is balanced by the additional costs for gas compression units, which are necessary in concept 1. But however, capital costs for concept 2 are still much higher than for concept 1 (see Figure 4).

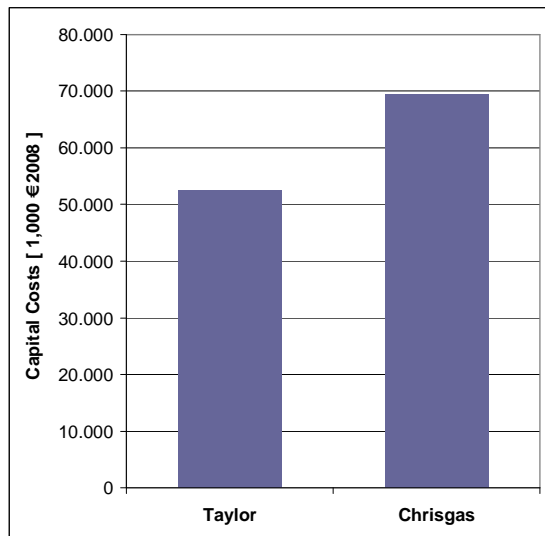


Figure 4: Capital cost

3.2 Operating cost

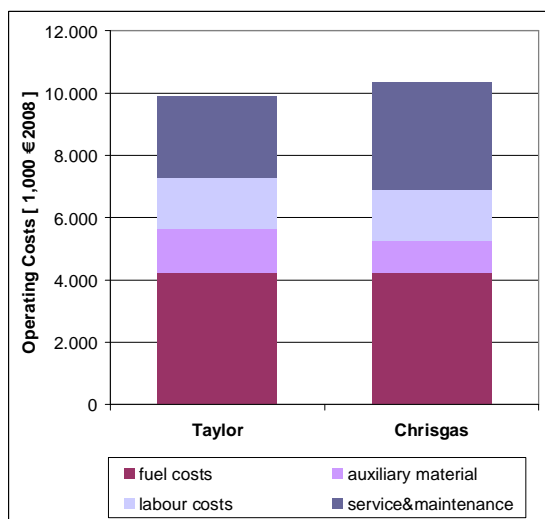


Figure 5: Operating cost

The most important factor included in the operating costs are fuel costs (see Figure 5). Here they are calculated for untreated wood chips with a water content of 50 % with a price of 57 €/t (C.A.R.M.E.N e.V., [16]). Drying of woodchips down to a water content of 25 %, which is necessary in order to prevent losses in the gasification process, is included in the process chain. As auxiliary materials for example catalyst material or gasifier bed material are taken into account. Other costs are labour costs as well as service and maintenance, which are calculated as 5 % of the total capital costs.

3.3 Revenues

From Figure 6 it becomes clear, that electricity generation has the highest share on the revenues from the production concepts. This is not only caused by high production (16.2 MW for concept 1 compared to 4.8 MW DME-Output), but also by high prices for electricity produced by renewable energy. Defined by the German government [17], a price of about 14 ct/kWh can be assumed as the revenue from electricity production for these production concepts. Also contributing to the total revenues is the use of surplus heat for district heating, where a price of 2 ct/kWh is used for the calculation. For DME, the price orientates on the price for LPG, since DME from these production concepts should primarily be used for energetic consumption. Therefore, revenues from DME production are calculated with a price for DME of 4.7 ct/kWh.

But even if the three different items contributing to the total revenues do not have equal shares for the two concepts, they sum up to nearly the same total amount in the end (18.6 Mio. € for concept 1 and 18.8 Mio. € for concept 2, respectively). So, for concept 1 for example lower DME production is balanced by the higher district heating and electricity revenues.

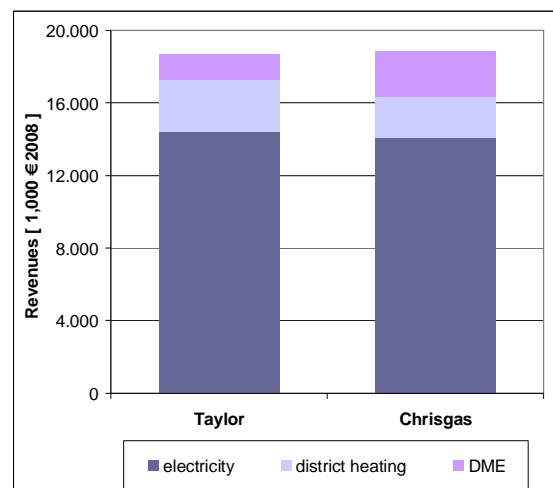


Figure 6: Revenues

3.4 Evaluation

For evaluation of profitability, the capital value method following VDI rule 6025 was adopted. As parameters the total project duration was assumed to be 20 years and an internal interest rate of 6 % was defined. The results from this analysis show good profitability (represented by a positive net present value) for both concepts. Overall production efficiencies (and therefore annual revenues) were nearly equal for the two concepts. But as expected, concept 2 (Chrisgas process) results in a

considerably lower net present value, since capital costs are higher for this concept (see Figure 7). Therefore, results of economic analysis reveal that concept 1 provides better overall profitability.

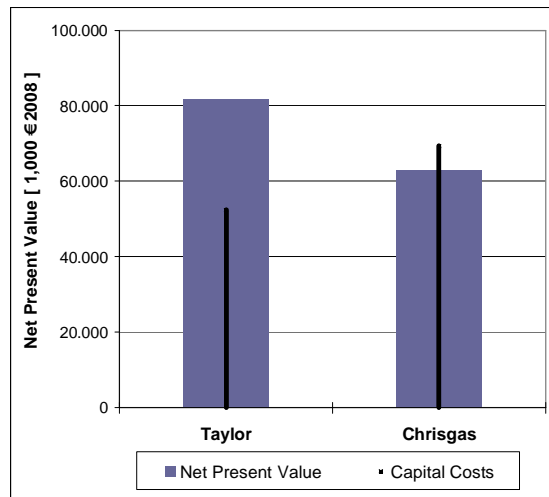


Figure 7: Net present value evaluation

4 CONCLUSION AND FUTURE WORK

4.1 Conclusions from modeling work

In this work, two concepts for the large-scale production of DME from wood are developed. These two concepts adopt different technologies concerning the gasifier; specifically one uses an atmospheric steam blown CFB gasifier (Taylor process), while the other employs a pressurised CFB gasifier blown by a mixture of oxygen and steam (Chrisgas process). For comparability purposes, both concepts are designed for a fuel input of 60 MW wood chips. As products DME, electricity and surplus heat for district heating were taken into account. And although the distribution of products is different for the two concepts, overall efficiency is nearly equal. Specifically, the energy equivalent of DME production (conducted in once-through mode in a slurry reactor) of concept 1 is 4.8 MW whereas for concept 2 only 8.6 MW DME is produced. Electricity is generated in a gas turbine by burning unreacted synthesis gas as well as in a steam turbine operated on process steam. For concept 1, a total sum of 16.2 MW electricity is produced and 15.8 MW for concept 2, respectively.

However, even if efficiency is nearly the same, economic analysis performed by means of the capital value method shows different results. For concept 2, capital costs are significantly higher than for concept 1. Therefore, results are better for concept 1, although both concepts show good profitability represented by a positive net present value. If the process of polygeneration of DME, electricity and heat is compared to a pure combined heat and power plant with the same fuel input of 60 MW, one would reach a much better profitability, because the net present value of such plant would be higher combined with a lower necessary investment.

In general, the concept of once-through synthesis should be reviewed for this process, since in comparison to electricity generation, DME production is considerably lower. But however, analysis of DME production from wood in terms of efficiency and also in economic terms shows positive results and therefore further investigations

in the future have a promising perspective.

4.2 Preparations for future work

The biggest drawback of the presented concepts is the low assumed CO conversion in the DME synthesis step. The profitability of the process chain could be increased to a large extend, if the real conversion in the synthesis reactor is higher than assumed. Therefore, the synthesis step will be experimentally analyzed in a project started recently. Fraunhofer UMSICHT installs a flexible laboratory test facility for continuous operation under technical conditions. The setup of this facility is shown in Figure 8.

The plant consists of “static” elements, which are fixed for all experiments (green elements in the layout), and “flexible” elements, which can be arranged differently for each experiment (yellow elements in the middle).

The synthesis gas, which is to be converted in the plant, is mixed from gas bottles of H₂, CO, CO₂, N₂ and Ar at a pressure of about 5 barg and room temperature. With this setup the synthesis gas composition of different gasifiers can be simulated. The individual gas flow rates, which are necessary to form the desired mixture, are regulated with mass flow controllers. The optional recycle stream is added to this gas mixture and the volumetric flow rate of the reactor feed then is measured with a drum-type gasmeter, whose output is independent from gas composition. The maximum volumetric flow rate of this mixed feed stream is 1 scm/h. Now the reactor feed is compressed to the reaction pressure of the synthesis. Up to 100 barg are possible. After compression the mixture is heated up to reaction temperature by means of 3 electrical heaters in series. Then the synthesis gas enters the modular part of the laboratory plant, which is described later. The remaining gas stream leaving the modular part is reduced in pressure in two steps and then released to atmosphere. The permanent gases are analyzed online for H₂, CO, CO₂, H₂O and CH₄ to close the material balances. Additionally, to increase the plants flexibility it is possible to install a recycle stream of permanent gases.

The construction kit for the modular part of the laboratory test plant consists of an optional steam generator, four different reactors, one air cooled heat exchanger, five twin pipe heat exchangers, which can be cooled with oil or water, two droplet separators, which can be cooled with water or other liquid heat carriers, and three product catch tanks, of which one can be cooled with liquid heat carrier. The superheated steam can be mixed to the synthesis gas between the second and third gas heater to avoid condensation. By this arrangement, the water content of the reactor feed is not limited to the pressure dew point at room temperature. Table IV gives the characteristic values for the four different reactors. All of them can either be used as fixed bed reactors or slurry reactors.

Table IV: Characteristic dimensions of available reactors

	R1	R2	R3	R4
Inner diameter [mm]	18	24	27	27
Length [mm]	900	1800	900	500
volume [ccm]	229	814	515	286

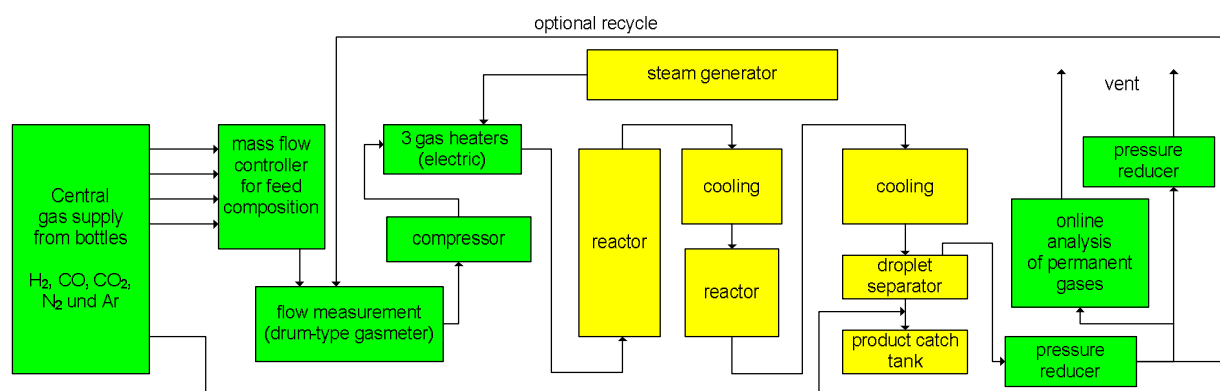


Figure 8: Laboratory plant layout

The construction kit allows for very flexible reactor set up. It is possible to use only one reactor, either as fixed bed or as slurry, or a series of reactors with or without intermediate cooling. With the high number of coolers and droplet separators it is also possible to condensate different fractions of liquid products/by-products at different temperature levels for a first separation. Along the plant several ports for taking gas samples for offline analysis and sample ports for liquid withdrawal are located.

After the plant is commissioned, tests with commercial methanol catalysts will act as starting point. Then the classical method of physically mixing methanol catalyst and dewatering catalyst for the single step DME synthesis [21] will be applied. The most promising approach however seems to be the development of a single catalyst that combines both functionalities of methanol synthesis and methanol dewatering on its surface.

For the development of such bi-functional catalyst, an Institute from the Max-Planck-Society could be enlisted as partner.

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