Mihael Dominko, Darko Lukec, Ivana Lukec, Ivan Pavošević, Marijan Utroša

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OPTIMIZATION OF HYDROGEN PRODUCTION FROM HEAVY OIL RESIDUES

Abstract

Hydrotreatment processes are the most important processes in a modern refinery. Hydrogen availability that enables flexibility in refinery production is a must for a modern refinery. Therefore, optimization in hydrogen production is in focus of both refinery modernization and through the design of new refineries.

On the other hand, to maintain the production of motor fuels being economical, production of fuel oils should be under the limit of 10%.

Integrated Gasification Combined Cycle process (IGCC) is a promising answer to these refinery needs: it is proven technology for the combined production of hydrogen, electric power or petrochemical components from heavy residues.

The goal of this paper is optimization of hydrogen and electric power production from vacuum residue produced from REB crude oil.

Introduction

Conversion of heavily evaporable fractions of crude oil

Today refinery industry is facing great challanges: there is increasingly more heavily evaporable components and contaminants (sulphur, metals) while the quality requirements for products are getting more stringent. There is an increased demand for the so called "white" petroleum products (motor gasolines, jet and diesel fuels), while the demand for heavy fuel oils is reduced. In order to fulfill these requirements for "white" petroleum products refineries started to invest in the processes that provide the conversion of heavy petroleum residues into easily evapourable products which meet the stringent quality requirements of products and ecology standards.

Refineries are still dealing with the problems of heavy residues containing considerable quantities of sulphur and metals. Regardless of whether coking or hydrocracking processes are used in the conversion of residues, great quantities of hydrogen are needed for achieving the required quality of products, which influences the growing requirement for hydrogen production. In refineries the catalytic reforming in hydrogen production is not sufficient anymore, so new processes such as vapour reforming of light hydrocarbons or partial oxidation of light and heavy hydrocarbons need to be designed[1].

Although the process of heavy oil residue gasification with electric power and hydrogen production (IGCC, Integrated Gasification Combined Cycle) is one of the most expensive investment processes, but due to its other advantages it has become a promising solution for refinery requirements. Since the least valuable refinery products such as vacuum residues, bitumen or coke can be used as raw materials in the gasification process, and one of the potential products in the refineries is hydrogen, an IGCC process is being increasingly used[2]. The integration of an IGCC process in a technological scheme of a refinery is shown in the Figure 1.

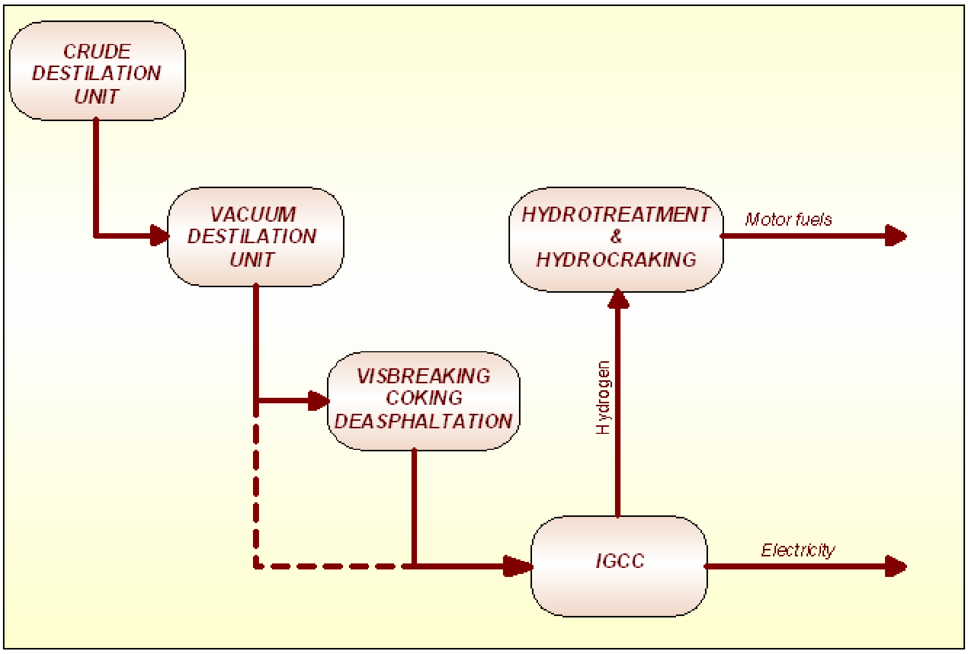

Figure 1: Integration of an IGCC process in technological scheme of a refinery

The basic purpose of an IGCC process is syngas production by the means of gasification which is actually a partial oxidation of a raw material in the solid or liquid state. Syngas (H_2+CO) can be used as a gas plant drive in electric power production, hydrogen production or as a raw material in the petrochemical industry. The scheme of the gasification process and possible raw material types and products is shown in the Figure 2.

The electric power production by the use of the gasification process is one of the least environmentally dangerous technologies considering the emissions of SO_2,

NO_x and CO which are considerably under the upper limit values[3,4]. All these factors justify their high price and substantiate the fact that we no longer live in the world of cheap energy-generating products.

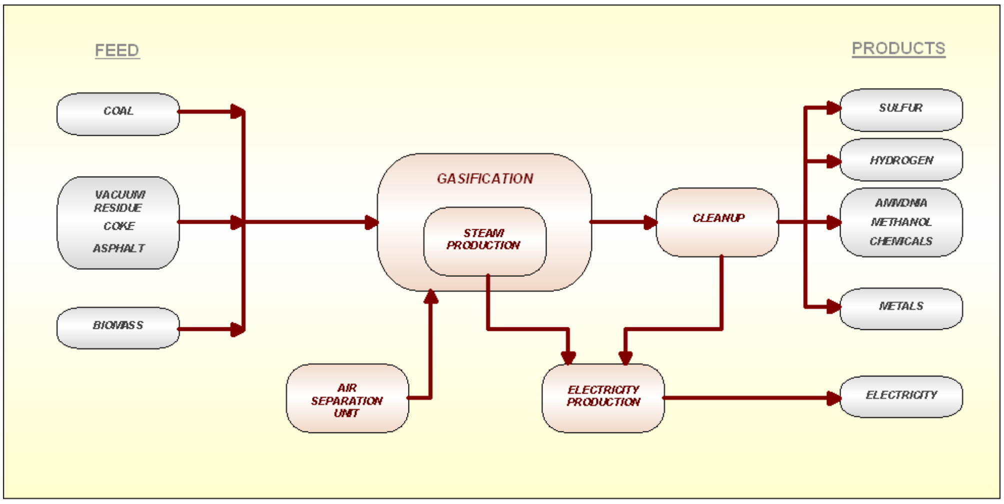

Figure 2: Scheme of gasification process.

Description of an IGCC process

Generally, the term gasification relates to the conversion of a raw material in the solid state (coal, coke, biomass…) or in the liquid state (fuel oil, bitumen) into syngas, which is basically made of hydrogen and carbon monoxide. Although in the past the gasification was mostly related to petrochemical processes in order to produce chemicals, today the gasification process is increasingly used in electric power production.

The gasification process is like a bridge which connects coal, coke, bitumen and fuel oils with electric power production in the gas and vapour turbines. Being designed in this way an IGCC is the only technology which provides the minimum ecologically harmful effect by coal or fuel oil firing. The contaminators such as sulphur and metals are extracted from syngas.

The IGCC process is combined of several units integrated in one complex (Figure 2). The process design can be optimized in accordance with requirements of hydrogen production, electric power production or other components.

The IGCC complex which provides the hydrogen production is shown in the Figure 3 and it includes the following basic units[2]:

– air separation unit,
– gasification unit,

– treatment of synthesized gas which includes acid gas treatment,
– hydrogen production,
– electric power production.

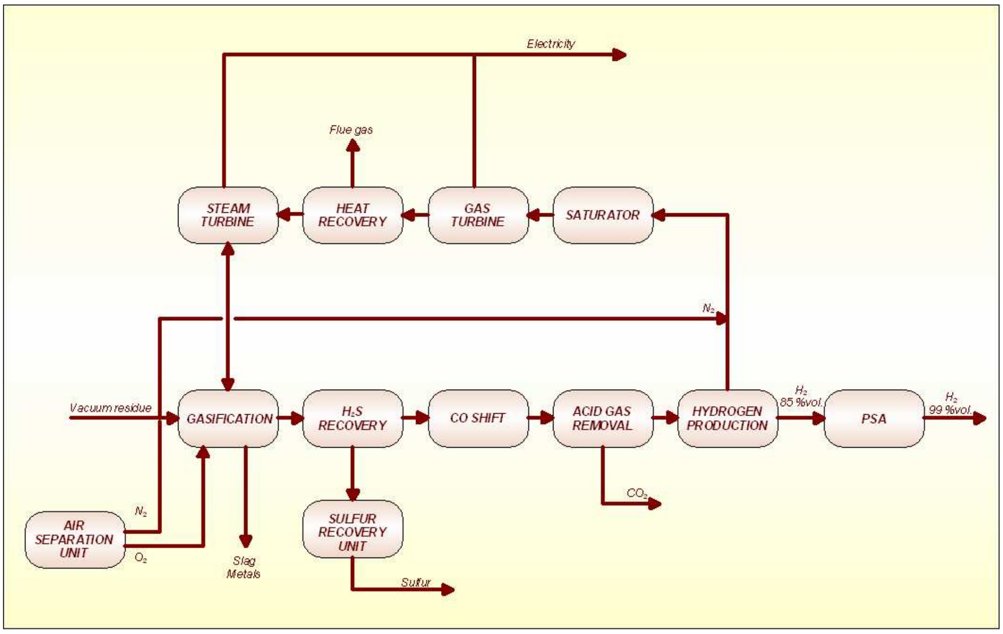

Figure 3: Scheme of an IGCC process with hydrogen production

Air separation unit
The purpose of air separation unit is the oxygen production for the needs of the needs of partial oxidation (99,5 % vol.) in the gasification process.

Gasification process
Raw material, heavy petroleum residues are brought into the gasification reactor where partial oxidation reactions are conducted and syngas H_2 + CO is produced. Other compounds made by partial oxidation are CO_2 i H_2O, impure H_2S, NH_3 and COS. These reactions occur at 1300 - 1500 ℃ and at the pressure of 40-65 bar. Released heat of gasification is used for the production of water vapor [3,5].

Treatment of syngas
Syngas is washed during the absorption with an appropriate solvent and then the impurities are removed. Gas enriched with H_2S is treated in the Claus process for sulphur production.

Hydrogen production
During hydrogen production, the IGCC complex is also equipped with a CO shift unit. In the reaction of CO and water additional hydrogen is produced while CO_2 is

made and removed from the process. Syngas is transported through the membranes for hydrogen separation in the concentration of 70 – 90 % vol. Afterwards hydrogen is additionally intensified to 99 % vol. in a hydrogen concentration unit (Pressure swing adsorption, PSA) [6].

Electric power production

After the separation through the membrane for removing hydrogen, the rest of syngas is used for electric power production in gas turbines, or in steam turbines. That is why this process is called "Combined Cycle”. A part of produced electric power is used in the refinery, while the rest is sold to the distribution network[2].

The analysis of an IGCC process in a refinery for Euro V quality fuel production

Within a refinery capacity of 80.000 BPSD (4,0 million tons/year), as an option for solving the problem of heavy residues, the possibility of using an IGCC process was analyzed. The quality requirements and product quantities define the structure of a refinery as a deep conversion refinery. [7]

The basic requirements of defining the refinery structure and the process capacity are the following:

- production of Euro V quality fuel in quantities defined in the Figure 4,
- minimal production of fuel oil,
- hydrogen production sufficient for the production flexibility,
- independent electric power production,
- minimal effect to environment.

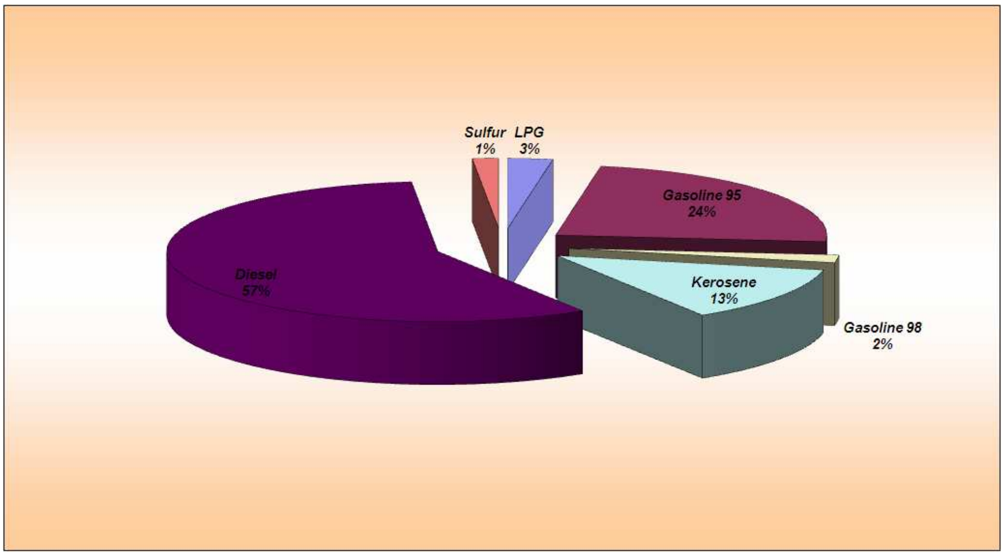

Figure 4: The definition of product quantity

Taking all the mentioned requirements into consideration, while defining the refinery structure the extensive analyses dealt with a quality solution of the treatment of heavy petroleum residues and vacuum residue: coking, solvent deasphaltation and IGCC process were considered.

A static model is made by mathematical modelling which defines a structure of refinery and process capacities which will meet the mentioned requirements.

Due to the characteristics of an IGCC process and the possibilities of electric power production according to the highest ecological standards, the IGCC process is included in the concept design of a refinery. The optimal solution for the selection of other processes for treatment of vacuum residues was analyzed by a static mathematical model. Three versions of process selection were analysed:

1. IGCC

Vacuum residue is used as the raw material for the IGCC process.

2. Solvent deasphaltation + IGCC

Before entering the IGCC process vacuum residue is treated by the solvent deasphaltation process which enables the production of deasphaltated oil as a raw material for the hydrocracking process, or production of diesel fuel, while asphalt as the residue of the deasphaltation process is used as a raw material in the gasification process. This version provides a flexibility of the production where the quantity of raw material for an IGCC can be increased or decreased, as well as electric power production.

3. Coking

Vacuum residue is used as the raw material for coking, where again the extraction of produced lighter products (gasolines, light gas oil) and heavy gas oil which is used as raw material for hydrocracking, while coke is used as a raw material for an IGCC.

A mathematical model of a refinery defines the process capacity and product quantity, as shown in the Table 1.

Table 1: Analyzed process of heavy residues

Process	**Process capacity,** t/y	**Quantity of raw material for IGCC**, t/y
Vacuum distillation	2,010.160	833.600
Solvent deasphaltation	833.600	500.160
Coking	833.600	208.400

Table 2: Quantity of IGCC product

Raw material	**Quantity of raw material for IGCC**, t/y	**Quantity of produced hydrogen,** t/y	**Quantity of produced electric power, MW**
Vacuum residue	833.600	73.888	111,6
Asphalt	500.160	44.333	67,0

Coke	208.400	18.472	27,9

As different quantities and characteristics of raw material are considered, there are different quantities of IGCC products which is shown in the Table 2.

During the analysis of an IGCC process, apart from the production of hydrogen and electric power, the independent electric power production from the listed raw materials was also analyzed. The results are shown in the Table 3. In this case, hydrogen for refinery needs would be produced from natural gas in the steam reforming process.

Table 3: Quantity of IGCC product

Raw material	Quantity of raw material for IGCC, t/y	Quantity of produced electric power, MW
Vacuum residue	833.600	484,1
Asphalt	500.160	290,5
Coke	208.400	121,0

Table 4: Prices of analyzed raw materials and products

Raw material	Price
€/MWh	35
Natural gas, €/Nm^3	0,2
Hydrogen, €/Nm^3	0,14

The Table 4 shows the prices of raw materials and products which were used in the economic analysis of the results.

The economic analysis of these three options is shown in the Figure 5.

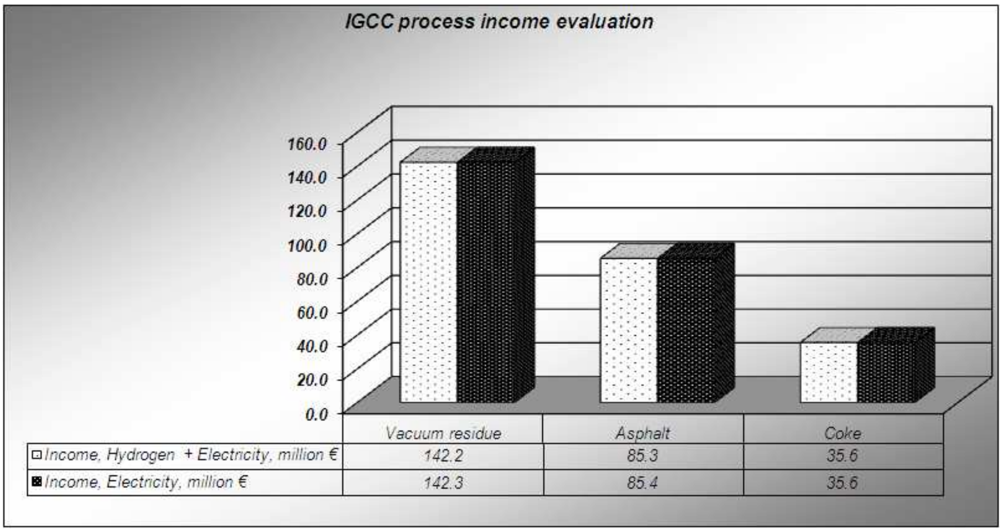

Figure 5: Assessment of raw material costs and incomes of IGCC process products

The assessment of investment costs of IGCC process is shown in the Figure 6.

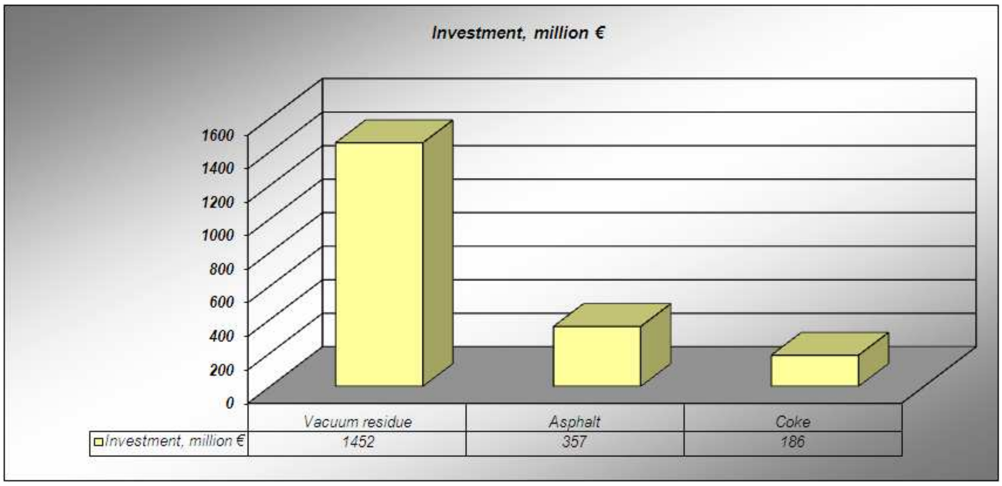

Figure 6: Assessment of investment costs of IGCC process

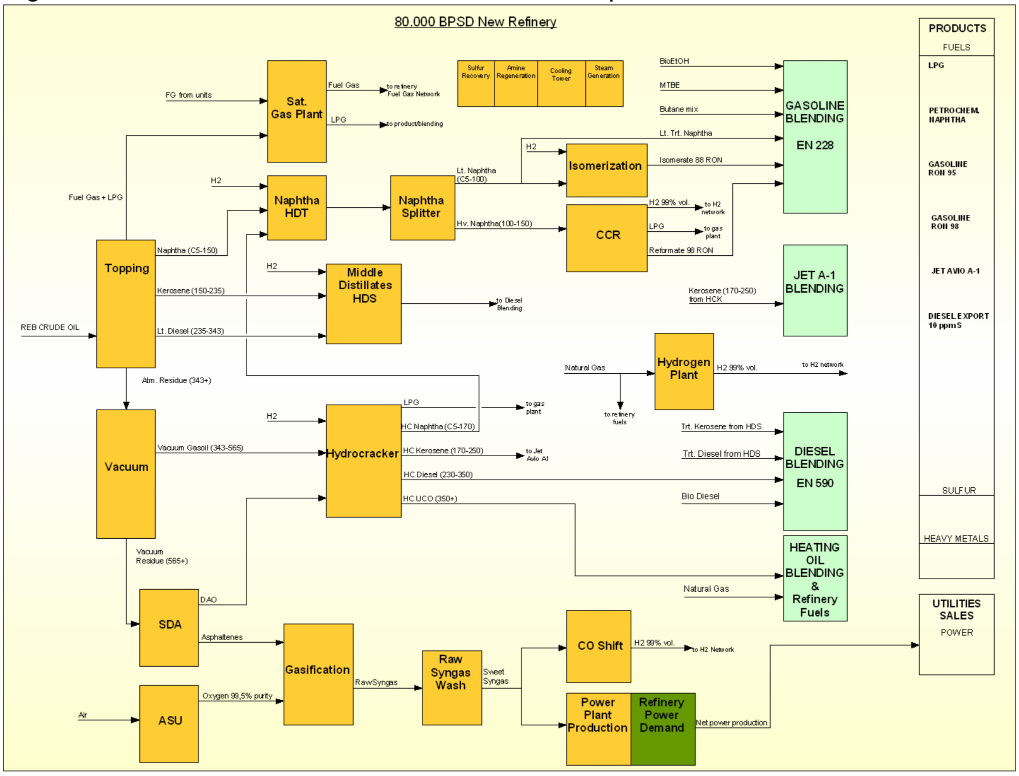

Figure 7: Final structure concept of the refinery

All these analyses of product quantity and investment costs show different options for sellecting the final structure. In the process of selection the production flexibility is one of the most important requirements. As you can see from the Tables 2 and 3 and the Figure 5, the option of the IGCC process which provides an independent electric power production, without hydrogen production, has a similar economic effect. Nevertheless, the sufficient hydrogen quantity for the needs of refinery can be produced by an IGCC process only in case of vacuum residue treatment of defined quantity. Therefore there is a tendency to choosing steam reforming as a solution for hydrogen production, but also with the possibility to apply an IGCC process in hydrogen production in order to increase the flexibility of the production.

In order to use the maximum quantity of raw material for hydrocracking from vacuum residue, the solvent deasphalting process was chosen as a possibility of the treatment of the vacuum residue. Choosing this process will provide for the sufficient flexibility in the production of fuels and electric energy or, in other words, for the increased or decreased production of raw material for hydrocracking or IGCC process.

The final structure concept is shown in the Figure 7.

Conclusion

This paper analyzes the possibility of using an IGCC process in a modern refinery in order to meet the quality requirements for products and production ecology standards for the moment and for the future.

Although we discuss a demanding investment here, it still stands for the flexibility, so its basic advantages are:

- solving the problem of heavy residues,
- electric energy production,
- possibility of hydrogen production,
- production of petrochemical raw materials,
- exhaust gas emission under the most stringent ecology requirements.

Apart from being important during the integration into the refinery system, the use of an IGCC process also provides electric power production and its distribution release.

The analysis that has been conducted proves the claim of energy-generating products today: the time of cheap energy-generating products is behind us and the sustainable development is reachable only by respecting the requirements of environmental protection.

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UDK	ključne riječi	key words
661.96	vodik iz sinteznog plina za rafinerijske procese	hydrogen from syngas for petroleum processing
665.658.2	hidroprerada, obrada vodikom	hydroprocessing
665.637.567	teški ostaci prerade	heavy residues
662.763	sintezni plin (CO+H2) uplinjavanjem teških ostataka	syngas (CO+H2) from heavy residues gasification
662.76	postrojenje za gasifikaciju (IGCC) u elektrani kombiniranog ciklusa	Integrated gasification combined cycle plant (IGCC)
621.311.22/.23	termoelektrana kombiniranog ciklusa	combined cycle power plant
621.438	sintetezni plin za plinske turbine termoelektrane	syngas for power plant gas turbines
621.165	para za parne turbine termoelektrane	steam for power plant steam turbines

Authors
Mihael Dominko[1], Ivan Pavošević[1], Marijan Utroša[1]
[1] Nafta inženiring, Mlinska ulica 5, Lendava, Slovenija
Darko Lukec[2], Ivana Lukec[2], e-mail: ivana.lukec@model.hr
[2] Model, Pazinska 36, Zagreb, Hrvatska

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