Croatian crude oils 30 years ago and today (analysis and distillation)

M. Fabulić Ruszkowski, M. Radošević, Š. Podolski, R. Gorup, Z. Marić

PROFESSIONAL PAPER

The work comprises processing of the Slavonija and Moslavina crude oil and gas condensate samples used in the Sisak Refinery production. The physical and chemical characteristics of crude oils, gas condensate and their fractions were determined. Laboratory distillation was carried out in accordance with ASTM D 2892 and ASTM D 5236.

The obtained data are used for preparation of crude oil assays, e.g. for optimisation of atmosphere and vacuum distillations in the Sisak Refinery production by mathematics models. It's pointed out of value of domestic oils as high-quality low sulphur feeds.

From the distillation curves, density and sulphur curves from domestic oils and gas condensate made over a period of thirty years it was concluded that there haven't been significant changes in the composition of oil and gas condensate.

Key words: Croatian oil, oil fractions, distillation

1. INTRODUCTION

Crude oil is a liquid to semi-solid natural substance, found predominantly in the Earth's crust. According to its chemical composition, oil is a very complex mixture of several thousands of hydrocarbons, which always contains sulphur, nitrogen and oxygen organic compounds. The composition and properties of oils from the same area, but from different reservoirs, can significantly differ.

In order to gain a comprehensive insight into the oil quality and processing parameters, all crude oil distillation fractions and residue need to be analysed and a detailed study of crude assays has to be made. In addition to technical value, the study also has an economic value since it facilitates the selection of feed for refinery units and processing conditions in accordance with market requirements.[14]

In the paper were analysed two samples of Croatian oils and gas condensates used in processing in the Sisak Refinery. Croatian oil is a mixture of Moslavina and Slavonia oils and gas condensate.

Croatian oils are produced from over 700 wells located in 35 oil fields. In 2008 the Croatian production amounted to 554 777 t of oil and 280 603 t of gas condensate. In 2008 processed quantities of Croatian oil amounted to 765 000 t. Processing of Croatian oil in the Sisak Refinery accounts for approx. 45% of total processed quantities in the refinery, which is 17.7 % of total processing in INA refineries.

Unfortunately, production and processing of Croatian crude oil is decreasing every year and in 2008 production and processing of Croatian oil in comparison with the year 2007 was less by 41 236 t and 24 000 t respectively.[1,2]

2. EXPERIMENTAL PART

2.1 Feeds

The Moslavina oil includes oils from the Pavljani, Šandrovec, Graberje, Žutica, Stružec and Jamarice fields (Table 1).

The Slavonia oil is a mixture of oils from the Beničanci and Đeletovci field, in the ratio of approximately 55% m/m : 45% m/m.

Gas condensate sample includes gas condensate from the gas stations Molve, Kalinovac and Stari Gradac. The ratio of gas condensate added to Croatian crudes is over 20-30%.

The physicochemical properties of analysed crudes and gas condensate are presented in Table 2.

According to solid paraffin content, the Slavonia and Moslavina oils are classified as middle paraffin oils, while according to density they fall into the category of medium density oils.[6,9]

The Moslavina and Slavonia oils are low-sulphur light or medium density oils, which contain significantly higher amounts of light fractions than high-sulphur content oils.[7] The ratio of sulphur in gas condensate is very low.

Table 1. Composition of Moslavina crude oil

Crude oil field	Ratio in crude oil Moslavina, % m/m
Stružec	22.43
Jamarica	18.04
Graberje	21.72
Žutica	17.36
Pavljani	0.98
Šandrovec	19.45

Table 2. Physicochemical properties of crude oils

Charasteristics	Crude oil Moslavina	Crude oil Slavonia	Gas condensate
Density, 15 °C, kg/dm^3, (ASTM D 5002)	0.8453	0.8746	0.7574
°API (DMA 4500)	35.74	30.15	55.16
Water, % m/m(ASTM D 4006e1)	< 0.5	< 0.5	0.0
Vapour pressure, RVP, kPa	23.0	29.0	60
Pour point ,°C (ASTM D 97)	+10	-3	-11
Sulphur ,% m/m (HRN EN ISO 20884)	0.400	0.390	0.0114
Paraffines ,% m/m (UOP 46)	6.9	7.76	1.06
Viscosity, 20 °C mPa s (ASTM D 445)	5.780	20.048	0.854
Viscosity, 20 °C mm^2/s (ASTM D 445)	6.780	23.007	1.133
Carbon residue (of 10 % distillate)	2.31	4.211	0.0
Ash content, % m/m	0.0	0.019	0.0
Asphaltenes, % m/m	0.48	1.74	0.0
Mercury, mg/dm^3	0.0360	0.0045	1.0741
ASTM distillation (ASTM D 86) start, IBP, °C	55.4	59.7	43.2
Yield 10% v/v	121.1	149.1	87.8
20 % v/v	154.5	208.1	107.5
30 % v/v	194.4	264.6	124.7
40 % v/v	242.7	306.0	144.1
50 % v/v	287.9	347.8	168.3
60 % v/v	332.7	364.5	197.5
70 % v/v	-	369.1	233.4
90 % v/v	-	-	366.3
End, FBP, °C	357.9	370.2	366.3

Gas condensate also contains a slight quantity of elemental mercury. In Sisak refinery the content of mercury in light gasoline fraction obtained from gas condensate is considerably lowered during the two-phase adsorption procedure.

2.2 Methods

Distillation curves on the basis of ASTM D 2892 test method were determined on oil samples applying the crude oil distillation method (fractionating column with 15 theoretical trays)[12] or the so-called TBP (true boiling point) distillation. Distillation up to 400 °C is carried out on the TBP device (atmospheric and vacuum distillation), and on the basis of ASTM D 5236 method is continued on the Potstill device under reduced pressure. In most cases the highest atmospheric equivalent temperature (AET) is about 570 °C. Distillation devices EuroDist System ASTM-D 2892, TBP and EuroDist System ASTM-D 5236 and Potstill are completely automated and have a control system enabling the monitoring and regulation of the distillation process, as well as data recording through measurement using EuroDist Control software.

The process of distillation of oil samples begins with the procedure of oil debutanization. The limits of boiling points for yields of crude oil fractions obtained from distillation are provided in Table 3.

The distillation curve shows dependence of temperature (T) on the mass ratio of predistilled product (% m/m). The tested crudes were compared based on the obtained material balance and product yield.

In tested oils sulphur content in fractions was determined by the method for determining sulphur in oil derivatives using WDX-ray spectrometer (HR EN ISO 20884 method). Research octane number (RON) and motor octane number (MON) for light and heavy naphtha have been determined by HRN EN 5164 and HRN EN 5163 method. Cetane number of diesel fuel was determined applying the HRN EN 5165 method.

3. RESULTS AND DISCUSSION

3.1 Distillation curves, material balance and fraction yields

Table 3 presents the fraction yields obtained from the TBP and Potstill distillations. Gas condensate predominantly contains light and middle fractions, and had significantly higher yields of light and heavy naphtha with regard to the Moslavina and Slavonia oil samples. Light gas oil (LGO) yields are approximately the same for all three tested samples.

The volume of heavy gas oil (HGO) is insignificant in gas condensate, as well as in atmospheric residue (AR).

Table 3. Yields of the crude oils fractions from TBP and Potstill distillation

Fraction, % m/m	Crude oil Moslavina	Crude oil Slavonia	Gas condensate
light naphtha (IBP-80 °C),	4.85	2.97	12.62
heavy naphtha (80-175 °C)	18.79	11.85	38.35
kerosene (175-225 °C)	9.19	6.92	1 473
light gas oil, LGO (225-340 °C)	23.29	23.49	22.27
heavy gas oil ,HGO (340-370 °C)	4.01	3.53	0.57
atmospheric residue, AR (+370 °C)	37.78	49.59	3.05
vacuum light gas oil, VLGO (370-430 °C)	7.75	10.58	-
vacuum heavy gas oil,VHGO (430-570 °C)	18.27	21.44	-
vacuum residue, VR (+ 570 °C)	11.56	17.45	-

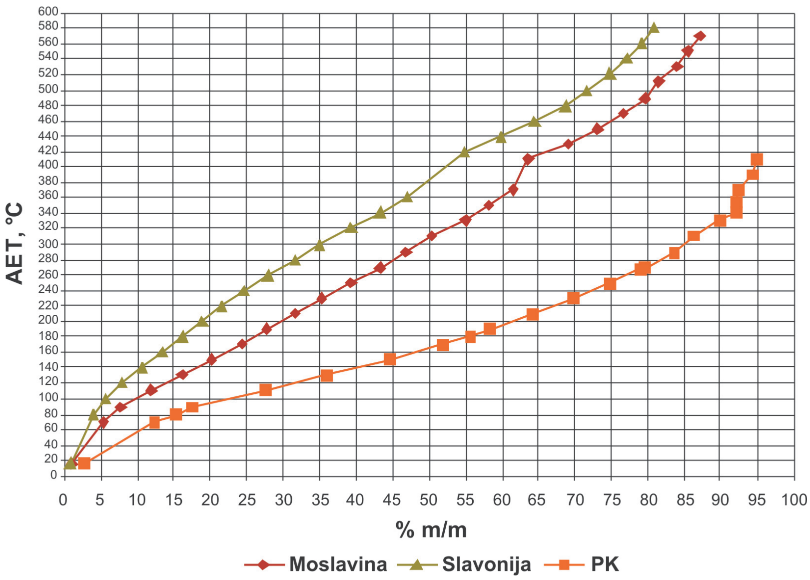

Fig. 1. Distillation curves of testing crude oils and gas condensate
Sl. 1. Destilacijske krivulje ispitanih nafti i plinskog kondenzata

With regard to Moslavina oils, the Slavonia oils contain considerably higher volumes of heavy fractions in AR, vacuum light gas oil (VLGO), vacuum heavy gas oil (VHGO) and vacuum residue (VR).

Figure 1 presents the distillation curves of Moslavina and Slavonia oils and gas condensate, with fractions taken per every 20 °C, obtained from the merged data of TBP and Potstill distillations

3.2 RON and MON for gasoline and kerosene cetane number

The obtained fractions of light and heavy naphtha were used to determine research octane number (RON) and motor octane number (MON), whose values are presented in Figures 2 and 3. The highest values were recorded in light naphtha obtained from gas condensate, and fractions of gasoline obtained from Slavonia oil also revealed the highest RON.

The cetane number was determined on fractions of kerosene and light gas oil (LGO) (Figure 4). The kerosene fraction of gas condensate has the highest value of cetane number, and LGO from the Moslavina oils has the highest cetane number.[7]

3.3 Analysis of sulphur in oil fractions

Sulphur content was determined in fractions of light and heavy naphtha and in fractions of medium and heavy distillates (Figures 5 and 6). The concentration of sulphur in light naphtha obtained from the Moslavina and Slavonia oils and in gas condensate ranges from 6 to 20 mg/kg. In heavy naphtha obtained from gas condensate, sulphur content amounts to only 6 mg/kg, whereas both oils contains higher

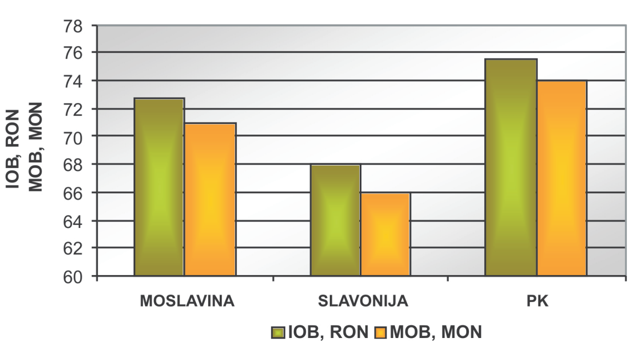

Fig. 2. RON and MON in light naphtha
Sl. 2. Istraživački (IOB) i motorni oktanski broj (MOB) lakog benzina

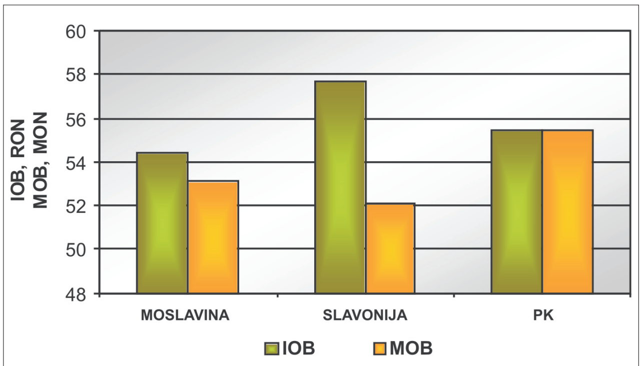

Fig. 3. RON and MON in heavy naphtha
Sl. 3. IOB i MOB u teškom benzinu

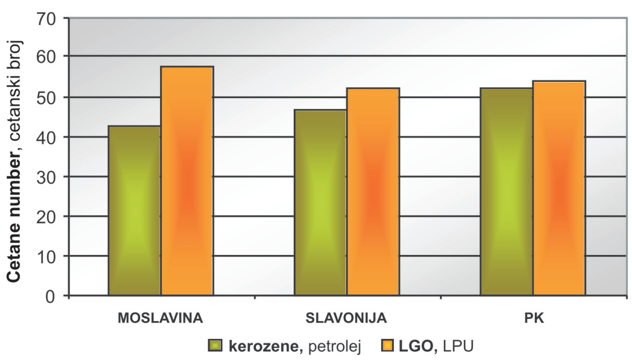

Fig. 4. Cetane number in kerosene and LGO
Sl. 4. Cetanski broj u petroleju i LPU

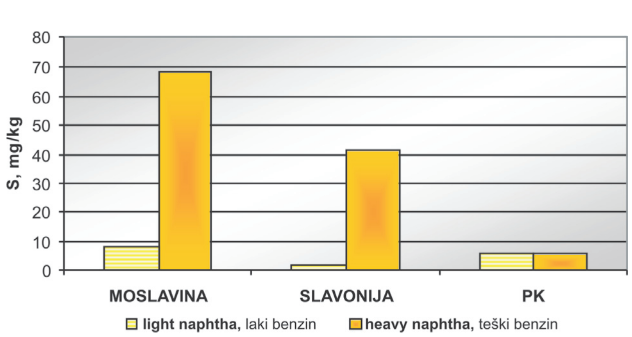

Fig. 5. Sulphur in light and heavy naphtha
Sl. 5. Sumpor u lakom i teškom benzinu

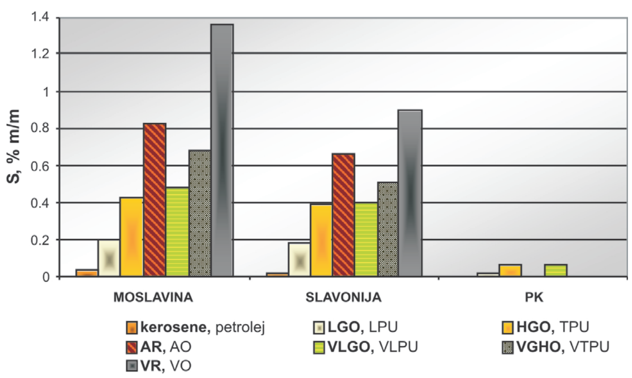

Fig. 6. Sulphfur in middle and heavy fractions
Sl. 6. Sumpor u srednjim i teškim frakcijama

volumes of sulphur in heavy naphtha fractions (41 and 68 mg/kg of sulphur).

Sulphur compounds are predominantly found in heavy fractions and in distillation residue in the form of benzothiophenic, dibenzothiophenic and naphtho-phenantrenic compounds.[14] Middle and heavy fractions obtained from the Moslavina oils contain higher concentrations of sulphur with regard to the same fractions obtained from the Slavonia oils. In all tested fractions the highest volumes of sulphur were recorded in atmospheric residue (AR) and in vacuum residue (VR).

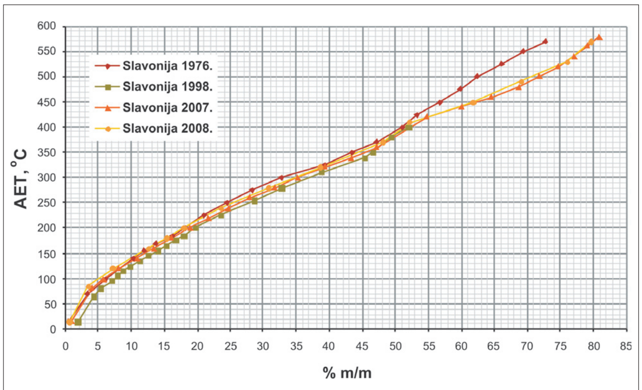

Fig. 7. Distillation curves of Slavonija crude oil from the year 1976, 1998, 2007 and 2008
Sl. 7. Destilacijske krivulje nafte Slavonija iz 1976., 1998., 2007. i 2008. godine

3.4 Comparison of distillation curves, density and sulphur curves in Croatian oils – before and today

It is extremely important to determine the basic properties of oils to make their classification and evaluation easier. The basic characteristics are density, sulphur content and distillation curve.

Since the data on above properties of both Croatian oils and gas condensate for the period from thirty years and two years ago were available, they were compared to determine changes in oil and gas condensate compositions.

Distillation curves and density curves for the Slavonia oils from 1976 to 2008[4,7,8,11] are presented in Figures 7 and 8. The obtained values are within the method's accuracy range, with a small variation in distillation curve from 1976. The density curves have similar values.

Distillation curves for Moslavina oils were prepared in 1976, 1998 and 2007 (Figure 9)[3,7,10] and their values are almost identical. Figure 10 presents a density curve for above years, and Figure 11 refers to sulphur content registered in 1976 and 2007. While density curves are almost identical, sulphur content curves slightly differ in higher fractions, which can be explained by use of different determination methods.

Figures 12 and 13 present the distillation and gas condensate density curves from the year 1994 and 2007.[5,7] The distillation curves confirm equal behaviour in gas condensate distillation. The shift in curves could be attributed to the loss of lighter fractions during sample handling (sampling, transportation, handling or distillation).

Based on above comparisons of distillation, density and sulphur-content curves over the last thirty years, it can be concluded that composition and quality of Moslavina and Slavonia oils and gas condensate has not changed.

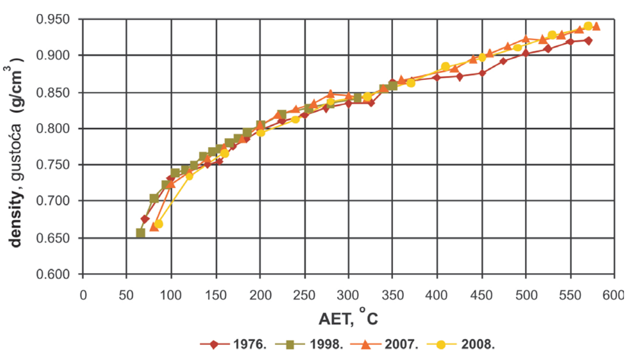

Fig. 8. Density curves of Slavonia crude oil from the year 1976, 1998, 2007 and 2008

Sl. 8. Krivulje gustoće Slavonija nafte iz 1976., 1998., 2007. i 2008. godine

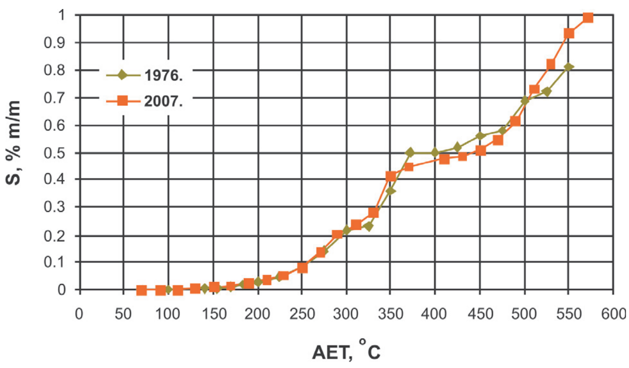

Fig. 11. Sulphur content curves of Moslavina crude oil from the year 1976 and 2007

Sl. 11. Krivulje sadržaja sumpora nafte Moslavina iz 1976. i 2007. godine

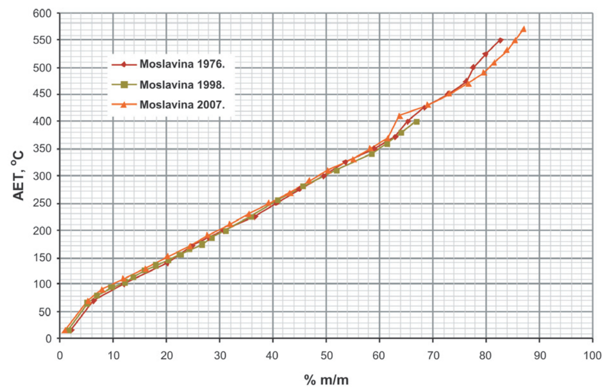

Fig. 9. Distillation curves of Moslavina crude oil from the year 1976, 1998 and 2007

Sl. 9. Destilacijske krivulje nafte Moslavina iz 1976., 1998. i 2007. godine

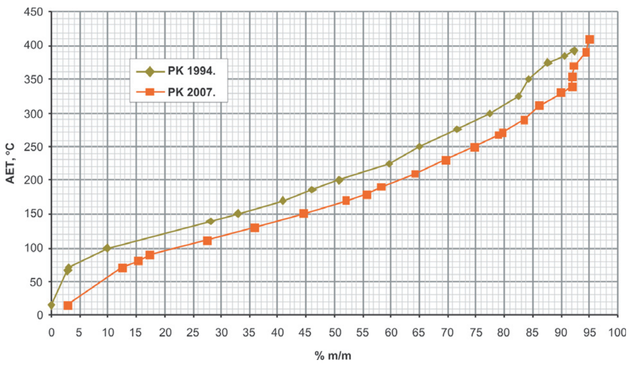

Fig. 12. Distillation curves of gas condensate from the year 1994 and 2007

Sl. 12. Destilacijske krivulje plinskog kondenzata iz 1994 . i 2007. godine

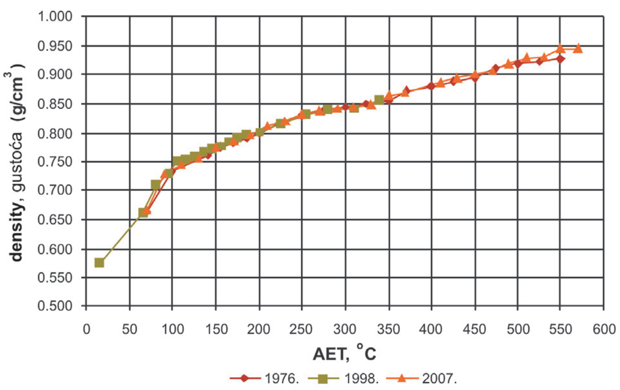

Fig. 10. Density curves of Moslavina crude oil from the year 1976, 1998 and 2007

Sl. 10. Krivulje gustoće nafte Moslavina iz 1976., 1998. i 2007. godine

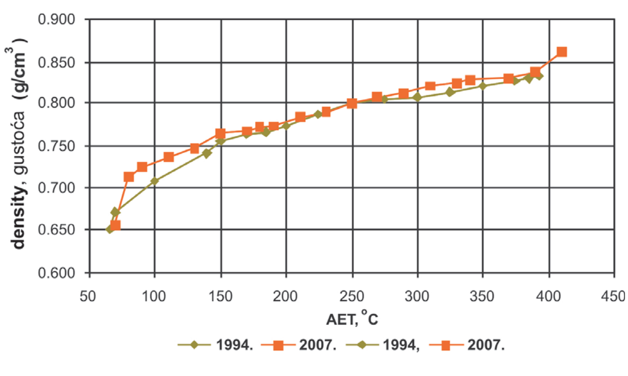

Fig. 13. Density curves of gas condensate from the year 1994 and 2007

Sl. 13. Krivulje gustoće plinskog kondenzata iz 1994. i 2007. godine

4. CONCLUSIONS

Croatian crude oils and gas condensate from the Slavonia and Moslavina region, processed at Sisak Oil Refinery, were analysed. The oils and gas condensate were compared based on the data obtained from distillation curve, material balance and yields of individual fractions. The obtained data are used as input data in Crude Manager and PIMS software used for optimizing the Sisak Oil Refinery production.

The Slavonia and Moslavina oils pertain to low sulphur oils and have high yields and good distribution of light and middle fractions. Gas condensate and the Moslavina oils have the best distribution and yield of light products.

The obtained results confirm the value and quality of Croatian low-sulphur content oils and justify its exploitation and processing.

It can be concluded from the presented data that the composition and quality of the Croatian oils and gas condensate have not significantly varied and that tested properties remained unchanged over the last thirty years.

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Authors:

Maja Fabulić Ruszkowski, DSc, INA industrija nafte d.d., Refining and Marketing Sector, Technological Development & Project Management Department, Lovinčićeva bb, 10000 Zagreb

Marko Radošević, INA, Technological Development & Project Management Department, Lovinčićeva bb, Zagreb

Štefica Podolski, INA, Technological Development & Project Management Department, Lovinčićeva bb, Zagreb

Roberta Gorup, Sisak Oil Refinery, A. Kovačića 1, Sisak

Zoran Marić, INA, Supply Chain Management Sector, A. Holjevca 10