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Low-temperature CO$_2$ removal from natural gas

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Abstract

As an alternative to chemical and physical solvents, membrane technologies and PSA, process principles for CO$_2$ removal from natural gas by low-temperature distillation are presented. A low-temperature process reducing the CO$_2$ concentration from an initial 50.6 vol-% to LNG specification (50 ppm) has been simulated in Aspen HYSYS. Main results such as product streams, power consumption for auxiliary refrigeration and steam requirements have been estimated. The process delivers the natural gas product for liquefaction at approximately 40 bar pressure and a temperature of -88°C and should be well suited for further cooling and liquefaction.

Keywords: Natural gas processing; CO$_2$ Removal; Low-temperature; Cryogenic; Extractive distillation.

1. Introduction

CO$_2$ removal from natural gas to meet specifications for pipeline transport (typically 2–3 vol-% CO$_2$) or LNG production (typically less than 50 ppm CO$_2$) can in principle be achieved through the use of different sweetening technologies. What technology is preferred depends on several case-specific criteria like for instance: natural gas feed condition and product specification; location and size of natural gas treatment plant; plant economics; ambient conditions and environmental aspects; process control and operation. Examples on applicable technology options for acid gas removal are chemical and physical absorption [1], membrane separation [2], pressure-swing adsorption (PSA) [3], membrane contactors [4] and cryogenic/low-temperature separation methods. Within the field of cryogenic/low-temperature CO$_2$ separation, various types of processes exist [5–7]. This work will focus on natural gas conditioning by low-temperature extractive distillation [8–10], with the main focus on obtaining a first numerical basis for estimating the energy requirements, both power and thermal energy, for producing natural gas for liquefaction and heavier natural gas products, and at the same time separating and compressing CO$_2$.

According to the International Dictionary of Refrigeration the consensual definition of cryogenics refers to temperature levels below 120 K or about -153°C [11]. The temperatures levels in consideration in this paper are above -90°C and hence, the natural gas conditioning process is not defined as 'cryogenic' according to [11], but rather low-temperature.

From the viewpoint of process integration, low-temperature CO$_2$ removal from natural gas may be well suited for LNG production [8,12]. The main reason for this is the low temperatures of the gaseous top products leaving the distillation columns, typically in the range of -80°C to -90°C. At these temperatures the methane-rich top product is to a large extent pre-cooled and also retained at a rather high pressure. Moreover, due to the requirement of feed gas

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drying to < 1 ppm-level water concentration, dehydration of natural gas (NG) feed for liquefaction is carried out upstream of the CO_2 removal process. The compatibility and overall power consumption for the CO_2 removal and liquefaction processes could therefore be advantageous due to these synergies.

Extractive distillation differs from normal distillation by the presence of a relatively non-volatile solvent/additive introduced to the distillation column. Due to low volatility the additive components will follow the heavy key component as bottom product in the distillation. For low-temperature natural gas conditioning, the extractive distillation additive can be a mixture of butane, pentane and heavier components. An important effect of introducing additive components in extractive distillation is breaking the azeotrope between light and heavy key components with low relative volatilities. A relevant example of this in the context of acid gas removal from natural gas is separation of ethane and CO_2 [13], where the obtainable CO_2 product purity would otherwise be constrained by a relatively pressure-independent azeotrope at approximately 67 mol-% CO_2 and 33 mol-% ethane [8]. Another important function is the effect of CO_2 freezing point depression. This in turn allows for operating at temperatures well below that of the point of CO_2 solidification that would otherwise occur in a low-temperature distillation column with no additives. By relaxing the low-end temperature constraint through additives circulation a higher degree of fractionation can be achieved.

A process for sweetening of natural gas with a relatively high CO_2 concentration before liquefaction will be presented as an example. On-going work for concepts with other feed CO_2 concentrations and end products will only be described briefly.

2. Process description

The chemical composition of the raw natural gas feed considered in this work is listed in Table 1 and is assumed to be available at 70 bar pressure, 40°C temperature and a molar flowrate of approximately 24 800 kmol/h. Furthermore, the gas feed is assumed to undergo pre-conditioning processes, removing water and H_2S, prior to the low-temperature distillation. Although co-removal of CO_2 and H_2S is a possible option for low-temperature distillation, only CO_2 removal is considered in this work. As can be observed, the composition is characterised by high CO_2 concentration, which makes low-temperature distillation a technology option for CO_2 removal especially worth investigating.

As the focus of this study has been on processing raw natural gas into LNG feed and CO_2 for re-injection, purification of other hydrocarbon products to standard specifications have not been emphasised. On the other hand, the process model shows principally how recovery of propane, butane and heavier components can be obtained through fractionation. The only rigid product specification of the model is CO_2 concentration in the natural gas stream for liquefaction, defined to be maximum 50 ppm. The purity of removed and captured CO_2 for re-injection should be as high as possible. However, any other component in this stream will be hydrocarbons, mainly ethane, leading to energy losses in terms of their heating value.

Table 1. Chemical composition of natural gas feed after pre-conditioning.

Component	Mole fraction
CH_4	0.397
C_2H_6	0.035
C_3H_8	0.024
i-C_4H_{10}	0.009
n-C_4H_{10}	0.009
i-C_5H_{12}	0.006
n-C_5H_{12}	0.006
n-C_6H_{14}	0.002
CO_2	0.506
N_2	0.005
H_2S	0.000
H_2O	0.000

The process flow diagram in Fig. 1 shows the principal layout of the low-temperature CO_2 removal process, including recovery columns for propane and butane. The diagram includes main process streams only and auxiliary refrigeration cycles as well as steam utility streams are not included. The raw natural gas is first assumed to undergo H_2S pre-removal and molsieve dehydration, denoted 'pre-conditioning processes', and subsequently pre-cooling to -10°C by the auxiliary refrigeration cycles and throttling to 40 bar before entering the Bulk column. In this distillation column the concentration of CO_2 is reduced from 50.6% to 10.6%. The top product is further separated in the 2nd low-

temperature distillation column with a top product CO_2 concentration of 0.9%. LNG specification (50 ppm CO_2) is obtained in the 3rd low-temperature column and is available at around 40 bar and -88°C. Data for all distillation columns are listed in Table 2. Given a three-column scheme for stepwise removal of CO_2 from methane, two central degrees of freedom are represented by the intermediate top-product CO_2 concentrations. The values for these variables chosen in the current configuration, 10.6% and 0.9% have been determined through rough minimisation with the total power consumption of the auxiliary refrigeration cycles as criterion. Too high degree of CO_2 removal in any of the three low-temperature columns will generally lead to higher reflux ratio and thus increased refrigeration power consumption, and the current parameters represent a trade-off with respect to power consumption.

For the Bulk column it is aimed at obtaining operating conditions not requiring recirculation of inhibitor in order to avoid freeze-out of CO_2. The 2nd and 3rd columns have an additional feed stream each, containing mainly pentane and hexane components. The purpose of this is primarily freezing point depression, allowing for operation at temperatures below that of the freezing point of CO_2. From each of the extractive distillations the heavy additive components are recovered and recirculated to the columns. From each recovery separator a waste stream of mainly methane and CO_2 is generated. In the process option described in the flow diagram of Fig. 1 these waste streams are not recycled and may be used as low-grade fuel for utility steam generation in boilers. Another alternative, as will be briefly discussed, is re-compression and recycling of these streams to the Bulk column.

CO_2 in the liquid bottom product of the Bulk column has a purity of approximately 85% and is fed to the CO_2 recovery column where purification to 94.35% is carried out. The CO_2 product is compressed to 110 bar while the bottom product, rich in heavier hydrocarbons, is further separated in the C_3 and C_4 recovery columns. About 18% of the stream 'C_5+' is recycled back to the 2nd and 3rd low-temperature distillation columns for freeze-out inhibition.

Chemical compositions for top and bottom products for each distillation column are listed in Table 3. As can be observed, the propane, butane and pentane products will likely have to undergo further purification if common sales gas specifications are to be obtained. The purity of propane obviously has to be increased from the current 85% and n- and i-butane should be split into separate product streams, but these processing steps have not been considered in the present study as the focus is mainly on CO_2 removal for LNG production.
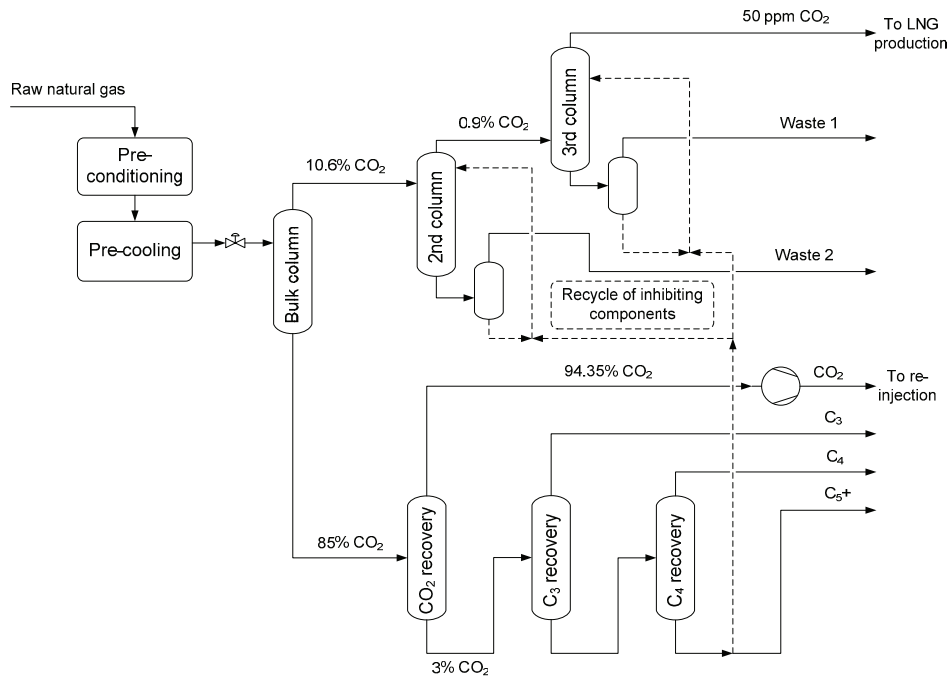

Fig. 1. Principal process flow diagram for the low-temperature CO_2 removal process

Table 2. Distillation column data of the process simulation model.

	Unit	Bulk column	2nd column	3rd column	CO2 recovery column	C3 recovery column	C4 recovery column
Theoretical stages[1]		19	14	62	62	62	77
Feed stage no. (from top)		4	4	10	34	20	20
Additive feed stage no.		n/a	1	57	n/a	n/a	n/a
Pressure	bar	40	40	40	30	16	10
Condenser temperature	°C	-67.5	-86.9	-88.0	-6.2	48.3	74.0
Condenser duty	MW	48.1	14.9	11.0	54.7	6.4	4.5
Reflux ratio		1.69	1.57	1.61	1.52	2.80	2.41
Reboiler temperature	°C	7.9	0.0	3.0	109.9	117.8	125.0
Reboiler duty	MW	40.4	11.4	11.3	87.8	7.4	5.7

[1] Including condenser and reboiler stages

Table 3. Distillation column product compositions.

	Bulk column		2nd column		3rd column		CO2 recovery column		C3 recovery column		C4 recovery column	
	Top product	Bottom product	Top product	Bottom product	Top product	Bottom product	Top product	Bottom product	Top product	Bottom product	Top product	Bottom product
CH_4	0.858	7 ppm	0.977	0.111	0.987	0.198	8 ppm					
C_2H_6	0.025	0.044	0.001	0.100		0.005	0.049	1 ppm				
C_3H_8		0.045	1 ppm	0.001		16 ppm	0.007	0.379	0.850	1 ppm	1 ppm	
$i\text{-}C_4H_{10}$	1 ppm	0.017		17 ppm				0.166	0.080	0.236	0.444	
$n\text{-}C_4H_{10}$		0.017				0.001		0.166	0.003	0.298	0.556	0.006
$i\text{-}C_5H_{12}$		0.011		0.104		0.144		0.111		0.200	422 ppm	0.426
$n\text{-}C_5H_{12}$		0.011	3 ppm	0.165		0.222		0.111		0.200	13 ppm	0.426
$n\text{-}C_6H_{14}$		0.004		0.161		0.357		0.037		0.067		0.142
CO_2	0.106	0.850	0.009	0.358	50 ppm	0.073	0.943	0.030	0.067			
N_2	0.011		0.013		0.013	3 ppm						

Process simulations have been performed in steady state using Aspen HYSYS with Peng–Robinson equation of state. The process is in this specific case assumed to be located in a rather cold environment. Assumed cooling water in- and outlet temperatures in water-cooled heat exchangers are set to 15°C and 20°C, respectively. Assumptions for compressor and pump efficiencies used are listed in Table 4.

A relatively simple cascade refrigeration cycle with pure propane and ethane as refrigerants has been assumed to supply the low-temperature CO_2 removal process with required cooling. Pinch temperatures for heat transfer have been set to 3°C for low-temperature heat exchangers in general and 4°C for the propane–ethane cascade heat exchanger. The refrigeration utility system has not been optimised with respect to refrigerant selection, energy consumption, equipment size or cost. However, it is still assumed that the resulting energy consumption of this cascade process gives a reasonable estimate for the power requirement associated with feed pre-cooling and condenser duties for the specified ambient conditions. On the other hand, the steam utility system design has not been included in the natural gas processing model. The described low-temperature CO_2 removal process is likely to be part of a larger processing plant, e.g. LNG production facility with adjacent utility systems.

Table 4. Compressor and pump efficiencies.

Isentropic efficiency	%
Propane compressors	80
Ethane compressors	80
CO_2 compressor	75
CO_2 pump	75
Cooling water pumps	75
Other pumps	75

3. Results and discussion

3.1. Product streams and energy requirement

An overview of molar flowrates and LHV-based energy flow for product streams is given in Table 5. For the process configuration shown in Fig. 1, the methane-rich natural gas product for liquefaction has an energy content of 58.0% relative to that of the raw natural gas feed stream. Of the total methane fed into the process, 93.73% is retained in this product stream.

The resulting CO_2 purity is 94.35% with the main part of the remainder made up by ethane (4.94%). The hydrocarbons entrained in the CO_2 stream account for a potential energy loss equivalent to 7.97% relative to that of the feed. Further fractionation of these components may be possible in order to recover ethane and increase CO_2 purity. This is however not further investigated in this work but 96% CO_2 purity is attainable by further extractive distillation according to ZareNezhad and Hosseinpour [10].

Waste streams account for a considerable part of the total energy, about 8.6% in total, as they contain hydrocarbons in addition to CO_2 removed in the 2nd and 3rd distillation columns. These streams could be considered to be utilised as low-grade fuel for e.g. steam generation for the utility system.

In addition to the 100.9 MW_{th} steam consumption estimated for the CO_2, C_3 and C_4 recovery columns, an additional 40.4 MW_{th} is required for the Bulk column reboiler duty if this is to be provided by condensation of steam. As can be read from Table 2 the reboiler temperature is 7.9°C for the current configuration and a water temperature of 15°C may therefore be too low from a practical point of view. Alternative heat sources for the Bulk column reboiler could be steam, heat pump or heat integration with intercoolers. The propane condenser has a duty of about 234 MW and hot-side in- and outlet temperatures of 37°C and 20°C, respectively.

Alternatively to the process configuration of Fig. 1, if no low-grade fuel is required for steam generation, the waste streams can be re-compressed and recirculated to the main feed stream. The low-temperature CO_2 removal process configuration will not change significantly, as the recycle of waste streams has limited impact on the Bulk column feed stream: molar flowrate will increase by an approximately estimated 9% while the chemical composition changes by 1 %-point or less for each component. A noticeable effect from changed Bulk column feed composition is the increased ethane concentration, resulting in slightly lowered CO_2 product purity from the CO_2 recovery column, down from 94.35% to about 92.64%. A higher purity upwards of 93% can be obtained by increasing the reflux ratio of the CO_2 recovery column, however at the cost of substantial increase in condenser and reboiler duties and thus power and steam requirement.

Recirculation of waste streams will increase the flowrate of the natural gas stream for liquefaction and the percentage of methane retained in this product stream is increased from 93.73% to 99.89% relative to the methane flowrate in the feed stream. Also propane, butane and C_5+ product flowrates are increased. On the other hand, more ethane is entrained in the stream of captured CO_2.

Although 50 ppm CO_2 concentration has been obtained for the LNG feed stream, this stream may be too lean for some specification and an enrichment of ethane and/or propane may therefore required. With the current configuration the propane stream will, as mentioned in section 2, need an additional purification step to be mixable with the methane without increasing the CO_2 concentration beyond LNG specification.

Table 5. Main results from process simulations.

	No recirculation of waste streams (Fig. 1)			With recirculation of waste streams		
	Molar flow [kmol/h]	LHV energy flow [MW]	Percentage of energy in feed stream	Molar flow [kmol/h]	LHV energy flow [MW]	Percentage of energy in feed stream
NG product to liquefier	9 356.2	2 058	58.0%	9962.3	2193	61.9%
CO_2 to re-injection	11 959	282.9	7.97%	13478	409.4	11.5%
C_3 product	605.81	329.4	9.29%	558.13	287.8	8.12%
C_4 product	399.17	294.6	8.30%	447.22	330.8	9.33%
C_5+ product	299.07	278.6	7.85%	348.39	324.5	9.15%
Waste 1	368.25	83.15	2.34%	—	—	—
Waste 2	1 808.6	220.5	6.22%	—	—	—
Percentage of CO_2 captured in re-injection stream	89.97%			99.57%		
CO_2 purity	94.35 mol-%			92.64 mol-%		
Power consumption						
Auxiliary refrigeration	78.5 MW			70.3 MW		
CO_2 compression	8.5 MW			9.5 MW		
Cooling water pumps	1.7 MW			1.7 MW		
Other auxiliary pumps	0.4 MW			0.2 MW		
Recycle compressors	—			7.5 MW		
Total power	89.1 MW			89.2 MW		
Total reboiler steam consumption (CO_2, C_3 and C_4 recovery columns)	100.9 MW$_{th}$ (141.3 MW$_{th}$)[1]			100.2 MW$_{th}$ (127.9 MW$_{th}$)[1]		

[1] including Bulk column reboiler

3.2. CO_2 freeze-out avoidance in distillation columns

While the Bulk column has only one feed and therefore no additive feed streams, the low-temperature extractive distillation columns (2nd and 3rd) have additive feed streams with relative flowrates about 0.14 and 0.10 mol additive per mol of column feed, respectively. Based on these assumptions, Figs. 2–4 show calculated tray temperatures for the three columns (Bulk, 2nd and 3rd column) together with estimates of the freeze-out temperatures for the respective liquid compositions of the different trays of the columns. Although freeze-out estimation must be done with caution and results handled and interpreted with great care [14], estimates made in HYSYS and MultiFlash indicate no temperature crossover between tray temperature and CO_2 freeze-out temperature in the three low-temperature distillation columns.

Controlling the freeze-out temperature in the low-temperature columns can in principle be done by controlling the amount of additive circulation and if wider temperature pinch between tray temperatures and corresponding CO_2 freeze-out temperature is required, this can be obtained by increasing the additive rates. For condensers where heat exchange occurs, pinch temperature should be large enough not only to avoid freeze-out at the equilibrium temperature, but also to avoid freeze-out on cold spots on heat exchanger surfaces. For the Bulk column the temperature pinch, with 1.5–3°C approach as indicated in Fig. 2, occurs in the condenser and introducing an additive stream can therefore be done to mitigate the risk of CO_2 freeze-out, if found necessary. The models for freezing point prediction indicate that it can be avoided but further complementary experimental verification would be preferable.
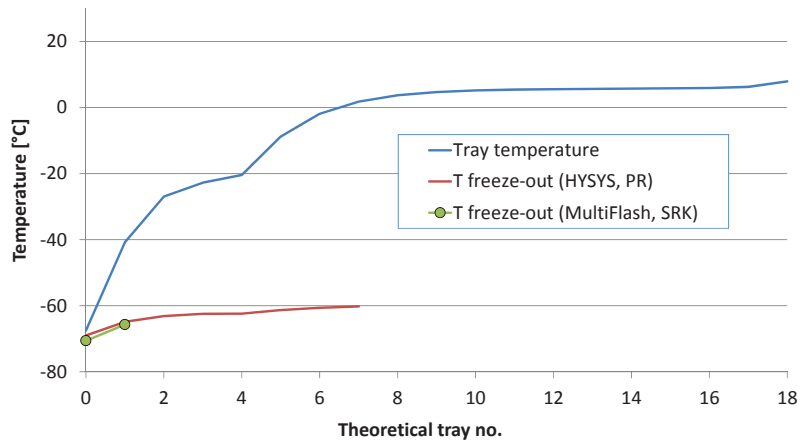
Fig. 2. Tray temperature and estimated CO_2 freeze-out temperature for Bulk column.
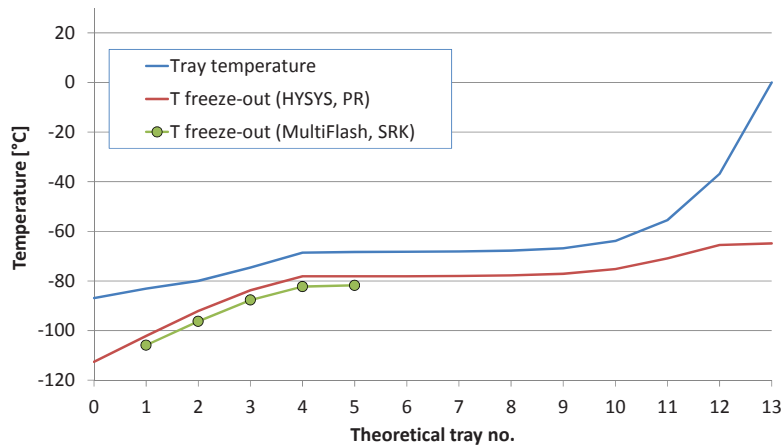

Fig. 3. Tray temperature and estimated CO_2 freeze-out temperature for 2nd column.
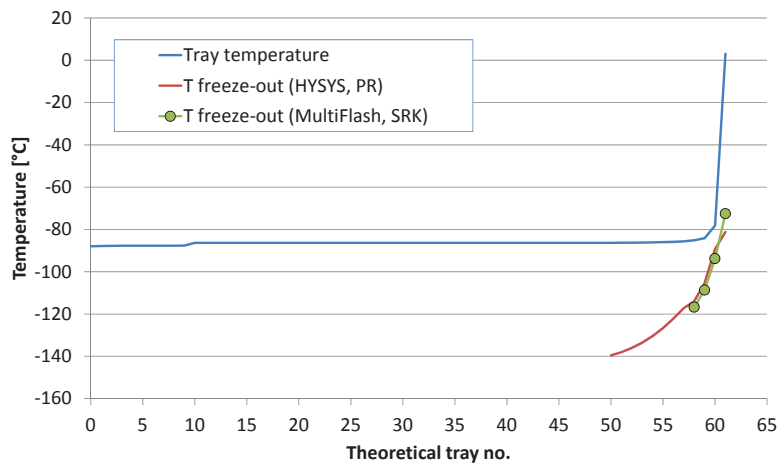

Fig. 4. Tray temperature and estimated CO_2 freeze-out temperature for 3rd column.

4. Conclusion and further work

A low-temperature process for CO_2 removal from natural gas before liquefaction has been presented. Three low-temperature columns reduce the CO_2 concentration from an initial 50.6% to 50 ppm through a combination of distillation and extractive distillation. An advantage of the low-temperature concept is that sweetened natural gas feed has a temperature of -88°C before entering the liquefier, and is therefore already partly pre-cooled for natural gas liquefaction. Hence, the process described must be regarded as an integral part of an LNG train rather than stand-alone. For benchmarking with other CO_2 removal technologies such as solvents, membranes or PSA, a global process approach is required, taking into account the whole process between raw natural gas feed and LNG product, as well as other product streams.

The overall process has not been fully optimised with respect to energy consumption. When column configurations and core process parameters have been settled more advanced and efficient auxiliary refrigeration processes should be elaborated upon. This becomes of significant importance in an integrated assessment where the natural gas sweetening process is combined with an LNG train.

The project will in the continuation consider different CO_2 concentrations of the raw feed gas, different CO_2 content in the sweetened natural gas (pipeline and LNG specifications), consider new and innovative low-temperature concepts, either as the only means for CO_2 removal or in combination with other technologies. Further, an important task will be to perform experimental verification for CO_2 freezing point for different natural gas compositions.

Acknowledgements

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