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D I S S E R T A T I O N A B S T R A C T

of dissertation

**MODELLING OF PROPERTIES OF PETROLEUM FLUIDS AND
PROCESSES IN OIL REFINING**

For acquiring educational and scientific degree „Doctor of Philosophy“

Disseration Supervisors: prof. Dobromir Yordanov, Ph.D.
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List of used abbreviations

%AAD	Absolute Average Deviation as per cent
¹ H NMR	Proton Nuclear Magnetic Resonance
AAD	Absolute Average Deviation
ANN	Artificial Neural Network
API	American Petroleum Institute
BEM	Bond-Electron Matrix
BO	Bayesian optimization
CAS	Computer Algebra System
CN	Cetane Number
ESI	Electrospray ionization
ESI-HRMS	Electrospray ionization high-resolution mass spectrometry
ESI-MS	Electrospray ionization mass spectrometry
FBP	Final Boiling Point
FCC	Fluidized bed catalytic cracking
FCCHCO	Fluidized bed catalytic cracking heavy cycle oil
FCCLCO	Fluidized bed catalytic cracking light cycle oil
FCCPT	Fluid Catalytic Cracking Pretreater
GA	Genetic Algorithm
GC	Gas Chromatography
HAGO	Heavy Atmospheric Gas Oil
HCO	Heavy Cycle Oil
H-Oil	Vacuum Residue Hydrocracking Unit
HSRGO	Heavy Straight-run Gas Oil
HTSD	High Temperature Simulated Distillation
HTVGO	Hydrotreated Vacuum Gas Oil
IBP	Initial Boiling Point
ICrA	Intercriteria Analysis
IFP	Intuitionistic Fuzzy Pairs
IFP	Institut Français du Pétrole
LCO	Light Cycle Oil
LSRGO	Light Straight-run Gas Oil
LVGO	Light Vacuum Gas Oil
ML	Machine learning
MON	Motor Octane Number
MTHS	Molecule-Type Homologous Series
MW	Molecular weight
NMR	Nuclear Magnetic Resonance
PINN	Physical Information Neural Network
REM	Reconstruction by entropy maximization
RON	Research Octane Number
RSE	Relative Standard Error
SARA	Saturates-Aromatics-Resins-Asphaltenes

SE	Standard Error
SG	Specific Gravity
SLO	Slurry Oil
SOL	Structure-oriented lumping
SR	Stochastic reconstruction
SSE	Sum of Squared Errors
SU-BEM	Structural Units and Bond-Electron Matrix
TBP	True Boiling Point
VBI	Viscosity Blending Index
VBR	Visbreaker Residue
ω	Acentric factor

Introduction

Petroleum continues to be a mainstay of the global economy and a vital raw material for modern industrial society. Despite the growing role of renewable sources, crude oil and petroleum products remain a major source of energy for transport and industry, as well as a key raw material for petrochemicals. This central role dictates the need to continuously improve the efficiency and economic feasibility of its processing. In this context, the characterization of crude oils and oil fractions is a fundamental step in the process simulation used in the petroleum industry.

The basic principle is that the more comprehensive and accurate this characterization is, the better and more adequate the simulation of the process will be.

The ability to accurately predict the physicochemical properties of petroleum fractions is fundamental for the design, optimization and management of the refining processes. The development of reliable models for predicting properties is essential for obtaining high-quality commodity products. Effective modeling allows not only to understand the behavior of the feedstock, but also to make accurate engineering calculations, preceding and replacing costly experiments.

Among the first steps in modeling crude oil and oil fractions is the interpretation of the fractional composition, for which data from a physical and simulated (obtained by gas chromatography) distillation curve are used. Each of these distillation curves must ultimately be converted into a True Boiling Point (TBP) distillation curve, which serves to generate pseudocomponents - a representation of fractions with a narrow boiling temperature range. Among the most important properties of a given pseudocomponent or oil fraction are the molecular weight and critical properties (temperature, pressure and volume). In addition to the fact that these parameters enter into numerous correlations for predicting other physicochemical properties of oil fractions, they also participate in thermodynamic models for predicting phase equilibrium and enthalpy, which are extremely important for performing a material and heat balance of the simulated process. Among the properties that are challenging to properly estimate are the dynamic and kinematic viscosity of liquid petroleum fractions, especially when it is necessary to model the viscosity of mixtures with heavy petroleum fractions.

Modern petroleum science has witnessed the emergence of a variety of advanced analytical techniques that allow for a more comprehensive characterization of petroleum and its derivatives. These techniques, in turn, contribute to the development of powerful methods for molecular modeling of petroleum fluids and molecular refining. These innovative approaches allow the generation of pseudocomponents and even the identification of real components that more accurately reflect the physical and chemical properties of narrow-boiling petroleum fractions. This leads to more accurate predictions of phase equilibria in the simulation model, its thermodynamic properties, the reactions taking place during the conversion processes, and the unit operation performance prediction.

However, as research highlights, these new methods remain largely unincorporated in the most widely used commercial process simulators (Aspen HYSYS, Aspen Plus, ChemCAD, etc.). Instead, commercial software often relies on unique lumping methods to represent petroleum at the molecular level.

Therefore, economic factors are the most powerful driver for the need for precise engineering calculations. In conditions of high competition, any improvement in modeling accuracy becomes a real economic advantage. Minimizing production losses, increasing the yield of valuable fractions, and reducing costs through virtual testing of operating modes are directly related to the ability to reliably predict properties. Inaccurate predictions, caused by outdated characterization methods, can lead to significant financial losses and inefficiency.

In light of the above premises, the aim of this dissertation is to focus on the critical analysis of the emerging gap between the latest advances in the characterization of oil fractions (including methods for converting distillation curves and determining molecular weight and critical properties); the methods implemented in widespread process simulators used for engineering calculations and process simulation and the constantly evolving methods for molecular reconstruction of crude oil and oil fractions. The present work aims to review the existing correlations for modeling key properties of petroleum and its fractions and models for molecular reconstruction of petroleum fluids available in the open literature and used in commercial software and to evaluate them against modern analytical techniques and tools for assessing influencing factors, such as nonlinear regression analysis, inter-criteria analysis and the use of artificial neural networks (ANN). This analysis is expected to serve as a basis for future development of integrated and more accurate tools for engineering practice, capable of significantly improving the efficiency and economic feasibility of modern oil refining plants.

Goals and objectives

The main purpose of this dissertation is to investigate the available analytical techniques, empirical correlations for calculating basic physical properties and methods for modeling the molecular composition of petroleum fluids in order to outline their limitations and determine the opportunities for improving the predictive ability of the correlations, the use of the correct analytical techniques and approaches for modeling petroleum fluids and related processes of their refining.

The following tasks were formulated to achieve the main goal:

1. To conduct a study on the use of distillation curves from physical vacuum distillation (ASTM D1160) and gas chromatographic high-temperature simulated distillation (ASTM D7169) to predict the yield of target products and to conduct an industrial experiment to validate the results obtained. To determine the distillation method that provides more reliable information for determining the amount of more valuable light fractions in the product undergoing separation.

2. To performing a comparison of the available and most commonly used correlations for predicting the molecular weight of hydrocarbons and petroleum fluids and to determine which of these correlations are most suitable for predicting the molecular mass in the range from 70 to 1685 g/mol. To use the collected molecular mass data to perform nonlinear regression and create a model based on an artificial neural network (ANN) to predict the molecular weight of petroleum fluids.

3. To compare the available and most commonly used empirical correlations for predicting the critical temperature and critical pressure of hydrocarbons and petroleum fluids and to determine the accuracy of their predictions across a wide range of hydrocarbons. To perform intercriteria analysis to assess the relationships between the different input variables, correlation analysis with the available data in order to obtain improved empirical correlations and use of artificial neural networks (ANNs) to predict these properties.

4. To analyze the available correlations for empirical and metaheuristic modeling of the viscosity of heavy fractions diluted with low molecular weight petroleum fluids, using experimentally obtained results from viscosity measurements of individual fractions and the resulting mixtures. Compare the result of the best empirical model with the predictions of the artificial neural network (ANN) model.

5. To analyze the available software libraries for automated properties prediction of libraries of components used for molecular modelling of oil and oil fractions. To analyze the accuracy of the most commonly used group-contribution models for predicting the properties of individual components in light fractions – gasoline and diesel and compare the results with the available experimental data.

I. Validation of Diesel Fraction Content in Heavy Oils Measured by High Temperature Simulated Distillation and Physical Vacuum Distillation by Performing a Commercial Distillation Test and Process Simulation

I.1. Laboratory Test Results

Figure 1 summarizes the variation of diesel fraction content (boiling temperature ≤ 360 °C) in H-Oil HAGO, and LVGO for 2021 and 2022, when ASTM D 7169 is used. It is evident from these data that diesel in HAGO varies between 10.4 and 53.4 wt.%, averaging at 21.7 wt.%. Whereas the diesel in LVGO varies between 18 and 42 wt.%, averaging at 24.8 wt.%. It is clear from these data that a sufficient amount of diesel fraction remains in the H-Oil heavy distillates, which is unfavorable from an oil refining economic point of view and presents a strong incentive to recover the diesel fraction from H-Oil HAGO, and LVGO. However, the physical distillation data obtained by the use of ASTM D 1160 exhibits much lower content of diesel fraction in H-Oil HAGO, and LVGO as shown in Figure 2. The data in Figure 2a indicate 2.3 vol.% diesel fraction content in HAGO, according to ASTM D 1160, versus 12.4 wt.% according to the ASTM D 7169 method. The data in Figure 2b indicate 5.0 vol.% diesel fraction content in LVGO, according to ASTM D 1160, versus 18.2 wt.% according to the ASTM D 7169 method. The ASTM D 1160 results disprove the opinion of poor diesel extraction in the H-Oil fractionator columns based on the ASTM D 7169 results.

In order to validate which method provides more reliable information about the content of diesel fraction in H-Oil heavy distillates, a decision was made to perform a commercial test in which the H-Oil heavy distillates were to be processed in the FCCPT main fractionator.

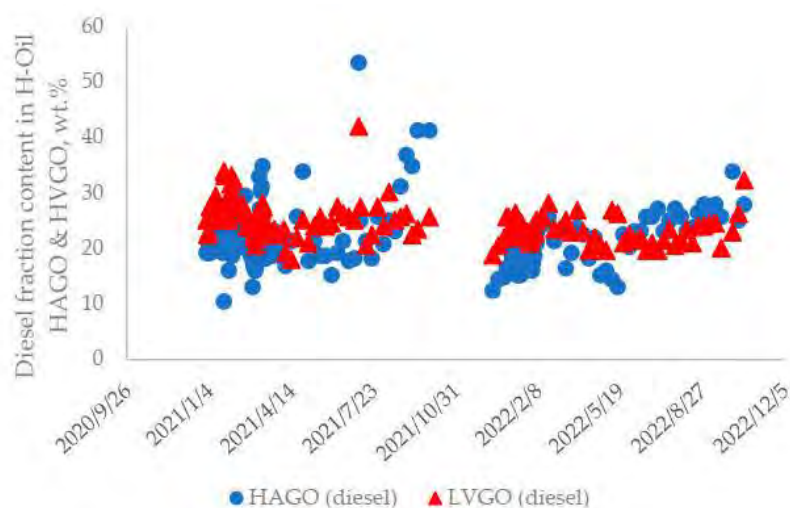


Figure 1. Variation of diesel fraction content (boiling ≤ 360 °C) in H-Oil HAGO and LVGO.

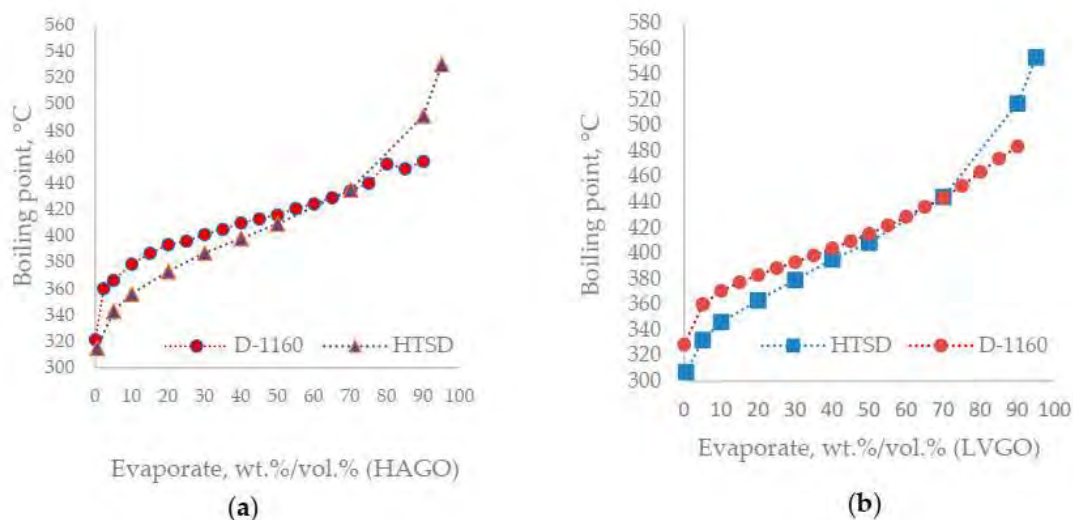


Figure 2. HTSD and physical vacuum distillation (ASTM D1160) data for H-Oil HAGO (a) and LVGO (b).

I.2. Commercial Distillation Test Results

Table 2 summarizes the operating conditions in the FCC feed hydrotreating section during the commercial test with and without processing H-Oil heavy distillates in the FCC feed hydrotreater stabilization column.

Table 1. Operating conditions during the commercial test without (Case 1) and with (Case 2) processing of H-Oil heavy distillates in the FCC feed hydrotreater stabilization column.

Process Parameters in the FCC Feed Hydrotreating Section	Unit	Case 1	Case 2
Charge heater inlet temperature	°C	339	340
Inlet pressure in the charge heater	bar	44	44
First hydrotreating reactor inlet temperature	°C	357	357
First hydrotreating reactor inlet pressure	Bar (g)	41	41
Inlet temperature in the heater, heating the stabilization column feed	°C	301	302
Stabilization column feed inlet temperature	°C	374	375
Stabilization column top temperature	°C	100	100
Stabilization column first packing bed temperature	°C	182	175
Stabilization column second packing bed temperature	°C	293	298
Stabilization column bottom temperature	°C	359	355
Stabilization column top pressure	Bar (g)	0.39	0.4
Stabilization column bottom pressure	Bar (g)	0.52	0.52

Steam rate in the bottom of the stabilization column	kg/h	3852	3952
Steam rate in the stripping column	kg/h	120	120
Hydrotreated VGO (bottom) product temperature	°C	374	376
Fuel gas rate in the heater, heating the stabilization column feed	Nm ³ /h	1562	1779
Stabilization column wash oil rate	m ³ /h	9	11.6
First pump around rate (below the first packing bed)	m ³ /h	127	125
Second pump around rate (below the second packing bed)	m ³ /h	30	31
First pass rate during the heater, heating the stabilization column feed	m ³ /h	72	69
Second pass rate during the heater, heating the stabilization column feed	m ³ /h	68	69
Third pass rate during the heater, heating the stabilization column feed	m ³ /h	83	83
Fourth pass rate during the heater, heating the stabilization column feed	m ³ /h	74	77
Fifth pass rate during the heater, heating the stabilization column feed	m ³ /h	131	126
Sixth pass rate during the heater, heating the stabilization column feed	m ³ /h	134	128
Feed flow rate of the FCC feed hydrotreating section	t/h	160	160
Flow rate of H-Oil heavy distillate blend	t/h	0	39
Percent of opening the valve providing recycling during the heater, heating the stabilization column feed	%	19	3

It is evident from the data in Table 1 that the operating conditions in the FCC feed hydrotreating section were almost the same for both studied cases. This may imply that any additional quantity of produced diesel in the FCC feed hydrotreating section should come from the additional H-Oil VGO blend processed in the stabilization column.

Table 2 presents data of the material balance of the LNB FCC feed hydrotreating section for both studied cases in this research: Case 1—without processing H-Oil heavy distillates (VGO = vacuum gas oil); and Case 2—with processing H-Oil VGO. The data in Table 2 indicates that the processing of 39 t/h H-Oil VGO blend resulted in 3.4 t/h higher amount of produced diesel fraction from the FCC feed hydrotreating section. This equals to 8.7 wt.% of the H-Oil VGO processed in the FCCPT stabilization column.

Table 3 presents data for the characteristics of FCCPT feed, HTVGO, and diesel, and those of the H-Oil heavy distillates measured by the ASTM D 1160 and the ASTM D 7169 methods for Case 2. It is worth mentioning here that the characteristics of the FCCPT feed, HTVGO, and diesel for Case 1 were identical with those of Case 2. The data in Table 3 indicates again a very big difference in the content of diesel fraction (boiling $\leq$ 360 °C) in the H-Oil VGO blend, that is additionally processed in the FCCPT stabilization column, measured by ASTM D 7169 (9.6 wt.%) and by the ASTM D 1160 (1.7 vol.%). If one takes a look at the data in Table 3, it can be seen that the additional amount of diesel separated from the FCCPT stabilization column, that comes from the H-Oil VGO blend, presents 8.7 wt.%

of the H-Oil VGO processed in the column. This value is very close to that measured by the ASTM D 7169 and too far from the value reported by the ASTM D 1160 method. It should be pointed out here that the characteristics of the diesel fraction separated from the FCCPT stabilization column and the following stripping column were the same for both studied cases. This means that the increased quantity of produced diesel fraction from the FCCPT stabilization column and the following stripping column comes from the increased content of diesel fraction in the H-Oil VGO blend.

Table 2. Quantity of feeds and products of the FCCPT (FCC feed pretreater) obtained during the commercial test without (Case 1) and with (Case 2) processing of H-Oil heavy distillates in the FCC feed hydrotreater stabilization column.

FCCPT Feed Component Flow Rate	Without H-Oil VGO Processing in the FCCPT Stabilization Column (Case 1)		With H-Oil VGO Processing in the FCCPT Stabilization Column (Case 2)		Δ Diesel fraction, t/h	% of Δ Diesel Fraction of H-Oil VGO Processed in the FCCPT Stabilization Column
FCCPT VGO feed rate, t/h	160		160			
H-Oil VGO entering in FCCPT stabilization column, t/h			39			
Hydrogen make up, t/h	0.85		0.83			
FCCPT Products	t/h	yields, wt. %	t/h	yields, wt. %		
FCCPT gas flow rate, t/h	1.1	0.7	1.2	0.7		
FCCPT H ₂ S flow rate, t/h	3.8	2.4	3.7	2.3		
FCCPT naphta flow rate, t/h	2.1	1.3	1.8	1.2		
FCCPT diesel flow rate, t/h	16.6	10.4	20.0	12.5	3.4	8.7
Hydrotreated VGO flow rate, t/h	137.0	85.6	172.9			
Losses, t/h	0.2	0.1	0.2			

Table 3. Characteristics of FCCPT feed, HTVGO and diesel, and those of the H-Oil heavy distillates, measured by ASTM D1160 and the ASTM D7169 methods for Case 2.

Parameter	FCCPT Feed	FCCPT Diesel	FCCPT HTVGO	H-Oil VGO Blend	H-Oil HVGO	H-Oil LVGO	H-Oil HAGO
Density at 15 °C, g/cm ³	0.93	0.89	0.91	0.94	0.95	0.95	0.93
Sulphur, wt. %	2.08	0.11	0.21	0.61	0.79	0.63	0.54
Distillation, wt. %/°C	ASTM D 7169						
0.5	349	213	348	320	397	317	313
5	367	240	365	347	416	341	342
10	381	260	377	361	429	354	355
30	418	303	411	397	463	390	386
50	446	330	439	428	489	419	410
70	485	352	474	466	515	452	438
90	535	397	525	524	553	515	495
95	561	434	551	556	577	543	531
99.5	638	521	615	633	655	593	625
Recovery, %	104.8	88.9	104.2	103	112.1	101.4	100.2

Boiling up to 360 °C, wt.%	3.3	76.4	3.7	9.6	0	13	12.8
Distillation, wt.%/°C				ASTM D 1160			
0.05	373	225	376	343	426	271	324
5	394	282	394	374	456	366	374
10	404	297	404	386	463	377	382
30	432	330	426	411	483	405	403
50	459	345	450	434	495	425	416
55	467	349	458	442	500	428	422
60	475	353	465	449	506	438	427
65	482	358	471	459	511	447	434
70	490		478	466	518	456	441
80	505		495	483	529	476	456
85	515		506	494	536	487	466
90	525		519		543	496	477
Boiling up to 360 °C, wt.%	0	66.9	0	1.7	0	4.5	1.1

Table 4. FCC section operating conditions and FCC yields registered for Case 1 and Case 2

Parameter	Case 1	Case 2
	Without H-Oil Diesel Separation	With H-Oil Diesel Separation
FCC feed rate, t/h	174	173
H-Oil VGO in FCC feed, wt.%	21.8	20.6
H-Oil diesel in FCC feed, wt.%	2	0
Riser outlet temperature, °C	550	550
Combined feed temperature, °C	313	318
Regenerator dense bed temperature, °C	704	703
Regenerator dilute bed temperature, °C	692	691
Air rate for coke burning, kNm ³ /h	105.3	106.3
CTO ratio	9.59	9.68
Heat of reaction, kJ/kg	599	617
Delta coke, wt.%	0.54	0.54
Yields and conversion, wt.%		
Dry gas	5.69	5.82
C3 fraction	8.59	8.62
C4 fraction	14.00	14.16
Gasoline	43.9	44.14
LCO	7.71	7.01
HCO	8.81	9.36
Slurry oil	6.05	5.68
Coke	5.22	5.21
Losses	0.03	0.01
Total	100.00	100.00
Conversion	77.43	77.96

I.3. Distillation Process Simulation Results

The feed for the FCCPT stabilization column has been reconstituted on the base of data for the distillation characteristics, the density of the liquid products, and the individual

component composition of the gaseous products. Three cases were simulated: Simulation Case 1 using ASTM D 86 for wild naphtha, and diesel distillation data characterization, and simulated distillation ASTM D 2887 extended for the stabilized HTVGO characterization; Simulation Case 2 with the H-Oil VGO blend, and the stabilized HTVGO (the bottom product from the FCCPT stabilization column) distillation characteristics measured by the ASTM D 1160; and Simulation Case 3 with the H-Oil VGO blend, and the stabilized HTVGO distillation characteristics measured by the ASTM D 7169 method. Characteristics of the hydrocarbon gas product, the wild naphtha, the diesel fraction, and the stable hydrotreated VGO for the three studied simulation cases are presented in Tables 5–8. It is evident from the data in the Tables 5–7 that the distillation characteristics of the wild naphtha, the diesel fraction, and the stabilized hydrotreated VGO (HTVGO) are almost the same, that is an indicator of the same efficiency of fractionation for all studied cases.

It is interesting to note that the sulphur content in the diesel fraction and the HTVGO is higher in Case 2 due to the higher sulphur content in the H-Oil VGO blend. This is also an indicator that the diesel fraction in Case 2 contains material from the H-Oil VGO blend

Table 5. Basic properties of the wild naphtha from FCCPT for Case 1 and Case 2.

Wild naphtha product from FCCPT			
Parameter / Method	Units	Value	
		Case 1	Case 2
Density at 15 °C, BDS EN ISO 3675	kg/m ³	766	759.4
Distillation curve acc. to BDS EN ISO 3405 (equivalent to ASTM D86)			
Initial Boiling Point	°C	37.8	38.5
5%	°C	83.5	85.8
10%	°C	96.1	95.3
50%	°C	133.6	129.8
90%	°C	169.9	163.8
95%	°C	178.5	170.9
End boiling point	°C	194.8	178.3
Recovery	vol. %	98.5	97.8

Table 6. Basic properties of the diesel fraction from FCCPT for Case 1 and Case 2.

Diesel fraction, product from FCCPT			
Parameter / Method	Units	Value	
		Case 1	Случай 2
Density at 15 °C, BDS EN ISO 3675	kg/m ³	891,2	889,4
Sulfur content, ASTN D 4294	wt. %	0.0301	0.105
Distillation curve acc. to BDS EN ISO 3405 (equivalent to ASTM D86)			
Initial Boiling Point	°C	220.6	217.6
5%	°C	242.1	241.3
10%	°C	255.4	255.2

50%	°C	321.4	323.6
90%	°C	355.9	356.4
95%	°C	-	364.8
Boiling above 360 °C	vol.%		

Table 7. Basic properties of the HTVGO (hydrotreated vacuum gasoil) from FCCPT for Case 1 and Case 2.

Hydrotreated Vacuum Gas Oil, product from FCCPT			
Parameter / Method	Units	Value	
		Case 1	Случай 2
Microcarbon content, BDS EN ISO10370	wt.%		0.12
Density at 15 °C, BDS EN ISO 3675	kg/m ³	901.1	910
Sulfur content, ASTN D 4294	wt.%	0.085	0.207
Distillation curve acc. to ASTM D 2887ext			
5%	°C	353	351
10%	°C	371	366
50%	°C	440	434
90%	°C	517	513
95%	°C	536	531

Table 8. Basic properties of the hydrocarbon gas from FCCPT for Case 1 and Case 2.

Method	Property	Case 1	Case 2
BDS EN ISO 6976	Density at 20 °C, kg/m ³	1.223	1.239
Proprietary (LNB)	Hydrogen, vol.%	23.7	23.1
Proprietary gas chromatography method (LNB)	CO ₂ , vol.%	<0.1	<0.1
	Oxygen, vol.%	0.5	0.5
	Nitrogen, vol.%	1.7	1.8
	Methane, vol.%	22.3	21.8
	CO, vol.%	<0.1	<0.1
Proprietary gas chromatography method (LNB)	C ₂ H ₆ , vol.%	17.6	17.8
	C ₂ H ₄ , vol.%	<0.1	<0.1
	C ₃ H ₈ , vol.%	15.9	16.6
	C ₃ H ₆ , vol.%	0.1	<0.1
	Σ C ₄ hydrocarbons, vol.%	10.2	10.5
	Σ C ₅ hydrocarbons, vol.%	4.6	4.7
	Σ C ₆ hydrocarbons, vol.%	3.4	3.2
	H ₂ S, ppmv	-	0.9
	Σ Sulfur compounds, ppmv	-	8.5

Table 9. Basic properties of the Vacuum Gas Oil from FCCPT for Case 1 and Case 2

Vacuum Gasoil, feed to FCCPT			
Parameter / Method	Units	Value	
		Case 1	Случай 2
Density at 15 °C, BDS EN ISO 3675	kg/m ³	923.9	927.3
Sulfur content, ASTN D 4294	wt. %	2.05	2.08
Microcarbon content, BDS EN ISO10370	wt. %	0.34	0.37
Distillation curve acc. to ASTM D 2887ext			
5%	°C	354	354
10%	°C	372	372
50%	°C	445	444
90%	°C	525	523
95%	°C	542	540

I.4. Discussion of the results from the performed studies

The proper characterization of petroleum oils is important not only for distillation column design but also for correct evaluation of the existent separation equipment performance [2-4]. *Kaes* [1] states that an ASTM D 1160 apparatus can be used to extend the crude TBP data. He pointed out that the ASTM D 1160 distillation better approximates a TBP distillation because it is carried out under vacuum; can distill heavier materials than a TBP; much simpler to run than TBP; and it is the best test for refinery vacuum distillation unit calculations [1]. *Kaes* considers the gas chromatographic simulated distillation method to be an unreliable method for conversion to TBP curve, and due to the fact that it derives the boiling data by using standard mixtures of n-paraffins, it is deemed to report inaccurate results for streams with significant aromatic content [1].

Golden et al. [2 – 4], however, argue that the use of the ASTM D 1160 method is worse than employing inaccurate TBP data in the design process of a vacuum distillation column. They conclude that few designers know the proper feed characterization techniques, including the use of a modern ASTM D 7169 chromatographic method. *Golden et al.* summarize that more than 50 vacuum distillation units have been field tested to confirm the validity of using ASTM D 7169 as a TBP curve to model crude and vacuum distillation unit operation [5].

The data shown in Figure 2 appear similar to the comparison of distillation curves of the ASTM D 86 and the simulated distillation (ASTM D 2887) reported by Riazi [6]. The data in Figure 2 also look similar to the ASTM D 86 and TBP curves reported by Riazi [6]. Both the TBP and simulation distillation curves lie below the ASTM D 86 and the ASTM D 1160 curves for evaporation lower than 50% and lie above these curves for evaporation higher than 50%. Riazi [6] argues that the ASTM D 86 distillation data do not represent actual boiling point of components in a petroleum fraction, while the TBP, due to the high degree of fractionation, gives accurate component distribution for mixtures. Riazi also

concludes that ASTM D 1160 distillation data is measured more accurately than ASTM D 86 since it is conducted at low pressure [7]. For this reason, ASTM D 1160 curves are closer to TBP curves at the same pressure base. Nevertheless, the similar appearance of the difference in the distillation curves between TBP and ASTM D 86 and that observed in the data of Figure 2 for ASTM D 7169 and ASTM D 1160 may suggest that ASTM D 7169 could be closer to TBP than the ASTM D 1160. Moreover, in earlier research [8], it was proven that the simulated distillation method ASTM D 2887 is equivalent to TBP, even for high aromatic oils like the fluid catalytic cracking light and heavy gas oils. All these findings suggest that the gas chromatographic HTSD (ASTM D 7169) should be closer to the TBP than the physical vacuum distillation method ASTM D 1160, and therefore, it should better characterize the heavy petroleum fractions.

The data in Table 1 show that the LNB FCC feed hydrotreating section operated at the same conditions in the hydrotreating reaction section (the same reaction temperature = 357 °C; the same feed rate = 160 t/h; and the same reaction pressure = 41 bar (g)) for both studied cases. Considering the same quality of the feed for the LNB FCC feed hydrotreating section (see the data in Table 9), one can expect the same vacuum gas oil conversion to take place in the hydrotreating reaction section, and thus, the same amount of generated diesel fraction in this section for both studied cases. Therefore, a different diesel fraction quantity registration in both cases must be ascribed to a separation of an additional amount of diesel fraction from the H-Oil VGO blend processed in the stabilization column during Case 2. The higher fuel gas consumption in the heater, heating the stabilization column feed during Case 2 suggests a higher extent of evaporation occurring in the stabilization column feed during Case 2, which could be due to a higher amount of low boiling material in the column feed in Case 2. The higher total fluid flow rate in Case 1, irrespective of the lower throughput (160 t/h feed rate for the FCCPT in Case 1) than in Case 2 (160 t/h feed rate for the FCCPT reaction section plus 39 t/h H-Oil VGO blend in the stabilization section), can be explained by the higher percent of recycling of stabilized HTVGO through the heater. This is evident from the higher percent of opening the valve providing recycling during the heater for Case 1.

The data in Tables 2 and 3 indicate much better agreement between the separated diesel fraction from H-Oil VGO blend (8.7 wt.%) in the FCCPT stabilization column and that measured in the H-Oil VGO blend by ASTM D 7169 (9.6 wt.%) than the measured by ASTM D 1160 diesel fraction content in the H-Oil VGO blend (1.7 vol.%). These results support the opinion of *Golden et al.* [2–4] that the gas chromatographic method ASTM D 7169 better characterizes heavy oils than the ASTM D 1160 method. The separation efficiency of the FCCPT stabilization column seems to be higher than that of the ASTM D 1160 apparatus, and it is better matched to the ASTM D 7169 method.

The data in Table 4 exhibit that the removal of the diesel fraction from the H-Oil VGO has a positive effect on the FCC unit performance leading to increased conversion by 0.53% that along with the increased diesel production in the FCCPT section resulted in

improved refinery performance expressed by increased margin with 7.2 MM USD/year (2022 basis).

I.5. Conclusions from the performed studies

The distillation characterization of heavy oils is an important petroleum characterization method because it provides information about the quality of separation taking place in the oil refining distillation columns. It is also important for the design of new separation equipment. Laboratory physical vacuum distillation tests (ASTM D 1160) and gas chromatographic simulated distillation analyses are typically used to evaluate the efficiency of separation occurring in the oil refining distillation columns which separate mixtures containing heavy oils. These laboratory methods are reported in the literature to be used for the design of new separation equipment. The results of this study support the opinion expressed by some researchers that the HTSD (ASTM D 7169) is superior for the characterization of heavy oils than the physical vacuum distillation test ASTM D 1160. The commercial test performed at a commercial FCC pretreater stabilization column showed that the yield of diesel fraction separated from a H-Oil VGO blend better matched to the content of this fraction in the H-Oil VGO blend measured by the ASTM D 7169 method than that measured by the ASTM D 1160 method. The better distillation characterization of the heavy oils by the ASTM D 7169 method was also confirmed by the use of software process simulator, demonstrating much better agreement between simulation results with the field observations than those obtained during the use of the ASTM D 1160 method. A conclusion could be made that the ASTM D 7169 method could be considered equivalent to TBP for heavy oils boiling above 360 °C.

Irrespective of the higher costs for single measurement by the ASTM D 7169 method, this method can deliver a substantial improvement in oil refining margin, which outweighs the costs many times over. Thus, we would consider using the ASTM D 7169 method instead of the ASTM D 1160 in our oil refining practice from now on.

II. Prediction of Molecular Weight of Petroleum Fluids by Empirical Correlations and Artificial Neuron Networks

Goosens [9] mentioned in his work that a great number of petroleum fluid molecular weight correlations exhibited marked deviations beyond molecular weights of 300 g/mol. That was the reason for us to select a data base with a very wide range of variation of molecular weight, boiling points, and specific gravity. Figure 1 shows a graph of dependence of molecular weight on boiling point for the selected data base of 430 petroleum fluids and individual hydrocarbons. It is evident from this data that molecular weight exponentially increases with boiling point augmentation. It can be also seen that some individual polynuclear aromatic hydrocarbons deviate from the general exponential dependence, displaying lower molecular weight at the same boiling point.

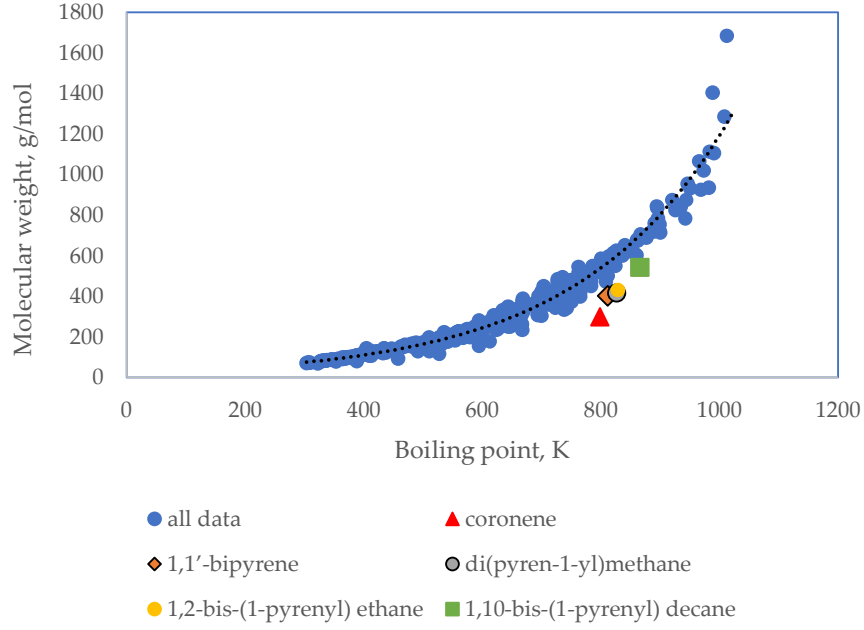


Figure 3. Dependence of molecular weight on boiling point for petroleum fluids and individual hydrocarbons..

The specific gravity, which well reflects the aromatic structure content [10], accounts for this deviation of the polynuclear aromatic compounds from the general exponential dependence of molecular weight on boiling point. By the use of CAS Maple and NLPsolve with Modified Newton Iterative Method and 306 points out of 430, the following new empirical correlation was developed:

$$MW = -552.982 + 453.095 * \exp\left(0.19239 * \exp\left(0.000421163 * \frac{BP^{1.22097}}{SG^{0.297075}}\right)\right) \quad (1)$$

where,

BP = boiling point of the petroleum fluid or individual hydrocarbon, K;

SG = specific gravity at 15.6 °C.

The remaining 124 data points were used to test the validity of Equation (1).

For the development of the artificial neural network, a 3-layer deep learning neural net-work with a structure of 9 inputs (SG, BP, T5%, T10%, T30%, T50%, T70%, T90%, and Kw), 12 neurons in the first layer, 1 neuron in the output layer, and 1 output was used.

Table 10. Statistical analysis of studied methods to predict petroleum fluid molecular weight for the whole range of studied molecular weights.

	Standard Error	Rel. st. Error	Sum of Squarred Errors	%AAD	SRE
ANN	23.0	7.2	1.6	4.3	-126.8
New empirical correlation (this work)	34.8	10.9	3.4	6.4	695.5
Hosseiniifar (2021)	84.4	26.6	8.6	9.4	-1851.7
Goosens (1996)	44.1	13.9	4.5	7.6	1970.2
Riazi and Daubert MW $\leq$ 700 g/mol (2005)	48.3	15.2	3.9	6.3	358.2
API (2011)	39.3	12.4	5.1	8.6	-999.1
Liñan (2011)	54.4	17.1	10.2	11.3	-2973.1
Twu (1986)	96.4	30.3	20.6	18.7	7840.0
Lee-Kesler (1976)	84.2	26.5	7.1	9.7	345.9
Riazi and Daubert $\leq$ 300 g/mol (2005)	117.3	36.9	12.4	12.5	4155.7
Lemus et al. (2016)	103.0	32.4	14.0	10.8	864.9
Soreide (1989)	84.1	26.5	12.2	9.4	-598

The data in Table 10 indubitably indicates that the ANN method provides the best accuracy of molecular weight prediction of petroleum fluids, following by the new empirical correlation developed in this work. If one compares the data for accuracy of molecular weight prediction of the methods tested in this work with the 430 petroleum fluid sample points with those reported by the authors who have developed the correlations, some discrepancies will be seen:

- *Goosens* [9] reported standard deviation for his method of about 2%, while the relative standard error (that can be assumed equivalent to the standard deviation shown in Table 10) is 13.9%.
- The %AAD of *Riazi and Daubert* MW $\leq$ 700 g/mol was reported as 4.7 [7], while that shown in Table 10 for this method is 6.3%.
- *Liñan et al.* [11] reported %AAD of 2.2, while that shown in Table 10 for this method is 11.3.
- *Lemus et al.* [12] reported %AAD of 5.3, while that shown in Table 10 for this method is 10.8.

The reason for these discrepancies may lie in the range for which the discussed correlations were developed, confirming again the statement of Schneider [13] that any molecular weight correlation should not be extended beyond the limits for which it is valid. Considering that some of the tested correlations were developed for a narrower range of boiling point and molecular weight variations, a statistical analysis of the studied methods was performed for the petroleum fluids whose molecular weight is $\leq$ 300 g/mol.

Table 11 presents data of standard error, relative standard error, and %AAD for the predictive methods employing only these petroleum fluid data whose molecular weight is ≤ 300 g/mol.

Table 11. Statistical analysis of studied methods to predict molecular weight for petroleum fluids and individual components whose molecular weight ≤ 300 g/mol.

	Standard Error	Rel. st. Error	%AAD
ANN	13.4	7.9	3.6
New empirical correlation (this work)	16.5	9.7	5.1
Hosseinifar (2021)	18.1	10.7	8.1
Goosens (1996)	17.8	10.5	5.4
Riazi and Daubert MW ≤ 700 g/mol (2005)	16.0	9.4	4.0
API (2011)	17.0	10.0	5.4
Twu (1986)	38.8	22.9	13.0
Lee–Kesler (1976)	18.3	10.8	7.3
Riazi and Daubert MW ≤ 300 g/mol (2005)	11.5	6.8	4.6
Lemus et al. (2016)	29.4	17.3	8.0
Soreide (1989)	32.0	18.8	7.6

The data in Table 11 indicates that the correlation of Riazi and Daubert MW ≤ 300 g/mol and the ANN model demonstrate the highest accuracy in molecular weight prediction, followed by the new correlation developed in this work. It is worth mentioning here that a great part of the data points which have molecular weight ≤ 300 g/mol 83 points out of 240 (35%), is taken from Riazi's work [14]. Therefore, the highest accuracy of the correlation of Riazi and Daubert MW ≤ 300 g/mol may be attributed to this fact.

It is also worth noting here that the accuracy of prediction of the lower molecular weight petroleum fluids (MW ≤ 300 g/mol) is understandably higher than that of the higher molecular weight petroleum fluids (MW ≥ 300 g/mol), because the heavy oil molecular weight is measured with a lower exactitude. Nevertheless, the correlations developed on the basis of extended molecular weight range also exhibit a satisfactory prediction for the lower molecular weight petroleum fluids (see, for example, the data for the ANN model, the new correlation, and Riazi and Daubert MW ≤ 700 g/mol from Table 11).

The ANN molecular weight model developed in this research, as shown in the data in Tables 10 and 11, distinguishes with the highest accuracy of prediction among all investigated empirical correlations. These findings support the opinion of *Hadavimoghaddam et al.* [15] that the artificial intelligence models provide the lowest average absolute relative error of petroleum property prediction. The use of *Hosseinifar and Shahverdi* [16] method to generate seven additional inputs for the ANN showed again that it is a successful approach to model not only viscosity, as reported in recent research [17], but also molecular weight of petroleum fluids.

The data in Table 10 indicates that the new empirical correlation (Equation (1)) demonstrates the best accuracy among the other empirical correlations available in the literature when the whole data base of 430 points is concerned. Then the correlations of *Goosens*, *Riazi and Daubert*, and that of *API* distinguish with better accuracy in molecular weight prediction than the remaining seven correlations. However, the new correlation (Equation (1)) and those of *Goosens* and *Riazi and Daubert* have been developed based on a great amount of data. That is why their comparison with data not included in their development may give a better indication of their molecular weight prediction ability. This was performed with 124 data points, and the statistical analysis of this comparison is summarized in Table 12.

Table 12. Statistical analysis of the new empirical correlation developed in this work, and of the correlations of *Goosens*, *Riazi and Daubert*, and *API* with 124 data points not used in their development.

	Standard Error	Rel. st. Error	%AAD
New empirical correlation (this work, test data)	42.1	11.6	8.8
Goosens (1996)	56.7	15.6	12.1
Riazi and Daubert MW $\leq$ 700 g/mol	52.7	14.5	8.7
API (2011)	47.1	13.0	9.0

The data in Table 12 again confirms the best performance of Equation (1) among the empirical correlations. It deserves mentioning here that 52 data points (42%) of all tested 124 data points were reported to be measured with repeatability of 15% [7]. This could explain the higher inaccuracy of molecular weight prediction for this test data set compared with that observed for the whole 430 data points and shown in Table 10.

The measurement of molecular weight of heavy oils is a difficult task associated with an error of about 15%. Thus, the correlations which satisfactorily predict molecular weight of various petroleum fluids can be an appropriate substitute for measurement.

Among the correlations existing in the literature examined in this work, three distinguished with a better precision of prediction: *Goosens*, *Riazi and Daubert*, and *API*. The new correlation developed in this work using a nonlinear regression technique demonstrated a higher accuracy of molecular weight prediction than that of the three correlations mentioned above. However, the molecular weight prediction by the ANN three-layered neural network with a back-propagation teacher model exhibited much better exactitude than the new nonlinear regression correlation. This observation confirms again that the ANN method can predict petroleum properties with a higher accuracy than the regression correlations.

Contrary to some statements in the literature that the other correlations developed after those of Lee–Kesler and Twu are not superior, the results of this research showed that the correlations of *Goosens*, *Riazi and Daubert*, *API*, and the new correlation predicted the molecular weight with a higher accuracy.

III. Comparison of the Methods for Predicting the Critical Temperature and Critical Pressure of Petroleum Fractions and Individual Hydrocarbons

The database of 176 pure hydrocarbons, critically evaluated by Hajipour and Satyro [18], was used for the purposes of this study. The five input variables used for the critical temperature (T_c) and critical pressure (P_c) predictions were: boiling point (T_b), specific gravity (SG), molecular weight (MW), H/C atomic ratio, and acentric factor (ω). The evaluation of the ICrA of the data for these variables, along with the data for the critical temperature in terms of μ and ν -values, is summarized in Tables 13 and 14.

Table 13 μ -values from the ICrA evaluation of the data for the 176 pure hydrocarbons used in this research for the purpose of modeling the critical temperature.

μ	T_b (K)	SG	MM	H/C ratio	ω	T_c (K)
T_b (K)	1.00	0.77	0.89	0.31	0.81	0.94
SG	0.77	1.00	0.69	0.14	0.62	0.81
MM	0.89	0.69	1.00	0.39	0.82	0.86
H/C ratio	0.31	0.14	0.39	1.00	0.40	0.28
ω	0.81	0.62	0.82	0.40	1.00	0.77
T_c (K)	0.94	0.81	0.86	0.28	0.77	1.00

Table 14 ν -values from the ICrA evaluation of the data for the 176 pure hydrocarbons used in this research for the purpose of modeling the critical temperature.

ν	T_b (K)	SG	MM	H/C ratio	ω	T_c (K)
T_b (K)	0.00	0.77	0.89	0.31	0.81	0.94
SG	0.77	0.00	0.69	0.14	0.62	0.81
MM	0.89	0.69	0.00	0.39	0.82	0.86
H/C ratio	0.31	0.14	0.39	0.00	0.40	0.28
ω	0.81	0.62	0.82	0.40	0.00	0.77
T_c (K)	0.94	0.81	0.86	0.28	0.77	0.00

The data in Tables 13 and 14 indicate that, except for the H/C atomic ratio, all four of the other properties have positive consonance with the critical temperature and, therefore, can be used for the purpose of critical temperature modeling. More precisely, the pairs T_b (K)— T_c (K): $\langle 0.94, 0.04 \rangle$ and MW— T_c (K): $\langle 0.86, 0.09 \rangle$ are in positive consonance, while the pairs SG— T_c (K): $\langle 0.81, 0.15 \rangle$ and Omega— T_c (K): $\langle 0.77, 0.17 \rangle$ are in weak positive consonance. The pair H/C ratio— T_c (K): $\langle 0.28, 0.59 \rangle$ is in weak dissonance. The properties of the H/C ratio— T_c (K) pair are neutral and independent—they do not have dependencies or opposite behavior. Therefore, the relationships/similarity properties between T_c (K) and T_b (K), MW, SG, and Omega are close, positive, and stable. This allows us to conclude that they can be used for the purpose of critical temperature modeling. The geometrical

interpretations of intuitionistic fuzzy sets (IFSs) are explained in ref. [19]. The results from ICrA have the form of the intuitionistic fuzzy pairs (IFPs), containing degree of membership and degree of non-membership (degrees of agreement and degrees of disagreement), and are visualized in the IFS interpretational triangle. A discussion and visualization of the ICrA results according to the scale from strong positive consonance to strong negative consonance is presented in ref. [20]. The μ - and ν -values from the ICrA evaluation of the data for the 176 pure hydrocarbons used in this research for the purpose of modeling the critical temperature (Tables 13 and 14) are visualized into the interpretational intuitionistic fuzzy triangle presented in Figure 4.

The evaluation of the ICrA of the data for the same variables, along with the data for the critical pressure in terms of the μ - and ν -values, is summarized in Tables 15 and 16.

It is evident from the data in Tables 15 and 16 that the boiling point, the molecular weight, and the acentric factor have negative consonances with the critical pressure. Unlike the critical temperature, where the specific gravity has a positive consonance, in the case of the critical pressure, the specific gravity is in a dissonance with it. The H/C ratio, similar to the critical temperature, is in dissonance with the critical pressure as well. Similar to the ICrA evaluation of variables that can affect the critical temperature, the μ - and ν -values from the ICrA evaluation of the data for the 176 pure hydrocarbons used in this research for the purpose of modeling the critical pressure are visualized in Figure 5.

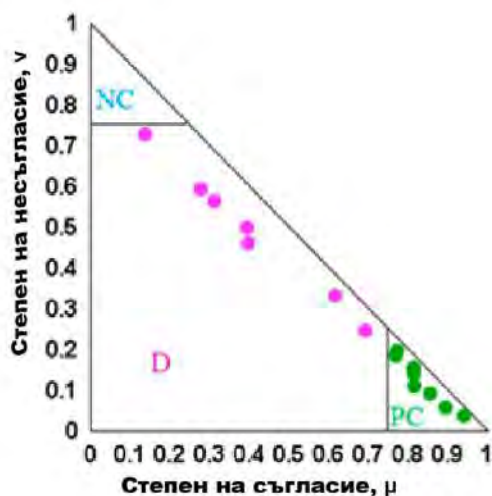


Figure 4. Results of the ICrA application for critical temperature visualized in the intuitionistic fuzzy interpretational triangle.

Table 15. μ -values from the ICrA evaluation of the data for the 176 pure hydrocarbons used in this research for the purpose of modeling the critical pressure.

μ	T_b (K)	SG	MM	H/C ratio	ω	P_c (kPa)
T_b (K)	1.00	0.77	0.89	0.31	0.81	0.24
SG	0.77	1.00	0.69	0.14	0.62	0.45
MM	0.89	0.69	1.00	0.39	0.82	0.17
H/C ratio	0.31	0.14	0.39	1.00	0.40	0.35
ω	0.81	0.62	0.82	0.40	1.00	0.14
P_c (kPa)	0.25	0.45	0.17	0.35	0.14	1.00

Table 16. ν -values from the ICrA evaluation of the data for the 176 pure hydrocarbons used in this research for the purpose of modeling the critical pressure.

ν	T_b (K)	SG	MM	H/C ratio	ω	P_c (kPa)
T_b (K)	0.00	0.19	0.06	0.56	0.14	0.73
SG	0.19	0.00	0.24	0.73	0.33	0.52
MM	0.06	0.24	0.00	0.50	0.11	0.77
H/C ratio	0.56	0.73	0.50	0.00	0.46	0.52
ω	0.14	0.33	0.11	0.46	0.00	0.81
P_c (kPa)	0.75	0.52	0.77	0.52	0.81	0.00

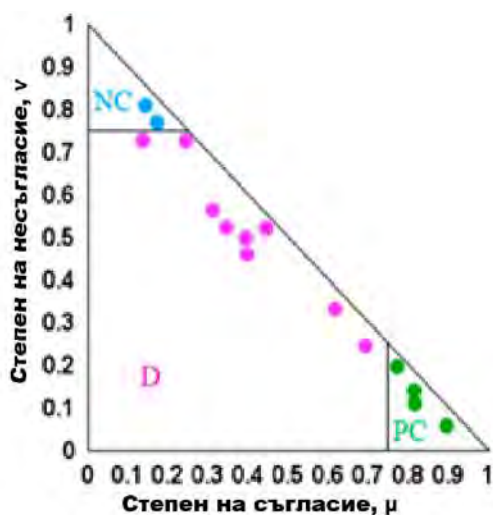


Figure 5. Results of the ICrA application for critical pressure visualized in the intuitionistic fuzzy interpretational triangle.

The data points in positive consonance are presented in the bottom right angle of the intuitionistic fuzzy interpretational triangle in Figure 5. The data points in positive consonance (PC) are visualized with green color. The data points in negative consonance (NC) are presented in the upper left angle of the intuitionistic fuzzy interpretational triangle.

The data points in negative consonance are colored in blue. All other points are marked in dissonance (D). They are presented in pink color in Figures 4 and 5.

After regression of the data, the following empirical correlations for predicting the critical temperature and critical pressure were developed:

$$T_c = \exp(2.80205583 - 0.04315009 \ln(MW) \ln(SG)) NBP^{0.642034} SG^{0.562092} MW^{-0.037658} \quad (2)$$

$$P_c = \exp(4.32148877 - 0.40020677 \ln(MW) \ln(NBP)) NBP^{1.22481398} SG^{1.7724661} MW^{1.72111379} \quad (3)$$

Where:

MW is the molecular weight of the hydrocarbon, kg/kmol;

SG is the specific gravity of the hydrocarbon at 15.6 °C;

NBP is the normal boiling point of the hydrocarbon, K;

T_c is the critical temperature of the hydrocarbon, K;

and P_c is the critical pressure of the hydrocarbon, kPa.

Non-linear regression with least squares fitting was employed to develop the new correlations for predicting critical temperature T_c and critical pressure P_c . The R^2 scores of these correlations are as follows:

- Critical Temperature Correlation (2): $R^2 = 0.9955$.
- Critical Pressure Correlation (3): $R^2 = 0.9832$.

These high R^2 values indicate excellent agreement between the predicted and experimental values, demonstrating the robustness of our new empirical models.

Figure 6 illustrates the fitness of the critical temperature predicted by the ANN versus the measured critical temperature. The ANN model demonstrates an exceptionally high accuracy in the prediction of the critical temperature, with $R = 0.99913$ and a standard error of 4.1 °C.

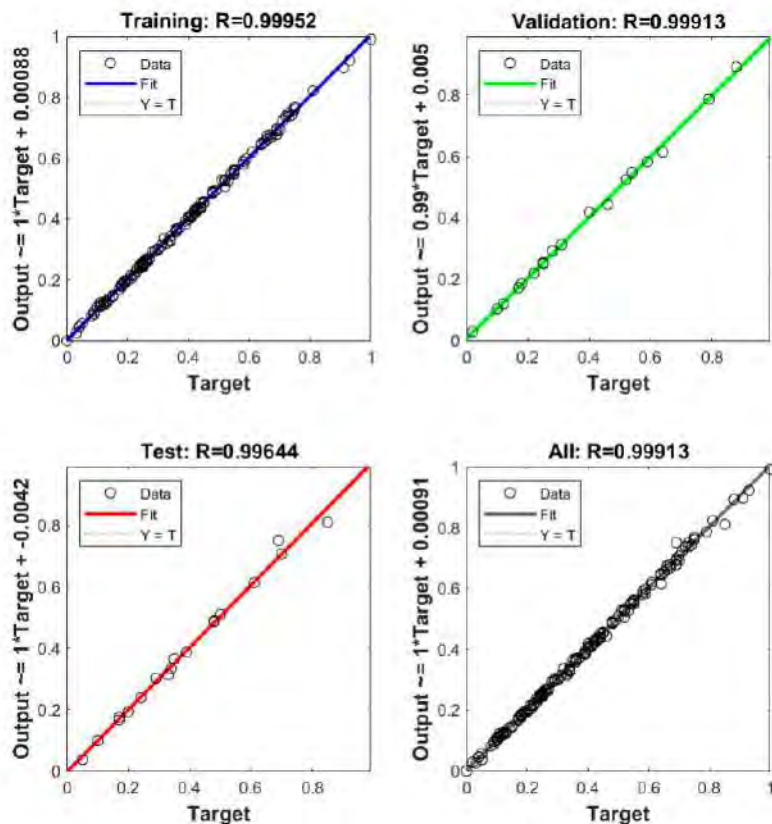


Figure 6. ANN-predicted versus experimental critical temperature values for training, validation, testing, and the overall dataset of 176 individual hydrocarbons.

As indicated in Figure 7, a mean squared error of 0.00010394 was achieved at epoch 4 of the training of ANN.

Figure 8 shows the fitness of the critical pressure predicted by the ANN versus the measured critical pressure. The ANN model demonstrates an exceptionally high accuracy in the prediction of the critical temperature, with $R = 0.99913$ and a standard error of $4.1\text{ }^{\circ}\text{C}$.

Figure 9 indicates that a mean squared error of 0.0019178 was achieved at epoch 10.

All the correlations for critical temperature and pressure estimation use two parameters—most commonly, the normal boiling point (T_b) and specific gravity (SG). In contrast, the correlations and ANN models proposed in this work introduce a third parameter: hydrocarbon molecular weight (MW). Although the molecular weight can be predicted using T_b and SG, as shown by Stratiev et al. [21], we found that incorporating MW significantly enhances the accuracy of critical property predictions.

Table 17 provides a detailed evaluation of the different correlations, along with the new correlation (Equation (2)), and the ANN model for predicting critical temperature, specifically for a selected set of hydrocarbon experimental data.

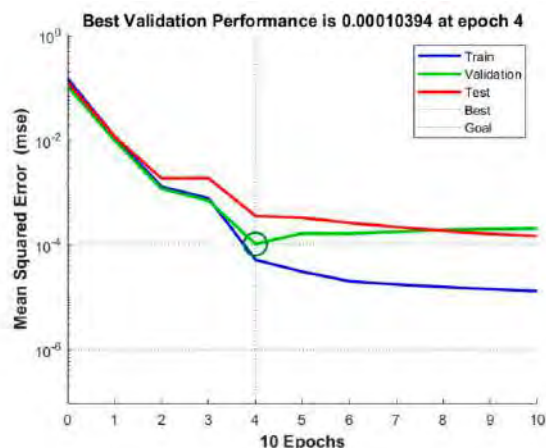


Figure 7. Neural network training performance for the prediction of critical temperature. The green circle indicates the point where the minimum mean squared error is obtained.

Table 17. Statistical analysis of the studied correlations in predicting the critical temperature of hydrocarbons.

Correlation	Standard Error	Relative Standard Error	Sum of Squared Errors	%AAD	SRE
New empirical correlation (this work)	6.94	1.1	0.0195	0.74%	-4.62
ANN model	4.1	0.66	0.006	0.39%	190.258
Winn-Mobil (1957)	9.74	1.6	0.0359	0.86%	-762.003
Cavett (1962)	9.99	1.6	0.0358	0.99%	-234.396
Lee-Kesler (1976)	7.35	1.2	0.0215	0.74%	-405.665
Riazi-Daubert (1980)	7.69	1.2	0.02341	0.75%	0.64
Riazi (1987)	8.205	1.3	0.0240	0.77%	412.145
Tsonopoulos (1986)	9.53	1.5	0.0312	0.88%	46.36
Twu (1987)	7.55	1.2	0.0212	0.73%	311.856
Lin-Chao (1984)	196.38	31.4	10.063	10.84%	-2896.87
Jianzhong et al. (1998)	7.95	1.3	0.0243	0.77%	392.453
Hosseiniifar (2014) from MW	20.84	3.3	0.1599	2.13%	-1016.19
Hosseiniifar (2014) from NBP	16.65	2.7	0.0845	1.47%	-673.57

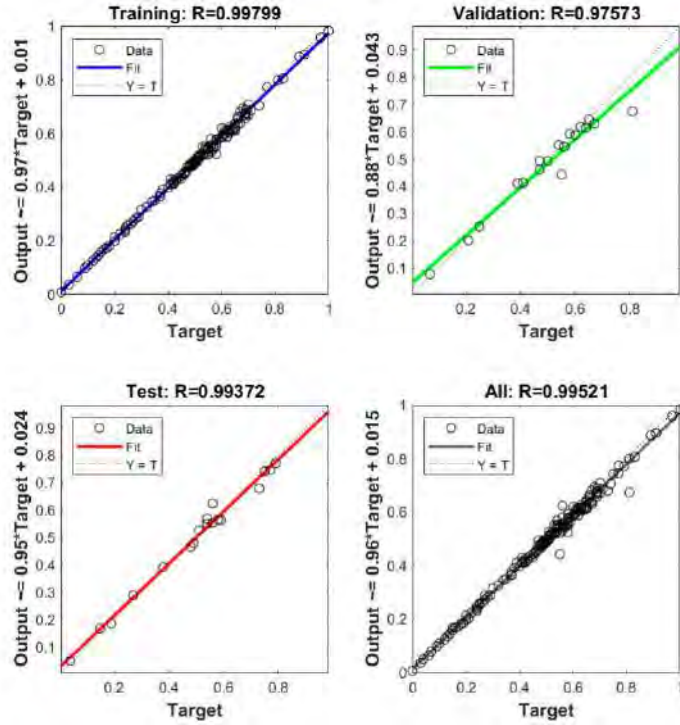


Figure 8. ANN-predicted versus experimental critical pressure values for training, validation, testing, and the overall dataset of 176 individual hydrocarbons.

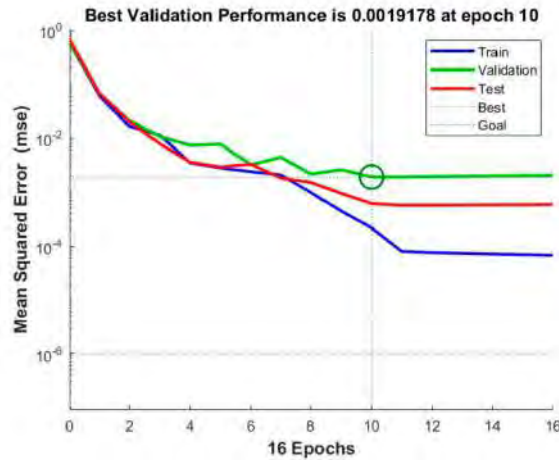


Figure 9. Neural network training performance for the prediction of critical pressure. The green circle indicates the point where the minimum mean squared error is obtained.

Table 18 provides a detailed evaluation of the different correlations, along with the new correlation (Equation (3)), and the ANN model for predicting critical temperature, specifically for a selected set of hydrocarbon experimental data.

Table 18. Statistical analysis of the studied correlations in predicting the critical temperature of hydrocarbons.

Correlation	Standard Error	Relative Standard Error	Sum of Squared Errors	%AAD	SRE
New empirical correlation (this work)	138.016	6.8	0.5317	3.39%	0.25
ANN Model	91.7	3.44	0.170	2.12%	-1.14
Winn-Mobil (1957)	182.536	6.8	1.879	5.66%	6.62
Cavett (1962)	183.363	7.3	1.611	5.02%	6.51
Lee-Kesler (1976)	160.420	6.0	1.007	4.48%	2.04
Riazi-Daubert (1980)	180.936	6.8	1.524	5.50%	0.64
Riazi (1987)	358.963	13.5	4.095	7.39%	8.06
Tsonopoulos (1986)	210.334	7.9	2.342	6.81%	4.15
Twu (1987)	689.905	25.9	7.904	14.79%	-21.50
Lin-Chao (1984)	104181.9	3907.6	328 939.3	798.89%	730.10
Jianzhong et al. (1998)	182.262	6.8	2.18	6.08%	6.11
HosseiniFar (2014) from MW	224.501	8.4	1.7616	7.16%	1.39
HosseiniFar (2014) from NBP	338.231	12.7	3.865	9.91%	-1.12

The calculated critical properties using the correlations evaluated here were utilized to perform vapor pressure predictions at each component's normal boiling point, employing the *Soave–Redlich–Kwong* (SRK) equation of state [22]. The predicted vapor pressure values were then compared to the calculated value using the database critical temperature and pressure data. The correct result for each data point is 101.325 kPa, representing normal atmospheric pressure.

A statistical analysis for each correlation method was calculated based on these vapor pressure predictions. Vapor pressure was calculated using the *Soave–Redlich–Kwong* (SRK) equation of state [22] and the *Lee–Kesler* equation of state [23], with original critical properties for comparison purposes. These equations are widely used in thermodynamic modeling, but they also have inherent errors in predicting vapor pressure. The results are summarized in Table 19, which provides a comprehensive statistical analysis of the studied correlations for predicting vapor pressure at normal boiling points for hydrocarbon components.

Table 19. Statistical analysis of the studied correlations in predicting vapor pressure at the normal boiling point for the hydrocarbon components.

Correlation	Standard Error	Relative Standard Error	Sum of Squared Errors	%AAD	SRE
SRK equation with original critical properties	2.329	6.649	0.092	1.21%	0.60
Lee-Kesler equation with original critical properties (for comparison)	1.164	-9.565	0.0229	0.61%	-0.21
New empirical correlation (this work)	8.705	20.35	1.284	6.46%	0.74
Winn-Mobil (1957)	16.482	0.889	4.604	8.13%	21.30
Cavett (1962)	14.037	1.9686	3.339	9.65%	11.00
Lee-Kesler (1976)	11.144	1.634	2.105	7.22%	10.07
Riazi-Daubert (1980)	9.473	-2.385	1.521	6.83%	-6.34
Riazi (1987)	9.532	-2.555	1.54	7.06%	-6.01
Tsonopoulos (1986)	9.611	3.818	1.565	7.16%	4.22
Twu (1987)	31.689	-1.172	17.019	20.45%	-35.59
Lin-Chao (1984)	10065.9	13.266	1687593.0	2483.99%	2373.21
Jianzhong et al. (1998)	9.165	-12.4707	1.4236	7.16%	-1.27
Hosseiniifar (2014) from MW	36.318	2.301	22.35	22.54%	25.06
Hosseiniifar (2014) from NBP	31.080	3.95	16.371	15.91%	13.19

The components which have highest deviations in the predicted properties primarily belong to the following categories:

- Branched alkenes, such as 3,3-dimethyl-1-butene and 2,3-dimethyl-1-butene.
- Cyclo-alkanes/alkenes, including cyclohexene, cycloheptane, and cyclooctane.
- Poly-substituted benzene derivatives, for example, indane, p-diisopropylbenzene, and 1,3,5-triethylbenzene.
- Poly-aromatics, such as naphthalene and 1-methylnaphthalene.
- Polycyclic compounds, including 1,1'-bicyclopentyl, decahydronaphthalene, tetralin, and triacontane.
- Heavy alkanes, like tricosane, tetracosane, hexacosane, and hexatriacontane.

The listed components show the highest deviations in critical pressure prediction. They are predominantly branched alkenes, cyclo-alkanes/alkenes, poly-substituted benzene derivatives, polycyclic compounds, and heavy alkanes.

III.1. Implications for Correlation Performance

No single correlation can address all the issues with critical pressure prediction across the entire range of hydrocarbons. The proposed correlation, while still showing some errors between experimental and calculated values, demonstrates smaller deviations compared to the

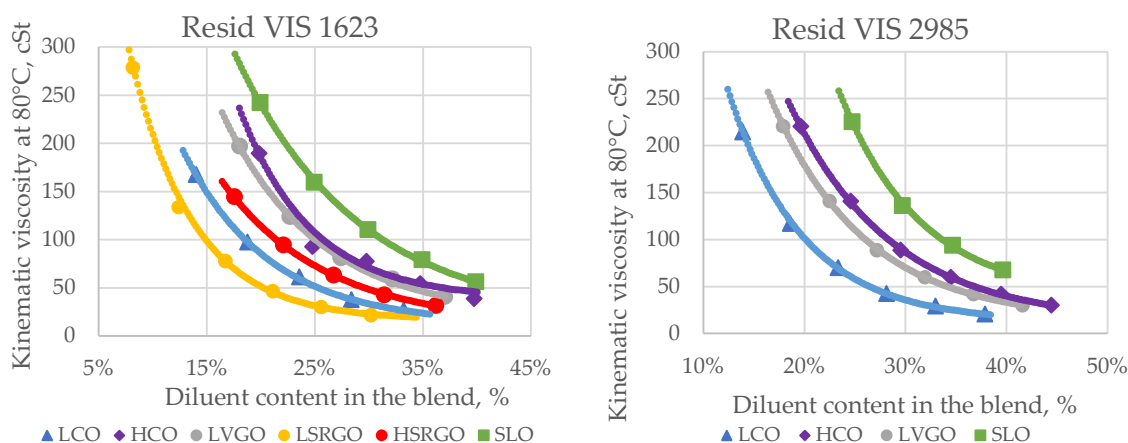
other correlations discussed in this work. This indicates its potential superiority over the existing methods for predicting critical pressures.

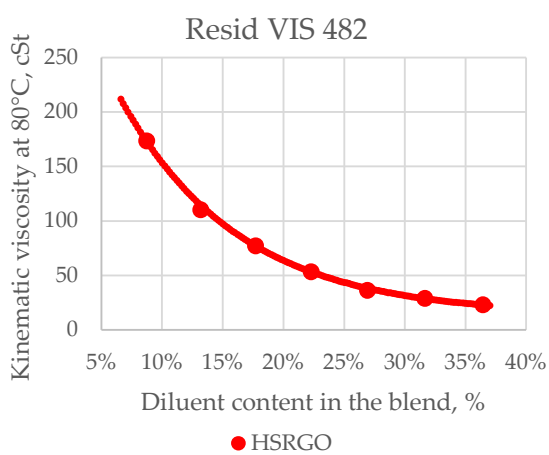
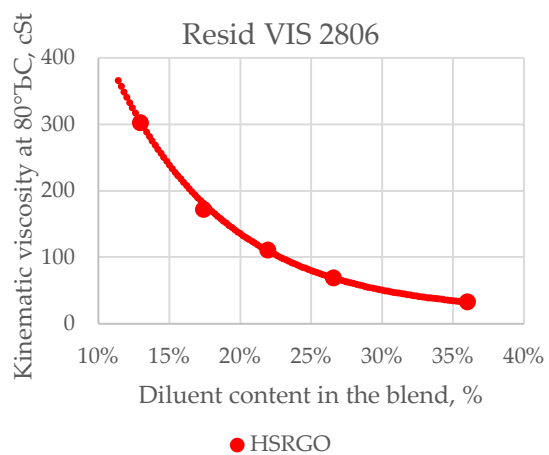
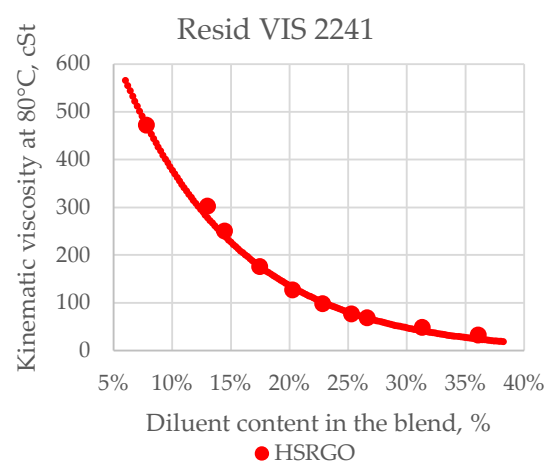
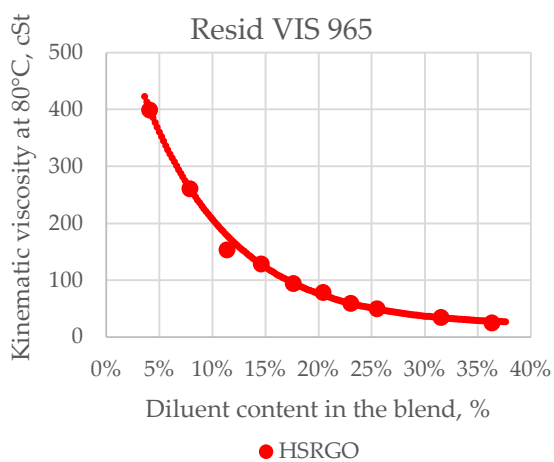
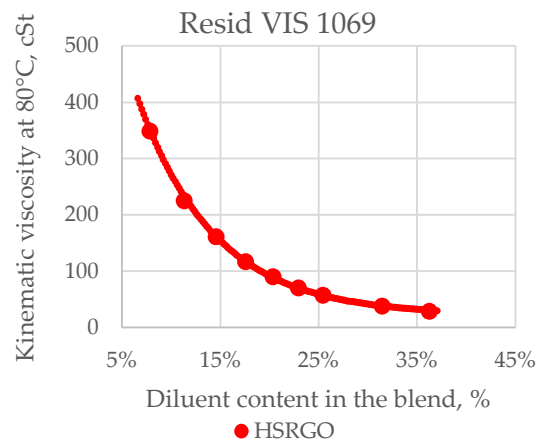
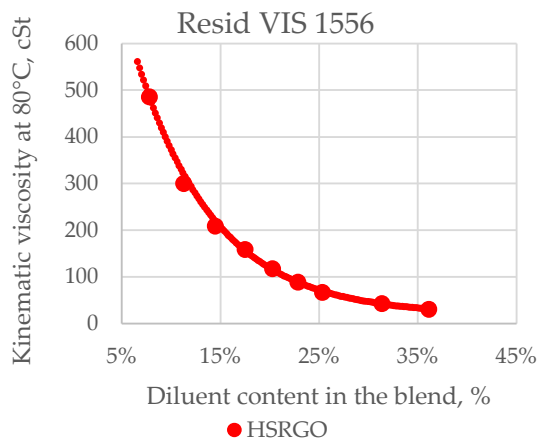
The novelty in the correlations presented in this work is the addition of one more parameter not included in the previous correlations, that is, the molecular weight. The ANN model, in addition to the molecular weight, also employs the acentric factor, which, as observed, further improved the accuracy of critical property calculations. For petroleum fractions and generated pseudo-components, the molecular weight can be calculated with higher precision, as discussed in source [24]. The cause for the bigger deviations in the critical property prediction is the complexity of the molecules of these hydrocarbons—including higher hydrocarbon chain length, branching, the presence of double bonds, and the presence of aromatic rings. The input parameters for the correlations cannot sufficiently address all the influences that the hydrocarbon structure has on the critical properties of the compounds.

IV. Prediction of viscosity of blends of heavy oils with diluents by empirical correlations and artificial neural network

IV.1. Modelling of viscosity of blends containing primary and secondary residues, and cutter stocks by the use of empirical correlations and ANN

Figure 10 presents graphs of variation of viscosity of the blends of studied nine residual oils with the six diluents as a function of diluent concentration in the blend. Table 20 summarizes the data shown in Figure 10.





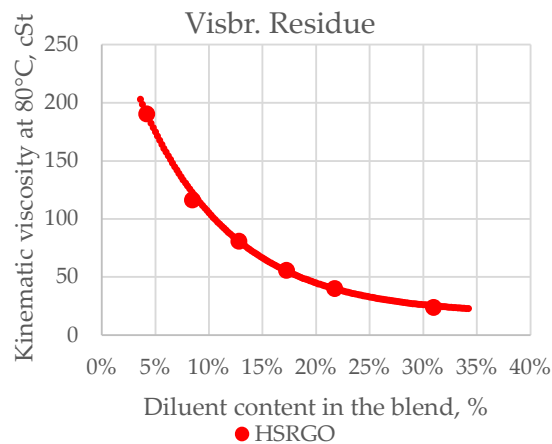


Figure 10. Variation of viscosity of the blends of studied nine residual oils with the six diluents, measured by the use of Engler specific viscometer operating under ASTM D 1665 requirements. (The title of each graph of Figure 10 contains number showing the kinematic viscosity (mm²/s) of the residual oil, measured at 80°C as a function of diluent concentration in the blend).

Table 20. Content of diluents and heavy oil blend kinematic viscosity.

Nr	Blend		Diluent content vol. %	Blend viscosity at 80°C, mm ² /s
	Resid	Diluent		
1	Resid VIS 1623	FCC LCO	15	167.4
2	Resid VIS 1623	FCC LCO	20	97.2
3	Resid VIS 1623	FCC LCO	25	61.1
4	Resid VIS 1623	FCC LCO	30	37.6
5	Resid VIS 1623	FCC LCO	35	26.4
6	Resid VIS 1623	FCC LCO	40	21.9
7	Resid VIS 1623	FCC HCO	20	189.7
8	Resid VIS 1623	FCC HCO	25	92.7
9	Resid VIS 1623	FCC HCO	30	77.3
10	Resid VIS 1623	FCC HCO	35	54.2
11	Resid VIS 1623	FCC HCO	40	38.6
12	Resid VIS 1623	LVGO	20	197.1
13	Resid VIS 1623	LVGO	25	123.9
14	Resid VIS 1623	LVGO	30	81.3
15	Resid VIS 1623	LVGO	35	59.1
16	Resid VIS 1623	LVGO	40	40.9
17	Resid VIS 1623	LSRGO	10	278.7
18	Resid VIS 1623	LSRGO	15	133.5
19	Resid VIS 1623	LSRGO	20	77.8
20	Resid VIS 1623	LSRGO	25	46.5
21	Resid VIS 1623	LSRGO	30	29.9
22	Resid VIS 1623	LSRGO	35	21.4

23	Resid VIS 1623	HSRGO	20	144.4
24	Resid VIS 1623	HSRGO	25	94.6
25	Resid VIS 1623	HSRGO	30	63.0
26	Resid VIS 1623	HSRGO	35	42.6
27	Resid VIS 1623	HSRGO	40	31.3
28	Resid VIS 1623	FCC SLO	20	242.4
29	Resid VIS 1623	FCC SLO	25	159.5
30	Resid VIS 1623	FCC SLO	30	110.6
31	Resid VIS 1623	FCC SLO	35	79.2
32	Resid VIS 1623	FCC SLO	40	56.2
33	Resid VIS 2985	FCC LCO	20	117.1
34	Resid VIS 2985	FCC LCO	25	70.0
35	Resid VIS 2985	FCC LCO	30	42.5
36	Resid VIS 2985	FCC LCO	35	29.0
37	Resid VIS 2985	FCC LCO	40	20.8
38	Resid VIS 2985	FCC HCO	20	220.7
39	Resid VIS 2985	FCC HCO	25	141.0
40	Resid VIS 2985	FCC HCO	30	88.8
41	Resid VIS 2985	FCC HCO	35	59.8
42	Resid VIS 2985	FCC HCO	40	41.9
43	Resid VIS 2985	FCC HCO	45	30.2
44	Resid VIS 2985	LVGO	20	220.7
45	Resid VIS 2985	LVGO	25	141.0
46	Resid VIS 2985	LVGO	30	88.8
47	Resid VIS 2985	LVGO	35	59.8
48	Resid VIS 2985	LVGO	40	41.9
49	Resid VIS 2985	LVGO	45	30.2
50	Resid VIS 2985	FCC SLO	25	225.6
51	Resid VIS 2985	FCC SLO	30	136.1
52	Resid VIS 2985	FCC SLO	35	93.7
53	Resid VIS 2985	FCC SLO	40	67.6
54	Resid VIS 1556	HSRGO	9	485.4
55	Resid VIS 1556	HSRGO	13	300.1
56	Resid VIS 1556	HSRGO	17	209.0
57	Resid VIS 1556	HSRGO	20	158.6
58	Resid VIS 1556	HSRGO	23	117.8
59	Resid VIS 1556	HSRGO	26	88.5
60	Resid VIS 1556	HSRGO	29	66.6
61	Resid VIS 1556	HSRGO	35	42.6
62	Resid VIS 1556	HSRGO	40	30.8
63	Resid VIS 1069	HSRGO	9.1	348.3
64	Resid VIS 1069	HSRGO	13.0	224.9
65	Resid VIS 1069	HSRGO	16.7	160.8
66	Resid VIS 1069	HSRGO	20.0	116.7

67	Resid VIS 1069	HSRGO	23.1	90.0
68	Resid VIS 1069	HSRGO	25.9	70.0
69	Resid VIS 1069	HSRGO	28.6	57.1
70	Resid VIS 1069	HSRGO	35.0	38.2
71	Resid VIS 1069	HSRGO	40.0	28.2
72	Resid VIS 765	HSRGO	4.8	399.4
73	Resid VIS 765	HSRGO	9.1	260.6
74	Resid VIS 765	HSRGO	13.0	153.4
75	Resid VIS 765	HSRGO	16.7	128.6
76	Resid VIS 765	HSRGO	20.0	94.1
77	Resid VIS 765	HSRGO	23.1	78.2
78	Resid VIS 765	HSRGO	25.9	59.3
79	Resid VIS 765	HSRGO	28.6	49.4
80	Resid VIS 765	HSRGO	35.0	34.1
81	Resid VIS 765	HSRGO	40.0	24.8
82	Resid VIS 2241	HSRGO	9.1	472.0
83	Resid VIS 2241	HSRGO	15.0	302.3
84	Resid VIS 2241	HSRGO	16.7	250.5
85	Resid VIS 2241	HSRGO	20.0	176.0
86	Resid VIS 2241	HSRGO	23.1	127.1
87	Resid VIS 2241	HSRGO	25.9	98.2
88	Resid VIS 2241	HSRGO	28.6	77.1
89	Resid VIS 2241	HSRGO	30.0	68.5
90	Resid VIS 2241	HSRGO	35.0	48.5
91	Resid VIS 2241	HSRGO	40.0	33.0
92	Resid VIS 2806	HSRGO	15	302.3
93	Resid VIS 2806	HSRGO	20	171.5
94	Resid VIS 2806	HSRGO	25	110.8
95	Resid VIS 2806	HSRGO	30	68.5
96	Resid VIS 2806	HSRGO	40	32.6
97	Resid VIS 482	HSRGO	15	110.4
98	Resid VIS 482	HSRGO	20	77.1
99	Resid VIS 482	HSRGO	30	36.3
100	Resid VIS 482	HSRGO	35	28.9
101	Resid VIS 482	HSRGO	40	23.0
102	Resid VIS 482	HSRGO	25	53.4
103	Resid VIS 482	HSRGO	10	173.4
104	Visbr. Residue	HSRGO	5	190.4
105	Visbr. Residue	HSRGO	10	116.3
106	Visbr. Residue	HSRGO	15	80.8
107	Visbr. Residue	HSRGO	20	55.6
108	Visbr. Residue	HSRGO	25	40.0
109	Visbr. Residue	HSRGO	35	23.7

The data points for each blend are interpolated by an exponential function in the form of equation (4). Table 21 presents values of equation (4) parameters (A, B, and C) for the studied 17 heavy oil blends.

$$VIS_{Blend} = A \times \exp(B \times vol.\%_{Diluent}) + C \quad (4)$$

Where:

- VIS_{Blend} = Viscosity of heavy oil–diluent blend at 80°C, mm²/s;
- A, B, C = equation parameters;
- $Vol.\%_{Diluent}$ = volume per cent of diluent concentration in the blend heavy oil–diluent.

Table 21 Values of regression coefficient A, B, and C from equation (4), coefficient of determination (R^2), % absolute average deviation (%AAD) of equation (4), and the range of variation of diluent concentration in the heavy oil blend.

Nr	Heavy Oil Blend	A	B	C	R^2	%AAD	Diluent concentration range, vol. %
1	VIS1623/LSRGO	1064.36	-0.171	16.483	0.9970	2.8	8.2–30.2
2	VIS1623/FCC LCO	900.16	-0.126	12.571	0.9995	2.2	14–38.1
3	VIS1623/HSRGO	819.65	-0.104	12.587	1.0000	0.6	17.5–36.2
4	VIS1623/LVGO	1361.29	-0.113	20.471	1.0000	1.2	18–37
5	VIS1623/FCC HCO	2999.99	-0.151	38.441	0.9989	8.9	19.8–39.7
6	VIS1623/FCC SLO	1303.70	-0.088	17.807	1.0000	0.8	19.9–39.9
7	VIS2985/FCC LCO	1316.86	-0.135	12.769	0.9996	1.2	13.9–37.8
8	VIS2985/LVGO	1424.54	-0.108	14.169	0.9999	0.7	17.9–41.6
9	VIS2985/FCC HCO	1465.28	-0.100	12.569	0.9998	0.7	19.6–44.4
10	VIS2985/FCC SLO	4000.00	-0.124	38.033	1.0000	0.9	24.7–39.6
11	VIS2985/HSRGO	1458.43	-0.125	16.634	0.9999	1.4	13–36
12	VIS1556/HSRGO	1243.95	-0.126	18.552	0.9927	3.0	7.8–36.1
13	VIS1069/HSRGO	894.16	-0.128	22.173	0.9992	1.9	7.9–36.2
14	VIS482/HSRGO	390.07	-0.103	13.701	0.9988	1.4	8.7–36.4
15	VIS965/HSRGO	620.20	-0.120	19.959	0.9959	3.7	4.1–36.3
16	VIS2241/HSRGO	1041.08	-0.101	-3.103	0.9952	6.3	7.8–36.1
17	Visbr.Residue/HSRGO	282.36	-0.117	17.798	0.9979	2.2	4.2–31

The data in Table 21 indicates an excellent fit of equation (4) to the experimental data of viscosity measurements of studied 17 heavy oil blends. This finding is in line with the results reported in references [25,26,27,28] and in another recent research [29], and suggests that the effect of diluent concentration variation on viscosity is similar to that of the temperature variation showing exponential dependence on. Thus, the form of the correlation predicting viscosity of blend of heavy oils with diluents can be similar to that predicting viscosity as a function of temperature. Hence, the form of double logarithm modified Walter' s equation discussed in the study of *Aboul - Seoud*, and Moharam [30] to predict petroleum fluid viscosity as a function of temperature could be used as starting point of data fit optimization. This can explain the low error of viscosity prediction of four crude oils with diesel at several proportions reported by *Centeno et al.*[31] by the use of *Walther* blending correlation with an additional parameter.

Besides the 21 correlations taken from the literature, a new additional correlation was developed in this work using computer algebra system (CAS) Maple and NLPSolve with Modified Newton Iterative Method as described in [32]. It has the form of equation (5).

$$VR \text{ blend viscosity} = 10^{10 \left(\frac{46.92799 - VBI_{blend}}{36.24710} \right)}$$

$$VBI_{blend} = \sum_{i=1}^n x_i VBI_i$$

$$VBI_i = 46.79831 - 35.361828 \times \log \log(CST_i + 0.89265) \quad (5)$$

Where:

VR blend viscosity – Viscosity of heavy oil–diluent blend, mm²/s;

VBI_{blend} – viscosity blending index of the heavy oil–diluent blend;

VBI_i – viscosity blending index of the i-th component in the blend;

CST_i – kinematic viscosity of the individual oil fraction at 80 °C, mm²/s.

Furthermore, an ANN blending viscosity model was developed. One of the great capabilities of neural networks is that they can perceive information and prognosticate afterwards. Artificial neural networks (ANNs) have several capabilities that make them effective for parameter prediction.

The estimated statistical parameters using the different correlations to evaluate the accuracy of prediction of viscosity of the 109 heavy oil blends are summarized in Table 22. It is evident from this data that the ANN model features with the highest accuracy of viscosity prediction which is much better than the best empirical correlation (equation (3)). This finding is in line with the results reported by *Ssebadduka et al.* [33] showing 4.7 times as low as %AAD of the ANN model relative to the best empirical correlation.

Table 22. Statistical analysis of studied methods to predict heavy oil blend viscosity, employing Engler specific viscometer.

No	Model	SE	RSE	SSE	%AAD	SRE	AAD	Max.dev.
1	Arrhenius	58622.0	51906.2	617.1	213.8	-23517.9	198.3	671.0
2	Bingham	18808.7	16653.9	85.8	88.1	9696.3	102.6	460.8
3	Chirinos	2158.7	1911.4	7.2	22.1	-1688.6	27.5	261.6
4	Cragoe	2954.6	2616.1	14.5	33.0	-3618.6	36.9	263.7
5	Reid	21347.2	18901.6	100.1	95.3	10485.4	110.0	483.0
6	Linear mixing rule	1807542.2	1600467.1	61551.0	1771.4	-194848.9	1193.4	2358.9
7	Chevron c VBI	2832.2	2507.8	13.5	31.5	-3451.6	35.3	263.1
8	Refutas c VBI	2541.7	2250.5	9.2	25.0	-2210.2	30.7	274.1
9	Al-Mulla c VBI	454487.8	402421.0	1071.5	278.9	-30676.4	400.4	3534.2
10	Walther with 1 parameter	597.1	528.7	2.2	10.7	571.9	11.9	147.8
11	Lederer with 1 parameter	753.8	667.4	3.2	13.9	425.3	16.5	128.9
12	Shu with 1 calculated parameter	10216.7	9046.2	495.7	127.9	-12124.0	84.3	290.9
13	Gao&Li with 1 parameter	12316.7	10905.7	32.0	47.0	3716.5	69.2	427.0
14	Power Law mixing rule	482.7	427.4	2.0	11.6	409.0	14.6	83.1
15	Miadonye	22167.2	10522.2	17.2	76.4	1933.7	130.7	264.2
16	Double Log mixing rule	1793.7	1588.2	16.5	34.5	3491.9	32.6	171.4
17	Double Natural Log mixing rule	3432.9	3039.6	14.9	32.0	-3207.9	37.3	297.3
18	Mehrota without interaction parameters	108379.9	95963.7	1452.8	320.9	-34978.7	278.0	862.8
19	4-th root mixing rule	1252.2	1108.7	6.9	22.1	-1627.1	23.4	171.3
20	Stratiev et al. (2008)	494.8	438.1	1.3	9.0	-477.3	11.0	175.6
21	Kolev et al.	395.7	350.3	1.2	8.2	358.9	9.4	159.7
22	New correlation (this work)	254.1	225.0	0.8	6.7	218.4	8.3	104.8
23	Artificial Neural Network	30.5	27.0	0.2	2.2	16.3	2.6	27.5

It deserves mentioning here that when viscosity of the blend was employed as ANN output instead of logarithm of viscosity, %AAD was 8.6%. This underlines the importance of the type of the output of the ANN to model.

Among the empirical correlations examined in this study one can see from the data in Table 22 that the best empirical correlations are those based on the linearized form of Walther's equation using the concept of viscosity blending index.

IV.2. Evaluation of VBI correlation and ANN model to predict viscosity of mixtures containing hydrocracked vacuum residue

The data discussed in section IV.1 concerned vacuum residual oils derived from different crude oils, and crude oil blends processed in a petroleum refinery. Typically, between 60 and 100% of crude oil blend processed in this refinery consisted of Urals crude oil. In order to test the applicability of best empirical correlations, established in section IV.1, for residual

oils with completely different properties two distinct hydrocracked vacuum residues (H-Oil VTB) were blended with four FCC gas oils and 24 mixtures were obtained. The viscosity at temperatures in the range 80°C – 145°C of mixtures was measured in accordance with ASTM D 1665 standard requirements. Table 23 presents data of characteristics of both H-Oil VTBs and four FCC gas oils being studied.

Table 23. Properties of two H-Oil VTBs and four FCC gas oils used to prepare 23 blends

H-Oil VTB/Diluent Properties	H-Oil VTB 5.5 2023	H-Oil VTB 10.7.2023	FCC LCO	FCC HCO-1	FCC HCO-2	FCC SLO
Density at 15 °C, gc/m ³	1.0721	1.0009	0.9412	1.036	1.0336	1.1146
Kinematic viscosity at 80 °C, °mm ² /s	4901	877	1.35	4.42	2.91	56.7
Kinematic viscosity at 90 °C, °mm ² /s		453	1.24			
Kinematic viscosity at 100 °C, °mm ² /s		254	1.11			
Kinematic viscosity at 120 °C, °mm ² /s	304	96			1.31	14.6
Kinematic viscosity at 130 °C, °mm ² /s	193				1.14	
Kinematic viscosity at 135 °C, °mm ² /s	149				1.07	
Kinematic viscosity at 140 °C, °mm ² /s	117				1.00	
Kinematic viscosity at 145 °C, °mm ² /s	96				0.94	
Softening point, °C	50.3					
Saturates, wt. %	19.7	26.2				
Aromatics, wt. %	54.1	52.0				
Resins, wt. %	7.7	8.1				
C ₇ asphaltenes, wt. %	29.4	13.7				
C ₅ asphaltenes, wt. %	36.3	21.9				
HTSD, wt. % (ASTM D-7169)						
IBP 0.5	362	407	138	202	196	196
10	480	514	188	275	267	341
30	554	565	220	306	296	383
50	590	598	234	328	321	413
70	631	638	255	354	344	444
90	698	697	279	391	379	487
95	726	719	290	410	397	506
FBP 99.5	834	774	333	452	446	539

Figure 11 indicates graphs of viscosity variation as a function of diluent concentration for the blends (H-Oil VTB (10.7.2023) – FCC LCO) at three different temperatures 80, 90, and 100°C. This data confirms again the exponential dependence of heavy oil blend viscosity on cutter stock concentration.

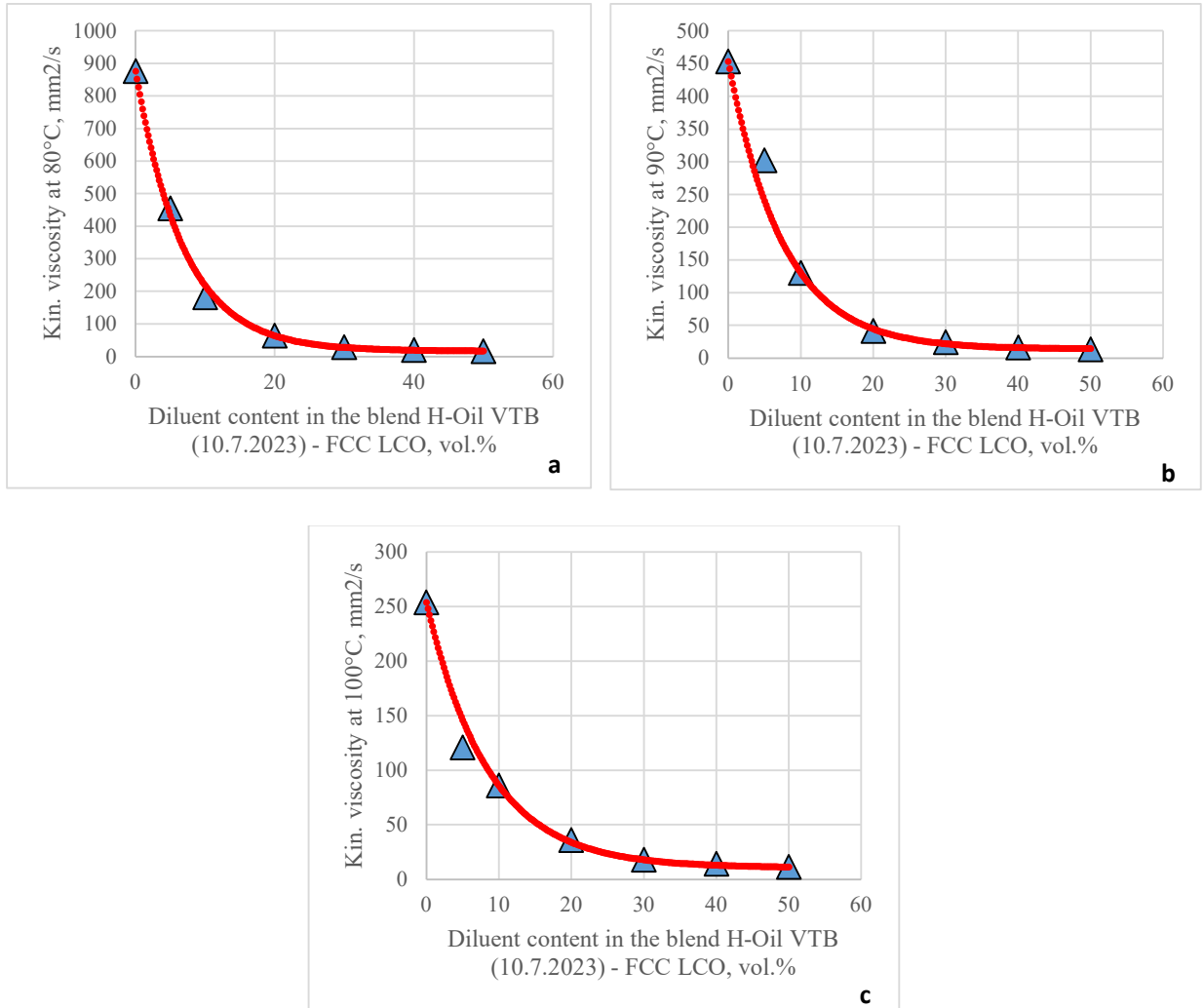


Figure 11. Dependence of viscosity of blends H-Oil VTB (10.7.2023) – FCC LCO measured at 80°C (a), 90°C (b), and 100°C (c) on LCO concentration.

The data in Table 24 acknowledges the excellent fit of equation (5) to the experimental data of viscosity measurements of the studied H-Oil VTB blends. Therefore, one may expect that the viscosity blending index model will be suitable for H-Oil VTB blends too.

Equation (6) used in this study is developed by *Kolev et al.* [17] and is as follows:

$$VR \text{ Blend Viscosity} = 10^{10 \left(\frac{41.10743 - VBI \text{ blend}}{49.08258} \right)} - 0.8$$

$$VBI \text{ blend} = \sum_i^n x_{vi} VBI_i \quad (6)$$

$$VBI_i = 41.10743 - 49.08258 \times \log \log (CST_i + 0.8)$$

Table 24. Values of regression coefficient A, B, and C from equation (4), coefficient of determination (R^2), % absolute average deviation (%AAD) of equation (4), and the range of variation of diluent concentration in the blend H-Oil VTB (10.7.2023) – FCC LCO

Nr	Temperature of measurement	A	B	C	R^2	%AAD	Diluent concentration range, vol. %
1	80°C	859.47	-0.145	17.233	0.9971	4.8	5–50
2	90°C	439.56	-0.133	13.941	0.9878	6.9	5–50
3	100°C	243.08	-0.117	10.704	0.9929	5.1	5–50

The employment of best empirical correlations established in section IV.1 to predict viscosity of the blends H-Oil VTB – FCC gas oils was tested against the data of 24 mixtures at the temperature range 80 – 145°C. Parity graphs of measured versus calculated by eqs. 21 and 31 H-Oil VTB – FCC gas oil mixture viscosity are presented in Figures 12 a, and 12 b. This data indicates that equation (6) outperforms equation (5).

Comparing %AAD and SSE from applying eqs. (6) and (5) to predict viscosities of H-Oil VTB – FCC gas oil blends (Figs. 12 a and 12 b) with these parameters from Table 25, it is seen that the forecast of H-Oil VTB – FCC gas oil blend viscosity is less accurate than that of the straight run vacuum residue – diluent blends. It is also obvious that eq. (5) being the best empirical correlation to predict viscosity of straight run vacuum residue – diluent blends seems to perform worse than eq. (6) for the blends of H-Oil VTB – FCC gas oil. This suggests that the specificity of interactions of blended oils affects the accuracy of prediction of eq. (5), and equation parameters may need to be optimized to reduce the error of prediction.

Table 25. Summary of values of slope, coefficient of determination R^2 of parity graphs of measured versus predicted heavy oil blend viscosity, together with %AAD, and standard error (SE).

№	1		2		3		4	
	Rahmes and Nelson (37.8°C)	Rahmes and Nelson (98.9°C)	Faris et al.		Shu		Centeno et al. (API = 9.89)	
	Eq.(6)	Eq.(6)	Eq.(6)	Mod.Eq.(6)	Eq.(6)	Mod.Eq.(6)	Eq.(6)	Mod.Eq.(6)
Slope	1.045	0.9972	0.9304	0.9706	0.7635	1.1402	0.5769	0.8019
R^2	0.9974	0.9985	0.9302	0.8963	0.9488	0.9546	0.9258	0.906
%AAD	3.87	1.75	12.3	10.5	43.5	10.1	27.9	11.7
SE	86.4	0.05	974	865	1.2×10^9	0.8×10^9	2234	894
SSE	0.2	0.04	0.441	0.568	4.52	0.40	1.91	0.50
Model parameters								
a	0.8	0.8	0.8	2.931	0.8	5.097	0.8	1.3033
b	41.10743	41.10743	41.10743	5.558	41.10743	92.732	41.10743	3.5588
c	49.08258	49.08258	49.08258	1.00	49.08258	1.00	49.08258	1.00

Table 25. (continued)

№	5		6		7	
	Centeno et al. (API = 12.42)	Centeno et al. (API = 15.93)	Centeno et al. (API = 21.31)		Centeno et al. (API = 12.42)	
	Eq.(6)	Mod.Eq.(6)	Eq.(6)	Eq.(6)	Mod.Eq.(6)	Eq.(6)
Slope	0.4737	0.9559	0.7811	0.4737	0.9559	0.7811
R ²	0.9807	0.9958	0.9872	0.9807	0.9958	0.9872
%AAD	27.5	4.8	15.2	27.5	4.8	15.2
SE	15610	270	1086	15610	270	1086
SSE	2.40	0.10	0.87	2.40	0.10	0.87
Model parameters						
a	0.8	2.05	0.8	0.8	2.05	0.8
b	41.10743	2.15	41.10743	41.10743	2.15	41.10743
c	49.08258	1.00	49.08258	49.08258	1.00	49.08258

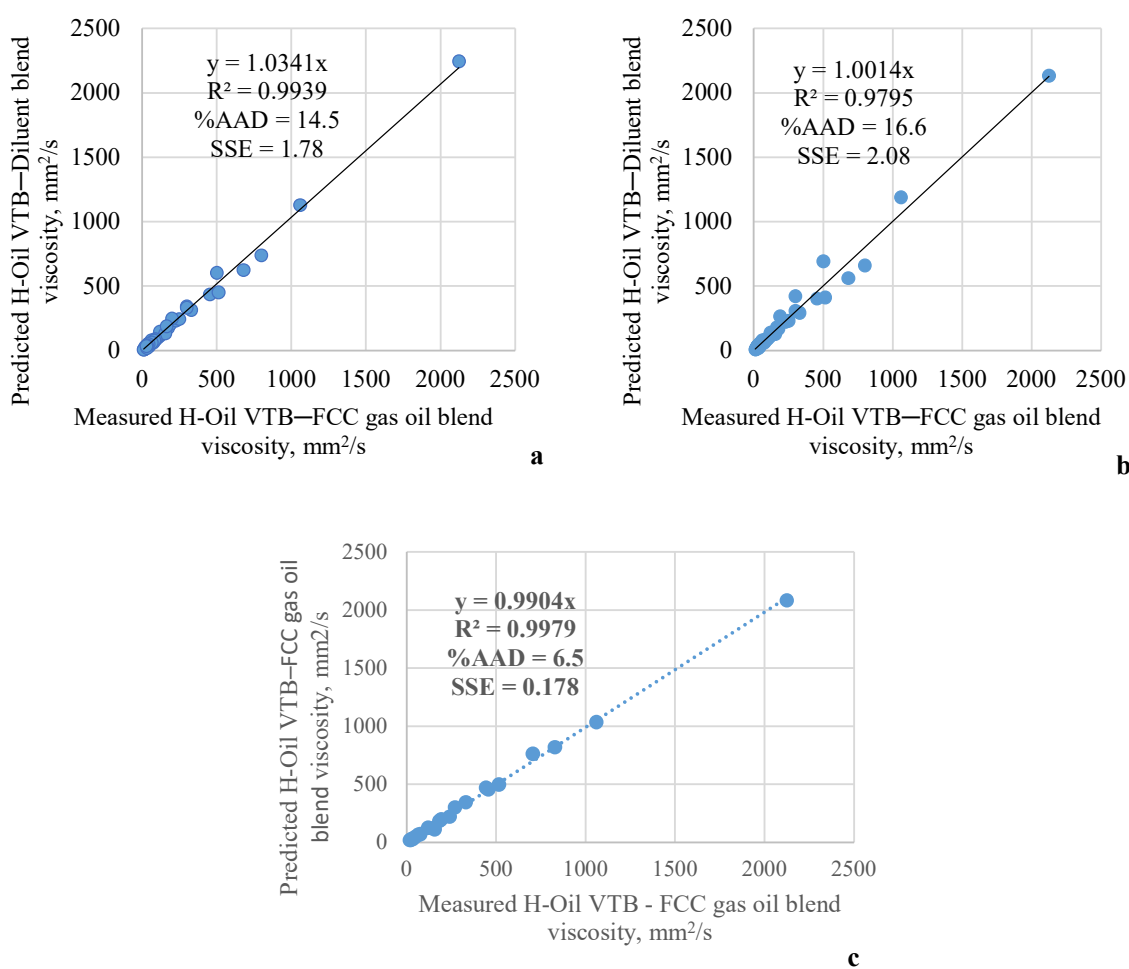


Figure 12. Parity graphs of measured versus calculated viscosity of blends H-Oil VTB – FCC gas oils by the use of eq.(6) (a), eq. (5) (b), and ANN model (c)

It is clear from the data in Figure 12 c that the ANN model again outperforms the empirical correlations. Similar to the empirical correlations, the ANN model also predicts the viscosity of H-Oil VTB – FCC gasoil blends with less accuracy than that of straight run vacuum residue – diluent mixtures.

IV.3. Assessment of VBI correlation to predict heavy oil blend viscosity.

The experimental viscosity data generated in this research and employed in sections IV.1, and IV.2 showed a variation in the range 260 – 4901 mm²/s at 80°C, while the empirical correlations available in the literature have been developed using oil viscosity data varying in the range between 31.9 mm²/s at 37.8°C and 1673698 mm²/s at 25°C. Considering that the heavy and extra heavy crude oils have viscosity between 100 and 10000 cSt it was decided to assess the capability of VBI correlation having the form of eq. (7) to predict viscosity of heavy oil blends ranging between 3.12 and 464 000 mm²/s at temperatures between 25 and 98.9°C using the literature data reported in the studies of *Rahmes and Nelson* [36], *Shu* [35], *Faris et al.* [37], and *Centeno et al.* [31]. As starting parameters in eq. (7) the ones of eq.(6) were used.

$$VR \text{ blend viscosity} = 10^{10 \left(\frac{b - VBI_{blend}}{c} \right)} - 0.8$$

$$VBI_{blend} = \sum_{i=1}^n x_{vi} VBI_i$$

$$VBI_i = b - c \times \log \log(CST_i + a) \quad (7)$$

Employing (CAS) Maple and NLPsolve with Modified Newton Iterative Method the initial parameters of eq. (7), which coincide with those of eq.(6) were optimized to achieve a better heavy oil blend viscosity prediction.

Table 25 summarizes the values of slope, coefficient of determination R² of parity graphs of measured versus predicted heavy oil blend viscosity, along with %AAD, and standard error (SE). It is evident from the data in Figure 12, and Table 25 that the modified eq.(6) with the new optimized parameters a, b, and c for each particular heavy oil – diluent blend provides a higher accuracy of viscosity prediction.

It is interesting to note the relatively high value of coefficient of determination R² of application of eq.(6) to the eight cases taken from the literature. This implies a good correlation between the data calculated by eq. (6) and the measured ones. The registration of poor %AAD (SE) suggests a need to optimize the parameters a, b, c, which seem to be specific to the heavy oil – diluent mixture.

If a comparison is made, for example, with the data reported by *Centeno et al.* [31] one can see that the modified eq.(6) demonstrates much better performance than any of studied correlations in their work. The standard errors for blends of crude oils with API of 9.89, 12.4,

15.9, and 21.3, and diesel fuel by the modified eq.(6) are much lower than the best correlations investigated by *Centeno et al.* [31]. They are as follows:

- API of 9.89 (SE = 894 versus 6.6x10⁴ announced by Centeno et al.7);
- API of 12.4 (SE = 270 versus 7.9x10³);
- API of 15.9 (SE = 156 versus 325);
- API of 21.3 (SE = 1.8 versus 13.1).

The attempt to correlate eq.(7) model parameters a, b from Table 25 with characteristics of heavy oils (API, and viscosity) failed implying that they are difficult to be preliminary predicted. In general, the accuracy of oil blend viscosity employing eq.(7) type model with the optimized parameters gets improved when API of oil is higher. This probably reflects the accuracy of viscosity measurement, which seems to be higher for the lighter oils.

The modified eq.(6) also shows a lower %AAD when the viscosity of bitumen — syncrude mixture studied by *Shu* [35] is predicted. %AAD of 16.4 of modified eq.(6) versus 25.0 reported by *Shu* [35] for his method applied to the bitumen — syncrude blend viscosity measured at 25°C is observed.

It deserves mentioning here that the accuracy of viscosity prediction is improved at higher temperature, and at lower heavy oil blend viscosity probably because the measurements at increased temperature, and for oils having lower viscosity are more precise.

The linearized double logarithm Walter's like viscosity blending index equation with three and five additional parameters seems to describe very well the relation of heavy oil blend viscosity to the concentration of diluent, and the viscosity of the pure heavy oil, and that of the diluents.

The same type equation was applied to the data reported by *Hernández et al.* [25] and the following equation (8) was obtained availing CAS Maple with Modified Newton Iterative Method:

$$VR \text{ blend viscosity} = 10^{10(-0.017852 \times VBI_{blend} + 0.81685)} - 0.8$$

$$VBI_{blend} = \sum_{i=1}^n x_i VBI_i$$

$$VBI_i = 41.10743 - 49.08258 \times \log \log(CST_i + 0.8) \quad (8)$$

Equation (8) was contrasted with the best 17th mixing rule with three interaction parameters of *Hernandez et al.* [25], and as evident from the data displayed in Figure 13 the accuracy of prediction of the three crude oils blend viscosity by eq.(5) is close to that of the 17th mixing rule with three interaction parameters of *Hernandez et al.* [25] Moreover, if the SSE of eq. (5) is compared with the 17 correlations studied by *Hernandez et al.* [25] it can be ranked as second best. This exemplifies the suitability of the form of the linearized Walther's equation using the concept of viscosity blending index to fit the experimental viscosity blend values.

The values of the fitting parameters in viscosity blending index equation, however seem to be specific to the experimental data as specific are the values of the interaction parameters reported by *Hernandez et al.* [25].

Unfortunately, the application of the ANN approach to model the crude oil blend viscosity data of *Hernandez et al.* [25] was not possible due to the fact that the number of data points was 47, and the ANN requires their number to be not lower than 100.

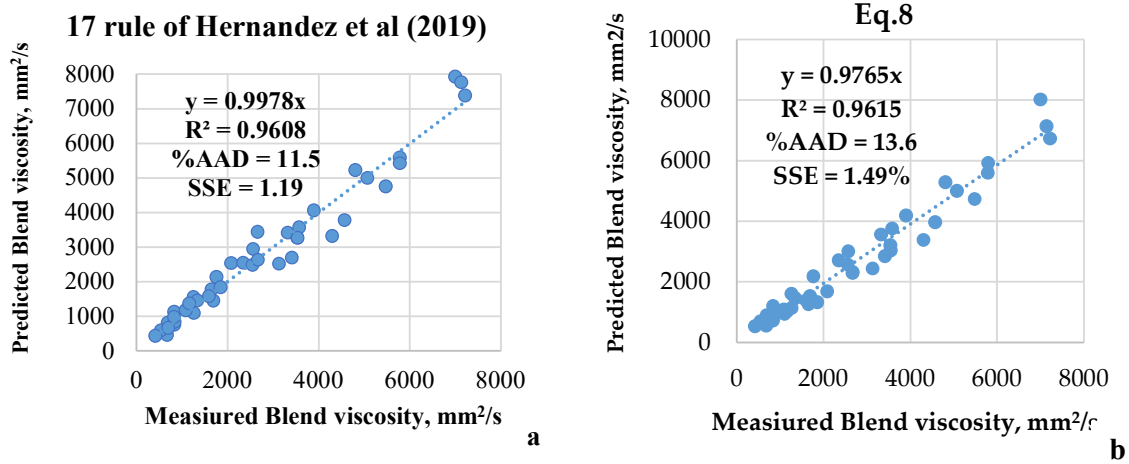


Figure 13. Parity graphs of measured versus predicted crude oil blend viscosity by the best 17th mixing rule with three interaction parameters of *Hernandez et al.* [25] (a), and by eq. 8 (b) using the data reported by *Hernandez et al.* [25] for 47 blends of three heavy crude oils.

IV.4. Conclusions

The viscosity of mixtures consisting of different heavy oils and distinct gas oil diluents follows an exponential relationship with diluent concentration. As such it is best modeled by the use of modified linearized double logarithm Walter's like viscosity blending index (VBI) equation. The viscosity blending index equations were found suitable for predicting viscosity of heavy oil, and bitumen blends. However, the parameters of these equations need to be optimized for the different mixtures to achieve a higher accuracy of prediction.

The availing of ANN approach provides the highest accuracy of heavy oil blend viscosity prediction in comparison with the empirical correlations confirming the statement made by other researchers that the metaheuristic models are superior to any empirical correlation. The viscosity blending index equation was found suitable to model heavy crude oil blend viscosity with an accuracy very close to that of the equation with interaction parameters. Similar to the values of the interactions parameters, the values of parameters of

the viscosity blending index equation seem to be specific to the experimental data being modeled.

V. Results from predicting the individual properties of the components in the data base for molecular reconstruction using group contribution methods.

The 110 compounds in the naphtha fraction from the data base for molecular reconstruction [42] for which experimental data was obtained were divided in several categories:

- Iso-alkanes, consisting of 20 compounds
- Normal alkanes, consisting of 11 compounds
- Mono-aromatic hydrocarbons, consisting of 16 compounds
- Naphthenes, consisting of 34 compounds
- Nitrogen-containing compounds, consisting of 5 compounds
- Sulfur-containing compounds, consisting of 14 compounds
- Oxygen-containing compounds, consisting of 10 compounds

The 139 compounds in the diesel fraction from the data base for molecular reconstruction [42] for which experimental data was obtained were divided in several categories:

- Normal alkanes, consisting of 18 compounds
- Iso-alkanes, consisting of 8 compounds
- Naphthenes, consisting of 42 compounds
- Mono-aromatic hydrocarbons, consisting of 23 compounds
- Di- and Tri-aromatic hydrocarbons, consisting of 14 compounds
- Sulfur-containing compounds, consisting of 10 compounds
- Nitrogen-containing compounds, consisting of 3 compounds
- Oxygen-containing compounds, consisting of 21 compounds

The results obtained for the performance of the Joback and Reid (J&R) and Abdulelah-Gani (A&G) (Constantinou-Gani (C&G) for Normal Boiling Point) Group Contribution methods are summarized in Table 26 below. The information in Table 26 contains the Average Absolute Deviation (AAD), the Maximum Absolute Deviation (MAD) and Bias for each property calculated for the different compound class in the naphtha or diesel range.

Table 26. Performance of the Joback and Reid and Abdulelah-Gani Group
Contribution methods for the calculated properties across different classes of compounds.

Compound Class	Property / Method	Range	AAD, %	MAD, %	Bias, %
N-alkanes	Normal Boiling Point, J&R	naphtha	4,54%	16,07%	-0,19%
		diesel	5,37%	14,30%	2,83%
	Normal Boiling Point, C&G	naphtha	2,62%	12,12%	-0,62%
		diesel	1,97%	5,08%	-1,87%
	Critical Temperature, J&R	naphtha	4,47%	15,64%	-0,34%
		diesel	5,82%	16,39%	2,88%
	Critical Temperature, A&G	naphtha	2,93%	15,03%	-2,27%
		diesel	0,53%	1,51%	-0,99%
	Critical Pressure, J&R	naphtha	2,14%	4,66%	1,03%
		diesel	5,54%	19,58%	-8,14%
	Critical Pressure, A&G	naphtha	1,33%	4,25%	2,14%
		diesel	3,87%	11,12%	-2,14%
	Acentric Factor, J&R	naphtha	2,74%	14,69%	5,17%
		diesel	9,87%	33,92%	-5,47%
	Acentric Factor, A&G	naphtha	7,76%	21,20%	-0,91%
		diesel	1,25%	9,57%	-7,57%
Isoalkanes	Specific Gravity, A&G	naphtha	2,08%	10,04%	1,77%
		diesel	0,65%	2,25%	-0,19%
	Normal Boiling Point, J&R	naphtha	2,08%	11,19%	-0,17%
		diesel	0,69%	2,77%	-1,88%
	Normal Boiling Point, C&G	naphtha	1,52%	7,35%	-0,51%
		diesel	0,64%	1,33%	0,24%
	Critical Temperature, J&R	naphtha	2,40%	11,77%	-0,11%
		diesel	0,66%	2,62%	-1,86%
	Critical Temperature, A&G	naphtha	1,36%	8,43%	-1,08%
		diesel	0,21%	0,65%	-0,21%
	Critical Pressure, J&R	naphtha	2,80%	7,90%	0,29%
		diesel	1,40%	4,42%	-1,77%
	Critical Pressure, A&G	naphtha	1,62%	8,17%	2,64%
		diesel	0,91%	4,14%	2,11%
	Acentric Factor, J&R	naphtha	1,49%	7,96%	0,84%
		diesel	0,92%	2,02%	-0,32%
Mono-aromatics	Acentric Factor, A&G	naphtha	6,59%	22,67%	-4,11%
		diesel	4,51%	11,96%	-6,80%
	Specific Gravity, A&G	naphtha	0,74%	2,76%	0,13%
		diesel	0,78%	2,70%	-0,52%
	Normal Boiling Point, J&R	naphtha	0,73%	1,95%	0,29%
		diesel	3,10%	12,05%	2,64%
	Normal Boiling Point, C&G	naphtha	4,52%	18,61%	10,33%
		diesel	6,12%	18,61%	6,36%
	Critical Temperature, J&R	naphtha	0,83%	2,18%	0,32%
		diesel	2,93%	11,50%	2,53%
	Critical Temperature, A&G	naphtha	0,88%	1,82%	0,18%

Di- and tri-aromatics	Critical Pressure, J&R	diesel	1,17%	2,62%	-0,72%
		naphtha	2,54%	8,73%	-1,21%
		diesel	3,61%	12,45%	-3,32%
	Critical Pressure, A&G	naphtha	2,13%	6,03%	-1,08%
		diesel	2,21%	6,61%	-1,75%
	Acentric Factor, J&R	naphtha	3,04%	8,86%	-0,72%
		diesel	2,77%	8,86%	-0,36%
	Acentric Factor, A&G	naphtha	4,12%	15,97%	2,76%
		diesel	4,19%	15,97%	-0,81%
	Specific Gravity, A&G	naphtha	0,46%	2,04%	0,20%
		diesel	0,31%	2,04%	0,27%
	Normal Boiling Point, J&R	diesel	3,35%	8,56%	1,50%
	Normal Boiling Point, C&G	diesel	2,28%	8,06%	-1,63%
	Critical Temperature, J&R	diesel	2,95%	7,22%	0,34%
	Critical Temperature, A&G	diesel	0,86%	2,23%	-0,25%
	Critical Pressure, J&R	diesel	6,26%	21,65%	-3,58%
	Critical Pressure, A&G	diesel	5,53%	19,88%	-0,01%
	Acentric Factor, J&R	diesel	8,24%	25,95%	14,22%
	Acentric Factor, A&G	diesel	7,89%	21,88%	7,82%
	Specific Gravity, A&G	diesel	4,05%	18,32%	1,56%
Naphthenes	Normal Boiling Point, J&R	naphtha	2,50%	34,93%	0,58%
		diesel	3,99%	15,47%	2,44%
	Normal Boiling Point, C&G	naphtha	3,51%	16,96%	-6,77%
		diesel	1,56%	13,83%	-6,58%
	Critical Temperature, J&R	naphtha	1,02%	3,62%	-0,28%
		diesel	4,02%	15,83%	2,68%
	Critical Temperature, A&G	naphtha	1,12%	3,37%	-0,54%
		diesel	1,09%	3,63%	-1,47%
	Critical Pressure, J&R	naphtha	2,59%	7,18%	0,24%
		diesel	6,90%	19,76%	1,38%
	Critical Pressure, A&G	naphtha	2,86%	8,61%	-0,18%
		diesel	8,29%	29,20%	4,27%
	Acentric Factor, J&R	naphtha	8,93%	35,98%	1,98%
		diesel	7,19%	35,98%	-0,30%
	Acentric Factor, A&G	naphtha	12,55%	40,71%	4,56%
		diesel	9,83%	40,71%	0,95%
	Specific Gravity, A&G	naphtha	3,99%	3,99%	2,61%
		diesel	1,92%	7,75%	-0,25%
Sulfur-containing compounds	Normal Boiling Point, J&R	naphtha	2,38%	8,97%	-2,57%
		diesel	1,92%	7,02%	-2,78%
	Normal Boiling Point, C&G	naphtha	15,80%	68,25%	-18,36%
		diesel	11,99%	49,32%	-13,81%
	Critical Temperature, J&R	naphtha	2,28%	8,79%	-2,40%
		diesel	2,06%	6,80%	-2,82%
	Critical Temperature, A&G	naphtha	2,02%	5,87%	-0,83%
		diesel	1,77%	3,90%	-1,03%

Nitrogen-containing compounds	Critical Pressure, J&R	naphtha	2,64%	10,72%	1,33%
		diesel	3,07%	10,72%	0,96%
	Critical Pressure, A&G	naphtha	2,64%	6,80%	-1,65%
		diesel	2,01%	6,80%	-1,92%
	Acentric Factor, J&R	naphtha	4,00%	13,65%	0,31%
		diesel	6,75%	22,89%	2,30%
	Acentric Factor, A&G	naphtha	6,16%	18,90%	0,95%
		diesel	7,25%	18,90%	2,59%
	Specific Gravity, A&G	naphtha	0,90%	4,25%	-0,75%
		diesel	0,87%	4,25%	-0,72%
	Normal Boiling Point, J&R	naphtha	3,88%	10,02%	-0,31%
		diesel	4,24%	10,02%	-3,66%
	Normal Boiling Point, C&G	naphtha	9,29%	35,64%	-18,81%
		diesel	2,46%	15,40%	-11,72%
	Critical Temperature, J&R	naphtha	3,64%	9,66%	-0,56%
		diesel	3,17%	9,66%	-4,91%
	Critical Temperature, A&G	naphtha	3,38%	6,80%	-0,13%
		diesel	2,28%	6,80%	-3,38%
	Critical Pressure, J&R	naphtha	4,70%	11,22%	0,59%
		diesel	6,20%	11,22%	1,93%
	Critical Pressure, A&G	naphtha	3,14%	12,24%	-5,97%
		diesel	5,36%	12,24%	-4,20%
Oxygen-containing compounds	Acentric Factor, J&R	naphtha	4,73%	13,72%	4,85%
		diesel	6,93%	26,33%	18,19%
	Acentric Factor, A&G	naphtha	5,35%	8,06%	-0,06%
		diesel	3,98%	6,02%	0,77%
	Specific Gravity, A&G	naphtha	1,26%	2,00%	0,10%
		diesel	1,48%	3,57%	1,35%
	Normal Boiling Point, J&R	naphtha	1,50%	3,72%	0,90%
		diesel	6,18%	19,78%	6,80%
	Normal Boiling Point, C&G	naphtha	5,01%	14,06%	2,97%
		diesel	3,19%	14,06%	0,28%
	Critical Temperature, J&R	naphtha	1,28%	3,30%	1,20%
		diesel	5,86%	20,05%	6,94%
	Critical Temperature, A&G	naphtha	2,64%	7,83%	3,93%
		diesel	1,87%	7,83%	2,76%
	Critical Pressure, J&R	naphtha	3,26%	8,14%	3,20%
		diesel	5,59%	18,12%	-0,69%
	Critical Pressure, A&G	naphtha	2,68%	6,82%	1,90%
		diesel	3,59%	22,33%	2,14%
	Acentric Factor, J&R	naphtha	5,15%	14,02%	-3,27%
		diesel	5,40%	14,02%	0,41%
	Acentric Factor, A&G	naphtha	5,36%	11,44%	-2,34%
		diesel	5,34%	11,44%	0,57%
	Specific Gravity, A&G	naphtha	1,18%	4,17%	-0,97%
		diesel	0,82%	4,17%	-0,43%

This study evaluated the predictive accuracy of group contribution methods for key physicochemical properties against experimental data for naphtha and diesel components. The findings reveal method-specific strengths and weaknesses, highly dependent on molecular class and the group contribution method employed.

V.1. Evaluation of the predictive accuracy of the group contribution methods in predicting the normal boiling point.

The normal boiling point (NBP) is a critical property, as it is directly used to fit the molecular composition to the experimental distillation curve. Our analysis shows distinct trends:

Alkanes: The *Joback and Reid* (J&R) method shows increasing error with molecular weight for n-alkanes, a trend less pronounced in the *Constantinou-Gani* (C&G) method. For iso-alkanes, both methods show decreasing error with increasing molecular weight.

Naphthenes: Prediction accuracy is poorer for the J&R method, while the C&G method maintains a more consistent, though not always superior, performance.

Aromatics: For mono-aromatics, the C&G method improves with molecular weight, whereas the J&R method becomes less accurate. For di- and tri-aromatics, absolute error fluctuates at lower molecular weights but increases significantly at higher weights, particularly for the J&R method.

Heteroatomic Compounds: The J&R method demonstrably outperforms the C&G method for sulfur-, nitrogen-, and oxygen-containing compounds. The C&G method shows large, unpredictable fluctuations in error for these classes, with peaks exceeding 50% for some sulfur compounds.

It is important to note that the C&G method (a second-order method) cannot benefit from the more precise third-order corrections available in the newer *Abdulelah-Gani* (A&G) method. Furthermore, the NBP calculation has not yet been implemented for the A&G method in the **ugropy** library.

V.2. Evaluation of the predictive accuracy of the group contribution methods in predicting the specific gravity.

Prediction specific gravity is another fundamental property for matching experimental bulk data. As the J&R method lacks a correlation for it, the A&G method was used exclusively. Despite using only first- and second-order groups (lacking third-order corrections), its accuracy is generally very good. The greatest deviations from experimental values were observed for naphthenes and aromatics, likely due to the absence of these higher-order corrections.

V.3. Possible origin of the observed errors in the predicted properties for the investigated Group Contribution methods

In their work [38] *Joback and Reid* (1984) state that multiple linear regression techniques were used to determine the group contributions for each parameter. These group contributions predict the change in the calculated property in linear fashion, which is most often not an accurate assumption. An example of this is the change in the normal boiling point in compounds within a certain homologous series (n-alkanes, n-alkylbenzenes and etc.) where the normal boiling point increases in non-linear fashion. Thus the error increases with the increase of the carbon number/molecular weight of the compound. Another drawback of the *Joback and Reid* method is the fact that a portion of the data used to regress the group contributions were actually estimated using additive methods during data compilation and nonexperimental sources may not have been screened out [39].

The calculation procedure in the work of *Constantinou and Gani* (1994) [39] uses the DIPPR databank and, additionally, experimental data of *Nikitin et al.* of the critical properties of heavy alkanes, not included in the DIPPR databank. The use of first and second order groups allows the increase of the accuracy of the predicted properties. Another important achievement of the *Constantinou and Gani* (1994) method is the ability to distinguish isomers in calculating their properties – while first order group contributions give the same result, the second order correction gives more accurate results. The optimization algorithm used for the regression of group contributions in *Constantinou and Gani* (1994) method is the modified-*Levenberg* approach, with objective function set to minimize the sum of squares of the difference between experimental and predicted values. Another feature worth noting is that the lefthand side of the equation for normal boiling point, normal melting point and critical properties is exponential, which is expected to better represent the exponential nature of the property value within the higher molecular weight members in the homologous series. The more recent and more advanced method of *Abdulelah-Gani* (2022) [40] uses the same framework as the *Constantinou and Gani* (1994) method, introducing third order groups to fine-tune the calculation accuracy of certain molecular fragments and configurations. The root cause of errors in the *Constantinou and Gani* (1994) and *Abdulelah-Gani* (2022) methods can be attributed to the wide variety of components used in the dataset for each property – presence of chemicals with high polarity, presence of multiple heteroatoms, hydrogen bonding effects which cannot be fully accounted for with group contributions.

Careful examination of the dataset published by the authors of the *Abdulelah-Gani method* [40] on their Guthub site [41] shows that:

- the normal boiling point group contributions were estimated with 5276 compounds with an average absolute error of -1.32 % and a maximum absolute error of -288.06%. The machine learning (ML) variant of the method provides a typical error below 1K between the predicted and the experimental value, with sudden values of 90.55 K error for certain compounds (210 compounds of 5276 total).

- the critical temperature group contributions were estimated with 776 compounds with an average absolute error of 0.11 % and a maximum absolute error of 94.77 %. The machine learning variant of the method provides a typical error below 1 K, with a maximum not exceeding 1.9 K.

- the critical pressure group contributions were estimated with 774 compounds with an average absolute error of -0.50 % and a maximum absolute error of 59.90%. The machine learning variant of the method provides an average absolute error of 0.87 %, with a maximum of 65.08 %.

- the acentric factor group contributions were estimated with 1723 compounds with an average absolute error of -2.65 % and a maximum absolute error of 77.55 %. The machine learning variant of the method provides an average absolute error of 1.08 %, with a maximum of 102.65 %.

V.4. Evaluation of the Molecular Library

A crucial finding of this work concerns the composition of the molecular library itself [42]. For the naphtha fraction (161 molecules), the inclusion of 23 nitrogen-containing and 12 oxygen-containing compounds (e.g., alcohols, carboxylic acids) is chemically unjustified. Straight-run naphtha typically contains only trace amounts of nitrogen (30-50 ppm, primarily as pyridines) and negligible oxygen; amines and acids are not present. Similarly, 30 sulfur-containing compounds are excessive for a fraction where sulfur rarely exceeds 400 ppm, and the absence of prevalent species like mercaptans is notable. This over-representation of heteroatomic species (58 components for <1 wt% of the fraction) artificially dilutes the hydrocarbon resolution.

This issue persists in the diesel fraction (885 molecules), where over 200 sulfur-containing and 200+ nitrogen/oxygen-containing compounds are used to represent heteroatom contents typically below 1 wt% and in the hundreds of ppmw, respectively. The presence of alcohols and carboxylic acids in straight-run diesel is also highly improbable.

This work underscores both the power and the limitations of current tools for the molecular modeling of petroleum fractions. The synergy of open-source molecular databases [42] and programming libraries like ugropy [43,44] provides an unprecedented foundation for research. The use of SMILES strings enables automated property prediction and database mining, significantly advancing the field.

V.5. Application and development prospects of the methods for molecular reconstruction of petroleum and petroleum fractions

Molecular modeling technology can be viewed as a tool to improve our understanding of petroleum itself and refining technology, as it incorporates as many fundamental principles as possible to quantitatively describe phenomena in their greatest details. Like most models,

the molecular composition models of petroleum can also be seen as an imperfect approximation of the real system [45]. This can be explained by the extremely high complexity of the diverse petroleum fluids, which cannot always be sufficiently well described by the algorithm used and the analytical procedure applied. For example in the study of *Campbell et al.* [46], who employed the same SR framework to reconstruct four vacuum residues (Hondo, Maya, Arabian Light, and Arabian Heavy), an excellent fit for the kinetic parameters of thermal cracking of Arabian Light and Maya resids and a poorer reaction model fit for the Hondo and Arabian Heavy resids was obtained. A possible explanation for the poorer modeling results for the Hondo and Arabian Heavy resids may be considered the poorer structural fits for these two resids, i.e., the structural model deviations propagated uncertainty into the reaction model. This highlights the great importance of the chemical nature of petroleum fluids modeled at the molecular level. The review articles dealing with the molecular modeling of petroleum appearing so far (*Ren et al.*[47], *Wang et al.*[48], and *Chen et al.* [49] were focused mainly on the progress achieved in the molecular modeling methods. Less attention was paid to the subject of the modeling — the chemical composition of petroleum. In reviewing the literature on the molecular reconstruction of crude oil, we found that the composition of the crude oils studied, which were modeled, did not cover the full range of variation in the chemical composition of crude oils worldwide. The studies of *Kheirollahi* [50], *Hinkle et al.* [51], and *Shishkova et al.* [52] present a good example of the limits of variation of crude oil chemical composition expressed by the contents of SARA fractions and density. The data in Table 27 can be considered representative for the limits in the variation of density and SARA fraction contents of the crude oils around the globe. A correlation analysis was performed to examine the relationship between density and the content of the different SARA fractions, as density has been a target in the optimization algorithms of the molecular reconstruction giving the best result [53]. The results of a correlation analysis of the data in Table 27 is given in Table 28.

Table 27. SARA analysis and density data of different crude oil samples from around the world.

Density at 20°C (D ₂₀), g/cm ³	Saturates, wt. %	Aromatics, wt. %	Resins, wt. %	Asphaltenes , wt. %	Hydrogen content, wt. %**
1.119	4.0	17.0	37.0	43.0	9.01
1.021	28.3	39.1	11.4	21.2	10.46
1.014	22.5	40.2	16.4	20.3	10.56
1.004	27.3	38.5	15.3	19.2	10.71
0.997	24.8	41.0	17.9	16.3	10.82
0.953	34.2	36.3	12.9	16.6	11.47
0.902	36.7	39.1	12.0	12.2	12.22
0.858	76.7	15.0	3.6	2.7	12.88
0.854	67.3	26.5	3.3	2.9	12.94
0.853	73.4	15.7	4.4	6.2	12.95

0.807	94.8	3.4	0.8	1.0	13.62
0.788	74.8	24.5	0.7	0.1	13.91
0.863*	70.1	19.8	9.5	0.0	13.55

Note: *The data in the last row from Table 14 are related to Daqing crude oil [56].

** Hydrogen content of crude oil was calculated using Equation (9) (in-house method)

$$\text{Hydrogen content in crude oil (wt. \%)} = -14.802 \times D_{20} + 25.575$$

$$R = 0.99 \quad (9)$$

Table 28. Correlation matrix of the data in Table 27.

	Density	Saturates	Aromatics	Resins	Asphaltenes
Density	1				
Saturates	-0.95	1			
Aromatics	0.51	-0.70	1		
Resins	0.91	-0.88	0.30	1	
Asphaltenes	0.96	-0.91	0.36	0.94	1

The data in Table 28 do indeed confirm that density is strongly correlated with the content of saturated hydrocarbons and asphaltenes, as well as with a slightly weaker, but still strong, correlation with the resin content.

The distribution of different molecular structures based on the number of carbon atoms in their molecule influences the distillation curve of crude oil, as shown in Figure 14.

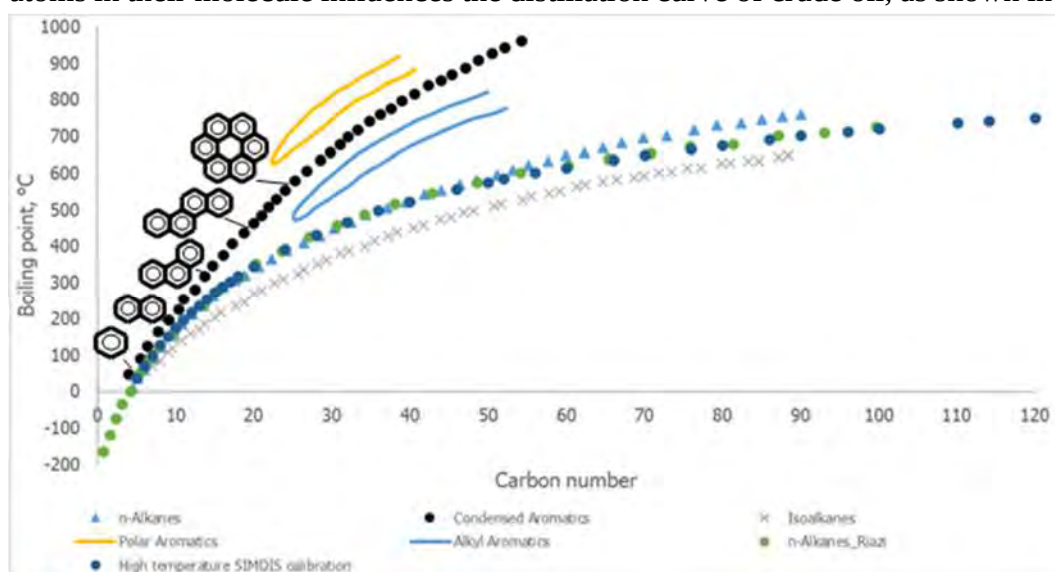


Figure 14. Relationship between the number of carbon atoms and the boiling point of the various hydrocarbons and their polar derivatives found in crude oil (Modified from Ramirez-Corredores [54] and Riazi [55]).

Figure 15 presents data of high temperature simulated distillation (HTSD, ASTM D7169) of the crude oils from Table 27.

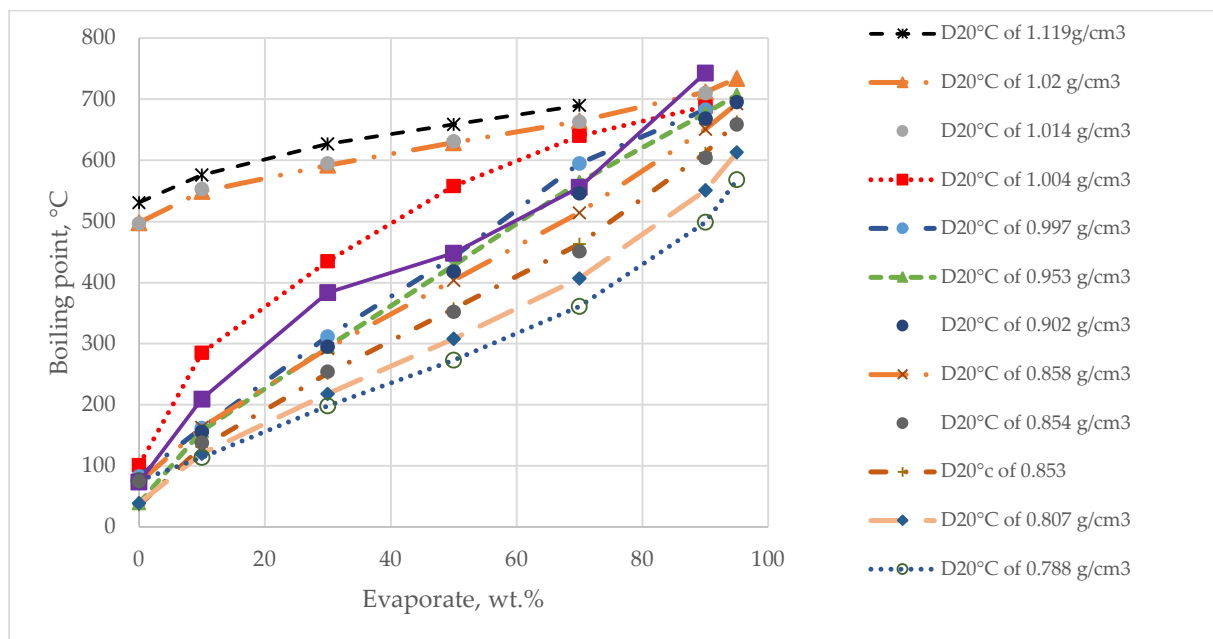


Figure 15. HTSD of crude oils from whose density and SARA composition was shown in Table 27.

It is evident from the data in Figure 15 that distribution of components according to the boiling points of the 12 crude oils is different as different is their SARA composition.

The data in Table 27 and Figure 15 show that the diversity in the group hydrocarbon composition (SARA) as well as the boiling point distribution and therefore the molecular weight distribution is so great that the proof of the ability of a given molecular modeling technique to adequately mimic the actual molecular composition of crude oil should be accepted when it is validate across the entire range of variation of density, SARA composition and boiling point distribution. *Zhou et al.* [56] discussed the catalytic cracking of Daqing crude oil, whose properties are presented in the data of Table 27 and Figure 15. *Zhang et al.* [57] mentioned that they examined their novel method SOHSL-CM by availing 42 sets of crude oil data without providing any information about these crude oil data. *Sihang et al.* [58] predicted the physical properties of five crude oils whose hydrogen content varied between 11.98 and 13.65 wt.%. *Xie et al.* [42] modeled the molecular chemical composition of 22 crude oils whose density varied between 0.830 and 0.970 g/cm³ and distillation characteristics oscillated for their initial boiling point between 273 and 398° C and 50% evaporate temperature in the range 537—765° C. All these investigations indicate that the full range of possible variations in the properties of crude oils being modeled as illustrated in the data of Table 3 and Figure 15 was not covered. This finding suggests that the future investigations of crude oil molecular reconstitution should be directed to cover all possible variations in

petroleum bulk properties, and especially these petroleum oils which have a higher concentration of resins and asphaltenes. These petroleum fractions are the most complex and therefore the most difficult to model.

It is obvious from the data on Figure 15 that distribution of the components of the 12 crude oils according to their boiling points is different, as is their SARA composition.

Broeke [59] calculated the number of potential organic substances for such a broad carbon number range to be in 10^{60} . Figure 16 shows the dependence of number of molecules in crude oil on the carbon number of its constituents.

Petroleum scientists consider that the number of different molecules in petroleum is formidable but not as astronomical as predicted by simple combinatorics. The number of molecules in petroleum oils used to reconstruct their molecular chemical composition was reported in several studies to affects the accuracy of property predictions [60,61], but this number ranges in the order of 10^4 – 10^5 [61,62].

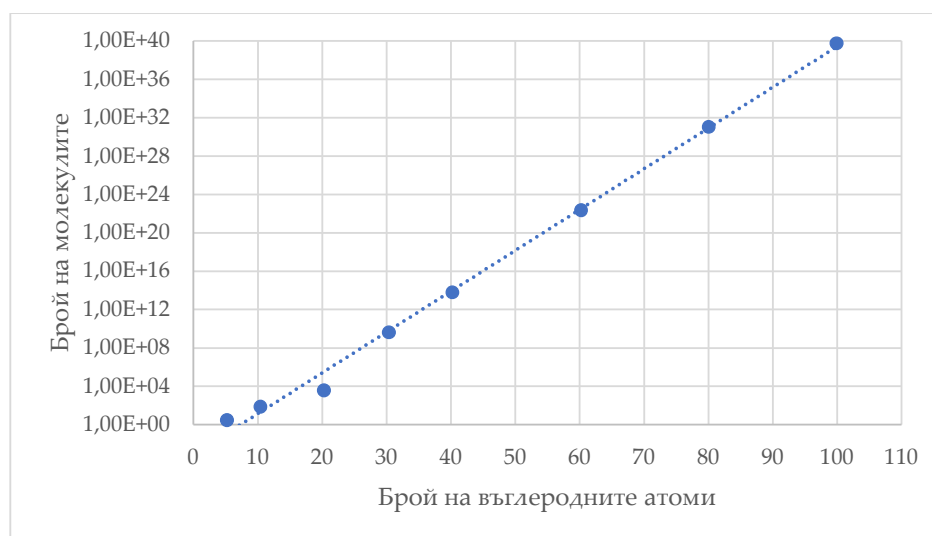


Figure 16. Number of molecules in crude oil as a function of their carbon number. (Adapted from Broeke [59]).

The greatest number of molecules used to reconstruct petroleum oil (Venezuelan vacuum residue) in all reviewed studies is 400,000 [63]. Despite the use of 400,000 molecules, built on the base of about 600 structure attribute, by *Zhang et al.* [63] the calculated SARA composition and simulated distillation curve featured with a lower accuracy compared to the calculations of *Yang et al.* [64] who availed 6,900 molecules and another molecular modeling framework (SOL). This comparison implies that the number of molecules is not as critical as the modeling strategy used to adequately reconstruct the molecular composition of petroleum.

The research of *Yang et al.* [64] proposed a molecular modeling strategy that seems easy to apply in terms of the availability of SARA and element composition data along with simulated distillation and report accurate calculations with a tractable number of molecules. However, it needs to be validated for vacuum residual oils featured with high resins and asphaltene content such as Boscan VR (Resins+asphaltenes of 57.6 wt.%), Vasconia VR (47.9 wt.%, Castilla VR (54.0 wt.%) whose hydroprocessing is very challenging [65].

The molecular weight of petroleum vacuum residues can vary between 600 and 1440 g/mol as reported in [64,65] and this should be taken into account in the process of molecular reconstruction. Vacuum residues reconstructed in the studies of *de Oliveira et al.* [67], *Campbell and Klein* [62], *Zhang et al.* [68], *Yang et al.* [64] and others reviewed in this work do not cover the whole diapason of variation of vacuum residue characteristics. Therefore, additional molecular reconstruction studies are needed to embrace the whole range of property variation of vacuum residues and prove that the applicability of the molecular modeling frameworks. The same is valid for the vacuum gas oils reconstructed in the research of *Wang et al.* [69], *Ren et al.* [47] and other researches reviewed in this article, which do not cover the full compositional diversity for VGO as reported in the research [66].

Most molecular modeling frameworks used in the various studies on the recovery of oil and its fractions during the considered period 1989-2025, beginning of 2026, show that they are capable of reconstructing all types of petroleum fluids, despite the fact that their original versions have shown some limitations, mainly for heavy oils. The SOL method was the most frequently explored, following by SR, Hybrid, and MTHS. MTHS was predominantly used for modeling of light oils, which restricted its usage [60]. However, the research of *Song et al.* [70] opened a new perspective for the MTHS approach showing that it can be used for reconstruction of not only light oils but also heavy petroleum fractions, reporting extremely low computation time (between 3 and 36 seconds). Over the years, the applied molecular reconstruction frameworks demonstrated a significant progress in terms of range of application, speed of computation, and accuracy of prediction. It is difficult to rank any of the investigated methodologies considering the achieved progress, although the observed predominance of SOL method utilized in the molecular reconstitution of petroleum. Each methodology investigated has its advantages and disadvantages, depending on the required application, but what is desired is a representation that preserves the maximum amount of molecular information while maintaining the necessary simplicity in computational manipulation.

Regarding the progress in the speed of molecular reconstruction, Figure 17 illustrates the huge improvement in the applied algorithms, hardware and modeling framework from 1997 to early 2026, allowing a 423-fold reduction in CPU time for the reconstruction of the most difficult to model petroleum fraction — vacuum residue. Different optimization algorithms (GA, SA, SQP, ANN+GA, nonlinear least squares optimization, PSO, GA-PSO, Bayesian likelihood-free inference) have been applied over the years.

Their successful performance was found to depend on the specificity of the modeling strategy and it cannot be deduced that a given algorithm exhibits the best performance in all petroleum molecular reconstitution studies. The improvement in the molecular reconstitution computation time observed lately enables using the reconstructed molecular composition of petroleum in process modeling and optimization [60,71,72].

Despite significant advances in molecular reconstitution methodologies, their integration with commercial process simulation software remains challenging. Most widely used simulators such as Aspen HYSYS, Aspen Plus and others continue to rely primarily on pseudo-component approaches for petroleum characterization [21]. This discrepancy creates a gap between the detailed molecular information generated by reconstitution models and the simplified representations employed in process simulation. Research in this field showed that the gap could be bridged by three approaches: 1) Molecular reconstitution is performed outside the process simulator environment and the resulting molecular compositions or pseudo-components with enhanced structural information are then imported into the simulator as user-defined components; 2) A hybrid approach combines traditional pseudo-component generation with molecular information. This strategy balances computational efficiency with molecular detail where it matters most for reaction kinetics [33]; 3) Development of custom reactor models that directly utilize molecular reconstitution outputs, bypassing the limitations of standard simulator components. These models often employ reduced reaction networks derived from detailed molecular kinetics [73,74]. The integration of molecular reconstitution models with process simulators faces several technical challenges such as computational overload, data consistency, reaction network complexity and lack of standardization. Recent developments in software architecture, particularly the adoption of CAPE-OPEN standards and the emergence of open-source simulation platforms like DWSIM, offer promising avenues for more seamless integration of molecular reconstitution approaches into the process simulators [75, 76].

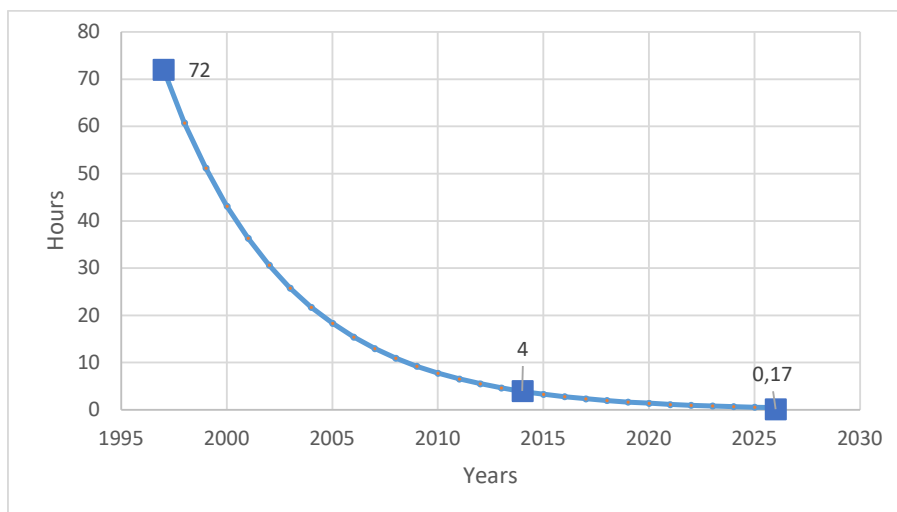


Figure 17. CPU time evolution for molecular reconstruction of vacuum residue over the years.

V.6. Conclusions and recommendations concerning the preparation of input data for molecular reconstruction

Based on the performed calculations using both group contribution methods that of *Joback and Reid* [38] (J&R) and the method of *Abdulelah-Gani* [40] (A&G) the following conclusions can be made:

1) The selection of the method for physical properties estimation is critical. No single group contribution method is universally superior. The J&R method performs better for most heteroatomic compounds, while the A&G method is required for specific gravity and shows strengths for certain hydrocarbon classes. The implementation limitations of these methods in software libraries must be carefully considered.

2) The empirical data is preferred: For lighter fractions like naphtha and diesel, the optimal strategy is to use available experimental property data (e.g., from DIPPR, API Databook) whenever a compound is identified. Group contribution methods should serve as a fallback for missing data, not the primary source. This hybrid approach will enhance the fidelity of molecular reconstruction optimization.

3) Molecular library realism is paramount: The accuracy of any molecular reconstruction is contingent on the chemical realism of its underlying molecular library. The over-representation of improbable or incorrect compound classes (e.g., acids in naphtha, excessive heteroatoms) introduces significant bias. Future libraries must be rigorously validated against typical petroleum fluid compositions to ensure they reflect plausible chemistry rather than just mathematical convenience.

4) A persistent challenge remains the scarcity of reliable experimental data. As noted by *Joback and Reid* [38], great care must be taken to avoid data contaminated by earlier predictions, a task that becomes increasingly difficult for heavier fractions where experimental data is exceedingly rare.

5) A possible good practice when dealing with fractions heavier than diesel, where experimental data is scarce, is to use the available methods for property prediction for pseudo-components to complement the properties calculated with the group contribution methods. Since these correlations are consistent with wide range of molecular weights, they can be used as pivotal data to compare the predictions of the group contribution methods. If a discrepancy of more than 10% between the two calculation approaches is observed, the result of the pseudo-component correlation shall be used instead of the group contribution method result.

VI. Dissertation conclusions

1. The superiority of gas chromatographic methods for simulated distillation over those of physical vacuum distillation in modeling separation processes in oil refining has been established.

2. Research has shown that the high temperature simulated distillation method (ASTM D 7169) can be considered equivalent to the true boiling point (TBP) for heavy petroleum fractions.

3. A detailed evaluation of the correlations available in the literature for predicting the molecular weight of petroleum fluids in the range from 70 to 1685 g/mol was performed.

4. A new correlation for predicting molecular mass has been derived using nonlinear regression and an artificial neural network model, which, with its increased prediction range and increased accuracy, outperforms the correlations published in the literature.

5. A detailed evaluation of the methods available in the literature for predicting critical temperature and critical pressure for oil fractions and individual hydrocarbons has been performed.

6. New correlations for predicting critical temperature and critical pressure have been derived using nonlinear regression and an artificial neural network model, which outperform correlations published in the literature with increased accuracy in predicting critical properties for individual hydrocarbons.

7. The change in viscosity of mixtures of various vacuum distillation residues with lighter fractions was investigated and it was confirmed that their viscosity decreases exponentially with increasing concentration of the lighter fraction.

8. An evaluation of existing correlations for calculating the viscosity of mixtures of light and heavy petroleum fractions was performed, and it was determined that the linearized form of the Walther equation using the viscosity blending index concept is most suitable for modeling mixtures of heavy fractions with or without the addition of a light fraction diluent, with an accuracy very close to that of equations using interaction parameters.

9. It has been confirmed that the use of an artificial neural network provides higher accuracy in predicting the viscosity of mixtures of heavy fractions and diluent compared to empirical correlations.

10. A new correlation for predicting the viscosity of mixtures of heavy fractions and diluents, obtained through nonlinear regression analysis of experimentally obtained results, is proposed. The proposed new correlation demonstrates increased accuracy in modeling the viscosity of this type of mixtures.

11. A new correlation dependence is proposed for predicting the viscosity of mixtures of heavy fractions and diluents based on the use of regression coefficients that are derived for different viscosity measurement temperatures, increasing the temperature range of the modeled mixtures.

12. An extensive literature review of the available methods and approaches for performing molecular reconstruction of crude oil and oil fractions was conducted, covering the period from 1989 to 2025 and the beginning of 2026. Progress in optimization algorithms and the applicability of molecular reconstruction in modeling various petroleum fluids and oil refining processes was tracked.

13. An evaluation of the most commonly used group contribution methods for generating properties of individual components in the molecular database for molecular reconstruction has been made. The errors in the prediction of the most important properties have been evaluated and recommendations for improving the accuracy of the input data used in the molecular reconstruction process have been presented.

VII. Dissertation contributions

1. The correlations derived in this dissertation for predicting the molecular mass, critical temperature and critical pressure of oil fractions and individual hydrocarbons can be used in simulating and modeling petroleum fluids and oil refining processes, improving or supplementing the predictions of existing correlations used so far.

2. The conducted studies show the superiority of gas chromatographic methods of simulated distillation over physical distillation methods in performing distillation analysis of petroleum fluids. The confirmation of the equivalence of the obtained data with those of a true boiling point curve reinforces the advantage of these methods, due to the elimination of the need to convert the obtained data into a true boiling point curve.

3. The proposed correlations for calculating the viscosity of mixtures of heavy fractions and diluents of light fractions provide an opportunity to model the viscosity of such mixtures in order to improve the transport properties of heavy fractions using an optimal amount of light fractions used as a diluent. These light fractions have a correspondingly higher cost and reducing their input has direct economic benefits.

4. The detailed review of the growing popularity and application of the molecular reconstruction approach and the analysis of the importance of the preparation of the input information on the properties of the molecules in the libraries used for molecular reconstruction can serve to further improve the accuracy of the obtained results and the scope of application of molecular reconstruction.

ДЕКЛАРАЦИЯ ЗА ОРИГИНАЛНОСТ

По чл.27, ал.2 от ПП ЗРАСРБ

От Светлин Петров Василев

/трите имена на докторанта/

Към катедра "Индустриални технологии и мениджмънт"

/наименование на катедрата, факултет/

При Бургаски държавен университет "проф. д-р Ас. Златаров"

/наименование на университета/

"Заглавие на дисертационния труд:

"Моделiranje свойствата на нефтени флуиди и процеси в нефтопреработването"

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Декларатор:

Дата: 15.07.2026г

Светлин Петров Василев
Подпис; трите имена

VIII. List of publications on the topic of the dissertation

1. Stratiev, D.; Shishkova, I.; Ivanov, M.; Dinkov, R.; Argirov, G.; **Vasilev, S.**; Yordanov, D. Validation of Diesel Fraction Content in Heavy Oils Measured by High Temperature Simulated Distillation and Physical Vacuum Distillation by Performance of Commercial Distillation Test and Process Simulation. Appl. Sci. 2022, 12, 11824. <https://doi.org/10.3390/app122211824>
2. Stratiev, D.; Sotirov, S.; Sotirova, E.; Nenov, S.; Dinkov, R.; Shishkova, I.; Kolev, I.V.; Yordanov, D.; **Vasilev, S.**; Atanasov, K.; et al. Prediction of Molecular Weight of Petroleum Fluids by Empirical Correlations and Artificial Neuron Networks. Processes 2023, 11, 426. <https://doi.org/10.3390/pr11020426>
3. Sotirova, E.; **Vasilev, S.**; Stratiev, D.; Shishkova, I.; Sotirov, S.; Nikolova, R.; Veli, A.; Bureva, V.; Atanasov, K.; Georgieva, V.; et al. Comparison of the Methods for Predicting the Critical Temperature and Critical Pressure of Petroleum Fractions and Individual Hydrocarbons. Fuels 2025, 6, 36. <https://doi.org/10.3390/fuels6020036>
4. Stratiev, D.; Nenov, S.; Shishkova, I.; Sotirov, S.; Sotirova, E.; Dinkov, R.; Yordanov, D.; **Vasilev, S.**; Stratiev, D.D.; Prediction of Viscosity of Blends of Heavy Oils with Diluents by Empirical Correlations and Artificial Neural Network, Ind. Eng. Chem. Res. 2023, 62, 49, 21449–21463 <https://doi.org/10.1021/acs.iecr.3c02472>
5. **Vasilev, S.**; Stratiev, D.; Shishkova, I.; Dinkov, R.; Yordanov, D.; Abdellatief, T.M.M.; Sotirov, S.; Sotirova, E.; Dimitrov, A.; Georgieva, V.; et al. Oil Characterization, Molecular Modeling and Process Simulation in Petroleum Research and Industry, Opportunities, Challenges and Perspectives. Molecules 2026, 31, 1645. <https://doi.org/10.3390/molecules31101645>
6. **Vasilev, S.**; Stratiev, D.; Shiskova, I.; Yordanov, D.; Abdellatief, T.M.M.; Nikolova, R.; Sotirov, S.; Sotirova, E.; Dimitrov, A.; Georgieva, V. Input Data for Molecular Reconstruction of Petroleum Fractions—A Reality Check. Processes 2026, 14, 1606. <https://doi.org/10.3390/pr14101606>

IX. Noted citations of publications related to the development of the dissertation

Stratiev, D.; Shishkova, I.; Ivanov, M.; Dinkov, R.; Argirov, G.; Vasilev, S.; Yordanov, D. Validation of Diesel Fraction Content in Heavy Oils Measured by High Temperature Simulated Distillation and Physical Vacuum Distillation by Performance of Commercial Distillation Test and Process Simulation. Appl. Sci. 2022, 12, 11824.

1. Kosolapova, S.M.; Smal, M.S.; Rudko, V.A.; Pyagay, I.N. A New Approach for Synthesizing Fatty Acid Esters from Linoleic-Type Vegetable Oil. *Processes* 2023, 11, 1534. <https://doi.org/10.3390/pr11051534>.
2. Kukharova, T.; Martirosyan, A.; Asadulagi, M.-A.; Ilyushin, Y. Development of the Separation Column's Temperature Field Monitoring System. *Energies* 2024, 17, 5175. <https://doi.org/10.3390/en17205175>.
3. Yan, H.; Zhao, C.; Zuo, X.; Shu, J.; Hua, W.; Guan, L.; Gu, K. Research on a Small Oil Detection Instrument Combining Micro-Distillation Range Analyzer and Raman Spectroscopy Technology. *Sensors* 2025, 25, 2130. <https://doi.org/10.3390/s25072130>.
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