



**IEA Bioenergy**

*Technology Collaboration Programme*

# Gasification applications in existing industrial and agricultural infrastructures for production of sustainable value-added products

Case Study 4: Gasification of RDF and integration into an existing naphtha cracker

IEA Bioenergy: Task 33

December 2021



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# Gasification applications in existing industrial and agricultural infrastructures for production of sustainable value-added products

Case study 4: Gasification of RDF and integration into an existing naphtha cracker

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TNO

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## Abstract

This report discusses the feasibility of using gasification technology to provide circular and biobased feedstock to an existing naphtha cracker of a petrochemical plant. This approach is different to a widely investigated approach of producing liquids to replace naphtha. This liquid can be produced from biomass or from pure plastic waste streams, and after hydrotreating will have similar properties as naphtha. Gasification allows the usage of more complex mixed streams (RDF), that produce a similar gas phase composition of olefins and aromatics, when compared to the outlet of a naphtha steam cracking unit.

Operating on a complex mixture of biomass and plastics (RDF), means that a surplus of oxygen is introduced to the recovery section after the naphtha cracker. This oxygen will end up in the gas as CO and CO<sub>2</sub> and for a naphtha cracker these components are generally not desired. Some crackers can operate with CO, but in all cases the bulk of the CO<sub>2</sub> needs to be removed. For this to work we have integrated the gasifier with a CO<sub>2</sub> removal technology that converts also CO at the same time, reducing both the level of CO and CO<sub>2</sub>. The desk study is not meant to provide the final solution but what it does show is that the feedstock base for naphtha crackers can grow much more and also a big share of biogenic components can be introduced to the product slate. Recycling of plastic is always suffering from losses, which means that fossil fuels remain necessary, unless biogenic replacements can be found.

The vision of this route is that it will be supplemental to pyrolysis based routes, and that via gasification of RDF the much needed addition of "lost carbon" is covered. This case study is not meant to provide off the shelf designs for integration of gasification technology into naphtha cracker settings. The aim of this case study is to show the potential and create awareness of other strategies to create circular and biobased products in traditional refineries.

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## TRADITIONAL NAPHTHA CRACKING PROCESSES

There are various routes to produce the building blocks of plastics. Ethane crackers and naphtha crackers are the most common technologies used. A naphtha cracker produces olefins and aromatics, mostly ethylene, propylene and benzene. This is one of the reasons that our plastics today are made from these building blocks. A traditional naphtha cracking process is a fully integrated design where mass and energy balances are tuned rather precisely in order to maximize product yield. Spallina et al. [1] wrote a paper on assessing different routes and in his publication a nice representation is given for a naphtha cracker including the downstream processing train. Impurities in the feedstock can have detrimental effects on the plant, therefore there are rather strict requirements to the quality of naphtha, which are translated also to naphtha replacements like pyrolysis oils.

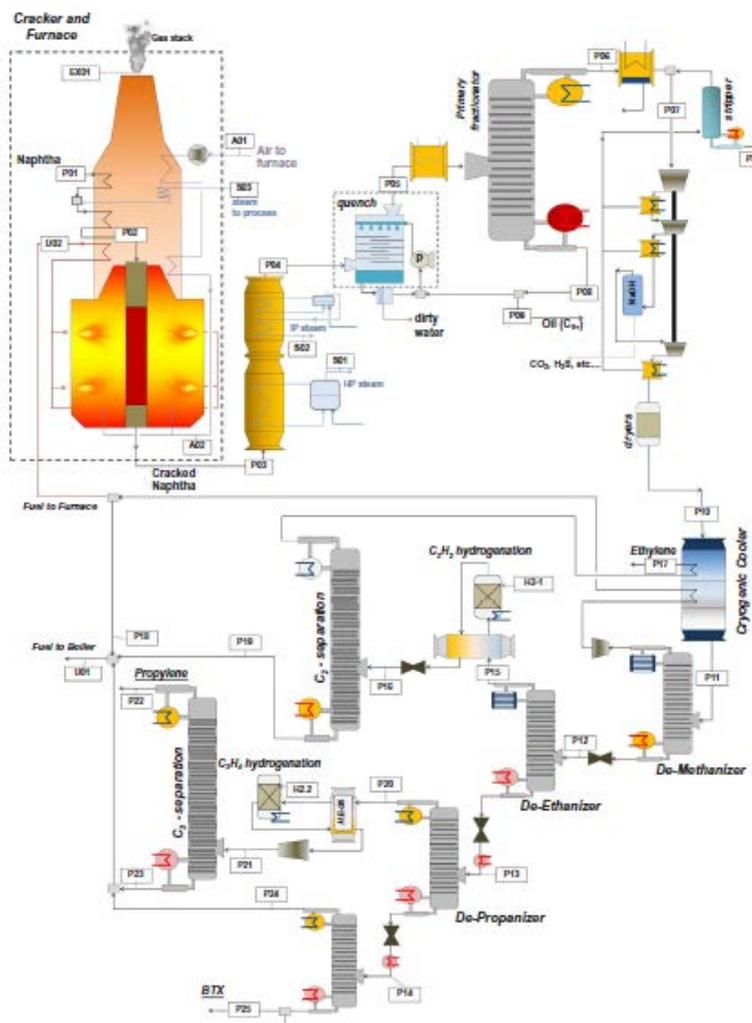


Figure 1: Schematic lay-out of a naphtha cracker, including downstream processing steps<sup>1</sup>

From this graph it becomes clear that most of the cleaning and downstream processing is done to produce ethylene, propylene and Pygas (BTX) and the off gasses tend to be used as fuel gas in the naphtha cracker. For this case study combination of a gasifier on RDF connected to the outlet of the naphtha cracker will be investigated combined to SEWGS technology for removal of CO and CO<sub>2</sub>.

## GASIFICATION PROCESSES

The naphtha cracking process is a thermally driven process, where liquid naphtha is evaporated and ran through series of tubes inside a furnace (see Figure 1). The tubes are heated via external combustion of gas. This fuel gas is the off-gas of the naphtha process as can be seen in Figure 1. In an oversimplified approach this would be called in indirectly heated gasification process, where feedstock is externally heated to produce gas components. The term gasification can have different meanings, but for sake of this case study the following definition is used.

*Gasification: The thermal conversion of a solid/liquid feedstock into a gas under mild conditions.*

The most common view of gasification is to produce synthesis gas. The production of CO and H<sub>2</sub> via gasification at high temperature, which in part is due to the fact that coal gasification tends to go in that direction. However, gasification can also lead to producer gas. This is produced in gasifiers that operate at lower temperature (mild condition) and a producer gas consists of much more than CO and H<sub>2</sub>, with methane, ethylene etc in there as well. In fact when evaluating the conditions used for naphtha cracking and RDF gasification, one will see that these two process have many similarities.

The starting point for the RDF gasification in this case study is the indirect gasification technology MILENA [2]. This technology is developed in the early 2000's and was eventually put into a joint venture with Synova. The technology operates under mild conditions, leaving many of the gas phase constituents intact. In Figure 2 the schematic lay out of the gasifier is depicted. The feedstock is fed to a vertical riser tube, which can operate between 600 - 850C. The bottom of this riser can be fluidized using steam (or nitrogen, air or other gases) to enable the inflow of hot bed material from the combustion zone. This hot material will convert the feedstock into gas and from the feedstock sufficient gas volume is produced to transport solids and char upwards in the riser. Exiting the riser tube creates a reduction in velocity, which will force the solids to separate from the gas flow and the bed material and char will fall down and flow into the combustion zone. This cyclic procedure allows for good temperature control and complete conversion of feedstock. The internal design is such that no solid circulation needs to be forced with for instance j-valves/l-valves, which are known to present complications during operation.

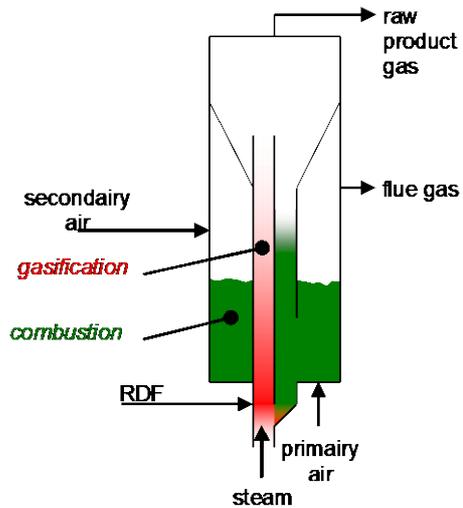


Figure 2: Schematic lay-out of the MILENA indirectly heated gasification reactor

Biomass gasification typically is performed at 750 - 850 C, but with plastics content the temperature can or needs to be lowered. Lowering the temperature will limit the cracking of biomass and would result in a few percent more char. However, for plastics the lower temperature will limit the cracking (less methane and hydrogen) but still maintain a high conversion to gas phase components (ethylene and benzene). The following graph is developed to identify what is happening with plastic waste streams in the MILENA gasifier. In Figure 3 the heating of plastics is shown on the x-axis, with chain length on the y-axis. The idea is that plastics will go through a melting phase into what is known as the pyrolysis phase. In this temperature window the main outlet is unsaturated long chained molecules (liquids), which after upgrading can be used to replace naphtha. The end of the curve represents the high temperature gasification and eventually combustion, where the feedstock is broken down into the smallest of molecules. Syngas for the high temperature gasification approach and flue gas (CO<sub>2</sub> and H<sub>2</sub>O) for the combustion. The mild conditions, here referred to as low temperature gasification (in fact cracking conditions) result in olefins and aromatics, which represents the naphtha cracker output.

*Low temperature gasification conditions can be considered as thermal cracking and produces a very different gas compared to high temperature gasification. A gas containing the molecular capital of the feedstock, such as ethylene, propylene and benzene.*

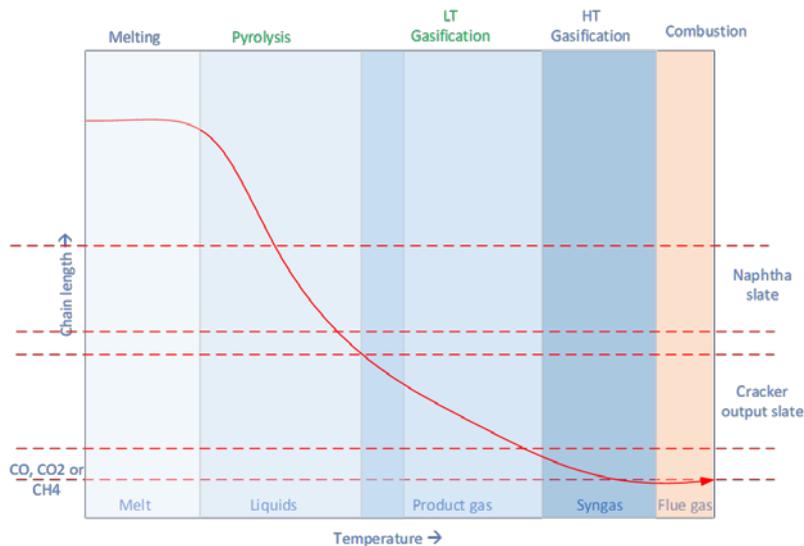


Figure 3: Thermal cracking of plastic waste stream, graphical representation.

In the MILENA gasifier, RDF can be converted at mild conditions, allowing the olefins and aromatics to remain intact. It also produces these molecules from the biomass in the feedstock whilst maintaining a complete conversion of feedstock. This set of unique features makes it an ideal technology to be used in waste management that allows biobased and circular products to be produced and recovered.

## SEWGS technology

The SEWGS technology (Sorption Enhanced Water-Gas-Shift) is a solid sorbent based separation technology for the capture of CO<sub>2</sub> from process gas. The system improves the capture by converting CO of the process stream to H<sub>2</sub> and CO<sub>2</sub>, which is then captured as well. The technology has been proven on large scale for the application of steel production off gases (EU 2020 project STEPWISE [3]).

The system is a pressure swing adsorption unit consisting of several columns filled with sorbent. The process gas is fed to a column where the CO<sub>2</sub> is adsorbed shifting the equilibrium of the WGS to produce H<sub>2</sub> and CO<sub>2</sub>. The stream exiting the column is CO<sub>2</sub> lean with a higher H<sub>2</sub> content. After the adsorption pure steam is added to remove as much gas from the void fraction of the column during depressurization. To improve the purity of the products and the energy recovery, the first part of the depressurization are pressure equalization steps. The product from the last depressurization step, to reach the purge pressure, is part of the final CO<sub>2</sub> product. Once the purge pressure level is reached, low pressure steam is fed into the column to desorb CO<sub>2</sub> and regenerate the sorbent. To get back to adsorption pressure level, the column receives the outlet from the pressure equalization steps followed by a repress with the CO<sub>2</sub>-lean product. The steps are shown in Error! Reference source not found. with counter-current blowdown and purge. To allow for continuous feed of process gas and pressure equalizations several columns are needed.

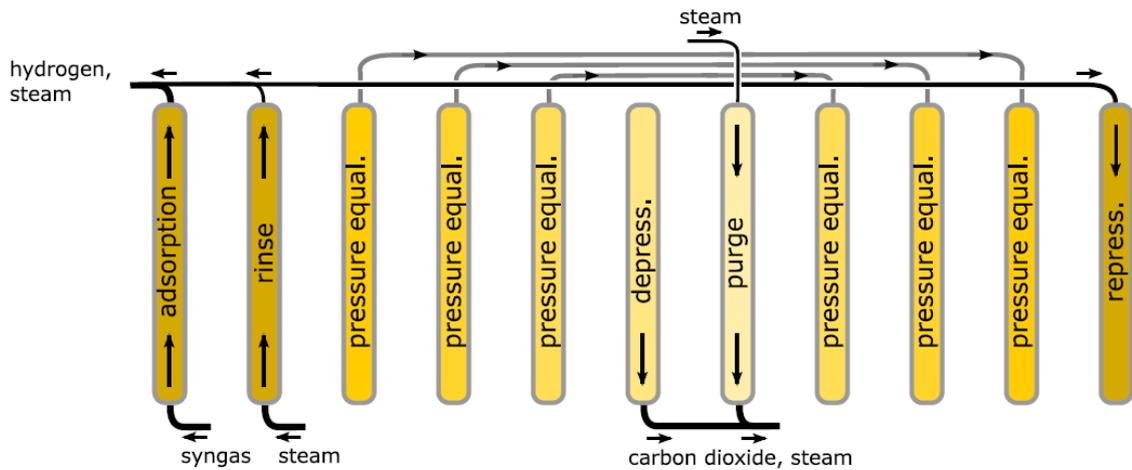


Figure 4: SEWGS cycle with 3 pressure equalisation steps [4]

A model has been developed and verified within TNO [4-6] which models a continuous operation of a cyclic PSA system for the SEWGS unit. This model is used to determine operation condition, cycle design and column sizing.

For the application of SEWGS in this project, a first study was conducted under the assumption, that the higher carbon molecules are inert to the sorbent and do not compromise its' characteristics. There has been testing performed on the sorbent with higher molecules which showed no changed behavior (internal communication). Furthermore COS is assumed to convert to H<sub>2</sub>S and CO<sub>2</sub> in the system.

## COMPARING PRODUCT SLATES

An important reason for this case study is the extensive R&D undertaken by TNO in the past on a broad range of feedstocks. With changing feedstock, the gas composition was also changing, some unexpectedly into direction of olefins or aromatics. The excursion into the RDF and plastic waste streams further supported the ideas that the technology of indirect gasification could also be used in the production of chemicals. The following graphs are to illustrate the unique effect the MILENA gasifier has on product output with varying feedstocks.

The three bars (Figure 5) represent the range from biomass to plastic waste. RDF is the mix and is the focus of this case study. As can be seen the product slate shifts from an oxygen rich (CO and CO<sub>2</sub>) product gas to an olefins rich product gas. The plastic waste clearly is interesting from a naphtha standpoint, since this is starting to resemble more and more the existing gas outlet. The RDF is chosen, since it represents part biogenic content and part circular content, which means that when obtaining the olefins and aromatics from this gas, it resembles both and it means that the plastics produced from this gas is partly circular and partly biobased. Secondly, in a fully circular world, losses are unavoidable and addition of a sustainable component is needed. Via de the RDF gasification route, this can be done in an easy manner.

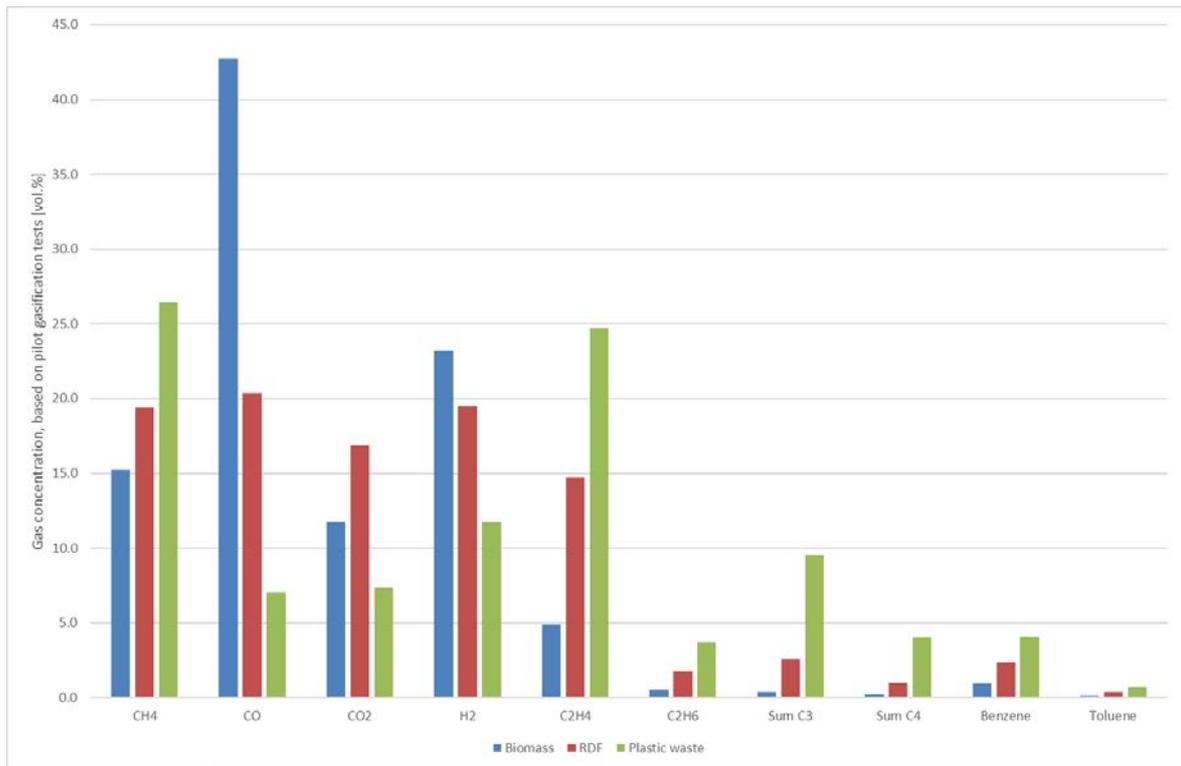


Figure 5: Gas composition for three different feedstock tests. Gas shifts from syngas rich to olefins and aromatics rich. All feedstocks have been tested on a 1 MWth Indirect gasifier

In order to relate the gas composition obtained with RDF to gas from a naphtha cracker the following approach is chosen. The gas is translated into energy yields, which mean that  $\text{CO}_2$  and  $\text{N}_2$  automatically fall out of the graph. Especially  $\text{CO}_2$  is relevant in a later stage with respect to the integration in a naphtha cracker process. Gas compositions from a naphtha cracker are mentioned in literature [1] and this was taken as input to make a graph representing the energy yield in the gas. In Figure 6 these energy concentrations are given for the gasification case and the naphtha cracking case. It is interesting to see when gasifying RDF the cracker off gas will have more methane, carbon monoxide and hydrogen as fuel gas. The yields in ethylene, benzene and toluene deviate from traditional gas, but the yield in propylene and butadiene are significantly lower. The integration of the RDF is described in the next chapter which involves tar removal (OLGA) and  $\text{CO}/\text{CO}_2$  removal (SEWGS), providing some more details to the steps considered in this case study.

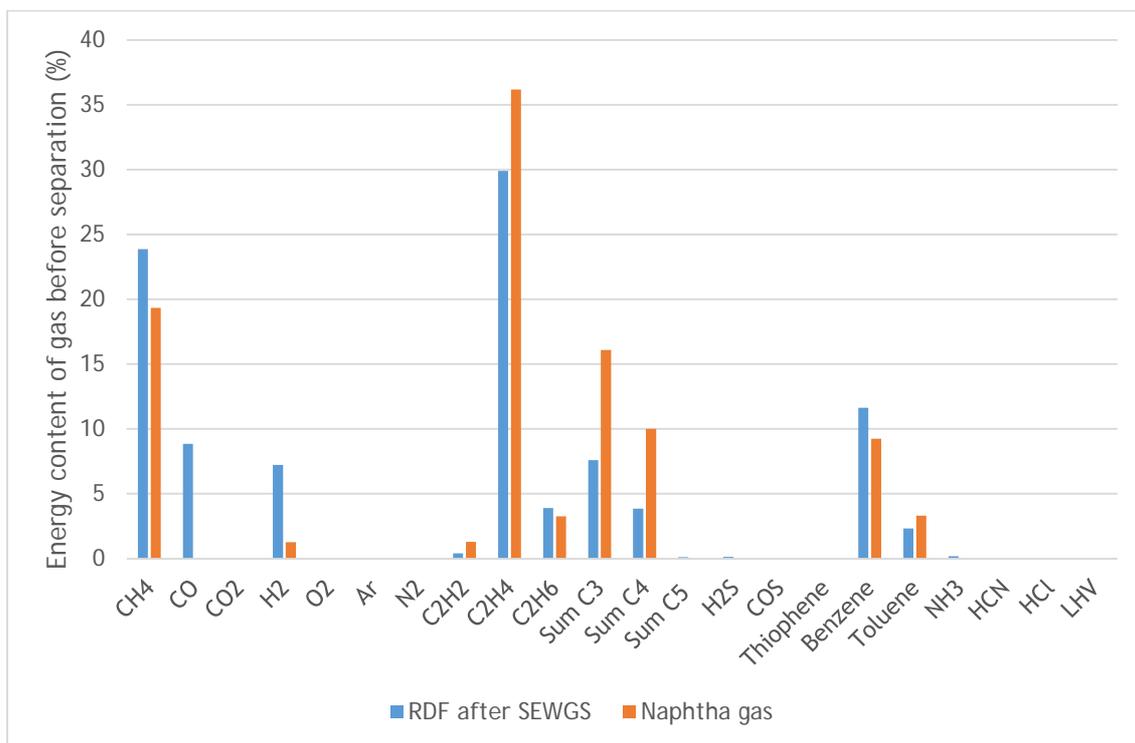


Figure 6: Energy content of gas produced by the conversion of RDF and removal of CO<sub>2</sub> compared to the gas produced by traditional naphtha crackers.

## INTERGRATING GASIFICATION INTO NAPHTHA CRACKERS

In order to integrate the gasifier into the recovery section of a naphtha cracker, certain gas cleaning is needed. The line-up considered in this case study is shown in Figure 7. The feedstock RDF (1) is fed to the MILENA gasifier and converted into gas. The gas is cleaned using OLGA in which tar components are removed and fed to the combustor of MILENA. The gas is subsequently cooled to about 30 degrees, removing some of the impurities (HCl and NH<sub>3</sub>) after which the gas is compressed to 12 bar. SEWGS technology is used to both convert CO as much as possible to CO<sub>2</sub> and H<sub>2</sub> and at the same time capture the CO<sub>2</sub>. This will result in a stream (11) enriched with H<sub>2</sub>, but still containing the olefins and aromatics from the gasification process. Second to that there is a rather pure stream of CO<sub>2</sub> (containing traces of H<sub>2</sub>S) produced from the feedstock, which can be used for sequestration purposes and reduce the carbon footprint of the installation significantly. The CO<sub>2</sub> is also a possible source for utilization (CCUS). More details on the numbers is given in the next chapter.

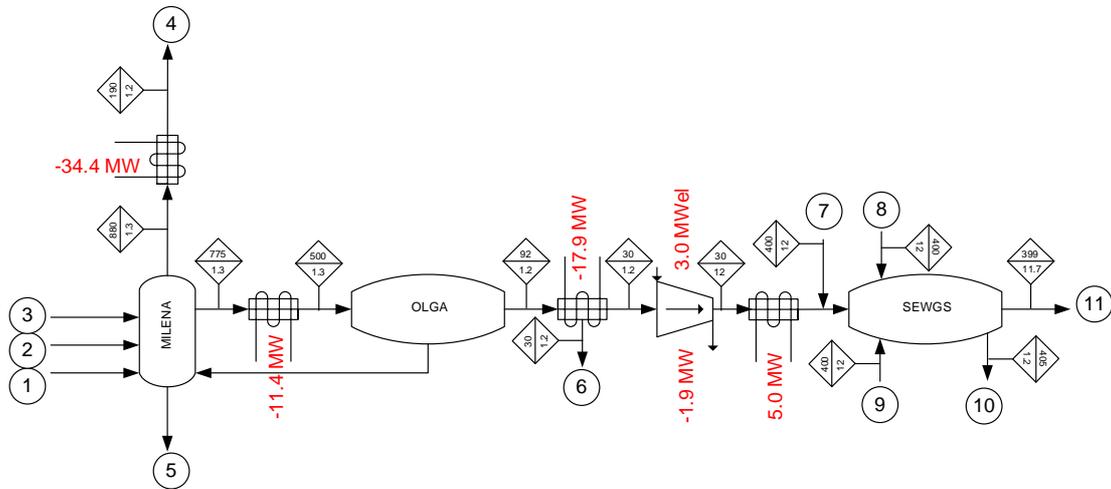


Figure 7: RDF gasification line-up considered for integration with a traditional naphtha cracker

## CASE STUDY BOUNDARY SETTINGS

This case study is meant to show the potential of integrating gasification in existing petrochemical plants. The particular case study on mild conditions for the RDF gasification, using the MILENA technology is based on a few assumptions.

1. Impurities relevant to naphtha cracker operators (oxygenates,  $\text{NO}_x$ , etc) are not in the product gas.
2. The final concentration of CO and  $\text{CO}_2$  is sufficiently low to be handled (either in the existing system or by dilution) in the total naphtha cracker outlet gas flow.
3. SEWGS technology will not affect the olefins/aromatics content in the producer gas.
4. For the modelling work on SEWGS the hydrocarbons are considered inert.
5. No additional gas cleaning is included.
6. No dynamic simulation has been included to see how the addition of this particular gas will affect the overall energy balance of the naphtha cracker operation / production side of the naphtha cracker.

## MASS AND ENERGY BALANCE

For the mass and energy balance the setup is shown in Figure 7. The flows in this system are given in the following table. The mass balance has an error of 0.4%, which for this case study is considered acceptable. The RDF input stream has a biogenic carbon content of 70% and 30% is of plastic (fossil) origin. These numbers become very interesting when interpreting the mass balance for this system.

*Interpretation 1. Allocate all  $\text{CO}_2$  emissions from the process as biogenic first.*

This feedstock contains 26588 kg/h of carbon, of which 7976 kg/h is of plastic origin (30%). In the flue gas of MILENA is 8211 kg/h of carbon in the form of  $\text{CO}_2$  and from SEWGS we obtain 5482 kg/h of carbon in the form of  $\text{CO}_2$ . This results in 13693 kg/h of carbon produced from the system as  $\text{CO}_2$ . Now we credit this to the biogenic content, which means that the remaining product from the system contains 12895 kg/h of carbon in the gas to be recovered as products. Which means that the products of this approach can be considered 61.8% circular and 38.2% biobased. After correcting for 28% of the carbon present as CO and  $\text{CH}_4$ , which will currently be diverted to the naphtha furnace, the products obtained have 88% circular content and 12%

biogenic content. It is perhaps playing with numbers, but this shows that gasification can have a major contribution to circular plastics, even with feedstocks that have a low plastic content. Furthermore this route, since the CO<sub>2</sub> is stored, contributes to net negative emissions.

Table 1: Carbon distribution by assuming all emissions to be of biogenic origin

	Feedstock RDF	Flue gas MILENA	CO <sub>2</sub> SEWGS	Carbon in off gas	Carbon in product	
Flow	74720	157998	45572	9525	10848	[kg/h]
C biogenic	18612	8211	5482	3870	1049	[kg/h]
C fossil	7976	0	0	0	7976	[kg/h]

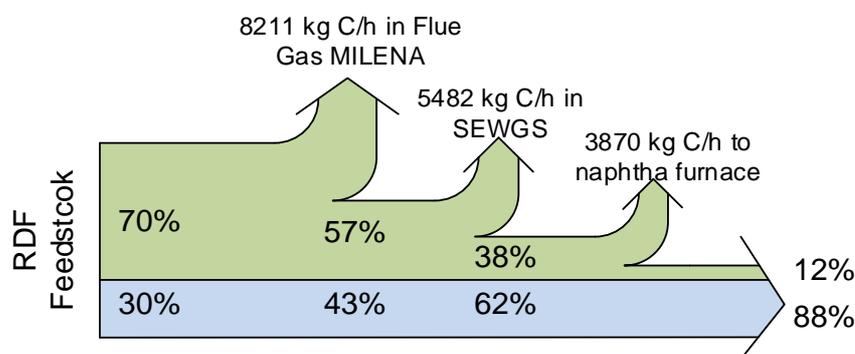


Figure 8: Flow scheme on how the carbon distribution in the end product might end up, based upon a simple accounting approach.

**Interpretation 2. Allocate MILENA flue gas CO<sub>2</sub> as biogenic carbon, the SEWGS CO<sub>2</sub> as fossil**

In this case the flue gas from MILENA is accredited to the biogenic content, but the CO<sub>2</sub> in pure form from SEWGS is considered to be of fossil origin, but can be used for sequestration. In that case the products that can be recovered in the downstream processing of the naphtha cracker are 80.7% biogenic in origin and 19.3% circular. Again after correction for the loss of CO and CH<sub>4</sub> in the product gas to the naphtha cracker furnace, the final product will contain 72% biogenic content and 28% circular plastics. This route should be considered more or less climate neutral and the product obtained in the downstream processing of the naphtha cracker has more or less the same split in carbon as the original feedstock has.

The interesting part of this exercise is that the fact that the feedstock contains biomass, allows the user of this process to maintain the claim that the end product is 100% circular, with over 10% or biogenic olefins/aromatics. If the feedstock had to be upgraded to very high quality (high plastic content), then part of the emissions sources had to be allocated to plastic molecules, reducing the overall circularity of the system. In thermochemical recycling of plastic waste materials, there is always an energy penalty to pay. This approach shows that having technology that can operate on both biomass and plastic waste streams, will have the highest circularity numbers for the plastic waste, with less sorting needed.

The overall mass balance for the gasifier with gas cleaning is given in Table 2. For the final gas composition of the flow number 11, the details are given in Appendix A.

Table 2: Mass flows for the proposed scheme depicted in Figure 7

Stream	Type	T [°C]	P [bar]	Flow [kg/h]	Flow [Nm <sup>3</sup> /h]
1	RDF	20	1.3	74720	
2	Steam-1	150	1.3	100	124
3	Air	174	1.3	143980	111774
4	Flue Gas	190	1.2	157998	113568
5	Bottom ash	700		2803	
6	Scrubber water	30		24056	
7	Steam-2	400	12	12869	15958
8	Rinse	400	12	5195	6549
9	Purge	400	1.4	12987	16371
10	CO <sub>2</sub> gas	405	1.2	45572	42518
11	Cracker feed	399	11.7	20374	28017

Considering the mass balance the 300 MWth input MILENA gasifier operating on 1800 tpd of RDF material can generate 260 tpd of hydrocarbons (C<sub>2</sub> → C<sub>7</sub>) with ethylene (142 tpd), benzene (55 tpd), propylene (55 tpd) and toluene (11 tpd) as the largest contributors.

## CONCLUSION

Operating existing naphtha crackers on alternative fuels is typically looking at replacing naphtha with a biogenic or circular alternative. A second solution is not looking at the naphtha, but at the gas which is produced from naphtha cracking and upgraded in the downstream section. This case study has shown that there is a large overlap in the gas obtained from RDF gasification using the MILENA technology and that substantial amounts of olefins and aromatics can be produced via this route.

The case study showed that to maintain 100% recycling efficiency for the plastics, a certain amount of biogenic residue is in fact crucial. This has a profound effect on recycling strategies, where to date a lot of effort is put into separation of all the different plastics and biogenic waste, with a rather low resulting recycling efficiency. Having technology that can operate on the more complex mixtures will simplify the sorting strategy.

Policy measures will have a major impact on how these process can or need to develop. If the focus is to generate as much circular materials from waste, the gasification route needs to be supported with CO<sub>2</sub> mechanisms favoring the sequestration of biogenic carbon. This will in itself also reduce the need of mechanical recycling, since residual paper/wood in the RDF is not an issue but a very attractive outcome. Secondly, the reduction in mechanical recycling steps, with all associated losses, also opens up a much larger potential of feed streams for the gasification process.

## Appendices

### Appendix A Gas composition of gas going to the downstream processing of a naphtha cracker

		Syngas after SEWGS (11)
CO	[mol%]	1.2%
H <sub>2</sub>	[mol%]	42.2%
CO <sub>2</sub>	[mol%]	0.6%
O <sub>2</sub>	[mol%]	0.0%
CH <sub>4</sub>	[mol%]	22.3%
N <sub>2</sub>	[mol%]	1.9%
Ar	[mol%]	0.0%
C <sub>2</sub> H <sub>2</sub>	[mol%]	0.2%
C <sub>2</sub> H <sub>4</sub>	[mol%]	15.8%
C <sub>2</sub> H <sub>6</sub>	[mol%]	1.8%
C <sub>3</sub> H <sub>6</sub>	[mol%]	1.8%
C <sub>4</sub> H <sub>y</sub>	[mol%]	0.4%
C <sub>5</sub> H <sub>y</sub>	[mol%]	0.0%
C <sub>6</sub> H <sub>6</sub>	[mol%]	2.2%
C <sub>7</sub> H <sub>8</sub>	[mol%]	0.4%
H <sub>2</sub> S	[ppm]	1.3
COS	[ppm]	0.0

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