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EVALUATION OF CALCULATIVE TOOLS INTENDED FOR THE PREDICTION OF LIQUID HYDROCARBON VISCOSITY

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Master's thesis carried out under the supervision of M.Sc. Kati Sandberg, Professor Reko Leino,
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ABSTRACT

The main purpose of this work was to comprehend and promulgate the process of predicting the kinematic viscosity of liquid hydrocarbon mixtures using empirical correlations and mixing rules. The performance of the most promising empirical correlations, describing the temperature dependence of the kinematic viscosity of liquid hydrocarbon mixtures, as well as mixing rules, describing the outcome of combining two fluids differing in kinematic viscosity, are evaluated by comparative means against a diverse experimental dataset attained exclusively for this work. The evaluated methods were chosen based on recognition and potentiality expressed in previous publications. A total of five empirical correlations, six mixing rules, and recent amended versions (where applicable) were investigated. The general results indicate that the most accurate and universal method of both types were found.

Keywords: Liquid viscosity, kinematic viscosity, hydrocarbons, empirical estimation, mixing rules

POPULÄRVETENSKAPLIG SAMMANFATTNING

Viskositeten hos en vätska utsäger hur "tjock" eller "tunn" en vätska är. En vätska som till exempel vatten har en låg viskositet och är mycket tunn, medan till exempel honung har en betydligt högre viskositet och är mycket tjockare. Viskositeten är en av de viktigaste egenskaperna hos kolvätevätskor (bränslen, smörjmedel, oljor osv.). En för hög eller för låg viskositet kan orsaka katastrofala problem i de flesta tillämpningarna. Standardiserade gränser för hur låg eller hög viskositeten hos produkter som består av kolvätevätskor får vara har fastställts på grund av detta. Gränserna är oftast temperaturbundna, dvs. en viss viskositet skall uppnås vid en viss temperatur. Viskositeten hos produkterna kan variera avsevärt, eftersom oljeraffinaderier är mycket komplicerade och allt fler nya råvaror tas i bruk tack vare den ökande klimatmedvetenheten. Det skulle därmed vara mycket nyttigt att kunna estimeras viskositeten hos kolvätevätskor vid olika temperaturer på basen av till exempel andra fysikalisk-kemiska egenskaper. I denna pro gradu-avhandling undersöktes flera olika metoder som kan lösa detta problem. Det visade sig att det bästa sättet för att estimeras viskositeten för en kolvätevätska vid en okänd temperatur var att använda kända värden för viskositet vid en eller två temperaturer. Med andra ord betyder detta att kända viskositetsvärden används för att bestämma viskositeten vid ytterligare temperaturer. Alternativt kan temperaturen då 50 volymprocent av ett prov har destillerats och i vissa fall densiteten vid 15 °C användas. Alla metoder som hittades visade sig vara mycket noggranna för proven som undersöktes. Estimering av viskositeten då två vätskor av känd konsistens blandas ihop undersöktes också. Två mycket exakta metoder för estimeringen av de resulterande blandningarnas viskositet hittades.

FOREWORD

This thesis was conducted as a part of a project at Neste Oyj, Porvoo, Finland during 2020. First and foremost, I would like to thank my supervisor Kati Sandberg at Neste for the opportunity to be able to conduct this work for a truly brilliant company and for the guidance, patience, and feedback over the course of the work. Secondly, I would like to express my sincerest gratitude to Cesar Araujo at Neste for both the mental and practical support regarding calculations and statistics over the course of the work. Furthermore, I would also want to thank the laboratory technicians at Neste for their hard work and dedication as well as everyone else at Neste for taking me in and making me a part of the group.

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ABBREVIATIONS

AAD	Absolute Average Deviation
API	American Petroleum Institute
API TDB	API Technical Data Book
ASTM	American Society for Testing and Materials
A-S & M	Aboul-Seoud and Moharam correlation
CEN	Comité Européen de Normalisation, European Committee for Standardization
cP	Centipoise
cSt	Centistoke
DEFSTAN	Defense standard
EN	European Norms, (European Standards)
ISO	International Organization for Standardization
JIG	Joint Inspection Group
LPG	Liquified Petroleum Gas
MBP	Mass Boiling Point
NFGW	New Focus on the General Walther equation-correlation
P	Poise
St	Stoke
VABP	Volume Average Boiling Point
VBI	Viscosity Blending Index
VBP	Volume Boiling Point
VI	Viscosity Index
WABP	Weight Average Boiling Point

DEFINITIONS

Blend	Mixture of two or more components (where component = pure compound/hydrocarbon mixture/fuel)
Cloud point	Temperature below which waxes in fuel solidify and cause a cloudy appearance (clogging filters and injectors)
Empirical correlation	A relationship or correlation supported by experiment or observation (not necessarily supported by theory)
Freezing point	Lowest temperature at which a fuel remains free of solid hydrocarbon crystals (crystals restrict flow of fuel through filters if present)
Hydrocarbon mixture	A mixture containing various hydrocarbon molecules
Mixing rule	An equation used for the estimation of viscosity when two or more known components are mixed.
Neat hydrocarbon mixture	Hydrocarbon mixture which has not been blended with another hydrocarbon mixture (e.g. a sample of a production run of fuel)

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1 INTRODUCTION

Traditional oil refineries are enormous facilities where crude oil is separated into different fractions and then processed to give a plethora of products. The most characteristic part of a traditional oil refinery is, among other process units, the primary atmospheric distillation tower (i.e. the topping unit). Here, the crude oil is distilled, giving different fractions, which are then processed further to produce various oil-based products. Traditional products of oil refining can be categorized into four different classes based on the targeted use. These include: 1) Industrial and domestic fuels (gas oils, fuel oils, or LPG (Liquified Petroleum Gas)); 2) Motor fuels (gasoline, diesel, kerosene, LPG); 3) Feedstocks for various chemical industries (virgin naphtha, LPG, olefins); and 4) Other products (e.g. lubricating oils, bitumens, paraffins, and solvents).¹ A simplified view of the various products produced in a traditional oil refinery is presented in **Figure 1**.

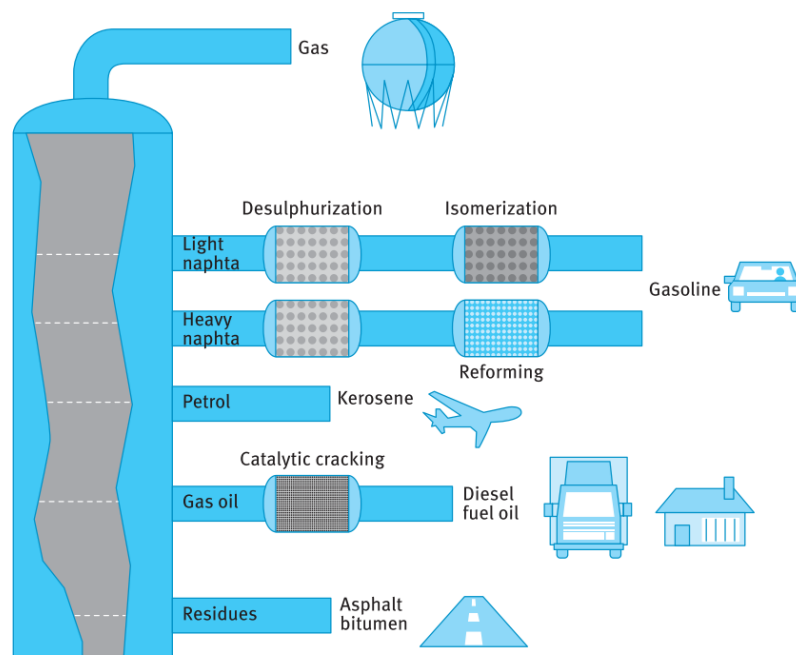


Figure 1: Simplified view of the products of a traditionally run refinery. Reproduced from: D. Y. Murzin, *Chemical Reaction Technology*; Walter de Gruyter GmbH: Turku, Finland, 2015, p.116 (see ref. 1.).

The chemically similar components of crude oil (hydrocarbons) are separated by distillation, as mentioned above. In distillation, separation occurs due to the differences in boiling points of the constituents of the mixture being distilled. The boiling points of the individual components are, on the other hand, related to the number of carbon atoms in the molecules (i.e. the size of the molecule). Fractions owning a higher boiling point (larger molecules) are

thus recovered at the lower parts of the distillation unit, while fractions with lower boiling points (smaller molecules) are recovered at higher sections of the distillation tower. A more detailed illustration of the atmospheric distillation unit, showing the approximate side stream draw-offs (side cuts) is depicted in **Figure 2**. Notice that some of the side streams are returned as reflux.¹

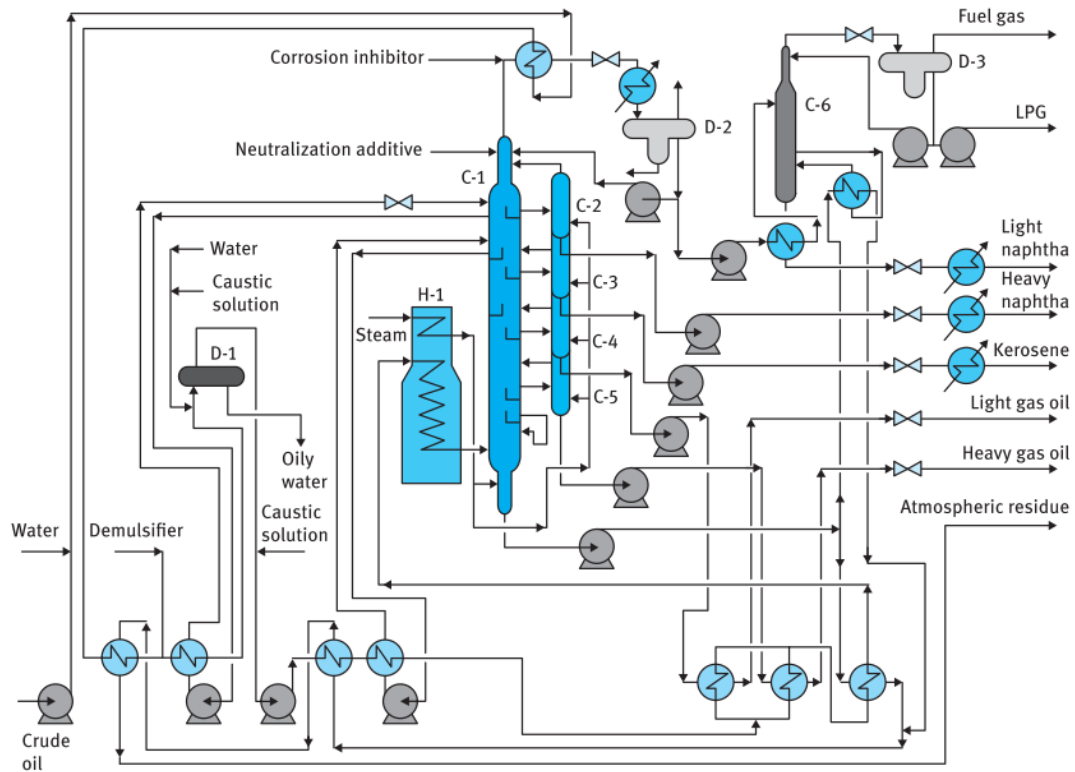


Figure 2: Illustration of the process scheme of a crude oil atmospheric distillation unit. Reproduced from: D. Y. Murzin, *Chemical Reaction Technology*; Walter de Gruyter GmbH: Turku, Finland, 2015, p.117 (see ref. 1.).

Various parameters such as reflux rate and temperature profile can be adjusted at this stage of the process to affect the properties of the side streams.¹ Further processing of the side streams introduces multiple parameters which may be altered to affect the properties of the final product. Examples of boiling point ranges and carbon number ranges of various oil fractions are given in **Table 1**.

Table 1: Boiling ranges of different oil fractions.¹

Fraction	Boiling range (°C)	Carbon number range	Use
Fuel gases	<20	1-5	Methane, ethane, propane, butane
Naphtha	70-170	6-10	Gasoline base, chemical feedstock
Kerosene	170-250	10-14	Jet, diesel, and heating fuel
Gas oil	250-340	14-19	
Heavy fraction	350-500	19-35	Lubricants, base stock, boiler fuel
Vacuum residue	>500	>35	Bitumen, heavy fuel oil, marine fuel oil

The complexity of a refinery ensures that two refineries with the same refining scheme are very unlikely to exist. Process schemes of refineries are usually designed based on market demand and crude oil characteristics. A general example of an oil refinery scheme including various process units for the reaction and workup of side streams, as well as the resulting products is shown in **Figure 3**.¹

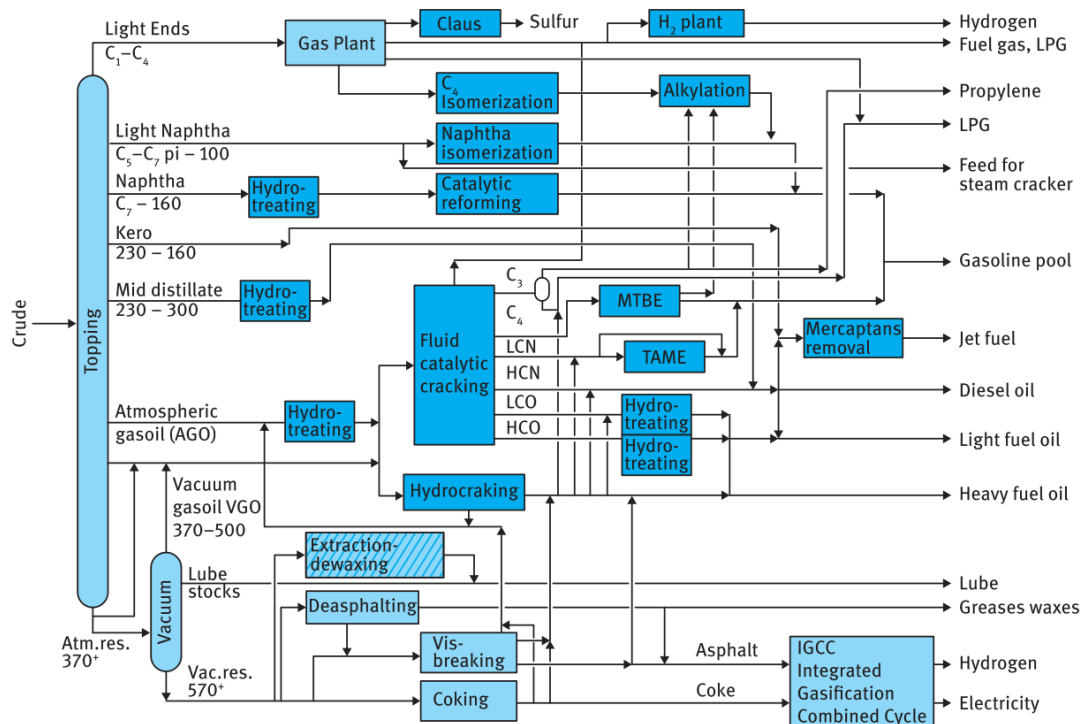


Figure 3: Process scheme of a generic refinery. Reproduced from: D. Y. Murzin, *Chemical Reaction Technology*; Walter de Gruyter GmbH: Turku, Finland, 2015, p.119 (see ref. 1.).

Middle distillates (e.g. diesel fuel, aviation fuel, and heating oil) are commonly among the main products of a traditionally run refinery. The complexity of a refinery results in a very wide range of grades within each product group. Most of the products produced in a refinery are specification products, meaning that the physicochemical properties of the products must meet certain limits.¹ The estimation of the final physicochemical properties of products has therefore always been important for the petroleum industry. The recent and future introduction of alternative fuel feedstocks and production methods due to the rising awareness of global warming has introduced added complexity to the estimation of key properties of the products.² Key properties of liquid hydrocarbons of the middle to heavy distillate range are, among others, the density, cloud point, freezing point, pour point, cetane number, and viscosity of the products.²⁻⁴

Viscosity is one of the most important properties of liquid hydrocarbon products.^{3,4} A precise theory expressing the viscosity of liquid fluids has not been found, despite a century of theoretical research, due to the complexity of the involved liquid momentum transfer mechanisms. Furthermore, the effect of temperature on the viscosity of liquids is characterized by a non-linear relationship. Simple methods for the accurate prediction of liquid viscosity do not exist and the introduction of alternative feedstocks introduces new aspects to consider.^{2,5,6} All the aforementioned arguments served as motivation for this thesis.

2 BACKGROUND

Recent increase in the production of heavy and extra-heavy crude oils has accentuated the importance of estimating physical and chemical properties, such as viscosity and density. These parameters are of utmost importance in for instance the pipeline transportation of oils.⁷ One of the main properties of interest in the field of base oils and lubricants has always been the viscosity, since the main function of the lubricants in a mechanical system is the control of friction and wear. Change in the viscosity of oil is well known to result from changes in temperature, pressure, and shear rate. The film-forming properties of oil are also known to be proportional to these dimensions. Lubricant viscosity is extremely sensitive to temperature change, which is why the temperature dependence of viscosity is of major concern for the lubricant industry.⁸ Efforts concerning the optimization of direct-injection diesel engines is primarily focused on the improved atomization of the fuel when sprayed into the combustion chamber. This is usually achieved by an increase in injection pressure, whereas the size of the droplets formed within the injectors is governed by fuel viscosity through a mechanism called droplet breakup. Higher viscosity translates to larger droplets as well as additional strain on all mechanical parts of the fuel system. Droplet size is, in addition, directly related to the emission characteristics of an engine, since smaller droplets favor vaporization and more complete combustion. Herein, a balance between emissions and viscosity of the fuel is found, which clearly describes the importance of accurate prediction of hydrocarbon viscosity.⁴ Aircraft fuel tanks can reach extremely low temperatures at high altitudes. A crucial characteristic of jet fuel is therefore the low-temperature fluidity of the fuel. Low-temperature fluidity of aviation fuel can be characterized by two intrinsic features: freezing point, and kinematic viscosity. These must be sufficiently low, ensuring proper fuel fluidity in the turbine engine systems of aircraft.⁹

Viscosities of fuels may be specified to fall within a maximum limit, minimum limit or even both, in standard specifications. Fuel viscosities exceeding specification limits may lead to issues related to emission characteristics (excessive droplet size), fuel pumpability and even filter plugging.³ On the other hand, viscosities significantly below the specification limit range may indirectly cause issues related to decreased lubricity, which may cause wear in the fuel system components by reduced film-forming properties. In fact, this is applicable for all cases mentioned above, including those cases where the specification does not specify a minimum limit for viscosity.^{8,9} However, desulfurization of fuels has complicated this mechanism and

an increased viscosity may not therefore provide increased lubricity in all cases. **See Section 2.3** for more information about liquid hydrocarbon specifications.

2.1 Viscosity of liquids

Viscosity is an intrinsic property of all fluids. A flowing fluid has an internal resistance to flow. Hence, the viscosity of a fluid is the measure of this resistance to flow (or shear). Viscosity is a function of both temperature and pressure. The viscosity of liquids and gases are affected differently by changes in temperature and pressure. The temperature dependence of liquid viscosity (including liquid hydrocarbons) is fully characterized by the structure of the individual molecules.¹⁰

The theories of fluid viscosity related to gases are very well developed in comparison to those of liquids. Momentum transfer between molecules results in the viscosity of a certain medium. The molecules within gaseous substances are separated by vast distances in comparison to the molecules in liquids. Momentum transfer occurring within gaseous substances is therefore governed by much simpler forces than the corresponding forces acting on momentum transfer within liquids, due to the proximity of the molecules within the liquids. Several theories have been formulated for the viscosity of gases, including accurate methods for viscosity prediction and temperature dependency.⁵ Nevertheless, the subject of the viscosities of gaseous fluids is out of the scope of the present work. Thus, only Newtonian liquids (i.e. liquids in which the viscosity remains constant while the amount of applied shear stress is varied) will be discussed in this thesis.

The viscosity of liquids may be expressed in two different forms: 1) Absolute or dynamic viscosity and 2) Kinematic viscosity.⁵ The two types are described in **Section 2.1.1 and 2.1.2**.

2.1.1 Dynamic viscosity

The dynamic viscosity is described as “the tangential force per unit area required to slide one layer (A) against another layer (B) when the two layers are maintained at a unit distance”.⁵ The system is depicted in **Figure 4** where the force F causes layers A and B to slide at velocities v_1 and v_2 , respectively.⁵ The viscosity of a fluid can be described mathematically as shown in equation (1).

$$\sigma = \eta \frac{dv}{dx} \quad (1)$$

where σ is the shear stress, η represents the dynamic viscosity and dv/dx is the shear rate.

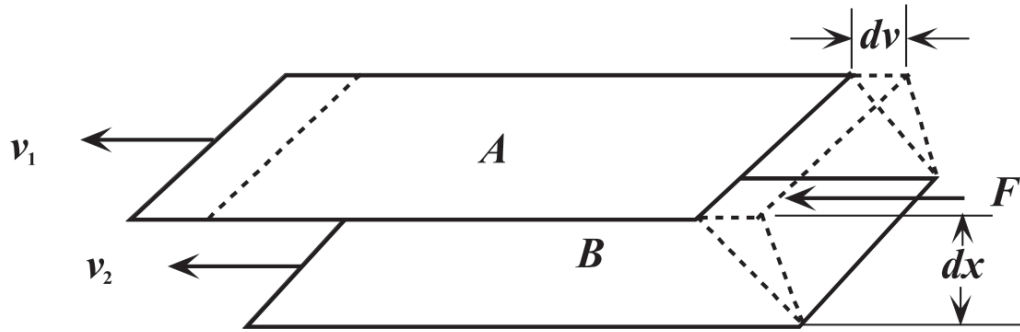


Figure 4: Shear of a liquid film. Reproduced from: D. S Viswanath; T. K. Ghosh; D. H. L. Prasad; N. V. K. Dutt; K. Y. Rani *Viscosity of Liquids*; Springer Netherlands: Dordrecht, The Netherlands, 2007, p.2 (see ref. 5.).

The dynamic viscosity may therefore be written in the form of equation (2).

$$\eta = \sigma \frac{x}{v} \quad (2)$$

where σ represents as the shear stress that is enacted when layer A moves in relation to layer B, x is the length that A moved in relation to B and v is the velocity at which that occurred.

Converting kinematic viscosity to dynamic viscosity:

The dynamic viscosity of a sample at the measured temperature can be calculated by multiplying the kinematic viscosity result with the density (ρ) of the sample, provided that both are known at the same temperature.¹¹ The most common units of dynamic viscosity are Pascal-seconds (Pa·s or kg/m·s), Poise (P, g/cm·s), and Centipoise (cP, 1/100 Poise).⁵

2.1.2 Kinematic viscosity

The kinematic viscosity of a sample can be obtained by dividing the dynamic viscosity (η) with the density (ρ) of the sample, provided that both have been determined at the same temperature.¹² The most common units for kinematic viscosity are m²/s, Stokes (St, cm²/s), and Centistokes (cSt, mm²/s).⁵

The laboratory test method used in this thesis (**see Section 5.3.1**) provides only the kinematic viscosity of a sample (density is not provided). All the empirical correlations and mixing rules described in **Section 4** either require or provide the kinematic viscosity of a sample. All further mentioning of viscosity in this work therefore specifically implies kinematic viscosity unless otherwise specified.

2.2 Hydrocarbon types and their influence on the physicochemical properties of fuel

Liquid hydrocarbon mixtures in the middle distillate range are primarily composed of *n*-paraffins (i.e. normal paraffins), *i*-paraffins (i.e. isoparaffins), olefins (i.e. unsaturated paraffins), cyclic paraffins, and aromatics. Each of the molecular group types supply specific properties to the products. Some of the most important properties provided by each group type, to middle distillate fuels, are listed below.^{13,14} The cold flow properties of middle distillate fuels are very important. The impact on these properties are therefore mentioned several times in the list provided below.

- Normal paraffins
 - Increased energy content and decreased cold flow properties. Positive impact on the cetane number of the fuel.
- Isoparaffins
 - Shape irregularity and branching provides improved cold flow properties compared to *n*-paraffin counterparts. Influences the resulting cetane number of the fuel negatively.
- Olefins
 - Good combustion characteristics, however, undesirable in fuels due to poor gum stability.
- Cycloparaffins
 - Improved cold flow properties and higher density than *n*- and *i*-paraffin counterparts of the same carbon number.
- Alkylbenzenes (substituted single-ring aromatics)
 - Provide increased energy density per unit volume as well as elastomer swelling, both crucial for fuel system integrity.
- Naphthalenes, alkyl naphthalenes, tetralins and indans
 - These multi-ring aromatics cause adverse effects on combustion through contribution to soot formation.

Every hydrocarbon class holds anywhere from tens to hundreds of individual chemical compounds. Each of the compounds contributes to the properties of a sample. The sum of these, result in the final properties of a sample, which can be measured by routine laboratory procedures.¹³ Complete analyses of middle distillates, involving the identification of the 1000

or more components in a sample, are possible by the use of complex and time consuming spectroscopic and chromatographic methods. Tracing the effect that each individual compound has on the physicochemical properties of a sample is, however, considered impractical, since the hydrocarbon component classes (e.g. *n*-paraffins) have been found to impart certain chemical and physical properties as groups. Researchers have therefore resorted to various “group-type” separations when working with petroleum-based products. Identification and quantification of these group-types can be achieved by spectroscopic methods like GC-MS (gas chromatography-mass spectrometry) and GCxGC (two-dimensional gas chromatography).^{10,13}

2.3 Typical standards governing the quality of fuels and oil products

Standards regulate the quality of fuels and oils by specifying limits for specific physical and chemical properties of the substances. Multiple standards for each product class are available since countries and/or continents are governed by local institutions, supplying their own standards for the products. Some of the largest standardization organizations in the world include ASTM International (American Society for Testing and Materials), API (American Petroleum Institute), CEN (Comité Européen De Normalisation), and ISO (International Organization for Standardization). Organizations governing the use of fuels in specific cases, exist as well. The United States military (MIL standards) for example, governs the quality of fuels for military use in the USA. Additionally, standards by organizations such as the British Ministry of Defense (DEFSTAN standards) include specifications for fuels intended for civil, commercial, and military use. Heavily standardized industries, such as the aviation industry, follow additional standards of organizations such as the Joint Inspection Group (JIG), whose main concern is the aviation fuel supply chain (i.e. refinery to aircraft). The standards published by ASTM International, CEN, and ISO were of interest in this work. The standards regulating the quality of the products relevant to this work, including tabulated viscosity limits for each product group, are described in this section.

2.3.1 Aviation turbine fuels

One of the main governing organizations for the quality of aviation fuel is ASTM International. Fossil aviation fuels are regulated by the “ASTM D1655 Standard Specification for Aviation Turbine Fuels”. This standard originally dictated the specification limits for “aviation fuel consisting predominantly of refined hydrocarbons derived from fossil raw materials”. Today, products originating from renewable raw materials must satisfy these limits as well. The fuels

grades included are Jet A and Jet A-1.¹⁴ Aviation fuels consisting of both fossil and synthetic blending components are additionally governed by the “ASTM D7566 Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons”. Specifications limits for the properties of currently approved synthetic blending components are defined in the annexes of the standard. The final fuel blends, however, have to satisfy the requirements of both D7566 and D1655, if synthetic components are present (as indicated above).¹⁵ Other commercial and military grade aviation fuels are governed by for example standards DEFSTAN 91-91, DEFSTAN 91-87, and MIL-DTL-83133 issued by the Ministry of Defense of the United Kingdom and the United States Airforce, respectively. The fuel grades included in these specifications are JP-8 and Jet A-1.^{16–18} Multiple additional aviation fuel specifications by various military and government organizations exist as well.¹⁹ Detailed descriptions of these can be found elsewhere in the literature. The viscosity limits of the mentioned specifications are given in **Table 2**.

Table 2: Viscosity limits of common aviation fuel specifications.

Specification	ASTM D1655 ¹⁴	ASTM D7566 ¹⁵	DEFSTAN 91-91 ¹⁶	DEFSTAN 91-87 ¹⁷	MIL-DTL-83133 ¹⁸
Fuel grade	JET A-1	JET A-1 containing synthesized hydrocarbons	JET A-1	JP-8	JP-8
Kinematic viscosity, max. (mm ² /s)	8.00 at -20 °C	8.00 at -20 °C (12.00 at -40 °C) *	8.00 at -20 °C	8.00 at -20 °C	8.00 at -20 °C

*required only for blends with specific components

2.3.2 Diesel fuels

Diesel fuels can be divided into two main groups based on use. Automotive diesel fuel or on-road diesel is a group of fuels which have been developed to be suitable for automotive use. Non-road diesel (i.e. red diesel, due to colorant) is a group of fuels which are intended to be used in applications excluding automotive use. In some countries, a colorant is added to non-road diesel to dissociate the two fuel types due to fiscal policies. Certain performance additives, beneficial for the automotive use of the fuels, may not have been added to non-road diesel.

2.3.2.1 Automotive diesel fuels, Europe

Automotive diesel fuels are governed by the European Committee for Standardization (Comité Européen De Normalisation, CEN) in Europe. EN 590 is the standard for fossil

automotive diesel fuel and EN 15940 is the standard for paraffinic automotive diesel fuel from synthesis or hydrotreatment. Both standards include generally acceptable limits as well as climate-related requirements. The climate related requirements are divided into classes 0, 1, 2, 3, and 4 in both standards. The classification is governed by the cetane number of the fuel in all cases. The generally acceptable requirements of EN 15940 are further divided into classes A and B due to the acceptance of cycloparaffins in class B (this decreases the cetane number of the resulting fuel). The viscosity requirements of classes A and B do not differ.^{20,21} The viscosity requirements of both standards are listed in **Table 3**.

Table 3: Viscosity limits of the European automotive diesel fuel specifications.

Specification	EN 590 and EN 15940 ^{20,21}				
Generally applicable limits:	Min. = 2,00				
Kinematic viscosity at +40 °C (mm ² /s)	Max. = 4,50				
Climate related requirements, categories:	0	1	2	3	4
Kinematic viscosity at +40 °C, min. (mm ² /s)	1,50	1,50	1,50	1,40	1,20
Kinematic viscosity at +40 °C, max. (mm ² /s)	4,00	4,00	4,00	4,00	4,00

2.3.2.2 Automotive diesel fuels, United States of America

The “ASTM D975 Standard Specification for Diesel Fuel” specifies the quality of diesel fuel in at least the United States of America. Diesel fuel quality is defined by a variety of different grades in the ASTM specification.²² The following grades are included:

- No. 1-D S15
- No. 1-D S500
- No. 1-D S5000
- No. 2-D S15
- No. 2-D S500
- No. 2-D S5000
- No. 4-D

The number after the S refers to the limit of sulfur content in each grade. Differences in other properties such as viscosity are defined as well.²² The viscosity limits of the grades are listed in **Table 4**.

Table 4: Viscosity limits of the American automotive diesel fuel specification.

Specification	ASTM D975 ²²						
Fuel grade	No. 1-D S15	No. 1-D S500	No. 1-D S5000	No. 2-D S15	No. 2-D S500	No. 2-D S5000	No. 4-D
Kinematic viscosity at 40 °C, min. (mm ² /s)	1,3	1,3	1,3	1,9	1,9	1,9	5,5
Kinematic viscosity at 40 °C, max. (mm ² /s)	2,4	2,4	2,4	4,1	4,1	4,1	24,0

2.3.3 Heating oil

A common European standard for the quality of heating oil and non-road diesel does not exist. The sulfur content of the fuels is capped by the Sulphur Content of Liquid Fuels Directive. All other properties of the fuels are governed by country-specific standards, the EN 590 standard for automotive diesel fuel or no standard at all, depending on the country.²³

The quality of heating oil and non-road diesel is governed by the “ASTM D0396 Standard Specification for Fuel Oils” in the USA. The fuels are divided into six grades of which No. 4 and 5 are further divided into “light” and/or “heavy” grades.²⁴ The specified viscosity limits of the grades are listed in **Table 5**.

Table 5: Viscosity limits of the American fuel oil specification.

Specification	ASTM D0396 ²⁴				
Fuel grade	No. 1 S15, S500 or S5000	No. 2 S15, S500 or S5000	B6-B20 S15, S500 or S5000	No. 4 (Light)	No. 4
Kinematic viscosity at 40 °C, min. (mm ² /s)	1,3	1,9	1,3	1,9	>5,5
Kinematic viscosity at 40 °C, max. (mm ² /s)	2,4	4,1	4,1	5,5	24,0
Fuel grade (continues)	No. 5 (Light)	No. 5 (Heavy)	No. 6		
Kinematic viscosity at 100 °C, min. (mm ² /s)	5,0	9,0	15,0		
Kinematic viscosity at 100 °C, max. (mm ² /s)	8,9	14,9	50,0		

2.3.4 Distillate marine fuels

Distillate marine fuel quality is governed by the ISO 8217 specification. The fuels are separated into seven different categories listed below.²⁵

- ISO-F-DMX

- ISO-F-DMA
- ISO-F-DFA
- ISO-F-DMZ
- ISO-F-DFZ
- ISO-F-DMB
- ISO-F-DFB

Distillate marine fuels are categorized into the grades by their kinematic viscosities at 40 °C. The last letter in the name of each category refers to the viscosity limits of the specific category.²⁵ Viscosity limits for the categories are listed in **Table 6**.

Table 6: Viscosity limits of the European distillate marine fuel specification.

Specification	ISO 8217 ²⁵						
Fuel grade (ISO-F-)	DMX	DMA	DFA	DMZ	DFZ	DMB	DFB
Kinematic viscosity at 40 °C, min. (mm ² /s)	1,4	2,0		3,0		2,0	
Kinematic viscosity at 40 °C, max. (mm ² /s)	5,5	6,0		6,0		11,0	

2.3.5 Base oils (lubricants)

One of the most relevant properties for the classification and marketing of base oils is the viscosity of the products. The API 1509 (API Engine Oil Licensing and Certification System, EOLCS) categorizes base oils into groups I, II, III, IV, and V based on refining method, viscosity, saturate content, and sulfur content.²⁶ The viscosity index (see **Section 2.4.2**) limits for these groups are listed in **Table 7**.

Table 7: Viscosity index limits of API base oil groups.

Specification	API 1509 ²⁶				
Base oil group	I	II	III	IV (PAO)	V
Viscosity index, min.	≥80		≥120	PAO manufacturer specification	All others
Viscosity index, max.	<120		-	PAO manufacturer specification	All others

The viscosity index of groups I – III are limited by EOLCS, whereas the PAO product specifications give rise to the limits of group IV. All other grades of viscosity index are covered by group V, as can be seen from **Table 7**.

2.4 Selected standard laboratory test methods for the determination of liquid viscosity

The viscosity (dynamic or kinematic) of hydrocarbon samples may be determined by multiple standardized methods. Results presented in the literature may have been determined by any of these techniques. A selection of important standardized test methods for viscosity determination are presented in this section.

2.4.1 ASTM D445

The “ASTM D445 Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids” describes the standard procedure for determining the kinematic viscosity (ν) of a transparent or opaque sample of liquid petroleum.¹¹ This method was used for all viscosity measurements presented in this thesis due to its widespread use, broad temperature range, and capability of processing multiple samples simultaneously. Furthermore, the method is generally accepted by most standards. A sketch of a Cannon-Fenske Routine viscometer used in this method is provided in **Figure 5**. The standard test method is discussed in more detail in the experimental section (see **Section 5.3.1**).

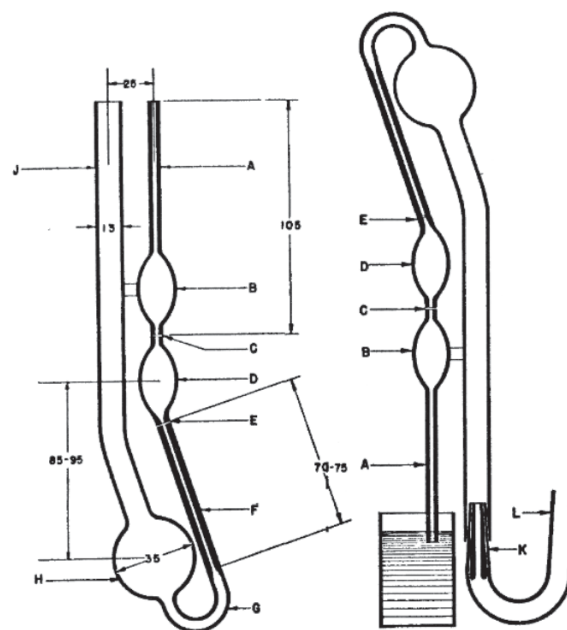


Figure 5: Dimensional illustration of a Cannon-Fenske Routine viscometer (left) as well as a presentation of the method of filling the instrument by suction (right). Reproduced from: D. S Viswanath; T. K. Ghosh; D. H. L. Prasad; N. V. K. Dutt; K. Y. Rani *Viscosity of Liquids*; Springer Netherlands: Dordrecht, The Netherlands, 2007, p.2 (see ref. 5.).

2.4.2 ASTM D2270

The “ASTM D2270 Standard Practice for Calculating Viscosity Index from Kinematic Viscosity at 40 °C and 100 °C” comprises the standard for calculating the viscosity index of a sample, given that the kinematic viscosity data of the sample is known at 40 °C and 100 °C. The viscosity index (VI) is a generally accepted measure of temperature dependence of the viscosity of a sample. The VI of a sample is in practice a single number which indicates the temperature dependence of the kinematic viscosity of the sample. The higher the viscosity index, the lower the decrease in viscosity of the sample with increasing temperature.²⁷

2.4.3 ASTM D7042

The “ASTM D7042 Standard Test Method for Dynamic Viscosity and Density of Liquids by Stabinger Viscometer (and the Calculation of Kinematic Viscosity)” describes the procedure for measuring both the dynamic viscosity (η) and the density of a liquid petroleum product or crude oil (provided that the sample is transparent and opaque) simultaneously using the Stabinger Viscometer. The precision of the method has only been determined for the materials, viscosities, densities, and temperatures indicated in the specification.¹²

The Stabinger Viscometer is a modified Couette-type coaxial rotational cylinder viscometer. A general illustration of a coaxial cylinder viscometer is given in **Figure 6**.⁵

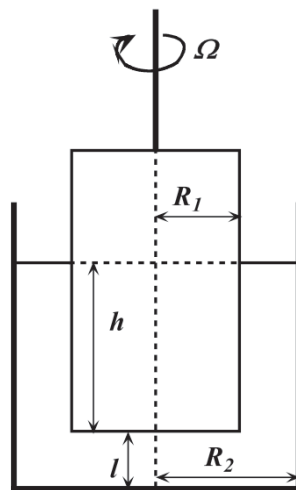


Figure 6: General structure of a coaxial rotational cylinder viscometer. Reproduced from: D. S Viswanath; T. K. Ghosh; D. H. L. Prasad; N. V. K. Dutt; K. Y. Rani *Viscosity of Liquids*; Springer Netherlands: Dordrecht, The Netherlands, 2007, p.2 (see ref. 5.).

2.4.4 ASTM D7945

The “ASTM D7945 Standard Test Method for Determination of Dynamic Viscosity and Derived Kinematic Viscosity of Liquids by Constant Pressure Viscometer” comprises the procedure for the determination of the dynamic viscosity and the density of a sample. These are determined for the purpose of deriving the kinematic viscosity of the sample based on the results. The dynamic viscosity and density are obtained by an automated apparatus. The kinematic viscosity is determined, based on these results, by the calculative procedure described in **Section 2.1.2**. The method also describes how the standard practice ASTM D341 (**see Section 4.1.1**) can be used for calculating the temperature at which a petroleum product attains a certain kinematic viscosity. The constant pressure viscometer is a capillary flow viscometer that uses the Hagen-Poiseuille principle of capillary flow to determine the viscosity of a sample (the time it takes for a specific volume of liquid to pass through a capillary is proportional to the viscosity of the fluid).⁵ It differs however from traditional viscometers in that, even though a capillary is used to restrict the flow of fluid and provide the means by which the viscosity of the sample is determined, a constant pressure of compressed air is used as the driving force for the fluid instead of gravity.²⁸

The unnecessary complexity and time-consuming task of measuring each sample separately, the introduction of an additional source of error by automation, and the mathematically derived kinematic viscosity were the grounds for not following this procedure in this work.

2.4.5 ASTM D5293

The “ASTM D5293 Standard Test Method for Apparent Viscosity of Engine Oils and Base Stocks Between -10 °C and -35 °C Using Cold-Cranking Simulator” encompasses a specialized approach for assessing the effects of the low temperature viscosity of oils on the performance in conditions simulating a real-life use case. The Cold-Cranking Simulator (CCS) result correlates with the cranking of an engine at low temperature and is known as the Apparent Cranking Viscosity. This approach produces results purely from a usability standpoint and should not be used for the prediction of low temperature flow in an engine. Information such as the determination of base stock suitability for engine oil formulations is gathered using this method. The method is calibrated using calibration oils that could be used for the formulation of an engine oil.²⁹ A picture of a Cold-Cranking Simulator is provided in **Figure 7**.



Figure 7: Picture of a Cold-Cranking Simulator produced by Cannon Instruments Co. Reproduced from: D. S Viswanath; T. K. Ghosh; D. H. L. Prasad; N. V. K. Dutt; K. Y. Rani *Viscosity of Liquids*; Springer Netherlands: Dordrecht, The Netherlands, 2007, p.2 (see ref. 5.).

This method is described in this section due to the alternative angle of interest toward the viscosity of a hydrocarbon mixture. The purpose of the method is to investigate, evaluate, and enumerate the effect of the viscosity of the product in the final use case. In other words, the method seeks to describe an entirely different aspect of the viscosity of a hydrocarbon mixture, expressed in terms of usability of the product in the intended application.²⁹

3 AIM OF THIS WORK

The viscosity of liquids is, among other things, a non-linear property with regards to temperature. This simple fact, arising from the complex molecular interactions involved in the seemingly straightforward physicochemical property of viscosity, complicates the predictive analytics involved in the estimation of the temperature dependence of liquid viscosity. Empirical correlations and mixing rules are still to this date one of the few feasible methods available for the prediction of liquid hydrocarbon mixture viscosities. Several empirical correlations and mixing rules are available in the literature, improved approaches have been proposed since the early 20th century. Several reviews regarding the most common “classical” methods as well as revisions of the methods are also available. Most of the aforementioned efforts have been aimed toward the estimation of the viscosities of liquid hydrocarbons derived from traditional fossil feedstocks. In fact, most of the methods described in this work have originally been developed for the estimation of crude oil viscosities. The suitability of these methods for the prediction of the viscosity of liquid hydrocarbon mixtures arising from the continuously growing alternative feedstock pool has not been evaluated in detail. The aim of this work is therefore to arrive at the best methods for the prediction of liquid hydrocarbon mixture viscosities of a diverse component pool including the blends thereof.

4 PREDICTION OF THE VISCOSITY OF COMPLEX HYDROCARBON MIXTURES

Several research groups have attempted to capture the intrinsic nature of liquid viscosity using various theories. Multiple mechanistic models have been proposed to describe the correlation of liquid viscosity, temperature, and pressure. The models most representative of this relationship are the Friction Theory and the Expand Fluid Theory. Multiple models exist that consider both the temperature and pressure when calculating the viscosities of liquids. The viscosity prediction model developed by Quiñones-Cisneros *et al.*³⁰ calculates the viscosity of pure compounds, such as individual *n*-alkanes, based on the Friction Theory and the van der Waals Theory at low to high pressures. The development of a three-single-parameter model based on the Friction Theory and the Cubic Equations of State, by the same group, expanded the application of the model to light, medium, and heavy oil systems.^{31–33} Yarranton *et al.*³⁴ developed a three-parameter correlation capable of calculating the viscosities of hydrocarbons, heavy oils, and heavy oil mixtures based on the expand fluid theory. Motahhari *et al.*³⁵ and Ramos-Pallares *et al.*³⁶ implemented the Expand Fluid Theory on mixtures of compounds as well as petroleum systems using binary interaction parameters. The mechanistic models described in the works by Quiñones-Cisneros *et al.*, Yarranton *et al.*, Motahhari *et al.*, and Ramos-Pallares *et al.* are capable of predicting the variation of fluid viscosity at high pressures and high temperatures with relatively low deviation. These models are therefore of great importance, for example, in the field of oil and gas reservoirs. Mechanistic models of this type, however, often contain an excessive number of parameters that require determination by regression, thus introducing an overwhelming complexity to the calculations.¹⁰

The liquid of interest in most chemical engineering processes, including the samples tested in this thesis, are under a medium- to low-pressure environment. The impact of the pressure on the viscosity of the liquid is negligible under these conditions and can therefore be excluded from the calculations. Variation in the viscosity of a hydrocarbon mixture can consequently be considered to occur only due to changes in temperature. The viscosity-temperature relationship of hydrocarbon mixtures can be described by a variety of empirical equations.¹⁰ These empirical correlations are usually much simpler than the mechanistic models, only containing a couple of basic parameters and one or more experimentally determined values, based on which the viscosity can be extrapolated to a different

temperature. The most common experimentally determined property used for this is the viscosity of a sample at a single temperature. Other common properties are for example the weighted average boiling point temperature and the specific gravity of a sample.³⁷

Most empirical correlations available in the literature are based on the equations developed by Vogel³⁸, Walther³⁹, or Andrade⁴⁰. A clear trend toward the use of the Walther correlation can, however, be distinguished. This can be explained by the simple fact that the approaches based on the Walther correlation exhibit much lower average absolute deviations (AAD) compared to the Vogel and Andrade counterparts.³⁷ The most promising correlations found in the literature are discussed in this section.

The equations evaluated in this work were chosen based on recommendations as well as performance presented in the literature and are therefore mostly concentrated on iterations of the Walther correlation. The performance of the most promising equations of this section were evaluated using the experimental data gathered in the experimental section of this work. The results can be found in **Section 6.2**.

4.1 Empirical correlations for the prediction of liquid hydrocarbon mixture viscosity

Each of the correlations described in this section can be thought of as solutions for different situations where a varying amount and type of input data is accessible. **Table 8** summarizes the required inputs and provided outputs of the empirical correlations of this section. The output of all empirical correlations discussed in this thesis is the viscosity of the studied sample at a desired temperature.

Table 8: Summary of inputs and outputs of empirical correlations.

Correlation	Input	Output
Walther ³⁹	Viscosity at two temperatures	Viscosity at desired temperature
NFGW ⁸	Viscosity at three temperatures	Viscosity at desired temperature
Aboul-Seoud and Moharam ⁴¹	Viscosity at one temperature	Viscosity at desired temperature
Mehrotra ⁴²	Weighted average of boiling points	Viscosity at desired temperature
Kotzakoulakis version of Mehrotra correlation ³⁷	50 % mass boiling point	Viscosity at desired temperature
Moharam ⁴³	Weighted average of boiling points and specific gravity	Viscosity at desired temperature

Kotzakoulakis version of Moharam correlation ³⁷	50 % mass boiling point and specific gravity at 15 °C	Viscosity at desired temperature
Puttagunta ⁴⁴	Viscosity at exactly 100 °F (37,78 °C)	Viscosity at desired temperature

4.1.1 Walther correlation

The Walther equation provides the foundation of the ASTM D341 standard. The ASTM D341 Standard Practice for Viscosity-Temperature Charts for Liquid Petroleum Products is a method for assessing the effect of temperature on the viscosity of various petroleum products. The method is based on conventional viscosity-temperature charts. These charts have traditionally been used for the approximation of the viscosity of a fuel or oil sample, at any temperature, provided that the viscosity of the sample is known at two separate temperatures. The two known data points are marked on the chart and a line connecting both is drawn. The viscosity at any other temperature can be established within the limits of the chart by the plotted line. Multiple charts with different scales are available.⁴⁵

The charts given in the standard have also been used for the approximation of liquid viscosities of blends of components. This requires manual plotting of the viscosity-temperature lines of each component on the chart and blending of the components by linear proportioning at constant viscosity or temperature (the horizontal or vertical distance is measured). The manual method is time consuming and the obtained results are known to be inaccurate.⁷ **See Section 4.2.1 and 4.2.5** for detailed information regarding the calculation approach to these methods and how the inaccuracy can be reduced.

The charts themselves are simplified practical tools that are governed by an equation. The underlying equation is therefore of greater interest regarding the scope of this work than the charts themselves. The first chart of this kind was published by MacCoull, it is based on equation (3)⁴² and features a static value of 0.7 in the double logarithm parenthesis.^{45,46} The equation is a two-parameter logarithmic viscosity equation:⁷

$$\log \log(v + 0.7) = b_1 + b_2 \cdot \log T \quad (3)$$

Subsequent development and publication of the equation by both ASTM⁴⁵ (subcommittee D02.07) and Walther³⁹ have resulted in the equation mostly being known as the ASTM equation or the Walther equation:

$$\log \log(v + 0.8) = b_1 + b_2 \cdot \log T \quad (4)$$

The Walther and ASTM forms of the equation (4)³⁷ differed from the original only by the value of 0.7 being 0.8 in the parenthesis (ASTM later reverted back to the original value of 0.7).⁴⁵ In both (3) and (4), ν is the kinematic viscosity (in cSt or mm²/s), T is the temperature in °K and, b_1 and b_2 are constants of the equation (determined for each sample separately).^{37,42}

Many forms of the equations (3) and (4) have been referred to as the Walther equation in the literature. Equations of this general type will therefore be referred to as the Walther equation in this work.

The Walther equation can be utilized for the prediction of the viscosity of a sample at any temperature, given that viscosity of the sample is initially known at two different temperatures. The equation should be modified in the following fashion:

Two data points should be used to solve for the constants b_1 and b_2 . The Walther equation (3) should be rewritten to isolate terms b_1 and b_2 , as shown in equations (5) and (6), respectively. The viscosity ν_3 at temperature T_3 can be calculated from the resulting equation (7) by inserting the values for b_1 and b_2 into their respective places.^a

$$b_1 = \log \log(\nu_1 + 0.7) + \frac{\log \log(\nu_2 + 0.7) - \log \log(\nu_1 + 0.7)}{\log T_1 - \log T_2} \cdot \log T_1 \quad (5)$$

$$b_2 = \frac{\log \log(\nu_2 + 0.7) - \log \log(\nu_1 + 0.7)}{\log T_1 - \log T_2} \quad (6)$$

$$\nu_3 = 10^{10^{b_1 - b_2 \cdot \log T_3}} - 0.7 \quad (7)$$

The viscosity-temperature relationship of a sample can be observed by altering the value of T_3 .

Researchers have long been relying on the Walther equation as given in equation (3) and (4), with the constant C in the general expression (8)⁸ owning a static value of 0.7 or 0.8. Some researchers, such as Nissan *et al.*, have suggested that the value of C should be a static value of 0.6 if the viscosity is expressed in centistokes.⁸

$$\log \log(\nu + C) = A + B \cdot \log T \quad (8)$$

Sánchez-Rubio *et al.* have more recently taken a new approach toward the determination of the C parameter of the Walther equation. The form of the Walther equation results in a

^a Determined by thesis author during the thesis work.

straight line on the viscosity charts of the form $\log\log(\text{viscosity})$ versus $\log(\text{temperature})$. Two points are needed for the mathematical construction of a line, just as was discussed in equations (5), (6), and (7). It was therefore reasoned that a third point between the two points already needed would improve the results significantly. This means that the Walther equation, at three known temperatures, should be solved. An iterative procedure in the solving of the combined “triple” Walther equation gives a different value of C for each sample studied (sample specific C). S  nchez-Rubio *et al.* studied lubricants, for which the common temperatures of viscosity determination are 40   C and 100   C. The best temperature to use for the third point was found to be the mean logarithmic temperature (i.e. 63.25   C). However, no mathematical reasoning was found to justify this.⁸

Solving for a fluid specific C value is performed in the following way. Three identical Walther equations are substituted with v_1, v_2, v_3 and T_1, T_2, T_3 , respectively.⁸ Rearranging the equations gives:

$$A = \log \log(v_1 + C) - B \cdot \log T_1 \quad (9)$$

$$A = \log \log(v_2 + C) - B \cdot \log T_2 \quad (10)$$

$$A = \log \log(v_3 + C) - B \cdot \log T_3 \quad (11)$$

The combination and rearrangement of equations (9) and (10) as well as (10) and (11) separately give: ⁸

$$\frac{1}{X} = \log \left[\frac{\log(v_2 + C)}{\log(v_1 + C)} \right] \quad (12)$$

$$\frac{1}{Y} = \log \left[\frac{\log(v_3 + C)}{\log(v_2 + C)} \right] \quad (13)$$

The subsequent combination and rearrangement of equation (12) and (13) lead to:

$$\frac{[\log(v_2 + C)]^Y}{[\log(v_1 + C)]^Y} = \frac{[\log(v_3 + C)]^X}{[\log(v_2 + C)]^X} \quad (14)$$

And if $(X + Y) = Z$, then the general expression (15) can be obtained:

$$[\log(v_2 + C)]^Z = [\log(v_3 + C)]^X \cdot [\log(v_1 + C)]^Y \quad (15)$$

The iteration of equation (15) will give the fluid specific value for parameter C . The new equation encompassing this process of deriving the fluid specific C was named the NFGW (New Focus on the General Walther equation) equation by the authors of the work.⁸

4.1.2 Aboul-Seoud and Moharam correlation

Replacing the parameter b_1 in the Walther equation (3) with the double logarithm of a known viscosity allows for the prediction of the viscosity of a sample at any temperature.⁴¹ This form of the equation is known as the Aboul-Seoud and Moharam correlation (16):

$$\ln \ln(v + 0.8) = \ln \ln(v_o + 0.8) + a_2 \cdot \ln \left(\frac{T}{T_o} \right) \quad (16)$$

where v is the kinematic viscosity (in cSt or mm²/s) at temperature T (K°), v_o is the known kinematic viscosity (in cSt or mm²/s) of the sample at temperature T_o (K°), and a_2 is a parameter of the equation estimated by Aboul-Seoud and Moharam to be equal to -3.7 based on experimental results (same as b_2 in equation (3) and (4)).⁴¹

The Aboul-Seoud and Moharam (A-S & M) correlation has been reported to be the best correlation to use when only a single viscosity measurement of a sample is available.³⁷

4.1.3 Mehrotra correlation

Mehrotra studied the parameters in equation (3) and found that the kinematic viscosity of his crude oil samples was in good correlation with the average boiling points (T_b) of the crude oils.⁴² The weighted average boiling point (T_b) of a sample is determined by equation (17)³⁷.

$$T_b = \sum_{i=1}^n \Delta x_i \cdot T_{bi} \quad (17)$$

where n is the number of distillation cuts, Δx_i the mass fraction of distillation cut i with $\sum \Delta x_i = 1$, and T_{bi} is the mid boiling point temperature of the distillation cut i (K°).

Mehrotra consequently modified the equation (3) to predict the kinematic viscosity of a sample at any temperature using the T_b of the samples. Examination of the parameters in the equation showed that the value of b_2 did not vary significantly with the T_b and could therefore be set to -3.7.⁴² The remaining parameter b_1 was expressed in terms of T_b and adopted the form:

$$b_1 = 5.489 + 0.148T_b^{0.5} \quad (18)$$

This resulted in the final form of the Mehrotra correlation (19)⁴⁷:

$$\log \log(v + 0.7) = 5.489 + 0.148T_b^{0.5} - 3.7 \log T \quad (19)$$

where ν is the kinematic viscosity (in cSt or mm²/s), T_b is the average boiling point (K°), and T is the temperature (K°).

Further improvement of the correlation has recently been performed by Kotzakoulakis *et al.*³⁷ They utilized a set of 137 crude oils to refine the correlation to the following form (20):

$$\ln \ln(\nu + 0.8) = 7.014T_b^{0.178} - 3.682 \ln T \quad (20)$$

where ν is the viscosity (cSt or mm²/s) to be estimated, T_b is the 50% mass boiling point (°K), and T the temperature (°K).³⁷

4.1.4 Moharam correlation

Moharam *et al.* combined the double logarithm relationship of the Wright blending model (further discussed in **Section 4.2.1**) with the previously established correlation of the T_b and the inverse of the absolute temperature. The resulting general empirical correlation (21) is said to describe the kinematic viscosity-temperature behavior of hydrocarbon liquids for the temperature range of 50-550 °C.⁴³

$$\ln \nu = A \cdot \exp \left[\left(\frac{T_b}{T} \right) \cdot \gamma^B \right] + C \quad (21)$$

where $A = 1.0185$, $B = \frac{T_b}{305.078} - 0.55526$ and $C = -3.2421$, ν is the kinematic viscosity (in cSt or mm²/s), T_b is the average boiling point (K°), and T is the temperature (K°), and γ is the specific gravity of the sample.

The specific gravity (i.e. relative density) is the ratio of the density of a material related to the density of pure water.⁴⁸ The specific gravity can be calculated using equation (22).

$$\gamma = \frac{\rho}{\rho_w} \quad (22)$$

where γ is the specific gravity, ρ is the density of a material, and ρ_w is the density of water.

The density of the material of interest should be known at the temperature of interest in order to calculate the specific gravity of a sample at the desired temperature.⁴⁸

Aboul-Seoud and Moharam later verified that the T_b of two oils could possibly be very close or even exactly the same. The Mehrotra correlation and other correlation relying only on the T_b of the sample were found to be ineffective in such cases. Aboul-Seoud and Moharam

therefore modified the Mehrotra correlation to consider both the specific gravity and the average boiling point of the sample.⁴¹ This resulted in the equation (23):

$$\ln \ln(v + 0.8) = 4.3414(T_b \cdot \gamma)^{0.2} + 6.6913 - 3.7 \ln T \quad (23)$$

where v is the kinematic viscosity (in cSt or mm²/s), T_b is the average boiling point (°K), T is the temperature (°K), and γ is the specific gravity of the sample.

A recent development of the Moharam correlation has been performed by Kotzakoulakis *et al.*³⁷ The effects of the parameters in equation (22) on the prediction of the viscosities of 137 crude oils was studied. Their investigations showed that using the 50 % mass boiling point instead of the average boiling point lowered the absolute average deviation (AAD) of the results by about 10 %. The modification of equation (22) by Kotzakoulakis *et al.* also permits the use of the specific gravity of the samples at 15 °C instead of using the specific gravity at the desired temperature, i.e. T in eq. (22) and (23). The reference water density at 15 °C for the calculation of the specific gravity of a sample was set to exactly 0.999099 g/cm³.³⁷ The resulting equation (24) takes the following form:

$$\ln \ln(v + 0.8) = 14.69T_b^{0.0684}\gamma^{0.267} - 3.682 \ln T \quad (24)$$

where v is the kinematic viscosity (in cSt or mm²/s), T_b is the 50 % mass boiling point (K°), T is the temperature (K°), and γ is the specific gravity at 15 °C of the sample.

Using the weighted average boiling point, the 50 % mass boiling point, or the 50 % volume boiling point for predicting the kinematic viscosity of a sample (in the Mehrotra or Moharam correlations) presents an issue for samples with incomplete distillation data. The equation (15) for the calculation of the weighted average boiling point requires the complete distillation range of a sample to be known.³⁷ The Riazi distribution model presented in **Section 4.1.6** may be used to solve this issue.

4.1.5 Puttagunta correlation

A five-parameter correlation was published by Puttagunta *et al.*⁴⁴ in 1992. The correlation predicts the viscosity of a sample at any temperature based on the viscosity of the sample at exactly 100 °F (37.78 °C) and atmospheric pressure. The required data can be obtained either by experimental determination or curve fitting.⁴¹ The Puttagunta correlation is defined by the equation (25)^{41,44}:

$$\log \nu = \frac{b}{\left(1 + \frac{T-37.78}{310.93}\right)^s} + c \quad (25)$$

where ν is the kinematic viscosity at temperature T (in cSt or mm²/s), T is the temperature (in °C), and b and s are functions of the kinematic viscosity at 37.78 °C.

It has been found that the equation is essentially the Walther equation expressed for the specific temperature of 37.78 °C.⁴² The correlation is nevertheless presented in this work, since it is also known as the API Procedure 11A4.1 of the API Technical Data Book (TDB). The API TDB is an annually updated book (a software nowadays) containing the latest technical data, methods, and standards regarding the areas of petroleum refining officially sanctioned by the API.⁴⁹

The API Procedure 11A4.1 discloses a correlation for the prediction of the viscosity of a liquid petroleum fraction as a function of temperature provided that the kinematic viscosity of the sample is known at 100 °F (37.78 °C) and atmospheric pressure.⁴¹ It features an absolute error of approximately 5.6 %, according to tests performed by the API and said to work best on light paraffinic fractions with API gravities over 30° API.⁵⁰

4.1.6 Riazi distribution model

Riazi has developed a distribution model for multiple properties of uncharacterized fractions of oils.^{51,52} The correlation exhibits excellent prediction of boiling points of oils with a correlation factor (R^2) of over 0.99 (see Section 6.1.1 for definition of R^2). The Riazi distribution model is therefore useful for the prediction of the entire distillation curve, the 50 % boiling point, and the weighted average T_b of a sample if only incomplete data is available.³⁷ The Riazi distribution model is described by the following equations (26) and (27)^{51,52}:

$$\frac{T_i - T_o}{T_o} = \left(\frac{A}{B} \ln \left(\frac{1}{1 - x_i} \right) \right)^{1/\beta} \quad (26)$$

Equation (26) in linear form:

$$Y = C_1 + C_2 X \quad \text{where} \quad Y = \ln \left(\frac{T_i - T_o}{T_o} \right) \quad \text{and} \quad X = \ln \ln \left(\frac{1}{1 - x_i} \right) \quad (27)$$

Where:

T_o = initial boiling point of sample (K°)

T_i = temperature at which i percent of the sample has been distilled (weight or volume percent based on what x_i is chosen to be)

x_i = volume or weight fraction of distillate

A and B = sample specific parameters (det. from exp. data, see below)

C_1 and C_2 = intercept and slope of the distillation curve

Partial distillation data can be used to plot the terms X and Y from which the slope and intercept (C_1 and C_2 respectively) can be determined.^{37,51,52} The sample specific parameters A and B can be determined from the equations (28) and (29):

$$B = \frac{1}{C_2} \quad (28)$$

and

$$A = Be^{C_1 B} \quad (29)$$

Equation (24) can be solved and used to derive the complete distillation curve of a sample.³⁷

4.2 Mixing rules for the calculation of petroleum blend viscosities

Mixing rules are calculative tools (i.e. equations) for the prediction of the viscosities of blends of hydrocarbon mixtures. A variety of mixing rules are available in the literature. Centeno *et al.*⁷ evaluated the performance of a total of 26 mixing rules on the prediction of the viscosity of various crude oil blends. The overall accuracy of the mixing rules on viscosity prediction of the crude oil blends were found to be relatively poor, which is why they expanded the investigation to naphtha, diesel, and vacuum gas oil blends. Only four of the seventeen generally accepted mixing rules for middle distillates were found to be acceptable in terms of accuracy when tested. These included the Chirinos, Refutas, Chevron, and Walther mixing rules.⁷ A summary of the inputs and outputs of all mixing rules discussed in this work is provided in **Table 9**.

Table 9: Summary of inputs and outputs of mixing rules.

Mixing rule	Input	Output
Wright blending method ⁵³	Viscosity at two temperatures and volume fractions for all components	Viscosity by volume fraction at desired temperatures
Kendall and Monroe correlation ⁵⁴	Viscosity (at the same temperature) and weight fractions of all components	Viscosity by volume fraction at the same temperature as the input
Refutas index method ⁷	Viscosity (at the same temperature) and weight fractions of all components	Viscosity by volume fraction at the same temperature as the input
Chevron mixing rule ⁵⁵	Viscosity (at the same temperature) and volume fractions of all components	Viscosity by volume fraction at the same temperature as the input
Walther mixing rule ³⁹	Viscosity (at the same temperature) and volume fractions of all components	Viscosity by volume fraction at the same temperature as the input
Chirinos mixing rule ⁷	Viscosity (at the same temperature) and weight fractions of all components	Viscosity by volume fraction at the same temperature as the input

4.2.1 Wright blending method

In 1946, Wright proposed a new method for using the ASTM chart (described in **Section 4.1.1** in conjunction with the Walther correlation) for predicting blend viscosities. The method has since proved to be a very effective tool for predicting the viscosity of all sorts of hydrocarbon blends and mixtures. The method is also referenced in the “ASTM D7152 Standard Practice for Calculating Viscosity of a Blend of Petroleum Products”, which is another reason why it will be discussed in this section.⁵⁶

The blending method proposed by Wright in 1946 was a method that utilized the charts of ASTM D341 to predict the viscosities of blends. Here the viscosity-temperature lines of the components are plotted on the chart and blended by linear proportioning along the $\log(T)$ axis. The advantage of this is that the “blending” is performed at “constant viscosity” instead of “constant temperature”, which would be the case if the chart were used as originally intended (see Section 4.2.5). An example of the use of a viscosity-temperature chart according to the Wright blending method is given in **Figure 8**, where Oil-A and Oil-B are the blending components and the long line between these, marked by intercepts O and R, is the “blend”.⁵³

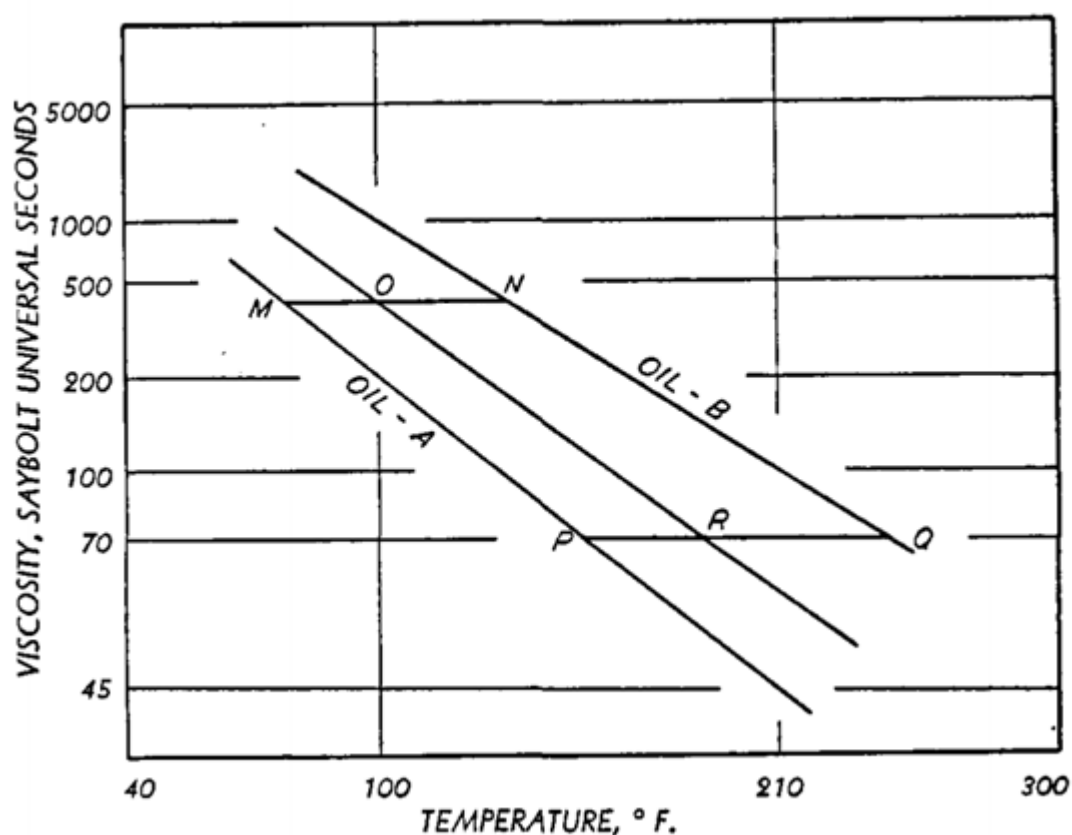


Figure 8: Using the viscosity-temperature charts according to the Wright blending method. Reproduced from: M. H. Rahmes; W. L. Nelson Viscosity Blending Relationships of Heavy Petroleum Oils. *Anal. Chem.* 1948, **20**, 912–915 (see ref. 53).

The equations for the lines and the intercepts in **Figure 8** can be used in a similar fashion to the Walther equation (see Section 4.1.1) to create a set of equations capable of predicting the viscosity of a blend mathematically.⁵⁷ Two viscosity values and the temperatures at which these were determined are needed for each “component”. This information can be used to calculate the inverse slope of each line. The information gathered thus far, including the intended volume fractions of each component, can be used to arrive at the viscosity of the

blend by linear proportioning. The prediction of the “blend” viscosity (slope) over a finite temperature range, as well as the prediction of the viscosity-temperature relationship of the individual components, similarly to the modified Walther equation (**see Section 4.1.1**), is then be possible. This method is referred to as "Modified Wright Method" if mass fractions are used.⁵⁷ A simple arrangement of input temperature values for the equation, within the temperature range of interest, in any spreadsheet software, allow for the graphical mapping of the resulting “blend” line (including accurate data points).

The “ASTM D7152 Standard Practice for Calculating Viscosity of a Blend of Petroleum Products” describes the procedures for calculating the estimated kinematic viscosity of a blend of two or more petroleum products. Two types of blending methods are described in this standard, the ASTM Blending Method and the Wright Blending Method.⁵⁸ The ASTM Blending Method is used for estimating the viscosity of a blend using the kinematic viscosity of each blend component at two separate temperatures and the blend fractions (volume fraction) of each component. The fraction of each component needed to prepare a certain blend, owning a specific viscosity value, can be estimated with this method. Mathematically transformed viscosity values for each component at the chosen temperature are used to produce the blend viscosity at said temperature. This method is referred to as "Modified ASTM Method" in case mass fractions are used. Reversion of the procedure allows for the determination of the amount of each component that has been used to create a blend of certain viscosity (only applicable for two component systems).^{56,57} The Wright Blending Method has a far more substantial base in theory, is more accurate, and has been described in the literature previously.⁵³ Only the Wright Blending Method (of the two) will therefore be subjected to further testing in this work.

4.2.2 *Kendall and Monroe correlation*

The mixing rules of the late 1920's were extremely inaccurate. Even the prediction of binary blends of pure compounds resulted in preposterous deviations since most mixing rules were based on the simple linear law of mixtures. Kendall and Monroe subsequently turned to experimental work; they measured the viscosities of binary systems where the properties of the components featured a significantly wider separation than those analyzed in previous studies.⁵⁴ The Kendall and Monroe equation (30)^{7,54} was developed based on these experimental results and adopted the following form:

$$\mu^{1/3} = w_A \mu_A^{1/3} + w_B \mu_B^{1/3} \quad (30)$$

Where μ is the kinematic viscosity (in cSt or mm²/s) and w the weight fraction of the components (w_A for A and w_B for B). The amount of components is undefined, however, $\sum w_i = 1$.⁷

The Kendall and Monroe equation has been added to the API Technical Data Book (**see Section 4.1.5 for definition**) due to the widespread use of the correlation in the petroleum industry. The equation forms the base for the API Procedure 11A3.1, which is one of the simpler procedures of the API TDB. The procedure is recommended to be used only for the estimation of the viscosities of mixtures of components owning very similar “molecular weights and general character”.⁵⁹

4.2.3 Refutas index method

The Refutas index method predicts the viscosity of a blend of components based on the viscosity blending indices of the individual components.⁷ The method was originally developed for the prediction of blend viscosities of all petroleum components ranging from gasoline to vacuum residue.⁷ The wide application range and satisfactory estimation errors for multiple products, including the close resemblance to the Chevron mixing rule, is the reason why the Refutas index method has been included in this work.⁷ The so called viscosity blending index (VBI) of each component is separately determined using the following equation:

$$VBI_i = 23.097 + 33.469 \log \log(v_i + 0.8) \quad (31)$$

where v_i is the viscosity of component i at a certain temperature (the same temperature should be used for all components).

The VBI of the individual components are then added together while considering the weight fractions of each component, arriving at the average VBI of the blend (VBI_β)⁷:

$$VBI_\beta = w_A VBI_A + w_B VBI_B \quad (32)$$

where w_i is the weight fraction of component i and VBI_i is the VBI of component i in the blend.

The VBI_β can be converted to the blend viscosity using the following equation⁷:

$$v = 10^{10 \left(\frac{VBI_\beta - 23.097}{33.469} \right)} - 0.8 \quad (33)$$

The temperature of the components or the blend is not considered at any point, as seen from the equations (31), (32), and (33). The viscosity of the blend is therefore calculated at the temperature at which the component viscosities were determined (i.e. a “constant temperature” approach). The Refutas index method is not suitable for the prediction of the viscosity of pure hydrocarbons or blends of only a few of them.⁵⁵

4.2.4 Chevron mixing rule

The Chevron mixing rule was developed by the Chevron Research Company.⁵⁵ It is based on the Refutas index method and features a simpler approach to the calculation of the viscosity blending index of a component. The total viscosity blend index of the components is calculated using volume fractions instead of weight fractions which is also more convenient since this data is usually more readily available. The Chevron mixing rule is not suitable for predicting the viscosities of blends of pure hydrocarbons just as its parent method, i.e. the Refutas index method.⁵⁵

The VBI of the individual components are calculated using equation (34), the total VBI by equation (35), and total VBI is finally converted to the blend viscosity using equation (36):^{7,55}

$$VBI_i = \frac{\log v_i}{3 + \log v_i} \quad (34)$$

$$VBI_\beta = \sum_{i=1}^n x_i VBI_i \quad (35)$$

$$v = 10^{\left(\frac{3VBI_\beta}{1 - VBI_\beta} \right)} \quad (36)$$

where v_i is the viscosity of the component i , VBI_i is the viscosity blending index of component i , x_i is the volume fraction of component i , VBI_β is the total VBI of the blend, and v is the viscosity of the blend. The Chevron mixing rule is a “constant temperature” approach similarly to the Refutas index method.

4.2.5 Walther mixing rule

The Walther equation described in **Section 4.1.1** can be transformed to a highly accurate mixing rule³⁹, known as the Walther mixing rule (37):

$$\log \log(v + C) = x_A \log \log(v_A + C) + x_B \log \log(v_B + C) \quad (37)$$

where v is the kinematic viscosity of the blend (in cSt or mm²/s), v_A and v_B are viscosities of the components, x is the volume fraction of each respective component and C is a parameter of the equation.⁷

The Walther mixing rule is the opposite approach to the Wright blending method. Here the “blending” happens at a “constant temperature” instead of happening at a “constant viscosity” as in the Wright method.³⁹ This difference in the approaches is displayed in **Figure 9**.

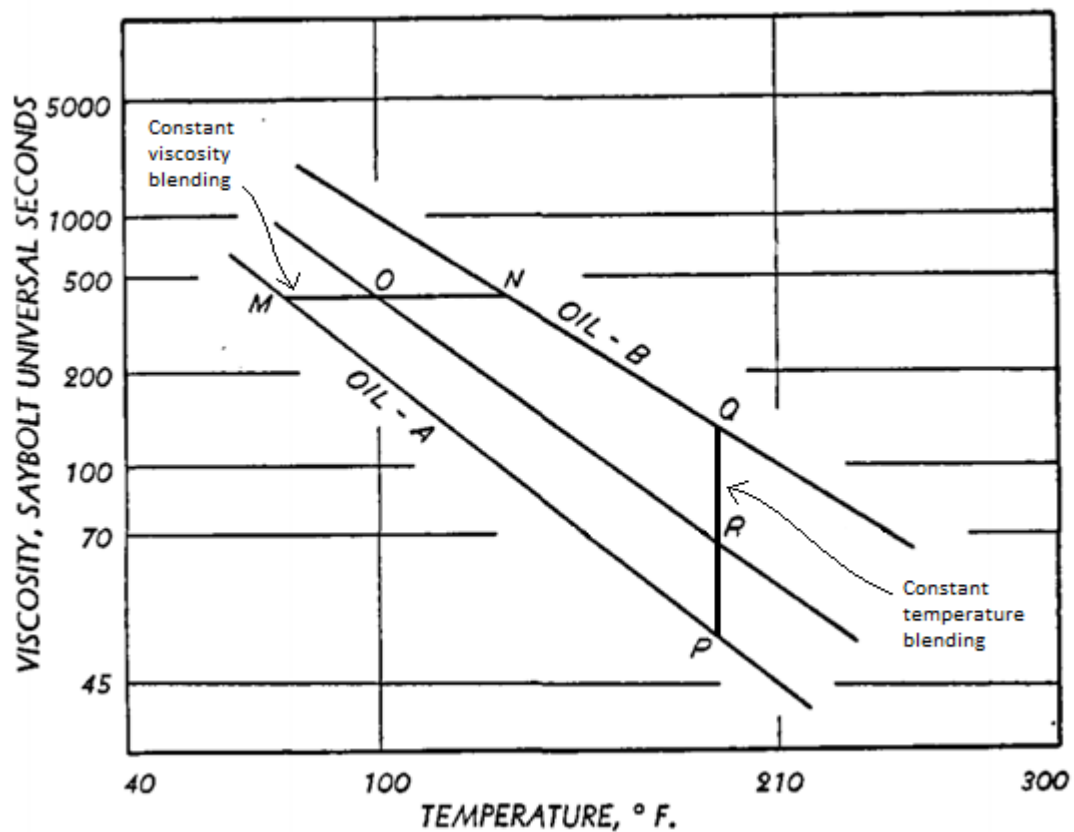


Figure 9: Graphical comparison of the constant temperature vs. constant viscosity approach. Adapted from: M. H. Rahmes; W. L. Nelson Viscosity Blending Relationships of Heavy Petroleum Oils. *Anal. Chem.* 1948, 20, 912–915 (see ref. 53).

The estimation taking place when using the Walther mixing rule is illustrated by the line owning the intercepts Q, R, and P whereas the estimation of the Wright method is depicted by the line with the intercepts M, O, and N. Here it can clearly be seen that the Walther mixing rule line follows a constant temperature value whereas the Wright method line follows a constant viscosity value.

This constant temperature nature of the Walther mixing rule is also the biggest drawback of the mixing rule (applicable for all constant temperature mixing rules). The lack of

temperature variance in the mixing rule requires the viscosities of the blending components to be known at the temperature of interest of the final blend, which might not be possible for all neat components (e.g. components owning a low flash point or high freezing point).

4.2.6 Chirinos mixing rule

The Chirinos mixing rule (38)^{7,60} is an iteration of the Walther mixing rule (37), where the parameter C has been fixed to a static value of 0.7 based on experimental determination and the volume fractions have been replaced by weight fractions.

$$\log \log(v + 0.7) = w_A \log \log(v_A + 0.7) + w_B \log \log(v_B + 0.7) \quad (38)$$

where v is the kinematic viscosity of the blend (in cSt or mm²/s), v_A and v_B are viscosities of the components, and w is the weight fraction of each respective component.⁷

This version of the equation was originally developed for bitumen-diluent mixtures⁶⁰ and is therefore included in this work for comparative purposes.

4.3 Examples of results obtained by previous research groups

All the empirical correlations and mixing rules described in **Section 4.1 and 4.2** have been investigated by a variety of research groups. Examples of previously reported deviations for the methods are provided in this section. The empirical correlations assessed in this work have mostly been investigated for the prediction of crude oils. A list of results from the works of Sánchez-Rubio *et al.*⁸, Aboul-Seoud and Moharam⁴¹, and Kotzakoulakis *et al.*³⁷ is presented in **Table 10**.

Table 10: Examples of previously reported deviations of correlations.

Equation	Absolute average deviation (%)	From work by
Walther, eq. (6)	3.84*	Sánchez-Rubio <i>et al.</i> ⁸
NFGW, eq. (13)	0.37*	Sánchez-Rubio <i>et al.</i> ⁸
Aboul-Seoud and Moharam, eq. (14)	1.47	Aboul-Seoud and Moharam ⁴¹
	13.7	Kotzakoulakis <i>et al.</i> ³⁷
Mehrotra, eq. (17)	5.0	Aboul-Seoud and Moharam ⁴¹
	218	Kotzakoulakis <i>et al.</i> ³⁷
Mehrotra by Kotzakoulakis, eq. (18)	199	Kotzakoulakis <i>et al.</i> ³⁷
Moharam, eq. (19)	5.54	Aboul-Seoud and Moharam ⁴¹
Moharam by Aboul-Seoud and Moharam, eq. (21)	3.05	Aboul-Seoud and Moharam ⁴¹
	101	Kotzakoulakis <i>et al.</i> ³⁷
Moharam by Kotzakoulakis, eq. (22)	52.9	Kotzakoulakis <i>et al.</i> ³⁷
Puttagunta, eq. (23)	1.59	Aboul-Seoud and Moharam ⁴¹
*Mean of standard deviations reported in the work		

Sánchez-Rubio results are the result of estimating 42 data points of 4 crude oils based on two (Walther equation) and three (NFGW equation) data points from each sample.⁸ Aboul-Seoud and Moharam results are obtained by estimating 478 or 316 data points of 16 or 14 crude oils respectively.⁴¹ Kotzakoulakis *et al.* AADs are the result of estimating the viscosities of 254 different crude oils at both 15 °C and 0 °C (i.e. 308 data points).³⁷

Centeno *et al.* investigated the accuracy of 17 different mixing rules by estimating the viscosities of naphtha, diesel, and vacuum gas oil binary blends. The percentage standard error (SE) for the predicted viscosities compared with experimental results are given in the original article.⁷ All mixing rules discussed in **Section 4.2**, except the Kendall and Monroe equation (30), performed very well according to the results reported by Centeno *et al.* (SE for Kendall and Monroe equation above 10 % at its worst, SE was below 5 % in all other cases). The Wright blending method, however, was not investigated by the group.

5 EXPERIMENTAL

Viscosity data for a variety of neat and blended hydrocarbon mixtures was needed for assessing the performance of the calculative tools found in the literature. Independent experimental determination of the kinematic viscosities was performed instead of using commercially available databanks due to repeatability and comparability concerns. Additional sample properties, required for specific correlations, were determined as well.

5.1 Methodology and plan

The sample matrix was designed to contain an extensive variety of hydrocarbon mixtures. These included market grade fuels, experimental fuels, oils, and model compounds of the middle to heavy distillate range. Neat sample properties, sample mixture properties as well as the effects of cumulatively raising the volumetric ratio of one of the components in the mixtures was of interest.

An assortment of mixtures was created for the purpose of this work. These included binary mixtures (mixtures of two components), tertiary mixtures (mixtures of three components), and quaternary mixtures (mixtures of four components). The mixtures were organized into five separate groups: four binary sample sets (BS1, BS2, BS3, and BS4) and one separate sample set for the tertiary and quaternary mixtures (TQ1). The TQ1 sample set was created and used for validation of the predictive capability of the methods. The tertiary and quaternary mixtures of TQ1 are mixtures of model compounds and an experimental fuel of the middle distillate range. This provided a highly complex set of viscosity data that could be used in the assessment of the models. The TQ1 sample set was, in other words, treated as a benchmark for the prediction flexibility of the correlations (in regards of input). The need for an additional group of samples arose during the thesis work, when the correlations requiring distillation data as input were found (see Section 4.1). An assortment of neat liquid hydrocarbons was analyzed, and the sample group was named Singular sample set 1 (S1). A summary of all sample sets are listed in Table 11.

Table 11: Summary of sample set details.

Sample set	No. of components per mixture	Use
Binary sample set 1 (BS1)	2	Mixing rules and correlations requiring viscosity as input
Binary sample set 2 (BS2)	2	Mixing rules and correlations requiring viscosity as input
Binary sample set 3 (BS3)	2	Mixing rules and correlations requiring viscosity as input
Binary sample set 4 (BS4)	2	Mixing rules and correlations requiring viscosity as input
Tertiary and quaternary sample set 1 (TQ1)	3 or 4	Mixing rules and correlations requiring viscosity as input
Singular sample set 1 (S1)	1 (neat components)	Correlations requiring distillation data as input

An assortment of the mixtures in the sample sets consisted of 0 – 100 vol-% of component A in a base of component B (applicable for most binary mixtures). Individual cases required more specific mixtures to be created and some combinations were of interest only at certain volumetric ratios.

The most relevant experimentally determined physicochemical property, regarding this work, was the kinematic viscosity of the neat samples and the mixtures thereof. Properties such as density and distillation data of the samples were determined as well, since these were needed for the assessment of certain correlations. Additional properties such as freezing point (see **Section 5.3.3** for further information regarding choice of this method) of the samples, were used to determine viable sample combinations and the temperature limit of reliable viscosity results for example.

The various individual, binary, tertiary, and quaternary samples discussed above, represent a scale between middle to heavy distillate liquid hydrocarbon mixtures, thus providing a good dataset for evaluating the calculative tools found in the literature. BS1-4 and TQ1 were used to evaluate empirical correlations that require 1, 2, or 3 viscosity data points as input (i.e. empirical correlations that are useful in situations where 1, 2, or 3 viscosity values of the sample at differing temperatures are known). The mixing rules were evaluated using BS1-4. The sample set S1 was in turn, used to evaluate empirical correlations that require the T_b and/or specific gravity of the samples as input (i.e. correlations that are useful situations where no viscosity data is available and the viscosity of the sample is needed).

5.2 Sample preparation

All binary, tertiary, and quaternary mixtures were prepared using volumetric pipettes and stored in 250 ml glass bottles. A final volume of 200 ml was chosen for the samples. This was done to simplify the volume ratios and thus ease the blending process in the laboratory. The volumetric ratios were identical for all binary sample series. 36 binary blends of the range 0 - 100 % were created. The tertiary and quaternary samples investigated in this work were created by a different logic (e.g. three components of varying vol-% in tertiary blends and four components of varying vol-% in quaternary blends).

5.3 Analysis

Test methods based on standardized procedures defined by ASTM International and EN ISO were used in this work. The standard procedures were used since product standards require all measurements in the industry to be conducted by following these methods. This ensured realistic results which could be of use when comparing the results to real-world cases. Additionally, empirical correlations such as the Kotzakoulakis *et al.* version of the Moharam correlation (see Section 4.1.4) require specifically the results of ASTM methods as input data.³⁷ Duplicate measurements were performed for all samples and the average result was used in further evaluations.

5.3.1 Viscosity, ASTM D445

The viscosities of the samples were determined by the practices defined in the “ASTM D445 Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids”. A suitable amount of each sample was transferred into a Cannon-Fenske routine viscometer of appropriate size by suction. The viscometers containing the samples were lowered into a temperature-controlled bath to control and stabilize the temperature of the samples. Heating and cooling of the bath was controlled by a Lauda Kryomat high performance thermostat. Multiple baths with different bath mediums were needed due to the wide temperature range of the determinations. The flow time of each sample was determined after an appropriate time was allowed for the samples to reach the target temperature. The viscosity value for each sample was calculated based on the flow time and the calibration constant of the viscometer. Two consecutive measurements of each sample were made and an acceptable reproducibility error, r , between each set of values was assured, wherever applicable. The parameter k is defined for each sample type/temperature combination separately, in the standard test method, and does not therefore cover the entire range of

samples in the sample matrix. The final viscosity value for each sample was reported as the average of these two parallel results (owning an acceptable r value if defined).¹¹

The procedure was repeated for all samples at temperatures of +30, +20, +10, 0, -10, -20, -30, and -40 °C. Some of the neat or mixed samples defined in the sample matrix were, however, limited by the relatively high freezing points or low flashpoints of the components.

Example of average result calculation:

Flow time 1 = F_1

Flow time 2 = F_2

Viscometer calibration constant = C_V

Viscosity of first measurement = $F_1 \cdot C_V = V_1$

Viscosity of second measurement = $F_2 \cdot C_V = V_2$

Average of results = $(V_1 + V_2) / 2 = V_A$

$r = V_A \cdot k$

5.3.2 Density, EN ISO 12185 (ASTM D4052)

The density of the samples was determined according to the standard procedure “EN ISO 12185 Crude petroleum and petroleum products – Determination of density – Oscillating U-tube method”. A Mettler Toledo DM45 DeltaRange density meter was used for the measurements.⁶¹

A small amount of sample (typically less than 1.2 ml) is introduced into a temperature-controlled sample cell (15 °C in this case). The oscillation frequency of the sample is determined when the sample has acclimatized to the correct temperature. The density of the sample is calculated from this value using cell constants (previously determined using calibration fluids with known densities).⁶¹

5.3.3 Freezing point, IP 529 (ASTM D7153e1)

The change in fluidity of a sample consisting of liquid hydrocarbons of the middle to heavy distillate range can be determined by multiple methods. These include for example the cloud point (i.e. when the first paraffins in the sample crystallize on a visually observable scale), the

pour point (i.e. when the sample becomes stagnant in nature instead of fluid), and the freezing point (i.e. when the last of the crystallized paraffins are liquified). The freezing point of the samples was chosen to be used in this work since even the slightest amount of crystallized paraffins could skew the delicate viscosity results, and none of these would be present above the temperature reported as the freezing point of the sample. The freezing point of the samples was determined in this work according to the standard procedure IP 529: Determination of the freezing point of aviation fuels – Automatic laser method using an ISL FZP 5G2s freezing point analyser.⁶²

The sample is cooled down at a rate of $10\text{ }^{\circ}\text{C} / \text{min} \pm 5\text{ }^{\circ}\text{C}$ while simultaneously being irradiated by a laser light. Two detectors within the instrument track the formation of paraffinic crystals and the opacity of the sample. The cooling of the sample is discontinued and heating of the sample at a constant temperature is initiated once both paraffin crystals and opacity has been detected. The freezing point of the sample is registered when all paraffin crystals have returned to liquid phase and the sample is clear.⁶²

5.3.4 Distillation range, ASTM D86

The boiling range characteristics of the samples in sample set S1 were determined according to the “ASTM D86 Standard Test Method for Distillation of Petroleum Products and Liquid Fuels at Atmospheric Pressure”. The test method comprises the atmospheric distillation of a sample of petroleum product to determine the boiling range of the sample. The distillation is performed in a laboratory batch distillation unit which can determine the entire boiling range quantitatively. In other words, the entire distillation range is recorded in relation to the volumetric ratio of product that has been recovered at each temperature (e.g. the temperature at which, for example, 50 volumetric percent of a sample has been recovered).⁶³

6 RESULTS AND DISCUSSION

The empirical correlations and mixing rules determined to be the most promising for our efforts in **Section 4**, were subjected to rigorous testing. The results are discussed in this section of the thesis. Results are presented in the form of adjusted R^2 values due to the impracticality of a detailed analysis of the substantial amount of experimental data generated in the present work. The detailed experimental results have been compiled in a separate report.⁶⁴

6.1 General results

The results for the viscosity determinations of the neat components of sample sets BS1, BS2, BS3, BS4 and TQ1 (BS1N, BS2N, TQ1N1 etc.) as well as selected mixtures from all sample sets (BS1M, BS2M, TQ1M1, TQ1M2 etc.) are presented in **Figure 10**. Selected components have been used in multiple sample sets and are therefore denoted by two sample set codes (e.g. BS1 + BS2).

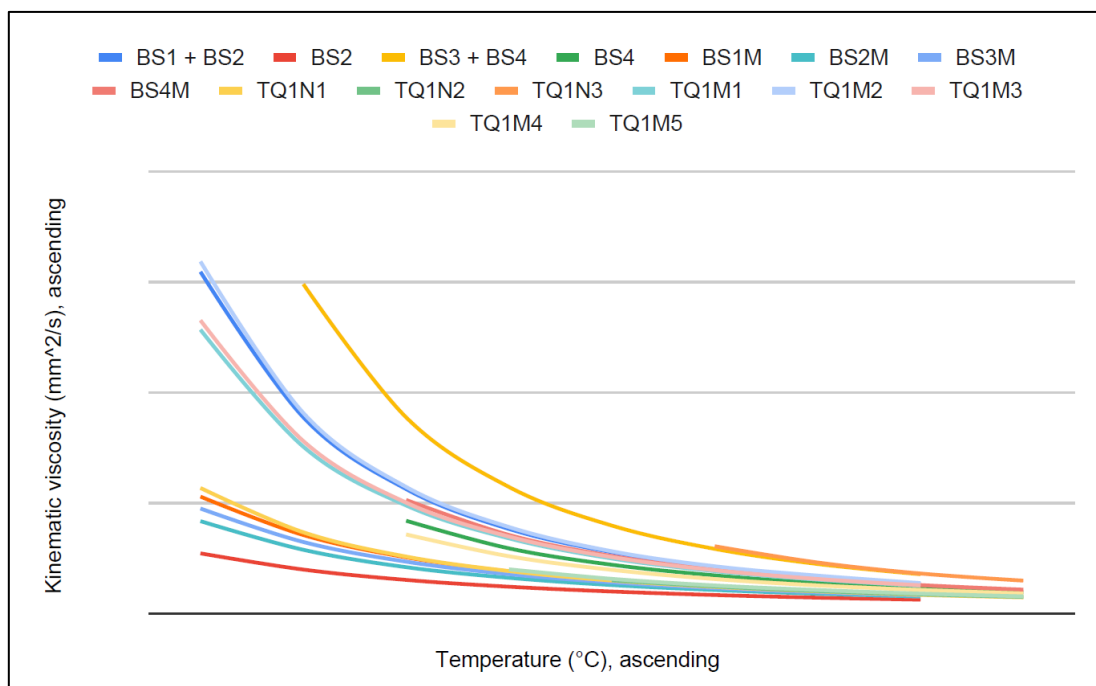


Figure 10: General results of viscosity determinations.

A surprising agreement between the temperature profiles of the neat components as well as the mixtures studied in this work was observed. It was speculated based on these results that the prediction of all sample sets would therefore be possible with relatively satisfactory accuracy.

6.1.1 R^2 adjusted

The coefficient of determination (R^2) is a quantity used for assessing the accuracy of a mathematical model (predictive description of experimental data). It relates the variance in the data which is explained by the mathematical model and that which is explained by simply assuming an average of the experimental points.⁶⁵ The R^2 of a model (or correlation) may be calculated using equation (40).

$$R^2 = 1 - \left(\frac{SS_{res}}{SS_{tot}} \right) = 1 - \frac{\sum_{N_{exp}} (\hat{\eta}_{exp} - \eta_{est})^2}{\sum_{N_{exp}} (\hat{\eta}_{exp} - \bar{\eta}_{exp})^2} \quad (40)$$

where SS_{res} is the sum of squared residuals of the model, SS_{tot} is the sum of total squared residuals, $\hat{\eta}_{exp}$ represents the experimental data, η_{est} represents the estimated data, $\bar{\eta}_{exp}$ is the average of all experimental data and N_{exp} is the number of experimental data points. It is a consequence from (40) that, very accurate models have R^2 values close to 1. In contrast, poorly accurate ones may have very low and even negative values of R^2 . However, assessment of model accuracy using R^2 should be done with caution as this parameter can be artificially improved by adding sufficient terms (parameters to a model). The adjusted R^2 , which considers the amount of terms in a model, should preferably be used instead.⁶⁵ All R^2 adjusted results presented in this work were calculated according to equation (41).

$$R^2_{adjusted} = 1 - \left((1 - R^2) \cdot \frac{(N_{exp} - 1)}{(N_{exp} - N_p - 1)} \right) \quad (41)$$

where N_{exp} is the number of experimental data points and N_p is the number of terms in the model. The adjusted R^2 results are presented in the form of $1 - \text{adjusted } R^2$ due to high accuracy of the correlations and mixing rules. The logic regarding the accuracy of a model for $1 - \text{adjusted } R^2$ is the contrary compared to the adjusted R^2 . In other words, very accurate models have a $1 - \text{adjusted } R^2$ close to 0 and poorly accurate ones may have very high or even negative values of $1 - \text{adjusted } R^2$.

6.1.2 Weighted average and 50 % boiling point

The volume specific boiling points of a sample (i.e. at which temperature a certain volume of sample has been distilled) may be determined by the method described in ASTM D86 (see **Section 5.3.4**). These results will give the Volume Average Boiling Point when calculations are performed according to equation (42).⁶⁶

$$VABP = 0.2 \cdot (T_{10\%} + T_{30\%} + T_{50\%} + T_{70\%} + T_{90\%}) \quad (42)$$

The temperatures at which certain weight percentages of a sample have been distilled are provided by the ASTM D2887 method. These results will provide the Weight Average Boiling Point (WABP) when used in equation (41).⁶⁶

$$WABP = 0.2 \cdot (T_{10\%} + T_{30\%} + T_{50\%} + T_{70\%} + T_{90\%}) \quad (43)$$

Both the VABP and the WABP can technically be used as input data in correlations where the Weighted Average Boiling Point is required as input (see Section 4.1.3 and Section 4.1.4). The 50 % boiling point can naturally be of two types as well. It can either be the 50 % mass boiling point (50 % MBP, determined by ASTM D2887) or the 50 % volume boiling point (50 % VBP, determined by ASTM D86). It was decided, based on early testing, that only the volume specific boiling points would be used to assess correlations where boiling point data was needed (the resulting accuracy of the model was found to be better).

6.2 Empirical correlations

The empirical correlations were investigated by testing the predictive accuracy of the methods based on experimental data obtained exclusively for this work. Two of the empirical correlations, the Walther correlation and the Aboul-Seoud and Moharam correlation, could be assessed using sample sets BS1, BS2, BS3, BS4 and TQ1 (i.e. binary, tertiary, and quaternary mixtures). The remaining two correlations of interest (the Kotzakoulakis version of the Mehrotra correlation and the Moharam correlation), were assessed using sample set S1. A list of the adjusted R^2 results of the correlations is provided in Table 12.

Table 12: Average adjusted R^2 of the investigated empirical correlations.

Empirical correlation	Average adjusted R^2 (original parameters)	Average adjusted R^2 (regressed parameters)
Walther*	0.996331	0.998997
Aboul-Seoud and Moharam	0.969477	0.999041
Kotzakoulakis version of Mehrotra correlation	-0.132616	0.998192
Kotzakoulakis version of Moharam correlation	-5.705039	0.997511
*No regression performed (see Section 6.2.1)		

An average of all sample set results is provided for correlations where multiple sample sets have been assessed (the average of multiple adjusted R^2 results has no statistical meaning, the results in **Table 12** are therefore merely suggestive).

6.2.1 Walther correlation

Primary investigations of the Walther correlation were focused on utilizing the traditional form of the equation (i.e. equations (3), (5), (6), and (7)). It was found at a very early stage that the parameters b_1 and b_2 could be calculated in two different ways. One was the traditional way described by equations (5) and (6), whereas the other was the method described in ASTM D341. The method described in the standard is meant to be used for situations where the kinematic viscosity to be predicted falls under $2.0 \text{ mm}^2/\text{s}$ (cSt).⁴⁵ This was a common occurrence in the dataset and both approaches were therefore investigated. The difference in adjusted R^2 for the entire BS1, for example, was found to be approximately $1 \cdot 10^{-9}$ (cold inputs were used, see below for more information). The method reported in the standard was, however, used in all subsequent calculations (precautionary action).



Another aspect of the Walther correlation is that the input temperatures can be varied. This was tested on all sample sets, where applicable (due to temperature (fluidity) constraints). The input viscosities used for comparing the calculations were taken at $+20^\circ\text{C}$ and 0°C in one case, and -20°C and -40°C in the other. The surprising result was that the accuracy decreased when the applied input values were taken from a higher temperature range. This can be speculated to result from the temperature dependence of liquid viscosities where the slope of the curve grows in a non-linear fashion when temperature decreases, thus increasing the uncertainty of the prediction toward the colder temperatures (see **Figure 10**). Using the colder temperature viscosity data as input can be speculated to have decreased the inaccuracy at the more critical temperature range with regards to viscosity prediction. A visual interpretation of the problem is given in **Table 13**.

Table 13: Visual interpretation of how the choice of input temperature affects the uncertainty of prediction.

Warm inputs (grey)		Cold inputs (grey)	
Temperature	Sample viscosity	Temperature	Sample viscosity
40 °C	x	40 °C	x
30 °C	x	30 °C	x
20 °C	x	20 °C	x
10 °C	x	10 °C	x
0 °C	x	0 °C	x
-10 °C	x	-10 °C	x
-20 °C	x	-20 °C	x
-30 °C	x	-30 °C	x
-40 °C	x	-40 °C	x

Expected accuracy of prediction due to increasing slope of viscosity-temperature curve:

Excellent:  Good:  Fair:  Poor: 

Improved accuracy:  Input (no inaccuracy): 

The uncertainty naturally decreases around the chosen inputs (notice the striped cells above, between, and below the chosen input values). Use of the warm inputs only affects the yellow and orange rows positively, whereas the cold inputs affect all the red and orange rows.

Let's, for example, assume that we know the viscosity of a sample at +20 °C and 0 °C. This will allow us to predict the viscosity of a sample at +30, +10, and -10 °C with increased accuracy, whereas the prediction accuracy of the +40, -20, -30, and -40 °C points are unaltered. When adding up the residuals of the results (estimated value – experimental value), the sum will simply be larger than if we would know the viscosity at -20 °C and -40 °C. The lower sum of residuals for the scenario where the colder values are known, is caused by the fact that the worst inaccuracies of the dataset (right half of **Table 13** fair and poor cells) are improved by the input values and surrounding effect (striped cells). The +40, +30, +20, +10, and 0 °C accuracy is naturally good to fair, which leads to a smaller sum of residuals.

Adjusted R^2 values for all sample sets studied are presented in **Figure 11**. The results have been separated into results for both cold and warm inputs.

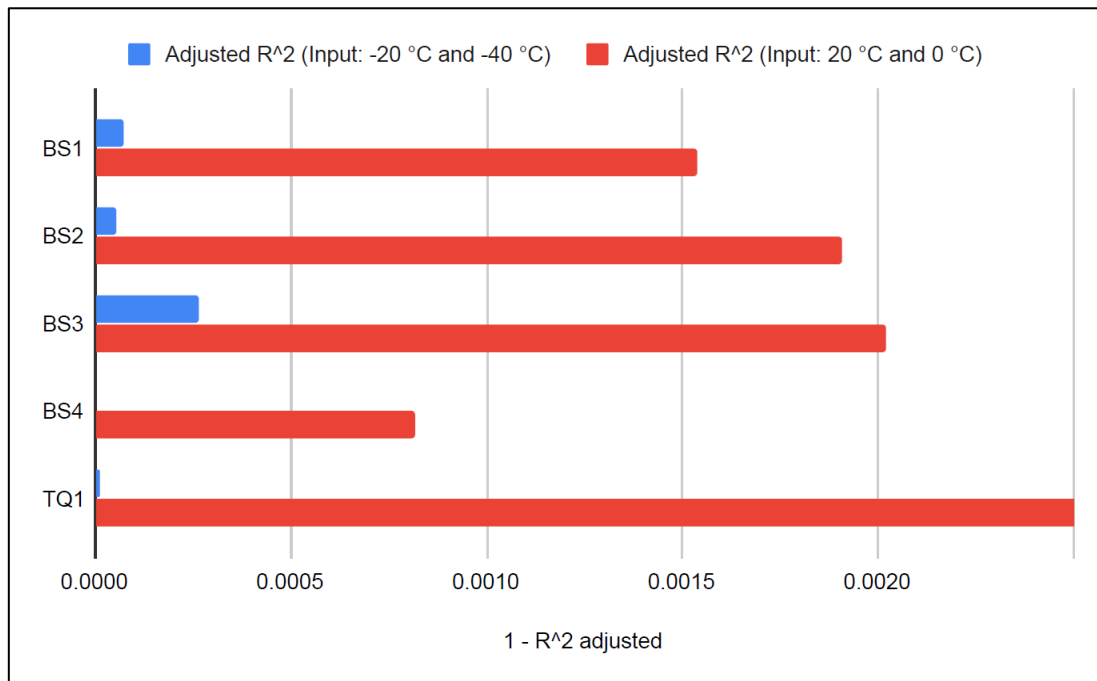


Figure 11: 1 - Adjusted R^2 results of the Walther correlation.

It was only possible to use the warmer inputs for BS4. The lack of cold data partially explains the significantly lower $1 - \text{adjusted } R^2$ for BS4. The prediction of TQ1 data with warm input values resulted, unsurprisingly, in the highest $1 - \text{adjusted } R^2$ result of all sample sets. The $1 - \text{adjusted } R^2$ for TQ1 was approximately 0.012058 when warm inputs were used. Switching to cold inputs surprisingly resulted in the largest $1 - \text{adjusted } R^2$ of the Walther correlation results ($1 - R^2 \text{ adj.} \approx 0.000012$). This will be the lowest $1 - \text{adjusted } R^2$ result reported in this thesis and is a strong indication of the flexibility of the Walther correlation. The use of cold input values was therefore concluded to be the best approach for lowering the local prediction uncertainty of the cold region. The difference in prediction accuracy when going from warm inputs (**Figure 12**) to cold inputs (**Figure 13**) is presented in the form of parity plots below.^b

^b The diagonal reference line is created by the equation $y = x$. This line represents the ideal relationship between experimental and estimated value.

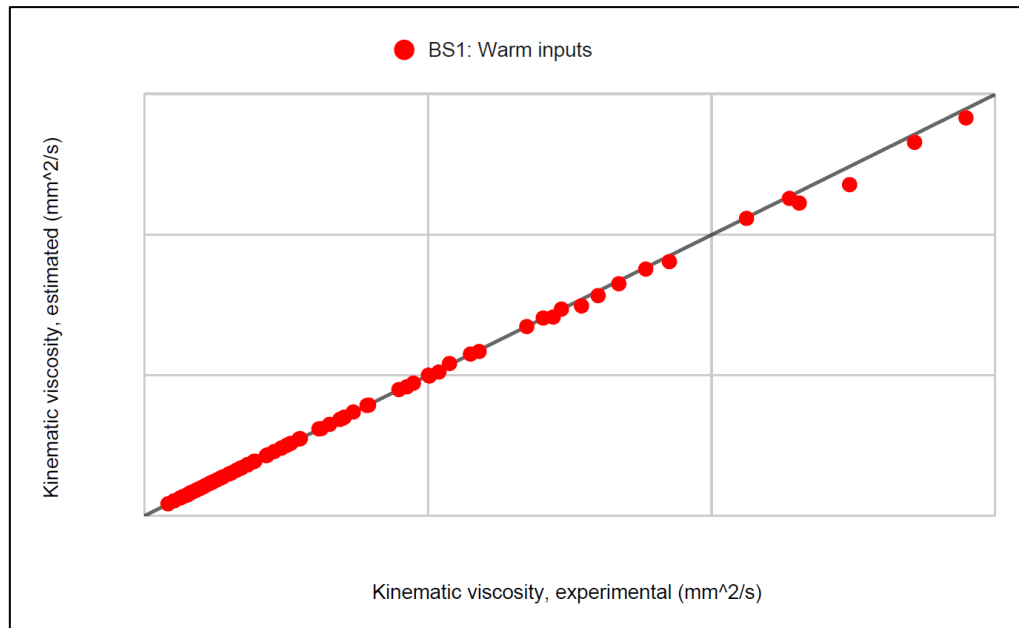


Figure 12: Parity plot of BS1 Walther correlation results using +20 and 0 °C data as inputs.

The inaccuracy of the results in the colder end of the plot (right half) in comparison with the warm result (left half) can clearly be seen from this figure.

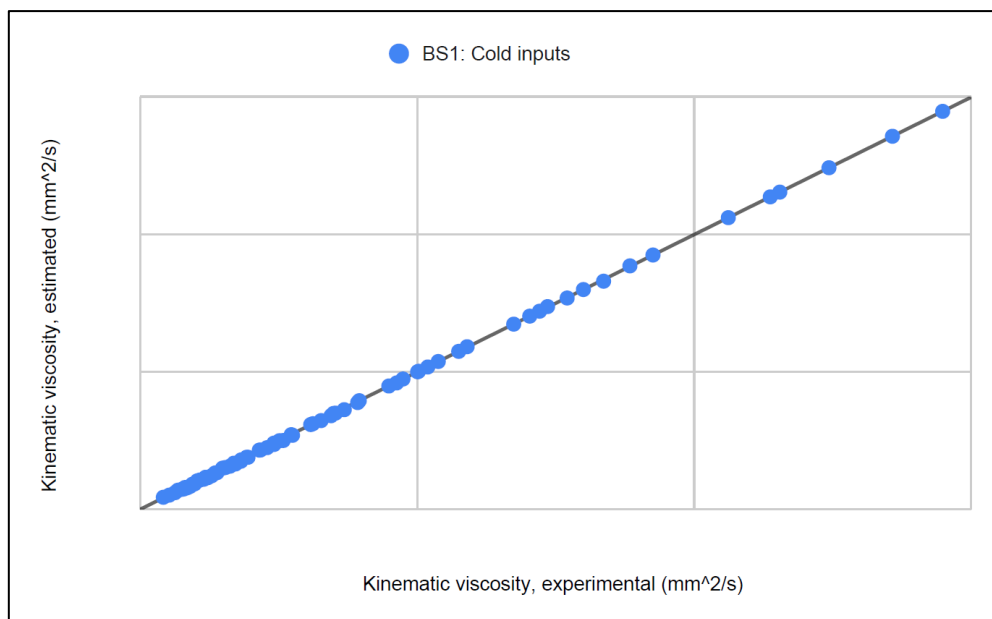


Figure 13: Parity plot of BS1 Walther correlation results using -20 and -40 °C data as inputs.

The general accuracy of the results is clearly greatly improved when cold input values are used. All the stray data points have been adjusted and most of the data points overlap the reference line. The spread of the results in the colder half of the plot has also been corrected.

Additionally, a general trend was observed where the R^2 adjusted of the individual sample sets would increase when the input range was broadened (e.g. +20 °C and -40 °C viscosity values were used as inputs).

The original correlation gave some promising results as can be seen in **Figure 11**, **Figure 12**, and **Figure 13** above. Previously reported results of the NFGW equation (see **Table 8**) attracted favorable attention and was therefore investigated despite the excellent results already obtained by using the first regression analysis. Unfortunately, the 1 – adjusted R^2 of the BS1 results had a value of 0.002807 when the NFGW approach was tested with cold inputs (1 – adjusted R^2 for BS1 using the original approach and cold inputs ≈ 0.000073). It could therefore be concluded that the NFGW approach is an unnecessarily complicated method for lighter hydrocarbon liquids than its original design.

A more straightforward approach of estimating the fluid specific C value was considered in the present work. The fluid specific value of the C parameter was derived by regression using the Solver function in ©Microsoft Excel. A comparison of the original parameter approach versus the regressed parameter approach showed that the Walther correlation is extremely well optimized in its native state. The adjusted R^2 of the prediction was found to decrease or increase by a maximum of $1 \cdot 10^{-5}$ only. It could therefore be concluded that the regression of the C parameter was unnecessary for the investigated samples.

6.2.2 *Aboul-Seoud and Moharam correlation*

The Aboul-Seoud and Moharam correlation was evaluated using the same sample sets as the Walther correlation (BS1, BS2, BS3, BS4, and TQ1). Even the additional sample set S1 could be utilized in this case. The amount of input values required for the A-S & M correlation is half of what is required for the Walther correlation (one vs. two viscosity values for each component, see **Table 8**). The difference in 1 – adjusted R^2 between the two methods was only approximately 0.04 for BS1 when the original parameters from the literature were used. The 1 – adjusted R^2 for all sample sets are provided in **Figure 14**.

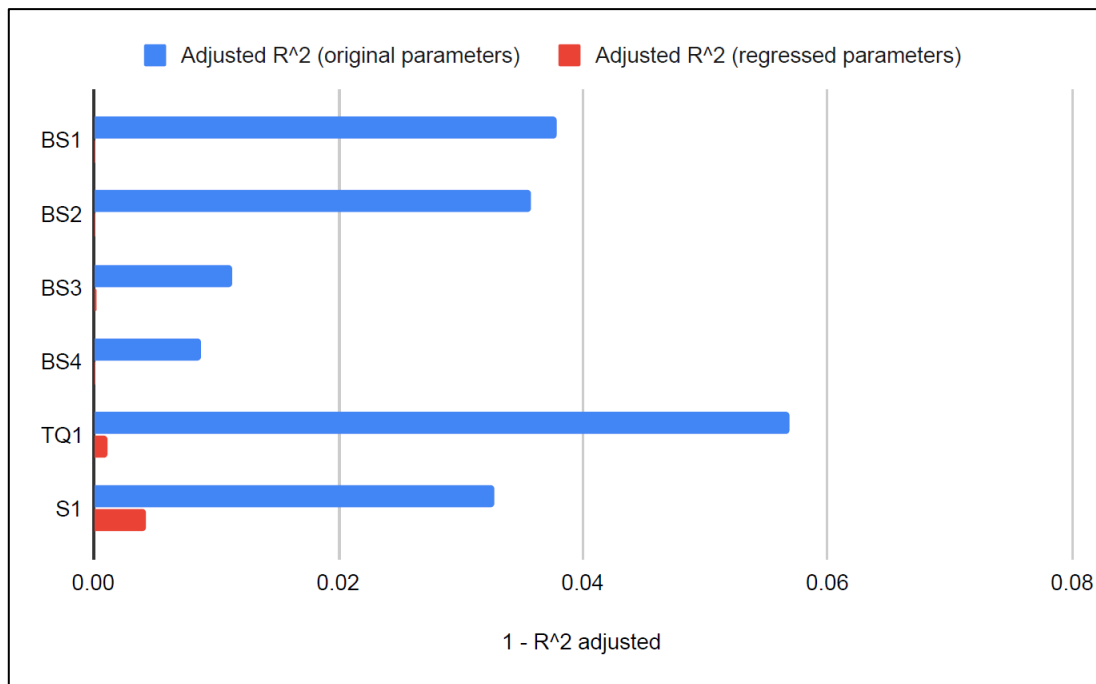


Figure 14: 1 - Adjusted R^2 results for the Aboul-Seoud and Moharam correlation.

The $1 - \text{adjusted } R^2$ for the binary sample sets decrease when going from BS1 toward BS4. This can be explained by the stepped decrease of the amount of data points to be predicted in each sample set. TQ1 presented again, unsurprisingly, the highest $1 - \text{adjusted } R^2$ of all sample sets studied. The size of the error, however, is very small when considering the content of the sample set. The excellent results for TQ1 suggests that this correlation may be able to reliably predict the viscosity of complex mixtures (i.e. is flexible regarding input variability).

The regression of the parameters using the Solver function in ©Microsoft Excel was tested for the A-S & M correlation as well. The parameters were regressed for each sample set separately. The results of the assessment are depicted by the red bars in **Figure 14**. A significant increase in the prediction accuracy can be achieved by regressing the parameters. The A-S & M correlation is nearly as accurate as the Walther correlation in the prediction of sample sets BS1, BS2, BS3, BS4, and TQ1, when the parameters are regressed for each set separately. The prediction of the viscosities of sample set S1 provided satisfactory results as well. Substantially less accurate prediction results are afforded when the parameters are regressed for all sample sets collectively. The substantial difference between regressed and original parameters is shown, as an example, for sample set BS1 in **Figure 15** and **Figure 16**.

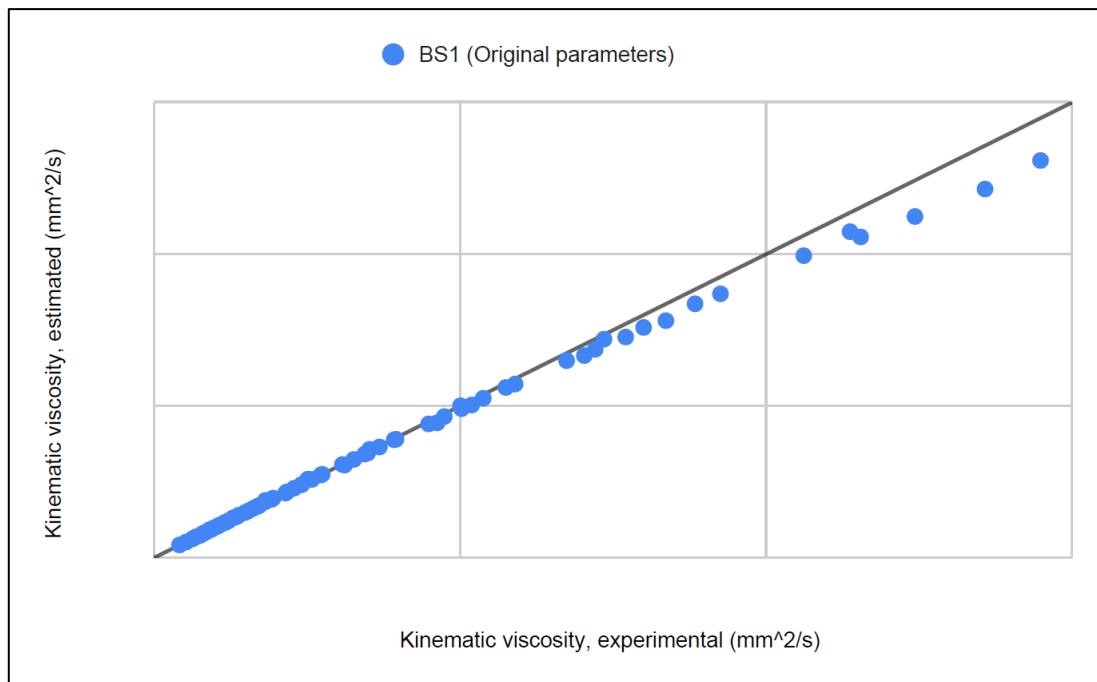


Figure 15: Aboul-Seoud and Moharam correlation results using original parameters.

The spread of the data points is substantial in the right half of the parity plot. This displays again the uncertainty of viscosity prediction in cold temperatures.

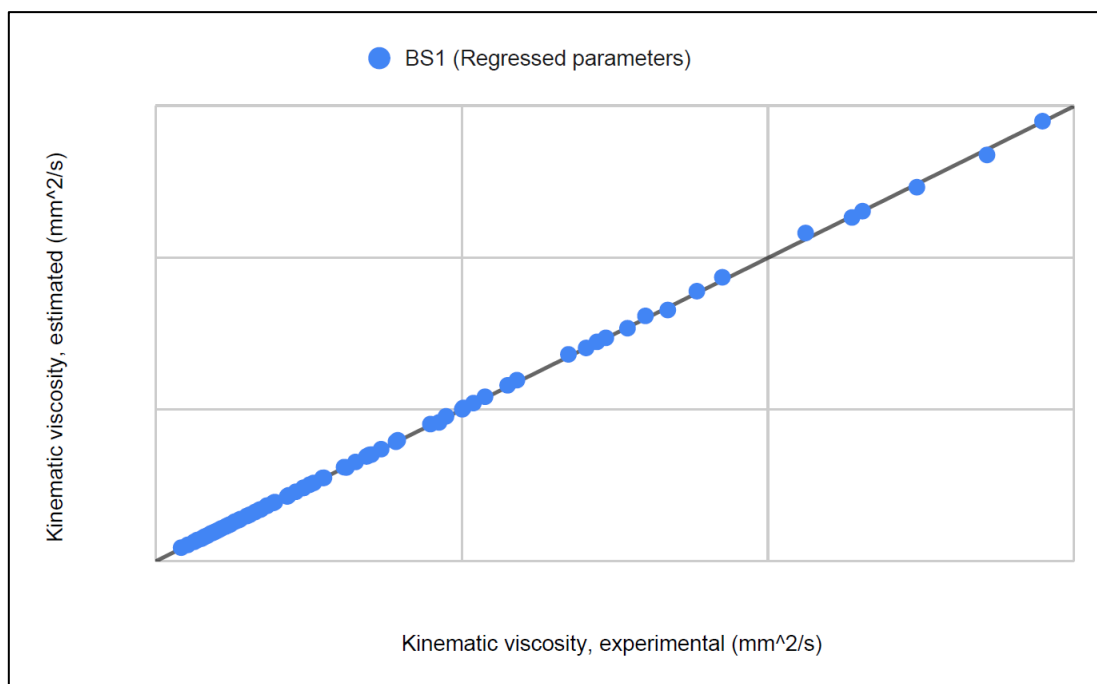


Figure 16: Aboul-Seoud and Moharam correlation results using regressed parameters.

The results are significantly improved when regressed parameters are used instead. Surprising similarity between the parity plot above and the Walther correlation results

(**Figure 12** and **Figure 13**) can be observed. It can therefore be concluded that the Aboul-Seoud and Moharam correlation is able to predict the viscosity of middle to heavy distillates if the parameters are regressed for a test data set.

6.2.3 Mehrotra correlation

The original Mehrotra correlation as well as the Kotzakoulakis version of the Mehrotra correlation were investigated using the sample set S1. The original correlation requires the weighted average boiling point to be used as input whereas the Kotzakoulakis version accepts the 50 % mass boiling point as input (**see Section 4.1.3**). Exact information was not found in the literature regarding the type of average boiling point to be used as input in the correlation. It was however decided, as previously mentioned, that only the volume average boiling points would be used as inputs. The Kotzakoulakis version of the Mehrotra correlation features an increase in accuracy (**see Table 10**), decrease in amount of variables, and simplification of required inputs. Excellent results were observed when the Kotzakoulakis version was tested (**see Section 6.2.3.1**). The performance of the original Mehrotra correlation and the A-S & M version were therefore not evaluated in this work.

6.2.3.1 Kotzakoulakis version of the Mehrotra correlation

Kotzakoulakis *et al.* explicitly report the use of the 50 % mass boiling point as input in their version of the correlation.³⁷ Only the 50 % volume boiling points (50 % VBP) was, however, investigated in the present work. The sample set S1 was used to evaluate this version of the Mehrotra correlation. Regression of the parameters of the correlation using the Solver function in ©Microsoft Excel was performed in this case as well.

The original parameters of the correlation provide extremely high 1 – adjusted R^2 results (1 – adjusted $R^2 \approx 1.13262$), indicating that the original parameters in fact are optimized for crude oils or other heavier hydrocarbon liquids. The results for S1, using the original parameters from the article, are presented in **Figure 17**.

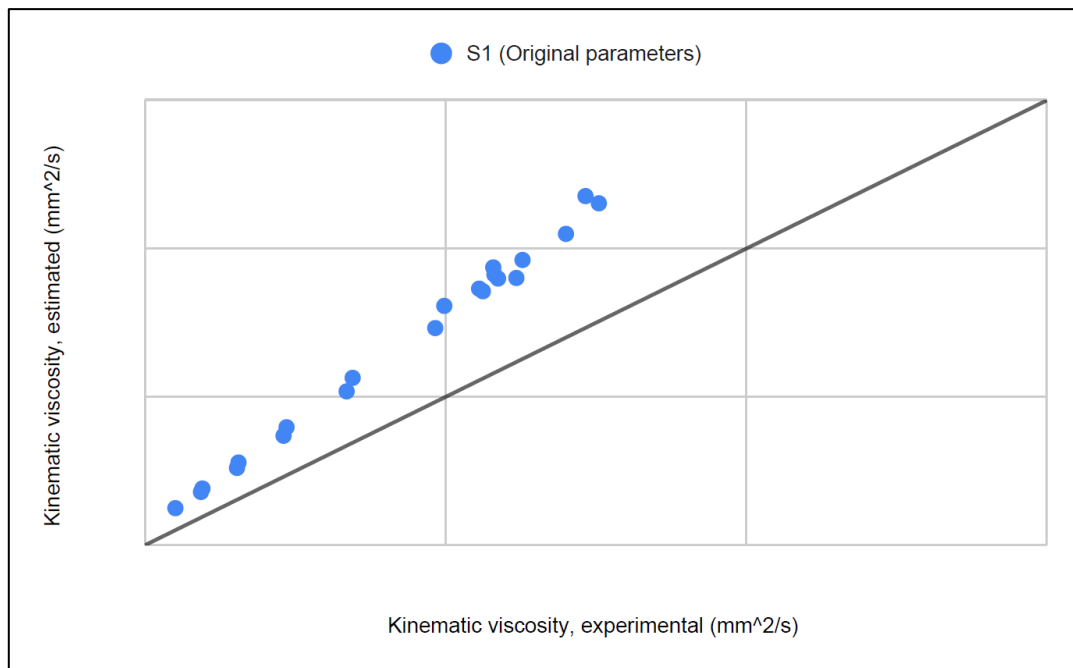


Figure 17: Results for the Kotzakoulakis version of the Mehrotra correlation using original parameters.

It is clear from the **Figure 17** that the results are far from ideal. The adjusted R^2 result also indicates that even the average of the viscosity results in S1 provide a better fit than the model (see **Section 6.1.1 for definition of R^2 adjusted**). Prediction accuracy can be improved substantially by regressing the correlation parameters. The results for S1, using regressed parameters, are presented in **Figure 18**.

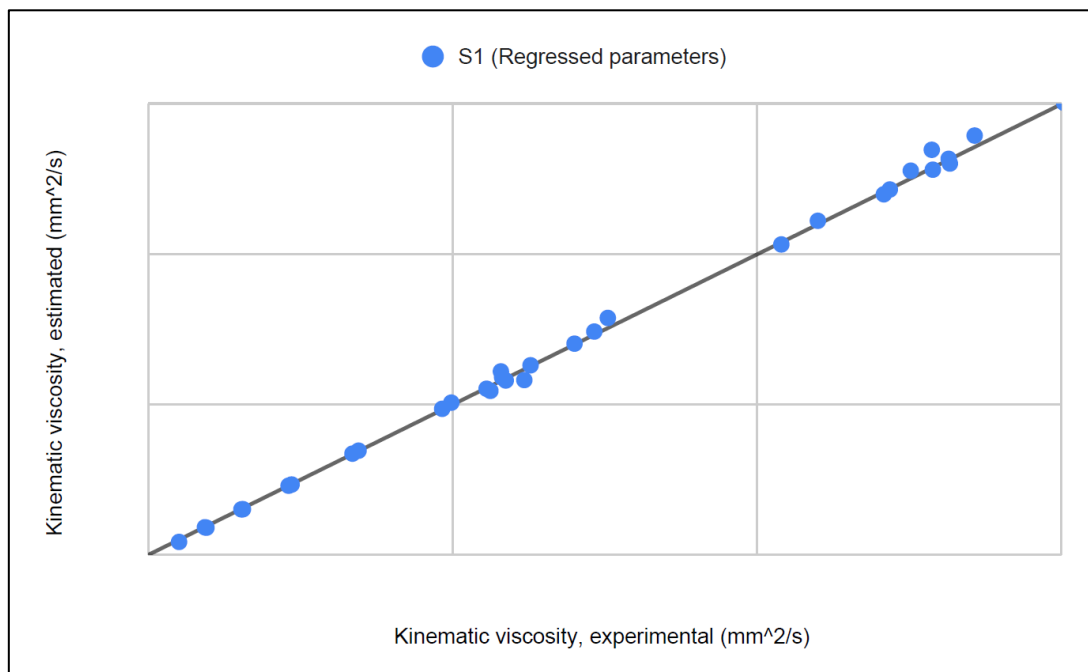


Figure 18: Results for the Kotzakoulakis version of the Mehrotra correlation using regressed parameters.

A substantial difference between the parity plots can be observed when the parameters are regressed. A significant increase in the $1 - \text{adjusted } R^2$ can also be observed ($1 - \text{adjusted } R^2$ of regressed correlation ≈ 0.001807). An additional observation can be made from the results. This is the fact that the 50 % VBP can be used as input instead of the 50 % MBP without issues. Overall, the Kotzakoulakis version of the Mehrotra correlation can be considered as a viable option for viscosity prediction of middle to heavy distillates. The correlation should, however, be considered only in cases where no viscosity data is available.

6.2.4 Moharam correlation

The original Moharam correlation (equation (21)) is said to describe the viscosity of a sample between 50 and 550 °C. The original version of the correlation was therefore not of interest regarding the efforts of this work (temperature range studied in this thesis = +40 to -40 °C). The version developed by A-S & M was excluded due to the same reason as the A-S & M version of the Mehrotra correlation was excluded (see Section 6.2.3). The Kotzakoulakis version of the Moharam correlation was, however, of interest and is therefore discussed in this section.

6.2.4.1 Kotzakoulakis version of the Moharam correlation.

The Kotzakoulakis version of the Moharam correlation has been reported to result in lower deviations than the original Moharam correlation (see Table 10). This version requires the 50 % mass boiling point and the specific gravity at 15 °C to be used as inputs. The 50 % VBP was used in this work due to the promising results obtained for the Kotzakoulakis version of the Mehrotra correlation (see Section 6.2.3.1). The reference density for water at 15 °C, needed for the calculation of specific gravity, was set to 999.099 kg/m³ as instructed in the original article.³⁷ Sample set S1 was used in the investigations due to the input constraints. Regression of the parameters of the correlation was performed using the Solver function in ©Microsoft Excel in this case as well. The results for S1, using original parameters reported in the literature, are presented in Figure 19.

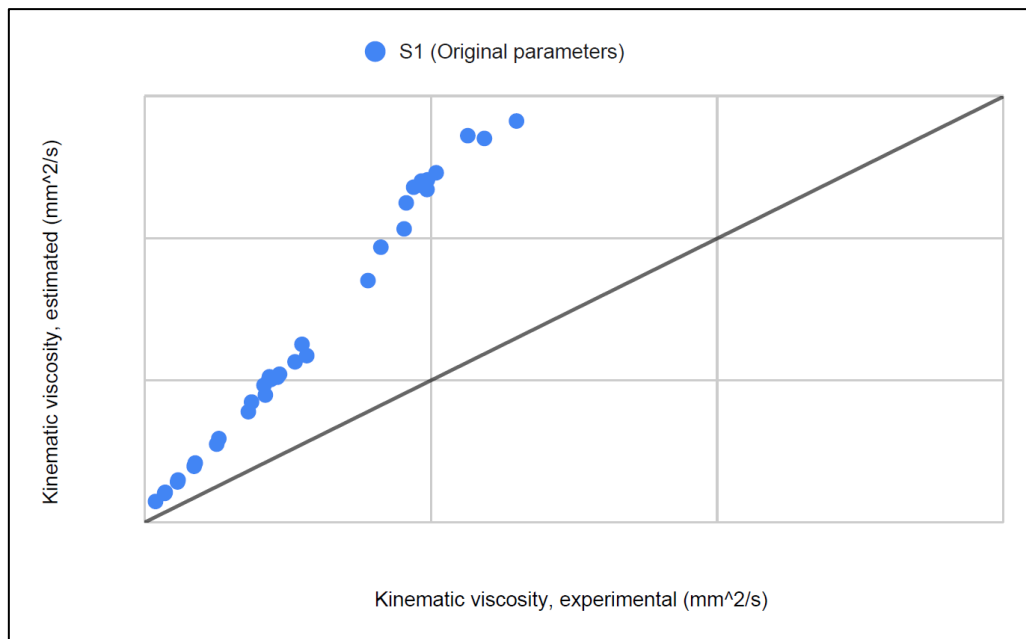


Figure 19: Results for the Kotzakoulakis version of the Moharam correlation using original parameters.

The difference between the Kotzakoulakis version of the Mehrotra and Moharam correlations is essentially only the addition of the specific gravity at 15 °C and a single parameter. The initial results portray a situation where the accuracy would decrease when an additional experimental input is provided. This, however, goes against the trend observed thus far. Regression of the correlation parameters was therefore performed. The results are presented in **Figure 20**.

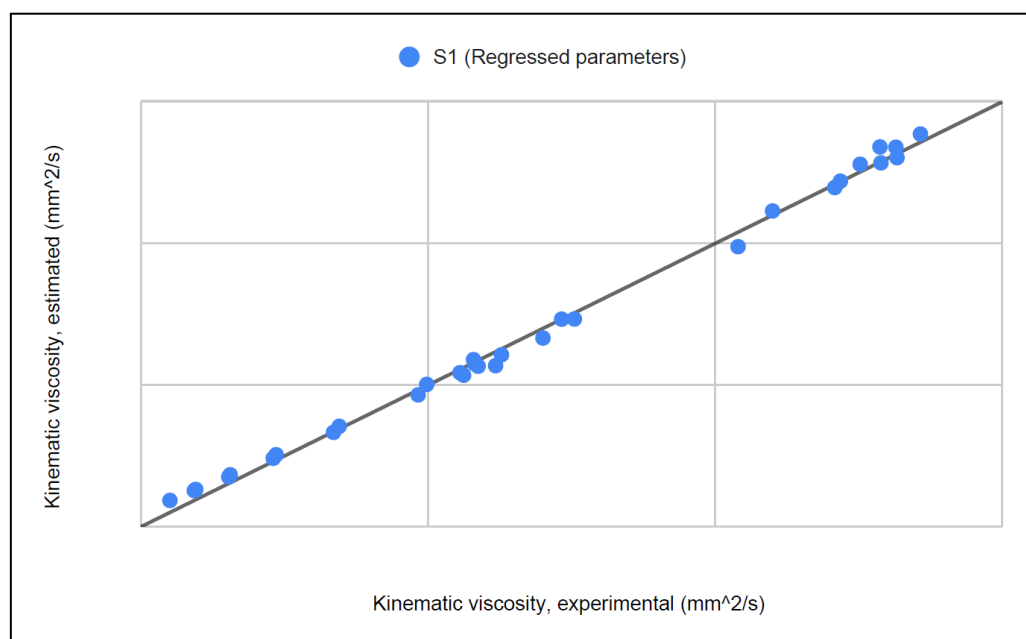


Figure 20: Results for the Kotzakoulakis version of the Moharam correlation using regressed parameters.

Remarkable improvement of the prediction accuracy and therefore $1 - \text{adjusted } R^2$ ($1 - \text{adjusted } R^2$ for regressed parameters ≈ 0.002489) is observed when comparing **Figure 19** and **Figure 20**. The $1 - \text{adjusted } R^2$ is, in this case, slightly higher for the Kotzakoulakis version of the Moharam correlation when compared to the Kotzakoulakis version of the Mehrotra correlation. The accuracy is, however, extremely similar in both cases and the Moharam correlation should, therefore, be considered if density data for the samples is available. A possible explanation for this is that two experimental points are relied upon in the Moharam correlation instead of only one in the Mehrotra correlation (Walther correlation vs. A-S & M correlation for example). This can be speculated to increase the probability of highly accurate predictions, as for example, in cases where significant error in the distillation point measurement has occurred. Furthermore, the use of the 50 % VBP as input was not found to cause issues in this case either.

6.2.5 Puttagunta correlation

The Puttagunta correlation was not investigated in this work because it is essentially the Walther equation expressed for the specific temperature of 37.78 °C.⁴²

6.3 Mixing rules

The mixing rules discussed in **Section 4.2** were evaluated using sample sets BS1, BS2, BS3, and BS4. The Chirinos mixing rule and the Refutas index method are iterations of the Walther mixing rule and the Chevron mixing rule, respectively. The Chirinos and Chevron rules are, however, included for comparative purposes. The Wright blending method and the Kendall and Monroe mixing rule are evaluated in this section as well due to their widespread use in the industry. A list of the average adjusted R^2 results of the mixing rules is provided in **Table 14** (results in **Table 14** are only suggestive).

Table 14: Average adjusted R^2 of the investigated mixing rules.

Mixing rule	Average adjusted R^2 (original parameters)	Average adjusted R^2 (regressed parameters)
Wright blending method	0.999354	-
Kendall and Monroe correlation	0.861519	-
Refutas index method	0.999381	-
Chevron mixing rule	0.998211	-
Walther mixing rule	0.999586	0.999894
Chirinos mixing rule	0.998968	-

The results for all sample sets and mixing rules are presented in the form of $1 - \text{adjusted } R^2$ values in **Figure 21**.

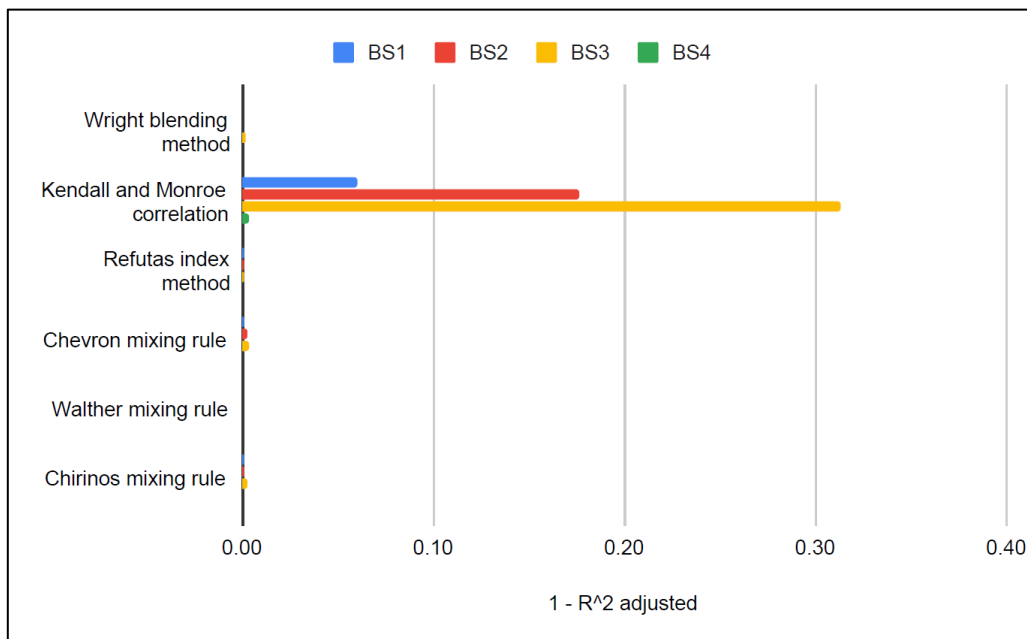


Figure 21: $1 - \text{Adjusted } R^2$ for all mixing rules.

It is clearly seen from **Figure 21** that the Kendall and Monroe mixing rule is the least accurate of all mixing rules. The Kendall and Monroe mixing rule should be used only for estimating viscosities of blends of components similar in nature (see **Section 4.2.2**, the inaccuracy of the results was expected). The Kendall and Monroe mixing rule was therefore excluded from all further investigations. An illustration of the $1 - \text{adjusted } R^2$ results excluding the Kendall and Monroe results is presented in **Figure 22**.

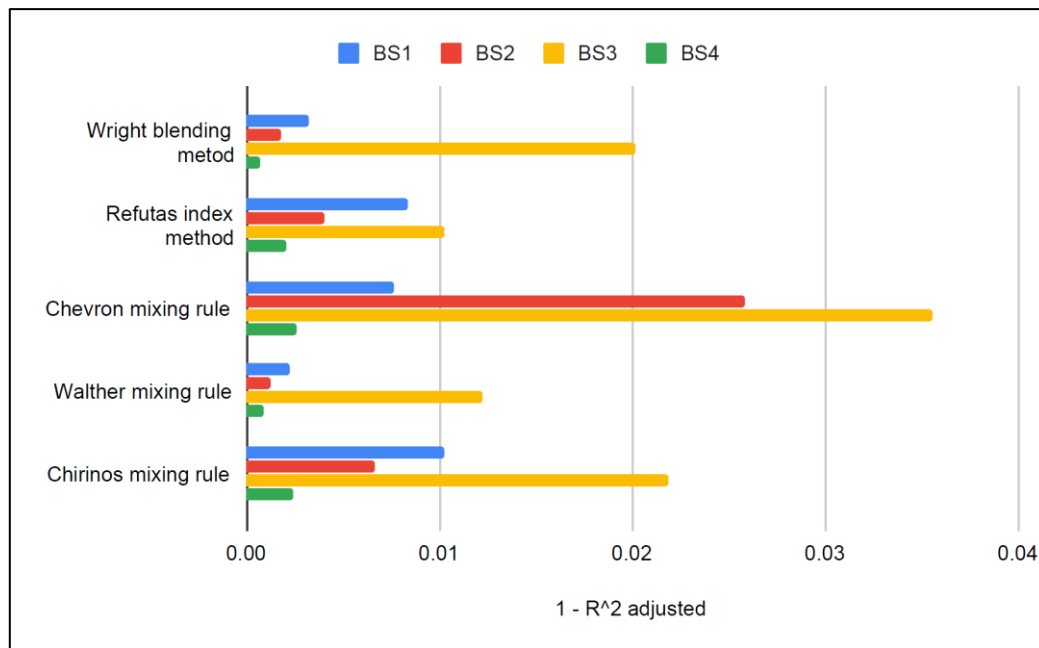


Figure 22: 1 - Adjusted R² for all mixing rules excluding the Kendall and Monroe results.

A considerably clearer overview of the results may be depicted when the Kendall and Monroe mixing rule is removed from **Figure 21**. The results displayed in **Figure 22** indicate that all of the remaining mixing rules are extremely accurate. The Chevron mixing rule and the Chirinos mixing rule, however, can be ruled out when compared to their respective analogues. The accuracy of the Wright blending method is unexpectedly high when considering the amount of inputs required for each of the mixing rules (see **Table 9**). The *C* parameter of the Walther mixing rule should be optimized for each individual situation in the same manner as the *C* parameter in the Walther correlation (see **Section 4.2.5**). The *C* parameter was set to a constant value of 0.7 in the initial tests (for which the results are presented in **Figure 22**). The effect of altering the *C* parameter was investigated in detail due to the promising results already obtained with the static *C* parameter. The *C* parameter of the Walther mixing rule was regressed using the Solver function in ©Microsoft Excel. The 1 – adjusted R² results for the regressed Walther correlation are presented in **Figure 23** (other results are unaltered and presented for comparative purposes).

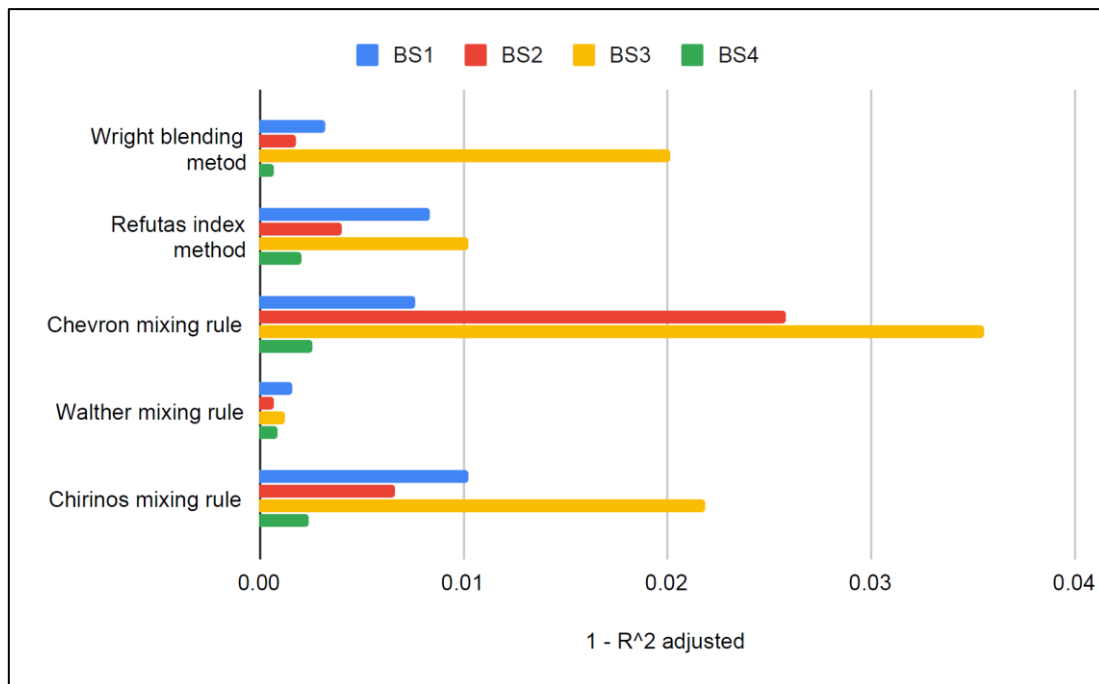


Figure 23: 1 - Adjusted R² for all mixing rules, Walther mixing rule regressed.

An example of the improved Walther mixing rule accuracy when going from the static C parameter to the regressed C parameter is presented for BS3 in **Figure 24** and **Figure 25**, respectively.

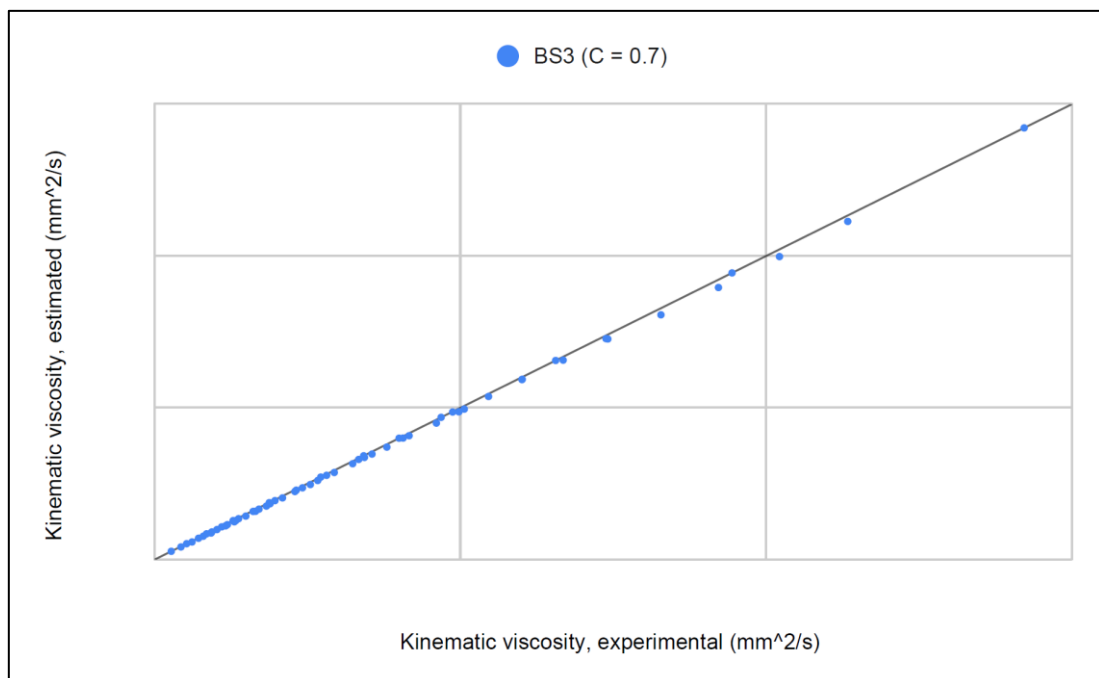


Figure 24: Parity plot of BS3 results for Walther mixing rule with C = 0.7.

The Walther mixing rule produces excellent results when a static value of 0.7 is used for the C parameter as can be seen from the parity plot above. The influence on the relatively high $1 - \text{adjusted } R^2$ for the BS3 sample set is caused by the inaccuracy of predicting the colder results (right half of **Figure 24**). This can be corrected by regression, however, at a cost in the accuracy of the warm results (left half of **Figure 25**).

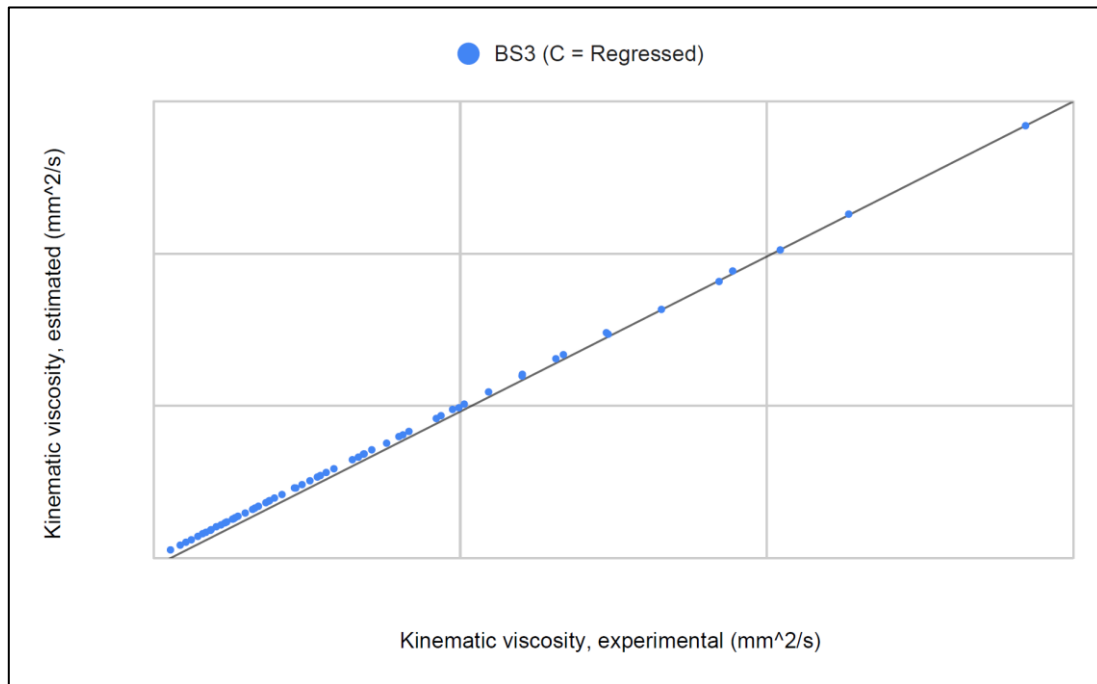


Figure 25: Parity plot of Walther mixing rule results using regressed parameters.

The parameter of the Walther mixing rule has been regressed in the results displayed in **Figure 25**. The colder results (right half of parity plot) have improved by the regression. This has however come at the expense of the accuracy of the warmer results (left half of plot) as they became slightly overestimated. Regression of the parameter in the Walther mixing rule should therefore be considered carefully and for each situation separately.

The accuracy of the Walther mixing rule is, nevertheless, excellent and it was therefore concluded that it is the best mixing rule, when the viscosity for both mixture components are known at the desired temperature (i.e. the temperature of interest of the resulting mixture). The Wright blending method produced impressive results with 75 % less input data than the rest of the mixing rules and should therefore be considered in cases where the viscosity of both components is not known at the temperature of interest (the Wright blending method is capable of predicting entire mixture datasets with only four inputs, 16 inputs are required for all other cases presented in this section).

7 CONCLUSION

A total of eight empirical correlations and six mixing rules were evaluated in this thesis. Four of the empirical correlations and all the mixing rules were investigated in detail using experimental data.

Effective methods for predicting the viscosity of a wide assortment of liquid hydrocarbons, using multiple types of input data, were identified. The Walther correlation proved to be an extremely effective method for predicting viscosity when two viscosity data points are known for a sample. It was also found that the input viscosities used in the Walther correlation for calculating the viscosity of a sample, should be determined at as distant temperatures as possible to improve the overall accuracy of the results. Further investigations should, however, be conducted to validate this claim.

The Aboul-Seoud and Moharam correlation proved to be effective in predicting the viscosity of liquid hydrocarbon mixtures using only one viscosity data point of a sample. The effect of varying the temperature at which this measurement is taken was not investigated. It can however be speculated that a colder temperature would be more beneficial regarding prediction accuracy for the temperature range studied in this thesis. The correlations requiring distillation data as input were initially found to be extremely inaccurate for the investigated samples. Situation specific regression of the correlation parameters was found to result in substantial improvements for all correlations, besides the Walther correlation. The Kotzakoulakis versions of the Mehrotra and Moharam correlations, which were initially found to be inaccurate for the samples tested in this thesis, were later found to be as accurate as the Walther correlation when the parameters were regressed.

The restriction of viscosity prediction was found to be the availability of input data and not the accuracy of the correlation as previously anticipated. The four correlations studied were found to provide incredibly accurate results. It can be concluded that the viscosity of hydrocarbon liquids of the middle to heavy distillate range was reliably explained based on a few selected experimental points. A list of required inputs, with increasing accuracy level, is provided below:

-
- 50 % volume boiling point and density at 15 °C
 - 50 % volume boiling point
 - Viscosity at two separate temperatures (preferably as far apart as possible)
 - Viscosity at one temperature

Further work on empirical correlations should concentrate on the development of the Kotzakoulakis version of the Moharam correlation. The viscosity data or the 50 % volume distillation point of two samples may be the same and would therefore result in the same prediction results. Including the specific gravity into the calculations may be beneficial for the prediction accuracy in situations of the aforementioned type (all other correlations utilize only one type of physicochemical data as input).

It was determined based on the investigations performed in this thesis that the most promising mixing rule for middle to heavy distillates is the Walther mixing rule. It is highly accurate in its native form and does benefit substantially from regression when it comes to complex blends. The Walther mixing rule requires substantial amounts of input data if the viscosity of a blend is to be predicted at multiple temperatures (due to the constant temperature nature). This is the situation for all mixing rules studied in this thesis, except for the Wright blending method. The Wright blending method is close to being as accurate as the Walther mixing rule without regression and can therefore be of great use when limited viscosity data of the blending components is known. Relatively high inaccuracy may, however, be expected when the viscosity of complex mixtures is estimated using the Wright blending method. The method should therefore be used with caution in these cases. Further work regarding the mixing rules should therefore be aimed toward the optimization of the Wright blending method by regression.

The general aim of the thesis was, in other words, achieved. Multiple precise methods for viscosity prediction of neat components as well as mixtures thereof were identified. A few of the approaches, however, require additional investigations to be optimized.

8 SUMMARY IN SWEDISH – SVENSK SAMMANFATTNING

8.1 Utvärdering av kalkylmetoder avsedda för estimering av kolvätevätskors viskositet

Traditionella oljeraffinaderier är massiva anläggningar där råolja separeras och omformas till diverse produkter. Flera processteg krävs för att förädla de olika fraktionerna till användbara produkter och egenskaperna hos slutprodukterna kan således variera kraftigt. Råvaruutbudet har dessutom utvidgats betydligt under de senaste årtionden tack vare den växande klimatmedvetenheten. De flesta produkterna som skapas i ett raffinaderi är därmed specifikationsprodukter, dvs. diverse standardiseringsorgan ställer krav på olika nyckelegenskaper hos produkterna.

Viskositet är ett mått på den interna friktionen av en fluid (dvs. vätska, gas eller ånga) och beskriver "tjockheten" av ifrågavarande fluid, till exempel är vatten "tunnare" än honung som är betydligt "tjockare". Viskositeten för vatten är därmed lägre än viskositeten för honung. Viskositeten kan uttryckas endera som dynamisk (absolut) viskositet eller kinematisk viskositet. Den kinematiska viskositeten används i de flesta metoderna som diskuteras i denna avhandling. Viskositet innebär därmed kinematisk viskositet i resten av denna svenska sammanfattning ifall inget annat meddelas.

Viskositet är en av de viktigaste egenskaperna hos produkter som består av kolväten i vätskefas. En för hög viskositet hos till exempel bränslen kan förorsaka problem med bränsletillförseln samt höja utsläppen eftersom droppstorleken vid insprutning i förbränningskammaren ökar (sämre förångning leder till ofullständig förbränning). En för låg bränsleviskositet kan däremot orsaka indirekta problem via den resulterande låga smörjförmågan hos bränslet. Resultatet är oftast total funktionsoduglighet av bränsletillförselsystemets väsentliga delar. Viskositet är även en av de viktigaste egenskaperna som ska tas i beaktade då kolvätevätskor transporteras i till exempel rörledningar. En pålitlig metod för att generellt kunna approximera viskositeten för olika kolvätevätskor skulle därför vara behövd. Syftet med denna avhandling var att utvärdera lämpligheten av välkända empiriska korrelationer för estimeringen av diverse kolvätevätskors viskositet. Även så kallade blandningsregler (mixing rules) undersöktes. Dessa används för att estimerar viskositeten hos en blandning som har skapats eller skall skapas genom att blanda en eller flera kolvätevätskor av känd konsistens.

8.1.1 *Estimering av komplexa kolväteblandningars viskositet*

Viskositeten hos en fluid uppstår i teorin som en följd av omplaceringen av rörelsemängd mellan molekylerna som fluiden består av (intern friktion). Omplaceringen sker i gaser och ångor genom kollisioner av glest stationerade molekyler. Omplaceringsmekanismerna hos vätskor är däremot mycket mera komplicerade eftersom molekylerna är mycket närmare varandra. Denna komplexitet härstammar från att krafterna som är involverade i mekanismerna är svårare att beskriva. Som följd av detta försvåras även estimeringen av vätskornas viskositet med hjälp av teoretiska mekanistiska modeller (som försöker förklara de komplicerade mekanismerna matematiskt). De flesta mekanistiska modellerna tar i beaktande både temperatur och tryck vid estimeringen av viskositet. Dagens mekanistiska modeller lyckas estimerar viskositeten för diverse fluider vid både höga temperaturer och höga tryck med relativt låga avvikelser. De mekanistiska modellerna innehåller dock oftast orimligt många parametrar som måste härledas genom regression. Regressionen av en stor mängd parametrar inför onödig komplexitet i beräkningarna samt ökar risken för förhöjda avvikelser i estimeringen. System som är under höga tryck eller temperaturer är dock inte av intresse i detta arbete. De flesta processerna inom kemiindustrin sker vid tryck som kan anses vara låga eller medelhöga. Tryckets inverkan på systemet kan därmed försummas i beräkningarna. Betydligt enklare (fast ändå svåra) empiriska korrelationer, som beskriver förhållandet mellan viskositet och andra fysikalisk-kemiska egenskaper hos kolvätevätskor, kan användas för att estimerar vätskornas viskositet i förhållande till temperatur.

De flesta empiriska korrelationerna som beskrivs i litteraturen är baserade på ekvationer utvecklade av Vogel, Walther eller Andrade. I litteraturen kan en tydlig trend gentemot korrelationer som baserar sig på Walther-ekvationen urskiljas. Den genomsnittliga avvikelsen för ekvationer av denna sort är nämligen betydligt lägre än tillvägagångssätten som baserar sig på tillämpningar av de andra ekvationstyperna. De mest lovande ekvationerna av denna typ, utvalda på basen av rekommendationer och i litteraturen uttryckt prestanda, beskrivs i detta arbete. Vissa av metoderna nämns som en följd av att de har en stark anknytning till standardiserade procedurer i oljeindustrin.

Walther-korrelationen baserar sig på den generella ekvationen (3). De kännetecknande dragen för Walther-korrelationen är dubbellogaritmen i vänstra ledet av ekvationen samt den enkla logaritmen i högra ledet.

$$\log \log(v + 0,7) = b_1 + b_2 \cdot \log T \quad (3)$$

där v är den kinematiska viskositeten (cSt eller mm²/s), T är temperaturen (°K) och b_1 samt b_2 är konstanter (bestäms skilt för varje prov).

Genom att skriva om ekvation (3) och utnyttja experimentellt fastställda värden för viskositet vid två skilda temperaturer kan man bestämma konstanterna b_1 och b_2 för ett specifikt prov enligt följande:

$$b_1 = \log \log(v_1 + 0,7) + \frac{\log \log(v_2 + 0,7) - \log \log(v_1 + 0,7)}{\log T_1 - \log T_2} \cdot \log T_1 \quad (5)$$

$$b_2 = \frac{\log \log(v_2 + 0,7) - \log \log(v_1 + 0,7)}{\log T_1 - \log T_2} \quad (6)$$

$$v_3 = 10^{10^{b_1 - b_2 \cdot \log T_3}} - 0,7 \quad (7)$$

Den ursprungliga Walther-korrelationen kan således användas för att estimeras viskositeten för ett prov vid godtycklig temperatur, då provets viskositet vid två temperaturer är känd.

Flera olika versioner av ekvationen bakom Walther-korrelationen existerar. Versionerna av ekvationen kan anses som lösningar för olika situationer där endast begränsad viskositetsinformation eller ingen viskositetsdata över huvud taget finns tillgänglig. Ekvationerna har utvecklats av diverse forskargrupper under det senaste århundradet. En grov lista på korrelationer (ekvationer), behövliga indata och typer av utdata som ges av ekvationerna framställs i **Tabell 1**.

Tabell 1: Empiriska korrelationer av intresse för detta arbete samt indata och utdata för respektive korrelation.

Korrelation	Indata	Utdata
Walther	Viskositet vid två temperaturer	Viskositeten vid godtyckligt vald temperatur
Aboul-Seoud och Moharam	Viskositet vid en temperatur	Viskositeten vid godtyckligt vald temperatur
Mehrotra	Vägt medelvärde av kokpunkter	Viskositeten vid godtyckligt vald temperatur
Moharam	Vägt medelvärde av kokpunkter och densitetstalet	Viskositeten vid godtyckligt vald temperatur
Puttagunta	Viskositeten av provet, bestämd vid exakt 100 °F (37,78 °C)	Viskositeten vid godtyckligt vald temperatur

Syftet för alla korrelationer är den samma, det vill säga utöka informationen gällande temperaturens inverkan på en vätskas viskositet (se kolumnen för utdata i **Tabell 1**). Kolvätevätskor, som till exempel bränslen, är blandningar av upp till tusentals olika föreningar. Varje förening har en unik kokpunkt vilket leder till att kokpunkten för

kolvätevätskor sprids över en relativt bred temperaturskala. Kokpunkten för kolvätevätskor rapporteras således som en skala på basen av mängden prov som har kokat över vid en viss temperatur (destillationsdata). Det vägda medelvärdet för denna skala (T_b) beräknas enligt ekvation (17).

$$\text{vägt medelvärde } T_b = \sum_{i=1}^n \Delta x_i * T_{bi} \quad (17)$$

Det vägda medelvärdet för T_b används som indata i Mehrotra-korrelationen och Moharam-korrelationen. Densitetstalet som används som ytterligare indata i Moharam-korrelationen kallas även relativ densitet och är ett mått på densiteten av en substans, jämfört med densiteten av rent vatten.

Korrelationerna som vi har diskuterat hittills kan endast användas för att estimerar viskositeten för en kolvätevätska då tillräckliga data för att tillfredsställa någon av korrelationerna finns tillgänglig. Då viskositeten för blandningar av en eller flera kolvätevätskor med känd viskositet (viskositetsinformation erhållen genom experimentellt arbete eller estimering med empiriska korrelationer) vill estimeras, måste så kallade blandningsregler (mixing rules) användas. Blandningsregler är alltså ekvationer som ger viskositeten för en blandning av kolvätevätskor på basen av utgångsmaterialens viskositetsinformation och diverse parametrar som endera beräknas med hjälp av experimentellt data eller bestäms genom regression. Centeno *et al.* undersökte prestandan på 26 olika blandningsregler genom att estimerar viskositeten för blandningar av nafta, diesel och vakuumgasolja. Endast fyra av dessa ansågs vara funktionsdugliga på basen av noggrannheten av estimeringarna. Blandningsreglerna som undersöktes i detta arbete samt indata och utdata för respektive regel framgår i **Tabell 2**. En del av reglerna beskrivs endast för att de har en stark anknytning till standardiserade procedurer i oljeindustrin och är därför väsentliga, men de ger nödvändigtvis inte de bästa approximationerna.

Tabell 2: Blandningsregler av intresse för detta arbete samt indata och utdata för respektive regel.

Blandningsregel	Indata	Utdata
Wright-blandningsregeln	Viskositet vid två temperaturer för alla komponenter	Viskositet enligt volymprocent vid godtyckligt vald temperatur
Kendall och Monroe-korrelationen	Viskositeten för alla komponenter vid samma temperatur	Viskositet enligt volymprocent vid samma temperatur som indata
Refutas-index metoden	Viskositeten för alla komponenter vid samma temperatur	Viskositet enligt volymprocent vid samma temperatur som indata
Chevron-blandningsregeln	Viskositeten för alla komponenter vid samma temperatur	Viskositet enligt volymprocent vid samma temperatur som indata
Walther-blandningsregeln	Viskositet vid en temperatur för alla komponenter	Viskositet enligt volymprocent vid samma temperatur som indata
Chirinos-blandningsregeln	Viskositet vid en temperatur för alla komponenter	Viskositet enligt volymprocent vid samma temperatur som indata

8.1.2 Experimentell del

Fem olika binära blandningar (BB1, BB2, BB3 osv.) av olika kolvätevätskor skapades för att undersöka prestandan av de olika empiriska korrelationerna och blandningsreglerna. Komponenterna som användes i blandningarna bestod av försäljbara och experimentella bränslen samt modellföreningar av medel- till tungdestillatsklassen. Blandningar med volymförhållandet 0 - 100 % undersöktes (inklusive utgångsmaterial). Viskositeten bestämdes mellan +40 och -40 °C med 10 °C intervall vid så många punkter som möjligt (beroende på frys- och flampunkt). I vissa fall undersöktes även tertiära och kvaternära blandningar. Dessa resultat inkluderades bland de fem olika binära blandningarnas resultat vid tillhörande platser. De empiriska korrelationerna som använder kokpunktsdata som indata hittades mitt i arbetet och utvärderades således med en skild datamängd som bestod av ett brett sortiment singulära kolvätevätskor (singulär datamängd 1, SD1).

8.1.3 Resultat

Storheten R^2 utsäger hur bra en modell beskriver experimentellt data. Modellens estimeringsfel jämförs med estimeringsfelet då ingen modell över huvud taget används (felet då beräknat medeltal och experimentella data jämförs). Justerat R^2 är en storhet som tar i beaktande mängden parametrar som modellen innehåller. En modell som beskriver experimentella data exakt uppvisar ett justerat R^2 på 1,00. Resultaten i denna svenska sammanfattning presenteras för det mesta i formen av $1 - \text{justerat } R^2$ eftersom metoderna som undersöktes uppvisar mycket höga värden för justerat R^2 . Logiken bakom $1 - \text{justerat } R^2$

är motsatt till vanliga justerade R^2 . Detta betyder att metoden är exaktare desto närmare 0 resultatet är. En mycket inexact metod uppvisar höga eller till och med negativa resultat för $1 - \text{justerat } R^2$.

Den stora mängden data som krävdes för att framställa dessa resultat har samlats i en separat rapport.⁶⁴

BB1-BB5 användes för att utvärdera två empiriska korrelationers prestanda (Walther-korrelationen samt Aboul-Seoud och Moharam-korrelationen). Walther-korrelationen visade sig vara mycket noggrann och uppvisade ett mycket lågt $1 - \text{justerat } R^2$ (resultatet för till exempel BB1 $\approx 0,00007$). Två olika tillvägagångssätt för att bestämma konstanterna b_1 och b_2 undersöktes (ekvationerna (5) och (6) samt metoden som framförs i standarden). En obetydligt liten positiv inverkan på $1 - \text{justerat } R^2$ observerades (förbättring på $1 \cdot 10^{-9}$ för till exempel BB1), men metoden ur standarden användes för säkerhets skull ändå. Det framgick också från resultaten att det lönar sig att använda viskositetsdata från kallare temperaturer som indata i Walther-korrelationen i vårt fall (**se Tabell 3**) och att noggrannheten i allmänhet växer då indata väljs för två temperaturer som är så långt ifrån varandra som möjligt.

Walther-korrelationen visade sig vara noggrannare än Aboul-Seoud och Moharam (A-S & M)-korrelationen. Detta var förväntat eftersom A-S & M-korrelationen inte avviker betydligt från den traditionella Walther-korrelationen och mängden indata i relation till Walther-korrelationen är hälften mindre. Resultaten är mycket imponerande med tanke på minskningen i mängden indata. Resultaten kunde förbättras betydligt genom att bestämma BB specifika parametrar för A-S & M-korrelationen genom regression (utfördes med hjälp av Solver funktionen i ©Microsoft Excel). Noggrannheten för A-S & M-korrelationen steg således till en lika hög nivå som Walther korrelationen. Det justerade R^2 för BB1 med ursprungliga parametrar samt med regressionsparametrar framförs som ett exempel i **Tabell 3**.

Tabell 3: BB1 resultat för Walther korrelationen och Aboul-Seoud och Moharam korrelationen.

Korrelation	Justerat R^2	Justerat R^2
	Ursprungliga parametrar	Regressionsparametrar
Walther	0,998461*	0,999926**
Aboul-Seoud och Moharam	0,962174	0,999887
*Varmt indata (+20 °C och 0 °C, ingen regression); **Kallt indata (-20 °C och -40 °C, ingen regression)		

SD1 användes för att utvärdera prestandan av korrelationerna som kräver kokpunktsdata som indata. Mehrotra-korrelationen använder endast det vägda medelvärdet av kokpunkterna (T_b) för att estimerar viskositeten av ett prov. Två olika versioner av T_b kan användas i beräkningarna, T_b beräknad på basen av kokpunkter registrerade då en bestämd massa har destillerats (WABP, Weight Average Boiling Point) och T_b beräknad på basen av kokpunkter som registrerats då en bestämd volym har destillerats (VABP, Volume Average Boiling Point). Endast kokpunkten då 50 volymprocent av en blandning har kokat över mättes för proven i SD1 eftersom endast Kotzakoulakis version av Mehrotra-korrelationen var av intresse för denna avhandling. Kotzakoulakis *et al.* uttrycker explicit att kokpunkten vid 50 massaprocent skall användas men 50 volymprocent användes ändå (logiskt sett mera noggrann då mätmetoder jämförs). Otroligt höga värden för justerade R^2 registrerades då de ursprungliga parametrarna användes (se **Tabell 4**), vilket tyder på att den ursprungliga versionen faktiskt är utvecklad för tyngre kolvätevätskor (till exempel råolja). Regression för att hitta de optimala parametrarna var det logiska nästa steget (genomfördes också i detta fall med hjälp av Solver funktionen i ©Microsoft Excel). En imponerande ökning i noggrannheten kunde urskiljas då de nya parametrarna användes. Resultaten framförs i **Tabell 4**.

Moharam korrelationen utnyttjar både T_b och densitetstalet för att estimerar viskositeten av provet. Densitetstalet är temperaturberoende och skall därmed bestämmas skilt för varje temperatur. Tillgång till detta data fanns inte vilket resulterade i att endast en modifierad version av Moharam korrelationen (Kotzakoulakis version, som använder kokpunkten vid 50 volymprocent och densitetstalet vid 15 °C, som indata) utvärderades. Denna korrelation visade sig också vara mycket inexact då de ursprungliga parametrarna användes för att estimerar viskositeten hos våra prov. Resultaten förbättrades betydligt då parametrarna optimerades genom regression. Resultaten framförs i **Tabell 4**.

Tabell 4: Resultat för Kotzakoulakis version av både Mehrotra och Moharam korrelationen.

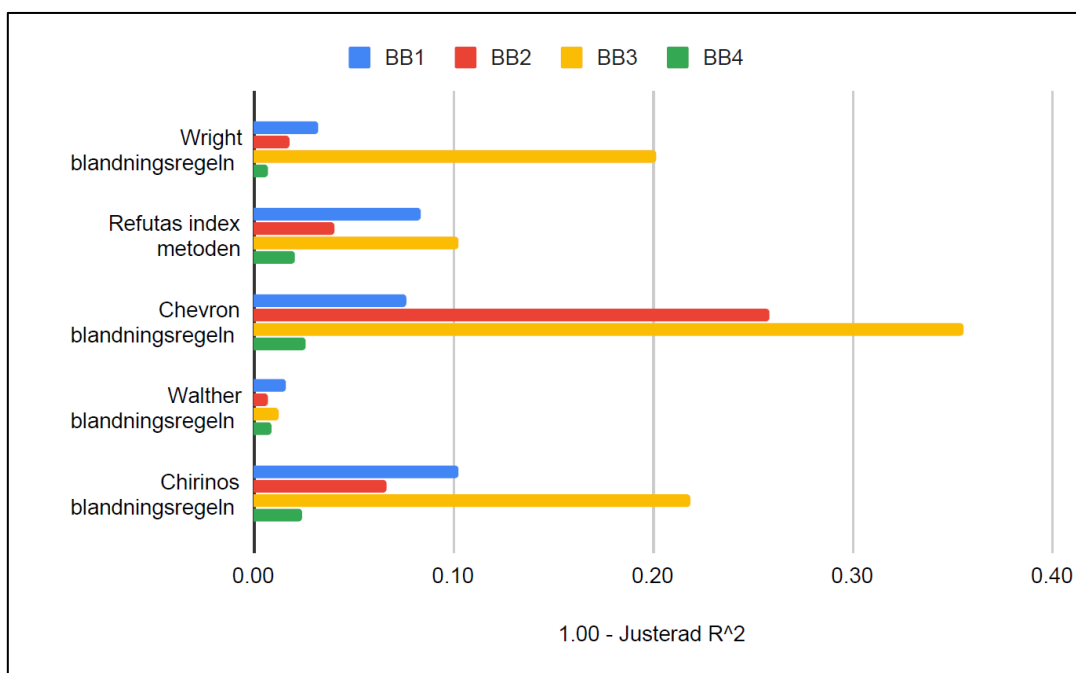
Korrelation	Justerat R^2	Justerat R^2
	Ursprungliga parametrar	Regressionsparametrar
Kotzakoulakis version av Mehrotra	-0,132617	0,998193
Kotzakoulakis version av Moharam	-5,705039	0.997512

Ur Tabell 4 går det tydligt att avläsa att de ursprungliga versionerna av Kotzakoulakis version av Moharam- och Mehrotra-korrelationerna inte har utvecklats för kolvätevätskor av den

typen som undersöktes i detta arbete. Imponerande resultat för båda korrelationerna kunde dock erhållas då parametrarna optimerades genom regression. Justerade R^2 för Kotzakoulakis version av Mehrotra korrelationen är något högre än justerat R^2 för Kotzakoulakis version av Moharam korrelationen. Detta tyder på att införingen av densitetstalet vid 15 °C i beräkningarna har en negativ inverkan på resultatet. Användningen av två fysikalisk-kemiska storheter i beräkningarna kan dock anses vara nyttigt för noggrannhetens skull i allmänhet (50 vol-% kokpunkten för flera kolvätevätskor kan till exempel vara exakt lika).

Puttagunta korrelationen undersöktes inte eftersom korrelationen visade sig vara Walther korrelationen skriven i en sådan form att indata kunde accepteras endast vid exakt 100 °F.

Blandningsreglerna undersöktes genom att jämföra $1 - \text{justerat } R^2$ som resulterade då blandningsreglerna estimerade alla datapunkter i BB1-BB5 (exklusive indata). Resultaten för detta framställs i **Figur 1**.



Figur 1: 1 - justerat R^2 för de bästa blandningsreglerna.

Av blandningsreglerna visade sig Walther-blandningsregeln vara exaktast. I **Figur 1** har parametrarna i Walther-blandningsregeln optimerats genom regression. Walther-blandningsregeln är exaktast fastän den inte skulle optimeras genom regression.

Wright-blandningsregeln kan anses vara så gott som lika noggrann med tanke på hur mycket mindre indata som krävs (se **Tabell 2**). Wright-blandningsregeln kan vara mycket nyttig i sådana fall där flampunkt eller fryspunkt inhiberar viskositetsbestämningen för en eller båda

av komponenterna vid den önskade temperaturen. Wright-blandningsregeln skall dock användas med försiktighet i sin nutida form, resultateten kan vara mycket inexacta ifall blandningen är komplex (se det höga resultatet för BB3 i **Figur 1**).

8.1.4 Konklusioner

Då viskositetsdata vid två temperaturer är tillgängligt för kolvätevätskan av intresse skall Walther-korrelationen i sin ursprungliga form definitivt användas. Ifall viskositeten vid endast en temperatur är tillgänglig skall Aboul-Seoud och Moharam-korrelationen användas. Kotzakoulakis version av Mehrotra- och Moharam-korrelationen är klart och tydligt i sin ursprungliga form optimerade för tyngre kolvätevätskor än de som undersöktes i denna avhandling. Dessa korrelationer skall således inte användas för estimeringen av medel- eller tungdestillat i sin ursprungliga form. Regressionen av parametrarna i Kotzakoulakis version av Mehrotra- och Moharam-korrelationen kan förbättra resultatet betydligt. Båda versionerna är därmed godtagbara för viskositetsestimering ifall det behövliga data finns tillgängligt. Av dessa undersökningar framgår det trots allt att Moharam-korrelationen högst antagligen är säkrare än Mehrotra-korrelationen eftersom densitetstalet tas i beaktande. Puttagunta-korrelationen är en förenklad version av Walther korrelationen och skall därmed undvikas. De bästa och mest universella blandningsreglerna presenterade i litteraturen är Walther- och Wright-blandningsreglerna. Walther-blandningsregeln borde dock prioriteras ifall tillräckliga data finns tillgängligt. Framtida insatser skall enligt dessa resultat fokusera på förståelsen och utvecklingen av främst Moharam-korrelationen. Vidare forskning gällande optimeringen av Wright-blandningsregeln genom regression kan även vara nyttigt för situationer där indata för Walther-blandningsregeln inte finns tillgängligt. De allmänna målsättningarna för denna pro gradu-avhandling uppfylldes.

9 REFERENCES

- (1) Murzin, D. Y. Oil Refining. In *Chemical Reaction Technology*; Walter de Gruyter GmbH: Turku, Finland, 2015; pp 116–122.
- (2) Saldana, D. A.; Starck, L.; Mougin, P.; Rousseau, B.; Ferrando, N.; Creton, B. Prediction of Density and Viscosity of Biofuel Compounds Using Machine Learning Methods. *Energy and Fuels* **2012**, *26*, 2416–2426.
- (3) Pires, A. P. P.; Han, Y.; Kramlich, J.; Garcia-Perez, M. Chemical Composition and Fuel Properties of Alternative Jet Fuels. *BioResources* **2018**, *13*, 2632–2657.
- (4) Aquino, M.; Ciotta, F.; Creton, B.; Féjean, C.; Pina, A.; Dartiguelongue, C.; Trusler, J. P. M.; Vignais, R.; Lugo, R.; Ungerer, P.; et al. Composition Analysis and Viscosity Prediction of Complex Fuel Mixtures Using a Molecular-Based Approach. *Energy and Fuels* **2012**, *26*, 2220–2230.
- (5) Viswanath, D. S.; Ghosh, T. K.; Prasad, D. H. L.; Dutt, N. V. K.; Rani, K. Y. *Viscosity of Liquids*; Springer Netherlands: Dordrecht, The Netherlands, 2007; pp 1–432.
- (6) Brush, S. G. Theories of Liquid Viscosity. *Chem. Rev.* **1962**, *62*, 513–548.
- (7) Centeno, G.; Sánchez-Reyna, G.; Ancheyta, J.; Muñoz, J. A. D.; Cardona, N. Testing Various Mixing Rules for Calculation of Viscosity of Petroleum Blends. *Fuel* **2011**, *90*, 3561–3570.
- (8) Sánchez-Rubio, M.; Chinas-Castillo, F.; Ruiz-Aquino, F.; Lara-Romero, J. A New Focus on the Walther Equation for Lubricant Viscosity Determination. *Lubr. Sci.* **2006**, *18*, 95–107.
- (9) Yang, J.; Xin, Z.; He, Q. (Sophia); Corscadden, K.; Niu, H. An Overview on Performance Characteristics of Bio-Jet Fuels. *Fuel* **2019**, *237*, 916–936.
- (10) Cai, G.; Liu, Z.; Zhang, L.; Zhao, S.; Xu, C. Quantitative Structure-Property Relationship Model for Hydrocarbon Liquid Viscosity Prediction. *Energy and Fuels* **2018**, *32*, 3290–3298.
- (11) *ASTM D445-19a, Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)*; ASTM International: West

Conshohocken, PA, 2019.

- (12) *ASTM D7042-19e1, Standard Test Method for Dynamic Viscosity and Density of Liquids by Stabinger Viscometer (and the Calculation of Kinematic Viscosity)*; ASTM International: West Conshohocken, PA, 2017.
- (13) Striebich, R. C.; Shafer, L. M.; Adams, R. K.; West, Z. J.; DeWitt, M. J.; Zabarnick, S. Hydrocarbon Group-Type Analysis of Petroleum-Derived and Synthetic Fuels Using Two-Dimensional Gas Chromatography. *Energy and Fuels* **2014**, 28, 5696–5706.
- (14) *ASTM D1655-19a, Standard Specification for Aviation Turbine Fuels*; ASTM International: West Conshohocken, PA, 2015.
- (15) *ASTM D7566-19a, Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons*; ASTM International: West Conshohocken, PA, 2019.
- (16) *Defence Standard 91-91, Turbine Fuel , Kerosine Type , Jet A-1 NATO Code : F-35*; Ministry of Defence, 2011.
- (17) *Defence Standard 91-87, Turbine Fuel , Aviation Kerosine Type , Containing Fuel System Icing Inhibitor NATO Code : F-34*; Ministry of Defence, 2002.
- (18) *MIL-DTL-83133E Turbine Fuel, Aviation, Kerosene Type, JP-8 (Nato F-34), Nato F-35, and JP-8 + 100 (Nato F-37)*; United States Air Force, 2008.
- (19) Warren, K. A. *World Jet Fuel Specifications*; ExxonMobil Aviation, 2008.
- (20) *EN 590, Automotive Fuels. Diesel. Requirements and Test Methods*; European Committee for Standardization, CEN: Brussels, Belgium, 2013.
- (21) *EN 15940, Automotive Fuels. Paraffinic Diesel Fuel from Synthesis or Hydrotreatment. Requirements and Test Methods*; European Committee for Standardization, CEN: Brussels, Belgium, 2016.
- (22) *ASTM D975-20a, Standard Specification for Diesel Fuel*; ASTM International: West Conshohocken, PA, 2020.
- (23) *CEN/TR 15738:2008, Petroleum Products - Heating Fuels - Need Feasibility and Required Deliverables for a Common European Specification*; European Committee for Standardization, CEN: Brussels, Belgium, 2008.

-
- (24) *ASTM D396-19a, Standard Specification for Fuel Oils*; ASTM International: West Conshohocken, PA, 2019.
- (25) *ISO 8217:2017, Petroleum Products - Fuels (Class F) - Specification of Marine Fuels*; International Organisation for Standardization, ISO: Vernier, Geneva, Switzerland, 2017.
- (26) *API 1509 - Annex E, API Base Oil Interchangeability Guidelines for Passenger Car Motor Oils and Diesel Engine Oils*; American Petroleum Institute: Washington, D.C., 2019.
- (27) *ASTM D2270-10(2016), Standard Practice for Calculating Viscosity Index from Kinematic Viscosity at 40 °C and 100 °C*; ASTM International: West Conshohocken, PA, 2016.
- (28) *ASTM D7945-16, Standard Test Method for Determination of Dynamic Viscosity and Derived Kinematic Viscosity of Liquids by Constant Pressure Viscometer*; ASTM International: West Conshohocken, PA, 2016.
- (29) *ASTM D5293-17a, Standard Test Method for Apparent Viscosity of Engine Oils and Base Stocks Between -10 °C and -35 °C Using Cold-Cranking Simulator*; ASTM International: West Conshohocken, PA, 2017.
- (30) Quiñones-Cisneros, S. E.; Zéberg-Mikkelsen, C. K.; Stenby, E. H. The Friction Theory (f-Theory) for Viscosity Modeling. *Fluid Phase Equilib.* **2000**, *169*, 249–276.
- (31) Quiñones-Cisneros, S. E.; Zéberg-Mikkelsen, C. K.; Stenby, E. H. One Parameter Friction Theory Models for Viscosity. *Fluid Phase Equilib.* **2001**, *178*, 1–16.
- (32) Quiñones-Cisneros, S. E.; Zéberg-Mikkelsen, C. K.; Stenby, E. H. The Friction Theory for Viscosity Modeling: Extension to Crude Oil Systems. *Chem. Eng. Sci.* **2001**, *56*, 7007–7015.
- (33) Quiñones-Cisneros, S. E.; Zéberg-Mikkelsen, C. K.; Baylaucq, A.; Boned, C. Viscosity Modeling and Prediction of Reservoir Fluids: From Natural Gas to Heavy Oils. *Int. J. Thermophys.* **2004**, *25*, 1353–1366.
- (34) Yarranton, H. W.; Satyro, M. A. Expanded Fluid-Based Viscosity Correlation for Hydrocarbons. *Ind. Eng. Chem. Res.* **2009**, *48*, 3640–3648.

-
- (35) Motahhari, H.; Satyro, M. A.; Yarranton, H. W. Predicting the Viscosity of Asymmetric Hydrocarbon Mixtures with the Expanded Fluid Viscosity Correlation. *Ind. Eng. Chem. Res.* **2011**, *50*, 12831–12843.
- (36) Ramos-Pallares, F.; Schoeggl, F. F.; Taylor, S. D.; Satyro, M. A.; Yarranton, H. W. Predicting the Viscosity of Hydrocarbon Mixtures and Diluted Heavy Oils Using the Expanded Fluid Model. *Energy and Fuels* **2016**, *30*, 3575–3595.
- (37) Kotzakoulakis, K.; George, S. C. A Simple and Flexible Correlation for Predicting the Viscosity of Crude Oils. *J. Pet. Sci. Eng.* **2017**, *158*, 416–423.
- (38) Vogel, H. The Law of the Relation between the Viscosity of Liquids and the Temperature. *Phys. Zeitschrift* **1921**, *22*, 645–646.
- (39) Walther, C. Über Die Auswertungen von Viskositätsangaben. *Erdöl und Teer* **1931**, *7*, 382–384.
- (40) Andrade, E. N. da C. XLI. A Theory of the Viscosity of Liquids.—Part I. *London, Edinburgh, Dublin Philos. Mag. J. Sci.* **1934**, *17* (112), 497–511.
- (41) Aboul-Seoud, A. L.; Moharam, H. M. A Generalized Viscosity Correlation for Undefined Petroleum Fractions. *Chem. Eng. J.* **1999**, *72*, 253–256.
- (42) Mehrotra, A. K.; Monnery, W. D.; Svrcek, W. Y. A Review of Practical Calculation Methods for the Viscosity of Liquid Hydrocarbons and Their Mixtures. *Fluid Phase Equilib.* **1996**, *117*, 344–355.
- (43) Moharam, H. M.; Al-Mehaideb, R. A.; Fahim, M. A. New Correlation for Predicting the Viscosity of Heavy Petroleum Fractions. *Fuel* **1995**, *74*, 1776–1779.
- (44) Puttagunta, V. R.; Miadonye, A.; Singh, B. Viscosity-Temperature Correlation for Prediction of Kinematic Viscosity of Conventional Petroleum Liquid. *Chem. Eng. Res. Des.* **1992**, *70*, 627–631.
- (45) ASTM D341-17, *Standard Practice for Viscosity-Temperature Charts for Liquid Petroleum Products*; ASTM International: West Conshohocken, PA, 2017.
- (46) MacCoull, N. *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*; Washburn, E. W., Ed.; McGraw-Hill Book Co.: New York, 1927.

-
- (47) Mehrotra, A. K. A Simple Equation for Predicting the Viscosity of Crude Oil Fractions. *Chem. Eng. Res. Des.* **1995**, *73*, 87–90.
- (48) Nakayama, Y.; Boucher, R. F. Characteristics of a Fluid. In *Introduction to Fluid Mechanics*; Butterworth-Heinemann: Oxford, 1999; p 8.
- (49) API Tech Data Book 10 <http://www.apidatabook.com/> (accessed May 19, 2020).
- (50) Correlation for the Liquid Viscosity of Petroleum Fractions at Low Pressure, Procedure 11A4.1. In *American Petroleum Institute (API) Technical Data Book*; American Petroleum Institute: New York, 1997.
- (51) Riazi, M. R. Distribution Model for Properties of Hydrocarbon-Plus Fractions. *Ind. Eng. Chem. Res* **1989**, *28*, 1731–1735.
- (52) Riazi, M. R. A Continuous Model for C 7+ Fraction Characterization of Petroleum Fluids. *Ind. Eng. Chem. Res* **1997**, *36*, 4299–4307.
- (53) Rahmes, M. H.; Nelson, W. L. Viscosity Blending Relationships of Heavy Petroleum Oils. *Anal. Chem.* **1948**, *20*, 912–915.
- (54) Kendall, J.; Monroe, K. P. Viscosity of Liquids. II. Viscosity-Composition Curves for Ideal Liquid Mixtures. *J. Am. Chem. Soc.* **1917**, *39*, 1787–1802.
- (55) Riazi, M. R. Characterization and Properties of Petroleum Fractions, ASTM Manual Series: MNL50; ASTM International: West Conshohocken, PA, 2005; pp 335–338.
- (56) *ASTM D7152-11(2016)E1, Standard Practice for Calculating Viscosity of a Blend of Petroleum Products*; ASTM International: West Conshohocken, PA, 2016.
- (57) Wagner, E. P.; Koehle, M. A.; Moyle, T. M.; Lambert, P. D. Predicting Temperature Dependent Viscosity for Unaltered Waste Soybean Oil Blended with Petroleum Fuels. *J. Am. Oil Chem. Soc.* **2010**, *87*, 453–459.
- (58) *ASTM D7152 - 11(2016)E1, Standard Practice for Calculating Viscosity of a Blend of Petroleum Products*; ASTM International: West Conshohocken, PA, 2016.
- (59) Liquid Viscosities of Defined Mixtures at Low Pressures, Procedure 11A3.1. In *American Petroleum Institute (API) Technical Data Book*; American Petroleum Institute: New York, 1997.

-
- (60) Miadonye, A.; Latour, N.; Puttagunta, V. R. A Correlation for Viscosity and Solvent Mass Fraction of Bitumen-Diluent Mixtures. *Pet. Sci. Technol.* **2000**, *18*, 1–14.
- (61) *ISO 12185:1996, Crude Petroleum and Petroleum Products - Determination of Density - Oscillating U-Tube Method*; International Organisation for Standardization, ISO: Vernier, Geneva, Switzerland, 1996.
- (62) *IP 529:2015, Determination of the Freezing Point of Aviation Fuels - Automatic Laser Method*; Energy Institute (formerly Institute of Petroleum - IP): London, United Kingdom, 2015.
- (63) *ASTM D86-19, Standard Test Method for Distillation of Petroleum Products and Liquid Fuels at Atmospheric Pressure*; ASTM International: West Conshohocken, PA, 2019.
- (64) Rautelin, W. M. W. (*CONFIDENTIAL*) *Compilation of the Experimental Results Attained for the Thesis: Evaluation of Calculative Tools Intended for the Prediction of Liquid Hydrocarbon Viscosity*; Helsinki, Finland, 2020.
- (65) Montgomery, D. C.; Runger, G. C. Simple Linear Regression and Correlation. In *Applied Statistics and Probability for Engineers*; Anderson, W., Welter, J., Pigliucci, N. M., Lesure, M., Aiello, G., Eds.; John Wiley & Sons, Inc.: New York, 2003; pp 397–398.
- (66) Average boiling point https://www.engineeringtoolbox.com/Average-boiling-point-VABP-MABP-WABP-CABP-MeABP-formula-d_1994.html (accessed Jun 17, 2020).