POLITECNICO DI TORINO

Collegio di Ingegneria Chimica e dei Materiali

Corso di Laurea Magistrale
in Ingegneria Chimica e dei Processi Sostenibili

Tesi di Laurea Magistrale

Modelling of the sediment content of heavy oil fractions

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A mamma e papà che mi accompagnano da una vita.
A nonno Ciccio e ai suoi stravaganti abbracci.
A nonna Ambrosina e alle corse intorno al tavolo.
A nonna Giovanna che c'è ogni giorno per una dolce parola.
Nulla sarebbe stato possibile senza voi. Grazie.

Summary

1. Introduzione

La richiesta mondiale di energia è in continuo aumento e la ragione va ricercata nello sviluppo economico e nell'aumento della popolazione, i quali causano il declino delle risorse petrolifere disponibili. Il mercato richiede tagli leggeri, come gasolio e diesel, e le raffinerie devono evitare, o limitare, la produzione di oli pesanti. Da analisi condotte, è emerso che la scoperta delle riserve petrolifere ha avuto un picco durante gli anni '60, che si è però arrestata in seguito. Per tale motivo risulta difficile, ai giorni nostri, rispondere alla richiesta energetica in quanto non ci sono scoperte di nuovi giacimenti di petrolio.

In tale contesto i processi di raffineria diventano molto importanti. Il taglio petrolifero pesante che un tempo non era utilizzato, diventa ora oggetto di studio per poter essere sfruttato. Il petrolio pesante possiede caratteristiche fisiche e chimiche diverse da quello leggero, questo a causa di resine e di asfalteni presenti, che rappresentano le molecole più polari all'interno del petrolio.

Poiché, la richiesta è di tagli leggeri, le raffinerie hanno bisogno di aggiornare e migliorare i processi degli oli pesanti. Uno dei processi più utili è quello di *miscelazione*: consiste nella creazione di una miscela tra un taglio pesante e uno leggero, per migliorare le proprietà del taglio pesante. all'interno del taglio pesante sono presenti delle particelle, chiamate asfalteni, le quali formano agglomerati e tendono a depositarsi, causando problemi nel trasporto o nella produzione. Il problema è che questo comportamento è favorito dal tipo di taglio leggero utilizzato, in quanto può destabilizzare la miscela e portare alla formazione dei sedimenti. Per i motivi appena citati è necessario diminuire la loro quantità e capire il loro comportamento tramite un modello matematico.

Nonostante il problema sia riconosciuto, il meccanismo che porta alla formazione dei sedimenti risulta difficile da spiegare. Il presente progetto di tesi è pertanto destinato alla ricerca di una legge universale, valida quindi per ogni miscela, che consenta di conoscere anticipatamente la formazione di sedimenti.

2. Stato dell'Arte

Il petrolio, o grezzo, è definito come l'olio che non ha subito alcun tipo di trattamento. Generalmente è riconosciuta la teoria secondo cui esso derivi da un processo di decomposizione di piante e di animali, durato milioni di anni. Il petrolio non è una miscela omogenea, consiste infatti in migliaia di idrocarburi diversi e piccole impurità. Il grezzo estratto da un giacimento non può essere utilizzato tale e quale, esso necessita di diversi processi di raffinazione. Tra i processi troviamo la *distillazione* ovvero la separazione dei componenti, basata sulla temperatura di ebollizione dei costituenti, oppure la *miscelazione* ossia la creazione di miscele tra un taglio leggero ed uno pesante, al fine di produrre prodotti con proprietà più specifiche.

In prima analisi è importante capire ciò che accade in una raffineria in cui avviene la distillazione. La raffineria ha il compito di trasformare il petrolio in un prodotto desiderabile. Per far ciò si opera con due colonne di distillazione: la prima a pressione atmosferica mentre la seconda operante in condizioni di vuoto. Il petrolio, dopo essere stato scaldato, entra nella prima colonna dotata di ribollitore e condensatore, ed esce sotto forma di benzina, cherosene, gasolio e residuo atmosferico: “tagli leggeri”. Il residuo atmosferico a sua volta entra nella seconda colonna, ed esce in seguito sotto forma di olio medio, lubrificante, olio pesante e residuo: “tagli pesanti”. All’inizio dell’era del petrolio era utilizzata una sola colonna e il residuo atmosferico non era sfruttato. Come è già stato riportato, le scoperte di nuove riserve petrolifere sono diminuite e si è presentata la necessità di sfruttare tutto il petrolio estratto, da qui la nascita della seconda colonna di distillazione.

Il residuo, prodotto della distillazione sottovuoto, è definito olio pesante. Esso contiene molecole con alto peso molecolare ed un elevato numero di eterocomposti (zolfo, azoto, ossigeno, metalli e aromatici). La struttura degli oli pesanti è difficile da capire a causa delle molecole presenti. Per tale ragione, numerose tecniche sono nate per capire la composizione del residuo, tra queste il frazionamento SARA, acronimo di Saturi, Aromatici, Resine (Malteni) e Asfalteni. Gli asfalteni sono definiti come composti insolubili in n-pentano o n-eptano e sono i composti più pesanti e polari tra i costituenti del petrolio. I malteni sono definiti come composti solubili in idrocarburi leggeri.

Il petrolio pesante ha generalmente una grande quantità di asfalteni, molecole che sono state oggetto di studio che hanno evidenziato il loro impatto negativo in diverse operazioni dell’industria petrolchimica. Nelle fasi di trasporto o di raffinazione ad esempio, gli asfalteni possono precipitare, depositare e ostruire i condotti in quanto sono un sistema colloidale. Essi sono solidi friabili di colore scuro e non hanno un punto di ebollizione. Da un’analisi elementare risultano costituiti prevalentemente da ossigeno (80% in peso) e idrogeno (8% in peso), con la presenza di eteroatomi.

Lo scopo è poter sfruttare il residuo petrolifero, quindi è necessario migliorare le sue caratteristiche chimiche e fisiche. Esistono diversi tipi di processi per trasformare il petrolio, tra cui il processo di miscelazione. Esso trasforma tagli petroliferi poco desiderabili in tagli più interessanti, attraverso la miscelazione di due o più sostanze in modo da produrre combustibile di viscosità intermedia che sia in grado di rispondere alle richieste di mercato. L’operazione risulta estremamente complicata in quanto è necessario seguire alcune regole di composizione, e nonostante sia oneroso da un punto di vista economico, risulta vantaggioso sul lungo periodo in quanto non si verificano lo spreco del residuo e l’utilizzo eccessivo di tagli leggeri.

Ogni proprietà può essere descritta tramite una legge matematica. Le mixing rules sono leggi matematiche che predicono il comportamento di una miscela conoscendo la composizione e le proprietà dei prodotti primari. Nel corso degli anni numerose mixing rules sono state identificate per diverse proprietà del petrolio, ma non per il contenuto di sedimenti. La sedimentazione è un processo molto difficile da descrivere e risulta ardua da predire specialmente su scala industriale.

Approccio teorico - Sundaram et Al.

Nel 2008 Sundaram et Al. lavorano ad un modello termodinamico in grado di predire il contenuto di sedimenti, il quale è valutato tramite un SHFT (Shell Hot Filtration Test method). Si capisce che gli asfalteni non sono semplici molecole, come il benzene, e proprio a causa della loro complessità sono definiti tramite il parametro di solubilità. Per il modello proposto da Sundaram et Al., gli asfalteni sono considerati in forma solida ed in equilibrio con la componente pesante (il solvente), è possibile applicare la relazione di equilibrio descritta dall'equazione 1:

$$K_i = \frac{X_s}{X_l} \tag{1}$$

X_s e X_l rappresentano la frazione molare rispettivamente di asfalteni e di fase liquida e K_i indica la costante di equilibrio, la quale può essere calcolata secondo l'equazione 2:

$$\ln(K_s) = 1 - \frac{V_s}{V_l} + ln\left(\frac{V_s}{V_l}\right) + \frac{V_s}{RT\,(\delta_1 - \delta_s)^2} \tag{2}$$

L'equazione predice la quantità massima di sedimenti che depositano. I parametri mancanti sono V_s e V_l, i quali rappresentano volumi molari di liquido e di solido, legati al peso molecolare, mentre R rappresenta la costante universale dei gas e T la temperatura assoluta. δ è il parametro di solubilità ed è calcolato mediante la definizione di Hildebrand, data dall'equazione 3:

$$\delta = \left(\frac{\Delta E}{V}\right)^{0,5} = \left(\frac{\Delta H_v - RT}{RT}\right)^{0,5} \tag{3}$$

In cui ΔE rappresenta l'energia interna di vaporizzazione mentre ΔH_v il calore di vaporizzazione, e la difficoltà principale consiste proprio nel calcolare quest'ultimo. I parametri chiave nel modello termodinamico consistono nel peso molecolare e dal parametro di solubilità, entrambi non possono essere calcolati direttamente ma solo estrapolati da dati sperimentali. Questo è ciò che rende complicato l'utilizzo di un modello termodinamico: nonostante la legge matematica sia stata sviluppata non sono presenti i parametri adeguati per poterla calcolare.

Durante lo studio anche l'effetto dei diversi diluenti è stato considerato. La figura 1 mostra, infatti, che non tutti i tagli leggeri contribuiscono allo stesso modo sul contenuto di sedimenti, ciò fa intuire che la sedimentazione dipende anche dalle proprietà del taglio leggero. Per il loro lavoro sono stati scelti VGO e HCO a verifica di tale ipotesi. La miscela contente VGO è risultata quella con il contenuto più alto di sedimenti. Hanno quindi concluso che il peso molecolare degli asfalteni, e quindi il contenuto di sedimenti, diminuisce alla crescita dell'aromaticità e al diminuire del rapporto H/C e che l'aromaticità del diluente potrebbe essere uno dei fattori chiave.

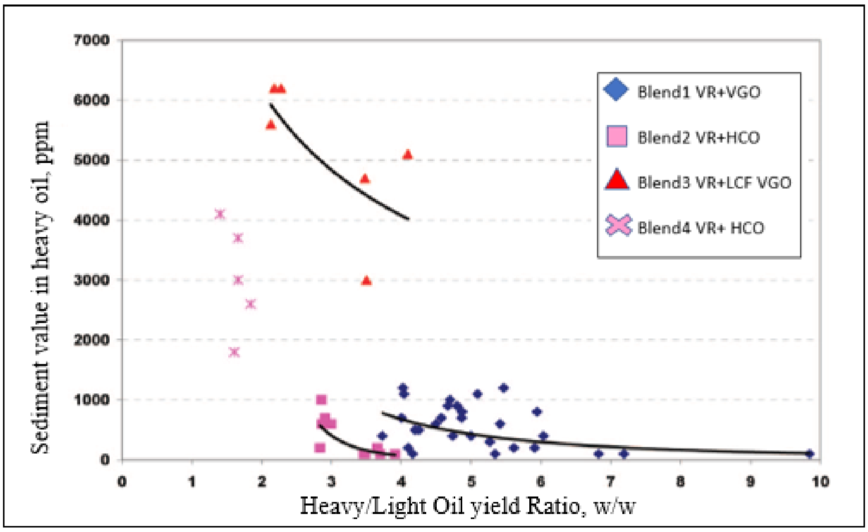

Figura 1. Effetto dei diversi diluenti sul contenuto di sedimenti per un residuo Arabico.

Quindi, è possibile utilizzare un approccio teorico e sarebbe ovviamente preferibile, ma risulta difficile correlare i parametri matematici dell'equazione al significato fisico e spesso è difficile trovare il valore di tali parametri.

Approccio empirico - Stratiev et Al.

Stratiev et Al. nel 2016 hanno lavorato con otto residui derivanti dalla distillazione in condizioni di vuoto (VRO) ed è stata studiata l'evoluzione del loro contenuto di sedimenti miscelati ai tagli leggeri LCO e HCO. In questo lavoro sono state poste basi fondamentali nella comprensione del fenomeno di deposizione degli asfalteni.

Inizialmente è stato dimostrato che il contenuto di asfalteni e la stabilità della miscela sono i parametri migliori per mettere in relazione la tendenza di un residuo a formare sedimenti. Poiché, gli asfalteni sono i componenti più aromatici, gli autori hanno seguito la regola de *il simile scioglie il simile* notando che all'aumentare dell'aromaticità del taglio leggero, il contenuto di sedimenti diminuiva. Inoltre, dalla figura 2 si nota che tanto più elevato è il contenuto iniziale di sedimenti tanto maggiore è la sua diminuzione una volta miscelato. In base ai diversi oli leggeri è possibile avere curve differenti, approssimabili da un'equazione polinomiale del terzo ordine.

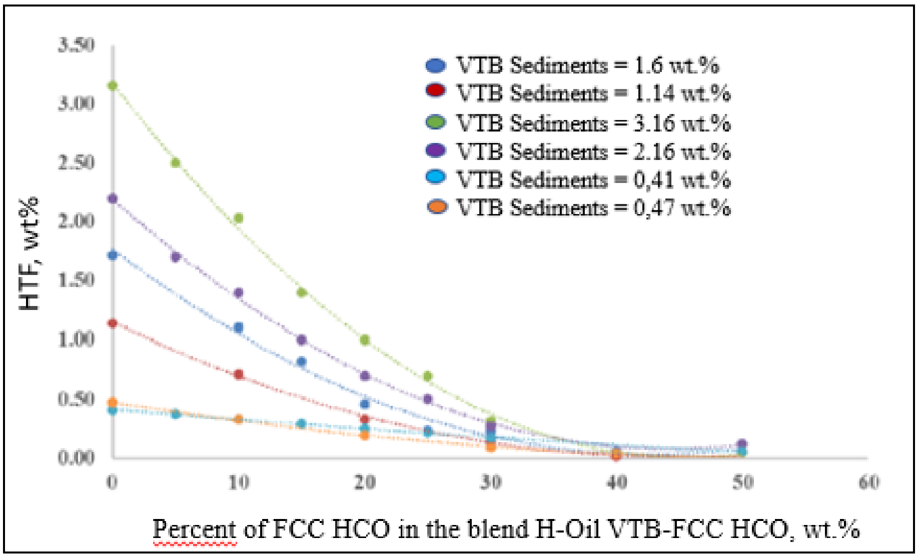

Figura 2. Evoluzione del contenuto di sedimenti per differenti residui miscelati a diverse quantità di HCO

Approccio empirico – Hajjami

Lo studio è stato condotto nel 2018 presso l'*IFP Energie Nouvelles* di Lione, il lavoro è basato sugli studi condotti da Stratiev et Al. Per costruire la legge che descrive il comportamento dei sedimenti, sono state seguite alcune regole:

- La legge deve essere relazionata alle proprietà fisico-chimiche dei componenti che costituiscono la miscela e alla composizione di quest'ultima.
- L'equazione deve essere applicata in campo industriale, per cui i parametri devono essere facilmente calcolabili in una raffineria.

Per costruire l'equazione Hajjami ha utilizzato sei residui e diversi tagli leggeri. Inizialmente il modello è stato calibrato per predire il contenuto di TSE (Contenuto Totale di Sedimenti) in un vasto range. Per far ciò, un unico residuo è stato miscelato con diversi tagli leggeri, ottenendo miscele con diverse composizioni. La figura 3 mostra l'evoluzione dei sedimenti in funzione della percentuale del taglio leggero. Si hanno diversi comportamenti: VGO ha un andamento quasi lineare, GO fa crescere inizialmente il contenuto di sedimenti per poi diminuire, mentre LCO ed HCO, che sono composti aromatici, fanno diminuire il contenuto di sedimenti. I risultati sono in accordo con lo studio di Stratiev.

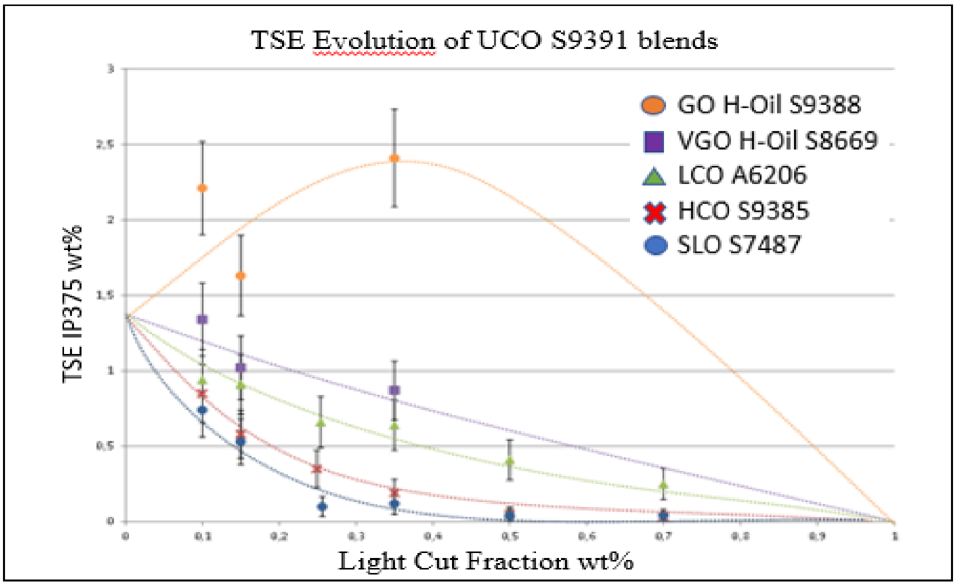

Figura 3. Contenuto di TSE di UCO S9391 miscelato a diversi tagli leggeri.

Hajjami assume un'equazione (equazione 4) di tipo esponenziale come modello:

$$TS_m = W_R \cdot TS_{0,R} \cdot e^{-k\, W_{CS}} \tag{4}$$

Dove TS rappresenta il contenuto di sedimenti, k la costante specifica per taglio leggero, W la composizione percentuale in peso, m indica la miscela, R il residuo e CS il taglio leggero, chiamato cutter stock.

L'equazione deve descrivere il comportamento dei due prodotti della miscela. La parte lineare dell'equazione esprime l'effetto di diluizione del taglio leggero, mentre quella esponenziale la stabilità/instabilità del taglio leggero. I due effetti avvengono allo stesso tempo, ma l'intensità del fenomeno dipende dal diluente scelto.

Secondariamente, per capire le proprietà del taglio leggero che giocano un ruolo nella formazione di sedimenti, sono stati effettuati altri esperimenti. Era chiaro che il parametro k dipendesse solo dal taglio leggero, in quanto è stato assunto che il residuo non gioca alcun ruolo nell'effetto di stabilità/instabilità. Poiché, i tagli che stabilizzano maggiormente sono aromatici, una delle proprietà considerate è proprio l'aromaticità. Un'altra proprietà molto importante è la densità. Risultava però difficile correlare aromaticità e densità nella medesima equazione, per tale ragione ne sono state ricavate due, l'equazione 5 considera l'aromaticità, mentre l'equazione 6 la densità.

$$k = a\, C_{aromatico} - b \tag{5}$$

$$k = a\, T_{SD} + b\, \rho + c \tag{6}$$

Il modello trovato da Hajjami descrive bene il comportamento delle miscele in quanto considera i parametri di entrambi i prodotti utilizzati.

Il lavoro si è basato su un approccio empirico, che ha evidenziato la difficoltà nel relazionare il modello matematico con le proprietà chimiche e fisiche.

3. Metodologia ed esperimenti

Per ottenere il modello matematico è necessario avere a disposizione numerosi dati sperimentali: conoscendo il contenuto di sedimenti per una determinata miscela e cambiando la composizione si può trovare la legge matematica che descrive tale comportamento. L'equazione di partenza è quella di Hajjami, equazione 4, il cui modello era costituito da un andamento sia esponenziale che lineare. Per quanto concerne questo lavoro di tesi, l'equazione prevede tre parti: la parte lineare, una parte per l'effetto del residuo e una per l'effetto del taglio leggero.

Il lavoro è stato suddiviso in tre parti:

1. Step 1- creazione e misura di sedimenti di nuove miscele, 60 miscele binarie utilizzando tre residui e cinque tagli leggeri utilizzati anche da Hajjami, oltre a tutte le miscele studiate nel precedente tirocinio. In questo modo il valore del parametro *k* è noto.

   Diversi modelli sono stati proposti. Per ogni equazione proposta è stato calcolato il valore di α che minimizzasse la differenza ai minimi quadrati tra il valore misurato con gli esperimenti e il valore che la nuova equazione proposta ci forniva. Tale parametro è però solo una prima approssimazione del valore reale. il quale rappresenta una proprietà caratteristica del residuo.
   In seguito, grazie alla creazione di nuove miscele, è stato posibile arrivare ad un valore del parametro *k* più corretto per ogni taglio leggero.

   È stato effettuato un calcolo iterativo di modo tale da arrivare a valori di α e *k* il più corretti possibili, ma non è possibile fornire i valori numerici dei due parametri.

1. Step 2- conoscenza dell'equazione matematica dei parametri α e *k,* in quanto nel primo step è stato trovato soltanto il valore numerico. Tali equazioni sono in funzione delle diverse proprietà del residuo per α e del taglio leggero per *k*.

2. Step 3- validazione del modello. Conoscendo la forma del modello e le equazioni dei parametri α e *k* è possibile validare il modello per miscele di tipo ternario. In questo modo è possibile dire se il modello risulta migliore o meno rispetto quello ottenuto da Hajjami.

Il contenuto di sedimenti dipende da molte proprietà che devono essere misurate. L'accuratezza di ogni misura può essere espressa tramite due valori: ripetibilità e riproducibilità. La ripetibilità consiste nel ripetere la stessa misura nello stesso laboratorio, con la stessa apparecchiatura e nelle stesse condizioni chimico-ambientali, mentre la riproducibilità è la capacità di differenti laboratori di ottenere lo stesso risultato.

Contenuto di sedimenti

Il contenuto di sedimenti è stato calcolato applicando il metodo IP375. Dopo la creazione della miscela (di residuo e taglio leggero), essa è posizionata su un agitatore magnetico con velocità

di rotazione pari a 300 rpm e alla temperatura di 70°C, per circa un'ora. In seguito, la miscela è scaldata in un forno per circa 20 minuti a 110°C, affinchè il composto risulti meno viscoso.
10 gr del campione attraversano un filtro, la cui porosità è 1,6 µm. Lo scopo è intrappolare i sedimenti sul filtro, i malteni invece sono in grado di attraversarlo. Durante la filtrazione è necessario inviare vapore per aiutare il filtraggio e successivamente raffreddare tramite acqua fredda. Una pompa posta a valle aiuta la filtrazione: è importante che il sistema sia freddo in quanto il filtro deve essere lavato con una soluzione di eptano e toluene per ottimizzare l'operazione, infatti se i solventi si presentano in stato liquido possono recare danni alla pompa.

La figura 4 rappresenta uno schema dell'apparecchiatura utilizzata per la filtrazione.

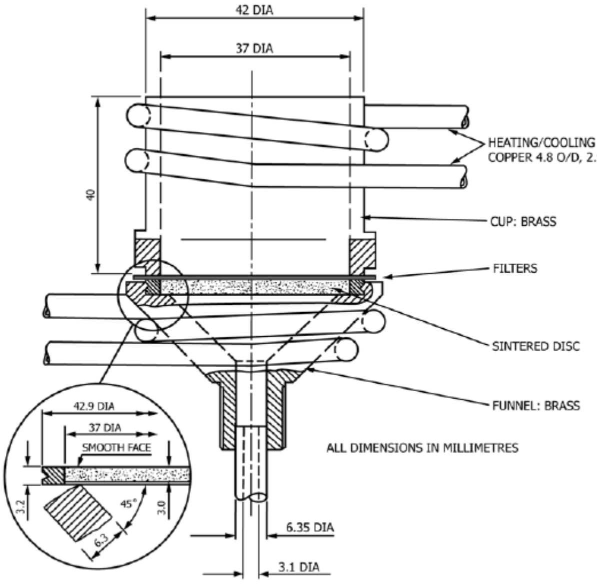

Figura 4. Apparecchiatura della filtrazione.

A filtrazione avvenuta, il filtro è recuperato e collocato in un forno a 110°C per qualche ora. Ciò che rimane sul filtro, chiamato torta, è pesato e rappresenta il contenuto di sedimenti.

Densità

La densità è misurata applicando il metodo ISO 12815. È necessario che la miscela venga scaldata, affinché la viscosità diminuisca, in un forno per 40 minuti a 70°C. Il metodo si avvale di un densimetro il quale contiene al suo interno un tubo oscillatore, composto da borosilicato, a forma di U. 0,70 mL di prodotto sono introdotti nel tubo, il quale vibra ad una frequenza caratteristica che dipende dalla densità del prodotto. La densità è calcolabile mediante l'equazione 7:

$$\rho = KA * Q^2 * f_1 - KB * f_2 \tag{7}$$

In cui *KA* e *KB* sono costanti dell'apparecchiatura, Q è il quoziente del periodo di oscillazione, f_1 ed f_2 sono termini correttivi.

Il campione introdotto all’interno dell’apparecchiatura possiede una temperatura di circa 70°C, mentre la misura della densità è restituita a 15°C.

Viscosità

La viscosità è misurata utilizzando il metodo ISO 3104. Dopo aver scaldato la miscela per 20 minuti a 70°C, 20 gr di campione sono introdotti all’interno del viscosimetro in cui avviene un secondo riscaldamento alla temperatura cui si desidera conoscere il valore di viscosità. Il fluido sale attraverso un tubo capillare, il quale possiede tre sfere di vetro in sequenza nel suo tratto superiore e il fluido si posiziona tra due sfere inizialmente, ciò conferisce una prima approssimazione della misura. Dopo di che il fluido raggiunge la sfera corretta. La viscosità è calcolata mediante l’equazione 8 come il tempo di flusso (τ) per la costante di calibrazione C (fornita dal costruttore del viscosimetro):

$$\upsilon = C * \tau \tag{8}$$

A causa delle elevate viscosità degli oli pesanti, per alcuni prodotti le viscosità sono calcolate a temperature superiori ai 100°C ed in seguito convertite a 50°C, tramite l’equazione 9:

$$\upsilon_T = exp\left\{ exp\ \left\{ln\ [\ ln(\upsilon_T - 0{,}7)] * B *\ ln\left(\frac{T}{T_1}\right)\right\}\right\} - 0{,}7 \tag{9}$$

Dove il parametro B è dato dalla relazione 10:

$$B = \frac{\ln\left[\frac{\ln\left(\upsilon_{T_1}+0{,}7\right)}{\ln\left(\upsilon_{T_2}+0{,}7\right)}\right]}{\ln\left(\frac{T_2}{T_1}\right)} \tag{10}$$

Frazionamento SARA

Il frazionamento SARA è utilizzato per separare il petrolio pesante nei suoi componenti principali: Saturi, Aromatici, Resine (Malteni) e Asfalteni, attraverso il metodo IFPEN 9305.

Separazione degli asfaltei dai malteni

In un’ampolla sono inseriti 20 gr di residuo a cui è aggiunto un quantitativo in peso superiore di 30 volte di n-eptano. L’ampolla è posizionata su un agitatore magnetico a 122°C e 800 rpm ed è inoltre collegata ad un piccolo condensatore che riflussa l’n-eptano. Il periodo di agitazione magnetica è di circa un’ora. La figura 5 mostra l’agitatore magnetico con l’ampolla posizionata al di sopra di esso.

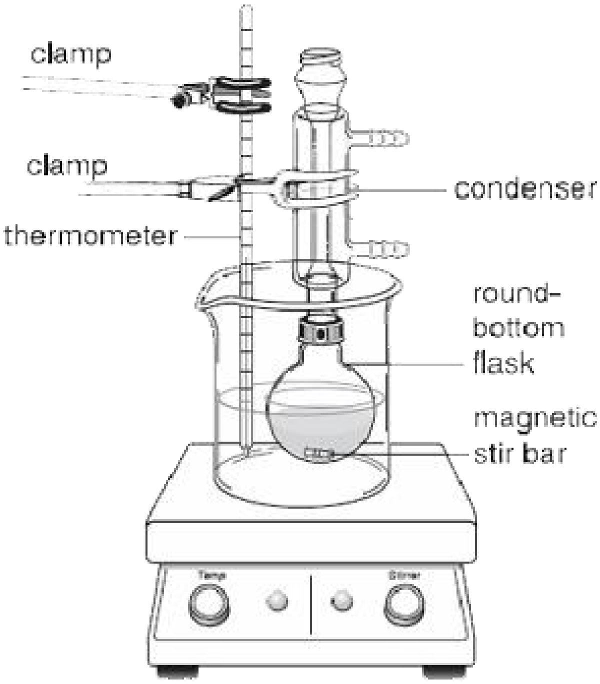

Figura 5. Agitatore magnetico con ampolla.

Successivamente, l’ampolla è messa a riposo per un’ora e 30 minuti in condizioni di buio e a temperatura ambiente. In questo periodo avviene la separazione degli asfalteni che hanno tendenza a depositare sul fondo dell’ampolla.

Avvenuta la precipitazione degli asfalteni si provvede a separarli dai malteni, e per far ciò la miscela è filtrata. Gli asfalteni rimangono bloccati sul filtro e posti in forno per un’ora a 60°C, per essere pesati in un momento successivo. I malteni e l’n-eptano sono raccolti separatamente, tale soluzione dovrà essere dapprima concentrata in condizioni di vuoto ed in seguito disidratata per avere solo il contenuto dei malteni.

Separazione dei malteni in Saturi, Aromatici e Resine:

Dopo la separazione dagli asfalteni, una piccola quantità di malteni è iniettata in una colonna, la quale è riempita con silicio e allumina. La separazione dei Saturi è effettuata mediante n-eptano, gli aromatici grazie all’introduzione di n-eptano e toluene mentre il contenuto di resine da una miscela di diclorometano, toluene e metanolo. All’uscita della colonna vengono pesati.

Composizione elementare

Il contenuto di carbonio, idrogeno, azoto, zolfo, nickel e vanadio è misurato tramite il metodo IFPEN 9422. I campioni considerati in questa analisi sono quelli maltenici che derivano dal frazionamento SARA. La spettrometria a fluorescenza a raggi X misura l’intensità di uno specifico picco emesso da un particolare atomo, il campione infatti è eccitato da un fascio di raggi X.

Il metodo è estremamente veloce e molto accurato.

AC7 (Precipitazione di asfalteni tramite eptano)

Il contenuto di asfalteni è misurato tramite il metodo NFT 60-115, ed è totalmente diverso dal frazionamento SARA o dalla filtrazione per misurare il contenuto di sedimenti.

La miscela costituita da residuo e taglio leggero è messa in un forno, la cui temperatura è regolata in base alla viscosità del residuo, successivamente 10 gr sono inseriti in un'ampolla e sono aggiunti 10 mL di toluene. L'ampolla è lasciata per circa 15 minuti su un letto di sabbia a 100°C per meglio solubilizzare il residuo in compagnia del toluene.

In seguito, 250 mL di n-C7 sono aggiunti alla soluzione contenuta nell'ampolla, la quale è posta su un agitatore magnetico ed è portato a ebollizione. Dopo un'ora, l'ampolla è messa a riposare al buio e a temperatura ambiente per circa due ore.

Passato il periodo di riposo la soluzione è filtrata e le particelle di asfaltene rimangono intrappolate. Una porzione di particelle rimane all'interno dell'ampolla, per tale ragione una piccola quantità di toluene é aggiunta per aiutare ulteriormente la loro solubilizzazione. Il filtro con le particelle è posto sull'ampolla e lavato con una soluzione di 100 mL di n-C7. Si ripete l'operazione precedente: l'ampolla è posizionata sull'agitatore magnetico e la soluzione è mandata a ebollizione, in questo modo il filtro è lavato nuovamente (grazie al riflusso) e il contenuto di malteni è smaltito.

L'ultimo step è mettere insieme i contenuti di asfaltene. Il filtro, sopra l'ampolla posta sull'agitatore magnetico per altri 45 minuti, rilascia completamente gli asfalteni che cadono e rimangono intrappolati nella sfera di vetro. Il contenuto è trasferito in una ciotola e messa in forno a 100°C. Il contenuto di asfalteni può essere ora misurato.

Distillazione simulata

Il metodo utilizzato in IFPE, IFPEN 1012 è molto simile ad ASTMD 7269, ed è utilizzato per conoscere la distribuzione della temperatura di ebollizione dei componenti del residuo. La distillazione simulata sfrutta la gas cromatografia (GC) per separare i componenti in base alle temperature di ebollizione. Il principio su cui è basata è che gli idrocarburi escono dalla colonna in base alla loro temperatura di ebollizione.

Il campione è inserito all'interno della colonna, la quale non è polare, in modo che riesca a separare i componenti per la loro volatilità: i più leggeri (polari) escono prima in quanto non hanno affinità con la colonna, mentre i pesanti (non polari) in un secondo momento. Un fascio di idrogeno colpisce le molecole che escono ed in base al picco di risposta si capisce di quale molecola si tratta.Per meglio separare, solitamente, a valle della seconda colonna, ne è posta una polare.

Carboni aromatici

Il contenuto di carboni aromatici in accordo al metodo IFPEN 9410. Il campione è solubilizzato con CD_3Cl. Il rapporto tra carboni saturi e carboni insaturi è misurato grazie alla tecnica NMR. Si assume che negli oli pesanti il contenuto di carboni insaturi corrisponde a quello dei carboni aromatici

4. Risultati

La letteratura scientifica non offre modelli matematici in grado di predire il contenuto di sedimenti all'interno di miscele di tagli petroliferi leggeri e pesanti. Il modello è stato costruito seguendo un approccio empirico.

Step 1: studiare l'effetto che il residuo ha sul contenuto di sedimenti, per poter far ciò numerose filtrazioni sono effettuate, per poter ottenere il maggior numero di dati possibili da studiare.

Basando il lavoro sull'equazione proposta da Hajjami, è aggiunto un nuovo parametro che possa descrivere le proprietà chimiche e fisiche del residuo, tale parametro è chiamato "α". In questa prima fase è possibile fornire al parametro solo un valore di tipo numerico, solo successivamente verrà ricavata una relazione matematica con le proprietà del residuo.

Per poter ricavare l'equazione è necessario conoscere: il contenuto iniziale di sedimenti, la composizione della miscela, il valore di k del taglio leggero. Proprio perché è necessario conoscere il valore del parametro k, i tagli leggeri scelti in questa prima fase sono gli stessi che Hajjami ha utilizzato nel corso del tirocinio precedente, in questo modo una prima approssimazione del parametro k può essere conosciuta.

Diverse equazioni vengono testate posizionando il parametro α in diversi modi, all'interno dell'esponenziale o a denominatore dell'equazione ad esempio. È stato utilizzato un solver sul programma Microsoft Excel in grado di fornire il valore di α che riuscisse a minimizzare la differenza della somma dei quadrati tra il valore predetto (con tale equazione) e il valore misurato attraverso gli esperimenti. Tra tutte le equazioni testate, l'equazione 11 risulta essere quella che meglio minimizza la differenza tra la predizione e la realtà.

$$y = W_R * \left(\frac{1}{\alpha} - TS_{0,R}\right) e^{-k\, W_{CS}} \tag{11}$$

La figura 6 mostra che c'è una relazione quasi lineare tra questi due valori, per tale motivo si ritiene che il modello fornito dall'equazione 11 possa essere ritenuto accettabile.

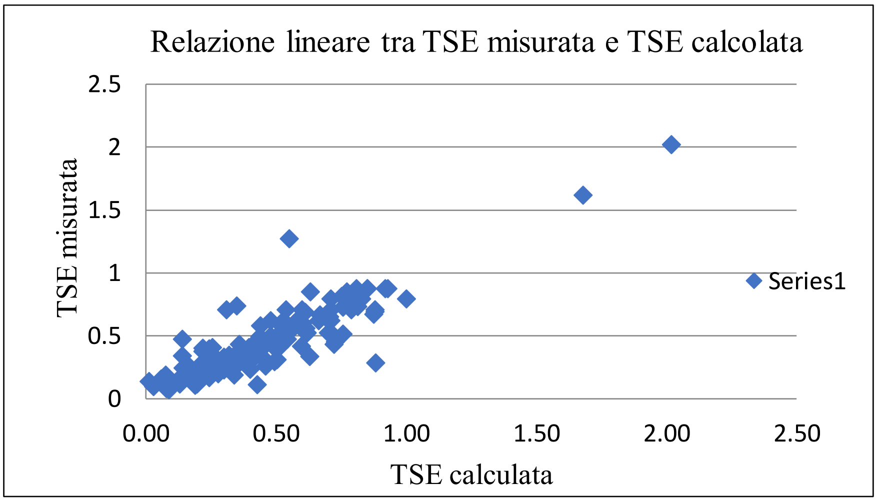

Figura 6. Relazione tra la TSE misurata e TSE calcolata.

Per poter trovare il valore di α per ogni residuo sono state considerate anche le miscele che Hajjami ha utilizzato lo scorso anno, in questo modo si può ottenere un valore più preciso del parametro. Infine, la definizione di RMSE è stata applicata per confrontare la nuova equazione proposta, con quella proposta da Hajjami, per avere la sicurezza che sia migliore. La nuova equazione, in effetti, risulta dare un errore minore rispetto alla precedente.

Successivamente lo stesso procedimento, appena descritto, è stato utilizzato per poter trovare un nuovo valore del parametro k. 52 filtrazioni sono state eseguite, utilizzando un solo residuo e 26 tagli leggeri. La scelta di utilizzare un solo residuo è dettata dal fatto che l'effetto che il taglio leggero ha è sempre lo stesso. Per poter calcolare il parametro k è necessario conoscere il contenuto iniziale di sedimenti del residuo, il parametro α (calcolato anche per il residuo utilizzato nel secondo step) e la composizione delle miscele.

Trovato il nuovo parametro k per ogni taglio leggero, è stato necessario un calcolo iterativo. Un nuovo parametro α_1è stato trovato utilizzando i parametri k_1, e un nuovo parametro k_2 è stato trovato utilizzando il parametro α_2. Le iterazioni sono ripetute fino a quando la differenza tra i valori non risulta essere sufficientemente piccola da non cambiare ulteriormente i valori successivi.

Studiando la relazione tra l'equazione predetta e i valori sperimentali ottenuti, si può notare in figura 7, che la relazione lineare migliora ulteriormente rispetto alla prima iterazione, seppur in modo lieve.

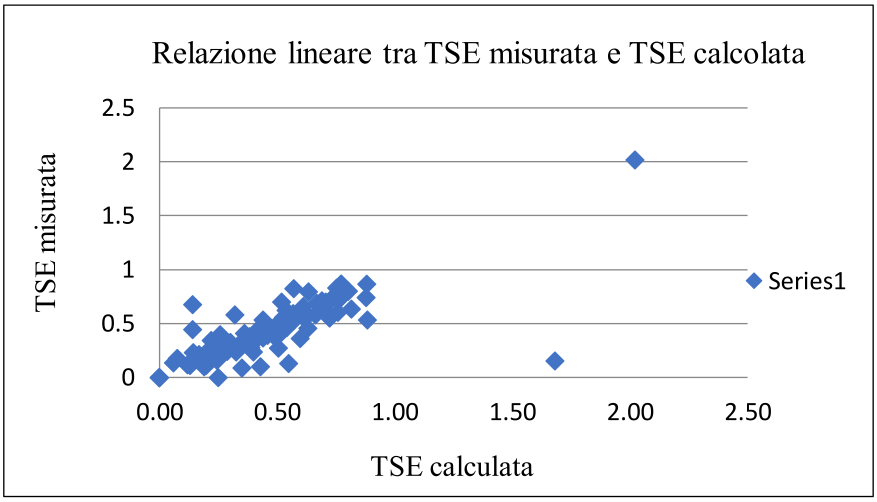

Figura 7. Relazione tra la TSE misurata e TSE calcolata

Step 2: trovare l'equazione matematica che descriva i parametri α e *k* legandoli alle proprietà del residuo e del taglio leggero, rispettivamente. Per questo step è stato utilizzato il software *visu3D*. Per poter utilizzare tale software è necessario creare due matrici (una relativa ai residui e una relativa ai tagli leggeri) le quali contengano il valore di ogni proprietà per ogni residuo ed ogni taglio leggero. Ovviamente ogni proprietà conferisce qualche informazione e probabilmente, seppur in modo poco evidente potrebbe giocare un ruolo nella sedimentazione, tuttavia solo alcune proprietà sono state prese in considerazione. *Visu3D* permette di trovare differenti modelli i quali possono prendere in considerazione anche differenti proprietà, la scelta del modello che meglio possa approssimare il valore dei parametri spetta a chi utilizza il software.

Per il parametro α è stato scelto il modello fornito dall'equazione 12:

$$\alpha = a + b * \rho + c * A + d * C + e * S + f * \gamma \tag{12}$$

in cui ρ rappresenta la densità, A il contenuto aromatico (ottenuto dal frazionamento SARA), C è il contenuto di carbonio, S rappresenta la quantità di zolfo, γ è la tensione superficiale dei malteni.

Per il parametro k invece sono state prese in considerazione due modelli che possono rivelarsi validi allo stesso modo e i quali sono descritti da differenti proprietà. L'equazione 13:

$$k_1 = a + b * \rho + c * H + d * DS5 + e * DS50 \tag{13}$$

In cui ρ rappresenta la densità, H il contenuto di idrogeno che è relazionato all'aromaticità, DS5 ovvero la temperatura che conduce alla distillazione del 5% del campione e DS50 che rappresenta la temperatura che conduce alla distillazione del 5% del campione.

Mentre l'equazione 14 descrive il secondo modello scelto.

$$k_2 = a + b * \rho + c * \gamma + d * H \tag{14}$$

In cui ρ rappresenta la densità, γ è la tensione superficiale e H il contenuto di idrogeno.

Step 3: validazione del modello. È necessario capire se il modello trovato può considerarsi una buona approssimazione del valore reale del contenuto di sedimenti e fornire inoltre un valore migliore rispetto a quello fornito dall'equazione suggerita da Hajjami.

Per poter validare il modello è necessario eseguire altri esperimenti di filtrazione con miscele ternarie, le quali possono essere costituite da due residui e un taglio leggero, o al contrario, due tagli leggeri e un solo residuo. È fondamentale validare il modello con miscele che non sono state utilizzate per la costruzione del modello: in questo modo si capisce se il modello trovato è universale o meno. Ed inoltre, fornisce anche informazioni anche sul contenuto di sedimento di miscele ternarie.

Le miscele create con due residui e un solo taglio leggero hanno un comportamento molto simile a quello delle miscele binarie. Mentre, le miscele contenenti due tagli leggeri no. Infatti, in queste ultime è presente anche il diesel, HYVAL S5177. Il diesel è un composto poco aromatico, per tale ragione destabilizza molto il sistema e il contenuto di sedimento aumenta.

Da una prima analisi appare quindi evidente che la scelta di considerare le caratteristiche aromatiche all'interno del parametro k è corretta

Per poter valutare l'accuratezza del modello è necessario conoscere: il contenuto iniziale di sedimenti, la composizione della miscela, i parametri α e k e il valore medio per le miscele. La validazione è stata eseguita sia con k_1 che con k_2.

Le figure 8 e 9 mostrano la relazione tra i valori misurati e quelli predetti delle miscele ternarie ottenuta con due residui, la prima applicando k_1, la seconda k_2. La relazione non è perfettamente lineare, ma non è un cattivo risultato in quanto per avere una relazione migliore è comunque necessario avere a disposizione un database più fornito di miscele con le rispettive proprietà. Non c'è molta differenza tra le due, i valori di k_1 e k_2 sono comunque molti simili tra loro.

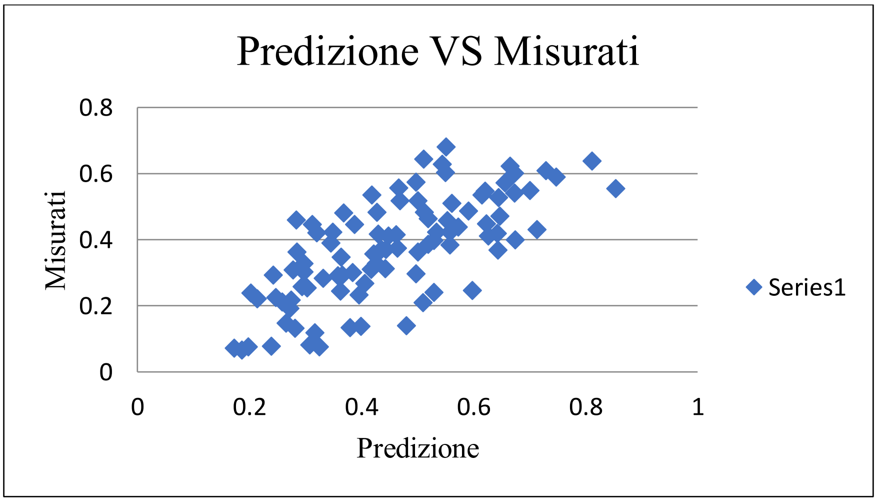

Figura 8. Relazione tra i valori misurati e quelli predetti delle miscele ternarie (due residui), con k_1.

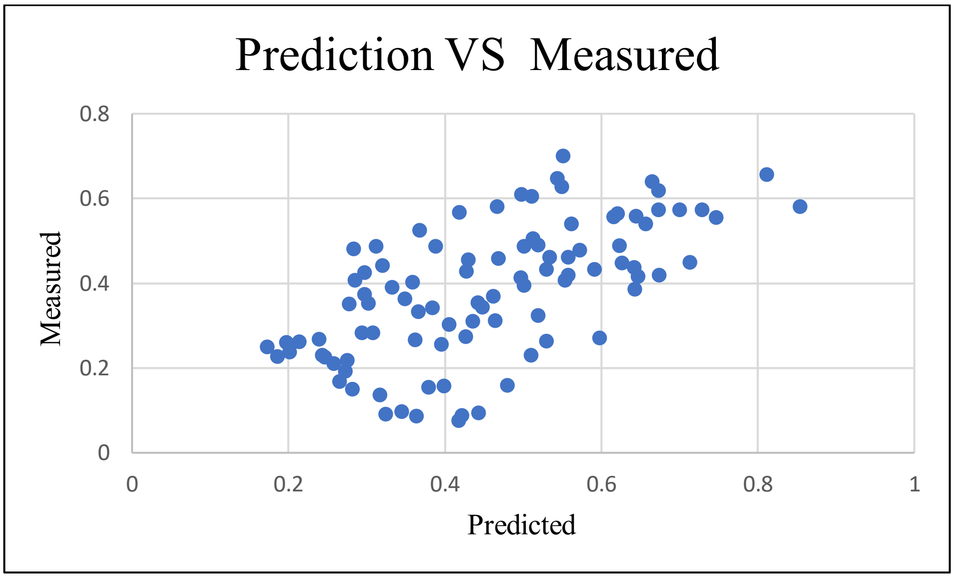

Figure 9. Relazione tra i valori misurati e quelli predetti delle miscele ternarie (due residui), con k_2.

Le figure 10 e 11 mostrano la relazione tra i valori misurati e quelli predetti delle miscele ternarie ottenuta con due tagli leggeri, la prima utilizzando k_1, la seconda usando k_2. La predizione non sembra molto buona, ma è necessario comunque ricordare che è stato utilizzato un diesel per la creazione delle miscele le quali risultano molto instabili. Per tale ragione risulta difficile riuscire a predire il contenuto dei sedimenti.

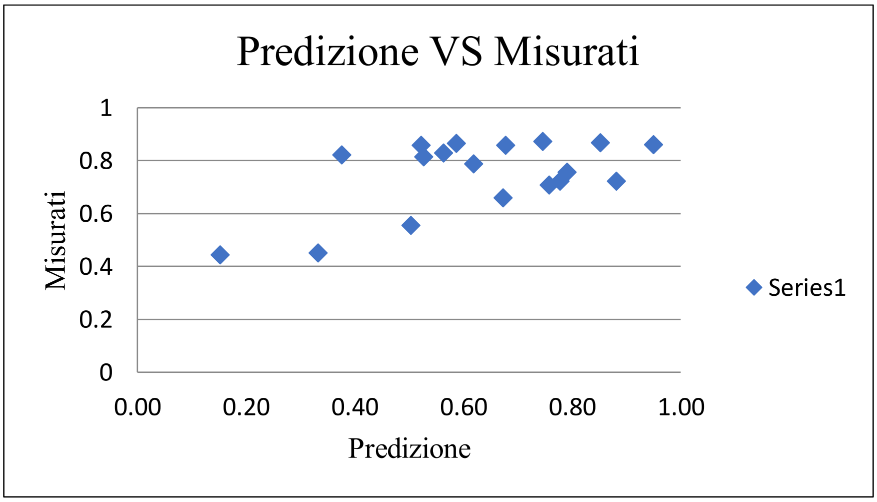

Figura 10. Relazione tra i valori misurati e quelli predetti delle miscele ternarie (due tagli leggeri), k_1.

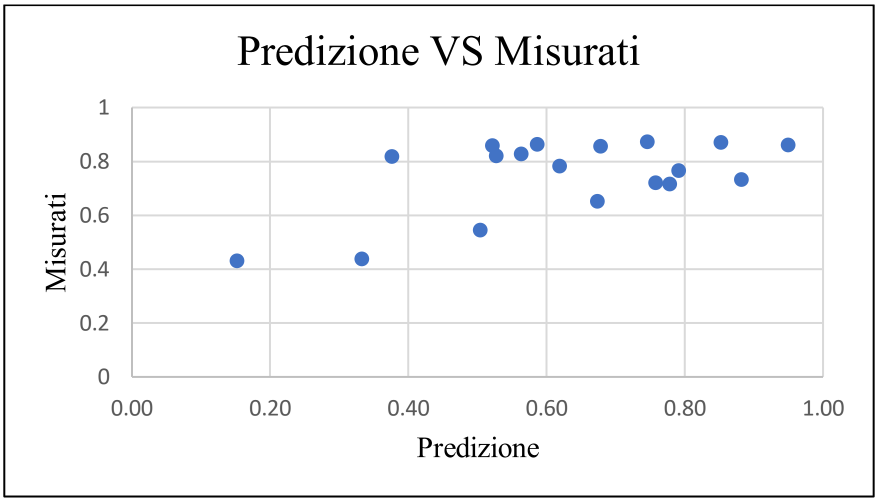

Figura 11. Relazione tra i valori misurati e quelli predetti delle miscele ternarie (due tagli leggeri), k_2.

Infine, è stato calcolato l'errore commesso utilizzando tre definizioni differenti:

RMSE valuta la deviazione standard della predizione.

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(\hat{y}_l - y_i)^2} \tag{5}$$

L'errore relativo (ε):

$$\varepsilon = \frac{1}{n}\sum_{1}^{n}\frac{|\hat{y}_l - y_i|}{y_i} \tag{6}$$

β per poter valutare se la predizione è sovra o sotto stimata:

$$\beta = \frac{1}{n}\sum_{1}^{n}(\hat{y}_l - y_i) \tag{7}$$

In cui n rappresenta il numero di misurazioni effettuate, ŷ è il valore predetto mentre *y* è il valore misurato.
La tabella 1 mostra l'errore dell'equazione applicando k_1.

Tabella 1. Errore dell'equazione per miscele con due residue e un taglio leggero.

Errore	*Valore numerico dell'errore per k1*	*Valore numerico dell'errore per k2*
RMSE	0,1471	0,1516
ε	0,2867	0,2815
β	0,1256	0,1234

La tabella 2 mostra l'errore dell'equazione applicando k_2.

Tabella 2. Errore dell'equazione per miscele con un residuo e due tagli leggeri.

Errore	*Valore numerico dell'errore per k1*	*Valore numerico dell'errore per k2*
RMSE	0,2062	0,1977
ε	0,3841	0,3633
β	0,1653	0,1594

Gli errori risultano accettabile quando si ha RMSE < 20 %, ε < 15 %, β < 15-20 %.

In questo caso ancora nessuno risulta essere minore della soglia accettabile (eccetto il valore di RMSE per il parametro α). Per tale ragione si può concludere che sarebbe opportuno eseguire altri esperimenti in modo tale da avere un database più fornito, e considerare anche altre proprietà.

5. Conclusioni

Lo scopo del tirocinio è stato quello di determinare una regola generale di miscelazione per la predizione del contenuto di sedimenti. In questo modo si è in grado di sfruttare il petrolio pesante conferendogli delle proprietà intermedie, appetibili per le richieste di mercato

Utilizzare un approccio di tipo termodinamico risulta migliore dal punto di vista della modellazione, nonostante ciò è stato seguito un approccio di natura empirica. Infatti, un modello termodinamico utilizza delle proprietà estremamente difficili da calcolare e per questo motivo è necessario ricordare che tale modello dovrà essere utilizzato in campo industriale. Le proprietà che devono essere considerate, quindi, devono essere facilmente misurabili e/o calcolabili in una ipotetica raffineria.

Oltre alla correttezza del modello è necessario che questo si adatti ad un numero elevato di residui e tagli leggeri, in quanto deve fornire un modello universale, e non corretto solo per i tagli petroliferi utilizzati per la costruzione dello stesso.

Il tirocinio è durato 6 mesi e numerose miscele sono state prese in considerazione, infatti i risultati ottenuti possono essere ritenuti accettabili. Tuttavia, per poter arrivare ad un modello migliore è necessario possedere un database ancora più fornito.

Un altro modo per poter migliorare il modello è quello di considerare nell'equazione la variabile temporale. Infatti, il contenuto di sedimento ha un'evoluzione nel tempo che è specifica per ogni residuo.

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1. Introduction

The world energy demand is increasing continuously during the years which is conducted by the economic development and the growth of the population, these events had caused the decline of petroleum resources available on the planet.

The product most requested by the market are the light components, deriving from distillation processes, while there is no request for heavy fuel oils, this makes refiners search new ways to reduce them or even totally avoid their production, but it is extremely difficult. Refineries are more and more dependent on heavy oil as the sources of light oils decrease. Some analysis about the oil fields have demonstrated that had reached a maximum volume during the 1960s (Campbell and Laherrère, 1998), since that period, reserves kept on declining [1]. It is highly difficult to respond to the energy demand, since the new discoveries of new oil fields are poor and scarce. The result is a gap between the worldwide energy demand and the availability of oil.

Figure 1.1 shows the discoveries of new fields, which had a peak during 1960s, but since that period have been drastically decreased and they will keep on decreasing in the future. The black line represents the production of the oil which does not care about the decreasing of the reserves but still increasing, and will not stop in the future.

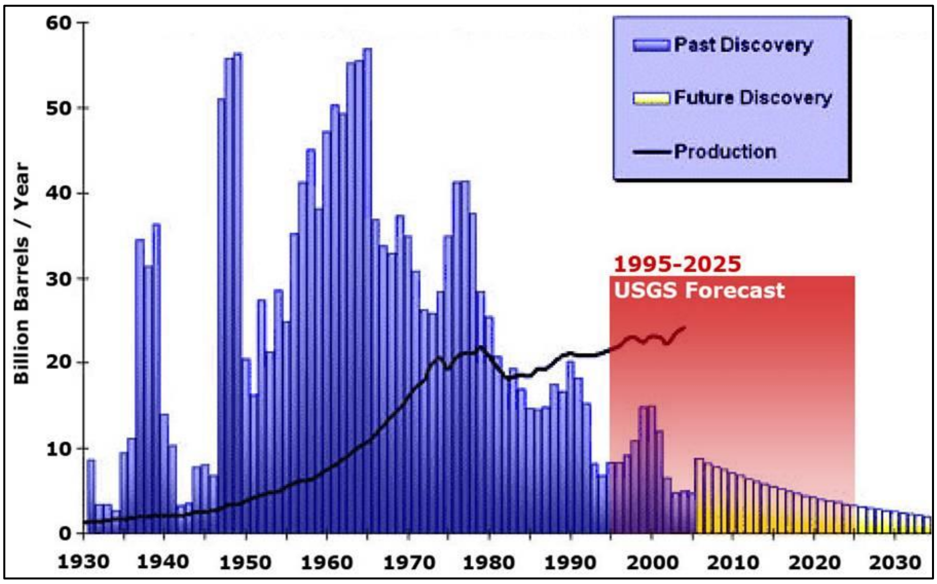


Figure 1.1 Discoveries of the reserves and energy demand production.

In this contest, refining process is increasingly concerning with the conversion of atmospheric or vacuum residues since the increase in demand of gasoline or middle distillates. The development of new technologies becomes extremely important for the economic production of unconventional oils, such as heavy oils and bitumens. Oil companies know that unconventional oil represents an alternative resource for the energy supply.

The main problem for unconventional oils is represented by their physical and chemical characteristics which are related to the presence of resins and asphaltenes, that represent the most polar fractions of these products. Probably the macrostructure is the cause of the high viscosity.

Since the high demand of light products, the target is to use heavy oils and convert them into light oils, therefore refiners need to upgrade the processes. One of the most used upgrading process is the *blending process*. It consists in a mixture between heavy oils and lighter cuts, called cutter stocks, in order to reduce the viscosity of the heavy oil and to provide it the characteristics of light oil, in order to be able to use it and do not waste it. The main problem is caused by the cutter stocks. The mixing can disturb the stability of the fuels and cause the sediments deposition. It is extremely important to study the compatibility between heavy fuels and cutter stocks to avoid the sediment formation.

In 2015 the start-up of the H-Oil process, in the LUKOIL Neftohim Burgas (LNB) refinery, had many technical problems. As it is reported in the articles of Stratiev et Al of 2016 [2], “Failures in the main pieces of equipment such as recycle treat gas compressors, feed pumps, washing water pumps, fuel gas compressors and many others were prevalent during the start-up process which lasted almost 3 months.”. During that period the H-Oil unit had to be stopped many times to solve the technical problems. Figure 1.2 shows the variation of the sediment level in the H-Oil unconverted vacuum tower bottom and atmospheric tower bottom products during the period July 21 – December 7 2015.

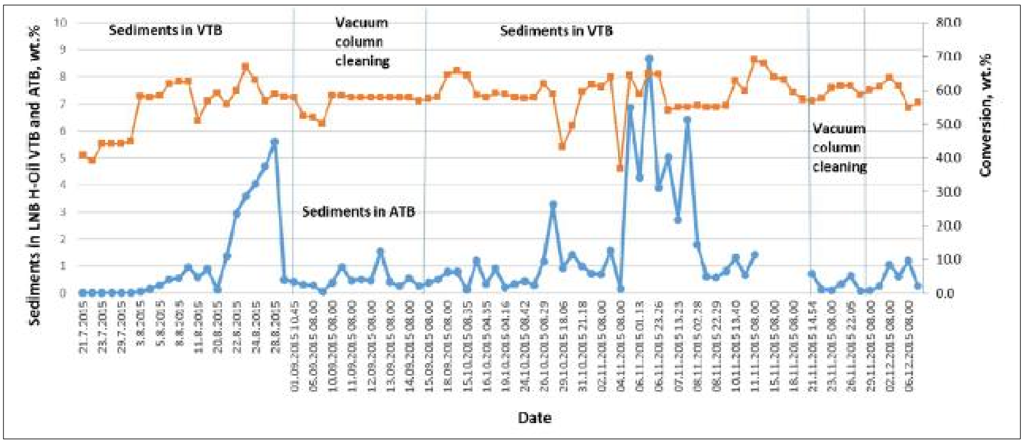


Figure 1.2. Variation of the sediment level in the H-Oil converted vacuum tower bottom and atmospheric tower bottom products.

Sediment deposition is extremely hard to be described. It is known that hydroconversion process modifies the power of the solvent, but many affects cause the sediment deposition such as the quality of the feedstock and the type of cutter stocks utilized for the blends. Many properties have to be involved to find a correct mathematical model able to describe and predict the sediment content. Finding a model means solve, at least in part, the problem. The knowledge of the mixture composition allows to know the future behavior and, anticipate if it is going to form sediments or not.

The aim of the internship is to validate a model able to predict sediment contents deriving from the mixtures of heavy and light cuts. The mechanism of this phenomena is extremely difficult to understand and the prediction of it still be challenging. Some models have been created, but it is not sure they describe the reality of the phenomena. All the thermodynamic models existed in the literature are perfect from the thermodynamic point of view, but impossible to realize because some properties are difficult to be measured.

The document contains four other chapters. *Chapter 2 – Literature review*, is about the knowledge of heavy fuels and moreover about sediment contents, their origins and their compositions. Many models found in the literature that try to describe the deposition of sediment are presented. *Chapter 3 – Methodology and experiment*, presents the methods followed in the internship as well as the experiments done and the data used. *Chapter 4 – Result and discussion*, present all the result obtained from the experiments and the discussion of the results. *Chapter 5 – Conclusion*, summarized what it has been done and the future possible perspective of the work.

2. Literature review

In this chapter, the different aspects related to oil refining are explained and heavy fuels are described in terms of composition and properties. Finally, the knowledge of the mixing rules suitable for the sediment content in heavy oil are presented.

2.1 Oil refining

Crude oil, mostly known as *petroleum*, is the definition for the "unprocessed" oil. The generally accepted theory is that crude oil was formed over millions of years from the remains animals and plants that lived in the sea. As they died, they sank to the seabed, were buried with sand and mud, and became an inorganic-rich layer [3]. Steadily, the layers piled up, tens meter of thick. Sand and mud became sedimentary rock while the organic remains became droplets of oil and gas.

The composition of crude oil is not unique and homogeneous, it consists of hundreds of different hydrocarbons molecules and a small amount of impurities. Hydrocarbons are molecules that contain mainly carbon and hydrogen atoms, with various lengths and several structures: chains, straight or branching, and also rings. Petroleum, as said, is not a specific compound, it can vary in color, from clear to black, and in viscosity, from like water to like solid. Even the properties are not unique: it is possible having different properties even if the petroleum derives from the same reservoir: time and depth influence this aspect.

Crude oil in its natural state has no value to consumers and must be transformed into products that can be used in marketplace. Different physical and chemical methods are used in refining process. Heat, pressure, catalyst and chemicals are applied under widely varying process designs, operating conditions and chemical reactions to convert crude oil and other hydrocarbons into petroleum products which can be used in everyday life fuels (gasoline, kerosene or diesel).

Separation and transformation of crude oil components take place in the oil refining, which is one of the most complex chemical industries and includes many different and complicated processes with several possible connections among them.

After crude oil is separated into its fractions, each stream is further converted by changing the size and the structure of molecules through cracking, reforming, and other conversion processes. The converted products are then subjected to various treatment and separation processes to remove undesirable constituents and improve petroleum quality.

Petroleum refining processes and operations are classified into five basic types [4]:

1. *Distillation* is the separation of crude oil in atmospheric and vacuum distillation columns into groups of hydrocarbon compounds based on their molecular size and boiling point.
2. *Conversion processes* change the size or the structure of hydrocarbon molecules

3. *Treatment processes* prepare hydrocarbon streams for additional processing and to prepare finished products using chemical or physical separation.
4. *Blending* is the process of mixing and combining hydrocarbon fractions, to produce finished products with specific performance properties.
5. Other refining operations.

In general terms, refineries operate under the physical laws and engineering specifications of the system and the economic principles. Complex interrelationships exist among the physical laws by which a system operates, the product demands required by the market, and the commercial rules and regulations established for the system.

In order to be closer to the cases of heavy fuels, this paragraph will be focused on residues distillation and upgrading process, a basic explanation will be given.

2.1.1 Distillation process and residue composition

A refinery is a group of manufacturing plants, which vary in number according to the variety of product produced. Refinery process must be selected to convert crude oil into more desirable products according to the daily market demands. A refinery must be flexible and be able to change the operative conditions. The conversion of high boiling feedstocks (residua and heavy oils) is not well known as the conversion of conventional petroleum. Significance investments in the processes of heavy feedstocks conversion will be necessary and lots of new technologies must be improved, in order to satisfy the changing pattern of product demand.

The distillation process is extremely complicated and it takes into account chemical reactions and physical separations. Because of the nature of crude oils which is composed of a huge variety of molecules, it would be nearly impossible to isolate every single molecule. For this reason, chemists and engineers deal with this problem by isolating mixtures of molecules according to the mixture's boiling point itself.

The first step is the separation of crude oil into fractions. Crude oil is heated in a furnace at a temperature of about 350°C and charged to a distillation tower. In the distillation tower occurs the separation which it is based on the boiling temperature of the petroleum compounds. The lightest fractions rise to the top of the tower and go out, they condense back to liquid and enters again the column while, the heaviest fractions, go down. The boiling point of the components increases going down the tower.

At the beginning of the petroleum age it was common to operate with one single column, obtaining GPL, gasoline, kerosene, gasoil and atmospheric residuum, without paying attention on the residuum. Since some decades the demand of the light product increase while, at the same time, the light oil reserves are decreasing, therefore a solution had to be found. Nowadays the process operates with two different columns. The first column is known as the "topping column" and from this one is obtained GPL, gasoline, kerosene, gasoil and atmospheric residuum (as before). The atmospheric residuum contains other components that are sent to another column, called the "vacuum column". During petroleum refining, the asphaltenes constituents are no distillable and remain in the residua fuels as the distillable fractions are removed.

Figure 2.1 shows the distillation process for a refinery, with atmospheric and vacuum distillation.

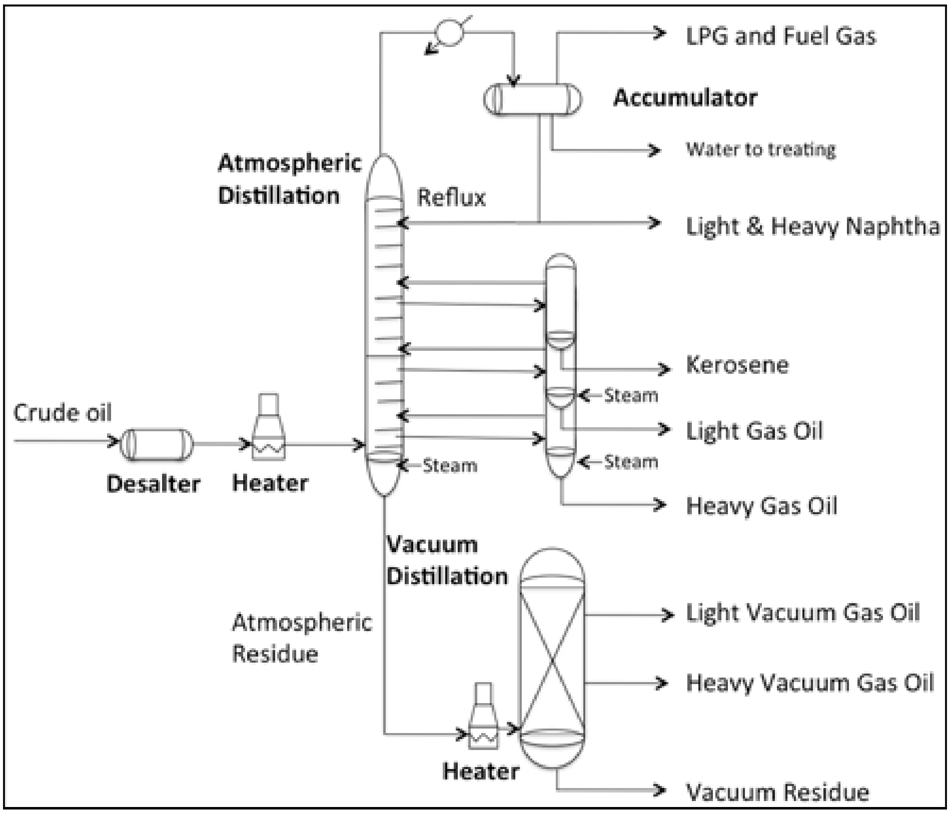


Figure 2.1. Distillation process in refinery.

Two columns are important because materials boiling below about 400° C may recovered by atmospheric distillation, whereas materials boiling up to 625 °C or higher are recovered by vacuum distillation. Residuum generally contains high concentrations of the high molecular weight organic compounds. At the exit of the distillation columns it will be possible to have different oil cuts based on the different boiling point of the compounds, each distillation cuts has a range of components which have similar boiling point and obviously similar properties but, and it is important to focus on this, they are not the same compound. For a certain family of hydrocarbon, the molecular weight, the complexity, the density, the aromaticity and the polarity are very similar to be possible exit the column together.

Finally, at the exit of the tower, the products will be better treated to remove all the impurities which can be presented in the final cuts, one of the treatments could be, for example, the desulfurization.

As said before different cuts are defined according to their initial and their final boiling points [5]. Figure 2.2 represents the distillation curve of different cuts obtained from the atmospheric distillation column.

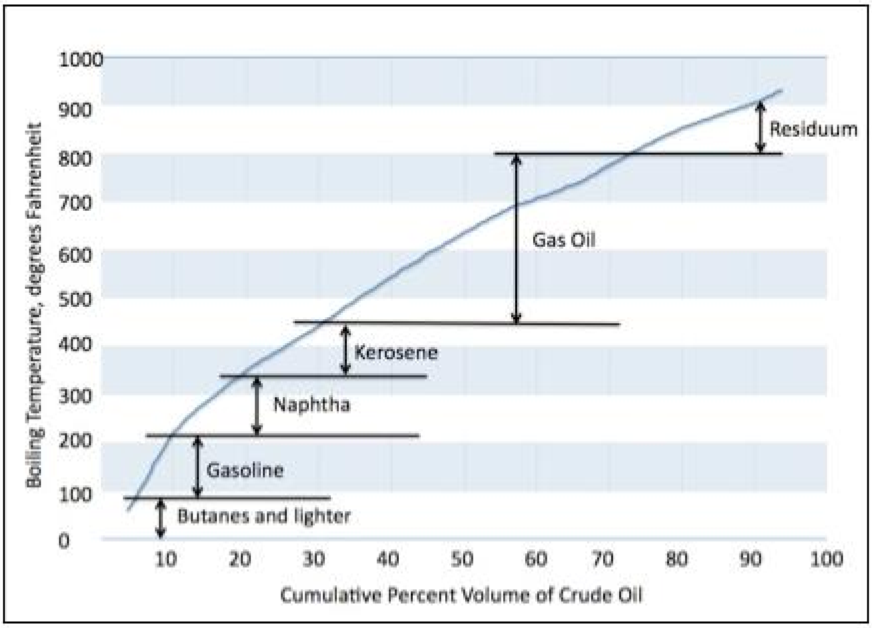


Figure 2.2. Distillation curve.

A list is presented, it is about the main cuts it is possible to recover from oil refining process.

- *Gasoline* is the most important refinery product, a blend of low boiling hydrocarbon fractions. It is distillated from ambient temperature to about 204° C.
- *Naphtha* intermediate that will be processed to make gasoline.
- *Kerosene* is a lighter middle distillate fraction from about 200°C to 250°C.
- *Gasoil* is a heavier middle distillate fraction from atmospheric column distillate from 250°C to 350°C.
- *Vacuum gas oil (VGO)* is the distillate fraction from the vacuum column which have distillation cut points between 350°C to about 550°C.
- *Atmospheric residue* (*AR*) is better known as long residue. It is known only the initial boiling point, around 350 °C. AR was used in the past as heavy fuel while now is used as feedstock for the vacuum distillation.
- *Vacuum residue* (VR) is also known as short residue. Since this residue contains non distillable components, only its initial boiling point is known, it is usually around the temperature of 550 °C.

Unconventional oil, known as heavy oils, extra heavy oils and bitumens, are defined as oils that contains a significant residual part left over petroleum distillation. They represent a significant share of the total world reserves. Heavy oils contain high molecular weight hydrocarbons and elevated levels of heterocompounds.

Due to the impossibility of a molecular characterization of petroleum because of the complex nature, a characterization that has been satisfactorily obtained is thank to fractionation. SARA analysis is the most used method, it classifies crude oil based on polarity through a chromatographic technique.

The chemical composition of residue is categorized in four fractions called *Saturates*, *Aromatics*, *Resins* (which represents the *Maltenes*) and *Asphaltenes* (the acronym is *SARA*).

- *Asphaltenes* are the components of crude oils or residues that are insoluble in light hydrocarbons such as n-pentane or n-heptane while are soluble in toluene. While, they are soluble in liquids of high surface tension such as pyridine, carbon disulfide and carbon tetrachloride.
  Asphaltenes correspond to the heaviest and most polar among all the constituents of oil and residues and, they are not single molecules since they consist in aggregates of different molecules: aromatic, naphtenic rings, methylenic, alkyl chains, sulfur and hydrogen bonds and metals. It is defined a multipolymer system. The average structure of 8sphaltene molecules can be simply described with condensed polynuclear aromatic rings connected to alkyl side-chains.

- *Maltenes composed by Saturates, Aromatic and Resins* is the fraction which is soluble in light hydrocarbon, contains a large variety of compounds that may be separated (usually by liquid chromatography) into the three classes cited up. Saturates are composed by nonpolar hydrocarbons with linear or branched chains. Aromatics correspond to the fraction that contains compounds with one or more aromatic ring linked to the aliphatic chain. Resins are defined as the most polar fraction of maltenes since they are polyaromatic compound.

Numerous investigations have been carried out concerning the *chemistry of the asphaltenes*. The molecular nature of petroleum asphaltenes have been studied for long time, analytical and spectroscopic techniques usually give the mean characteristics of asphaltenes fractions, which is composed of highly differentiated and very complex aromatic molecules, surrounded and linked by aliphatic chains and heteroatoms. It must be specified that asphaltenes and resins are two contiguous classes of components separated from a continuum of molecules according to their solubility in a low molecular weight alkane solvent. Therefore, the size and the chemical composition of some asphaltenes molecules can be very closed to those of some resins.

2.1.2 Heavy fuels

Heavy Fuel Oil (HFO) is a term utilized to describe a huge range of several marine residual oils and some distillate fuels.

Heavy fuel oil are products which derive from the mixtures of residual fuels and distillate. Marine diesel oil or marine gas oil can be added and mixed to heavy fuel in order to arrive to the intermediate viscosity desired. Heavy fuels can have several applications, the main is on the production of electric energy, for the big ships or like alternative to the petroleum for refinery.

Chemical and physical properties and the chemical composition can vary, depending on the native origins and the quality of the heavy oil, the variations of the distillate (cutter stocks) added in order to produce the viscosity required and the different refinery process.

Heavy oils usually have a bigger amount of asphaltenes and resins than light oils components. The importance of the asphaltenes in the petroleum industry is due to its negative impact on various petroleum operations, such as exploration, production, transportation and refining. In exploration, asphaltenes could alter the flow phase of the reservoir; in production, it may plug the wellbore; in transportation, it may precipitate and clot up the pipeline; in refining, it hinders the refinery yields [3].

2.1.3 Characteristics of asphaltenes

- *What is the origin of asphaltenes?*

Asphaltenes can derive from any kind of fossil fuel sources. These sources include the virgin components, all the intermediate which lead to a finished or processed products. The properties and the behavior of asphaltenes and bitumes strongly depend on the nature of the constituents.

There are many different techniques for obtaining the narrow fraction such as vacuum distillation, solvent extraction, thermal diffusion, crystallization and other techniques.

All fossils which are based on oils contain some asphaltenes, ranging from 0,1 to 50 %, however heavy oils contain the highest amount of asphaltenes compared to the lightest fractions. The content and the types of asphaltenes will influence the constitution and the properties of a particular oils.

- *What asphaltenes are?*

There are many definitions for the asphaltenes. In this work it is referred to asphaltene like to the material that is not soluble in light paraffins such as n-pentane or n-heptane. Asphaltene is a colloidal system similar to petroleum, obviously the difference consists in the removal of the light fractions. Since the low boiling molecules have been removed during the distillation process the particles of asphaltenes are grouped together to form larger particles [6].

Asphaltene constituents are from dark brown to black and they are friable solid, they have not definite the melting point. The consistency varies from a viscous liquid to a glassy solid. The elemental analysis shows a predominant amount of carbon (80% w/w), hydrogen (8% w/w), and heteroelements (sulfur, oxygen, nitrogen, nickel and vanadium, whose proportion of them may vary considerably for asphaltenes fractions having different sources). Due to the relatively low amount of hydrogen, the structure is considered as condensed polyaromatic.

Among all the heteroatoms which are presented, the sulfur is one of the most important in petroleum-derived asphaltenes. The distribution of the sulfur in asphaltenes is essentially in the sulfide form. Sulfur is very essential in the generation of the asphaltene, which is colloidal in nature and consists of micelles. The formation of micelles in two no miscible liquids may start with the emulsion polymerization of an associated locus, in fact, in some polymerization processes, the sulfide or mercaptan radical is a useful and necessary chain-transfer agent. During the diagenesis, sulfur may control the size of the micelle.

Furthermore, heteroatoms are essential in the control of the asphaltenes derived from source materials. For example, sulfur is basic for petroleum origin, nitrogen is fundamental for oil shale origin and oxygen is staple for coal origin. The origins of the sulfur in asphaltenes may also be an addition process during geochemical time.

Numerous techniques have been performed to understand the structure of the asphaltene molecule. Figure 2.3 represents a possible structure of the asphaltenes molecule.

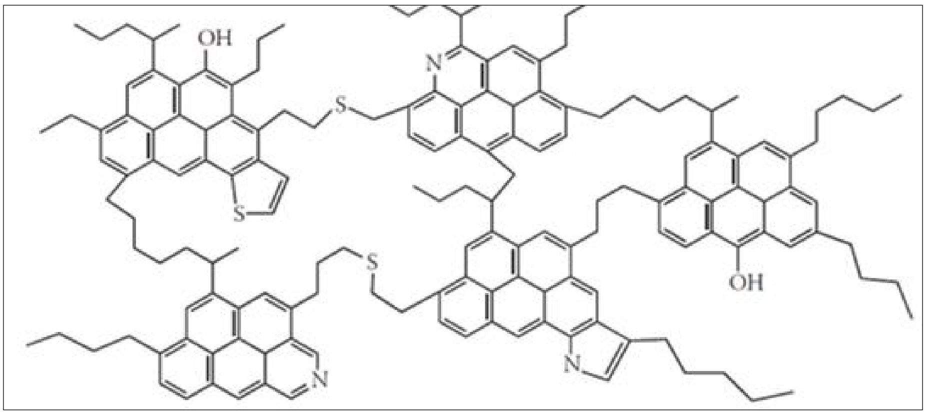


Figure 2.3. Illustration of an average structure for a molecule of asphaltenes.

Wiehe et Al. had the opinion that the molecular weight of asphaltenes is of order of 3000 g/mol and contains multiple islands of polynuclear aromatics of four aromatic rings. Thanks to the methods of Mullins and others, nowadays the most popular vision of asphaltenes molecular weight is of the order of 700 g/mol with only one large polynuclear aromatic ring per molecule [7].

- *Do asphaltenes cause some problems?*

Because of their colloidal nature, the precipitation and the deposition of asphaltenes during production, processing and transportation are the major challenges faced by industries in the last 30 years. In fact, asphaltenes may flocculate during the reservoir exploitation as a result of a change in the thermodynamic (pressure, temperature, composition) or flow conditions. Flocculation and deposition also induce severe damages by fouling and by plugging production and by surface handling facilities.

Below some examples of the problems that arise due to asphaltenes flocculation and/or sedimentation:

- Well bore plugging and pipeline deposition during recovery and transportation operation.
- Water contamination during wellhead storage and in pipelines can lead to the formation of emulsions.

- Sedimentation and plugging during crude oil storage (and during product storage) can occur due to oxidation of the asphaltene constituents.
- Thermally degraded asphaltene constituents are more aromatic and less soluble and appear as sediment during visbreaking and cracking processes.
- A high content of asphaltene constituents in fuel oil often causes ignition delay and poor combustion leading to boiler fouling, diminished heat transfer, stack emission and corrosion.

For these reasons it is necessary to try to decrease their amount.

- *Stabilility of the asphaltenes*

Incompatibility and instability are responsible of the asphaltenes precipitation in crude oil and in the blends with light oil. Stability does not depend only on the properties of the asphaltenes fractions, but also on how good the solvent acts. The first step toward predicting and avoiding problems is knowing how to evaluate asphaltenes stability. Various studies have been leading in order to understand asphaltenes precipitation, and some models and parameters have been proposed to take into account the changes in crude oil composition.

Saleh et Al. determined the compatibility parameters of oil based on flocculation titrations and SARA analysis. The fouling rate for individual crude oils diminished with decreasing asphaltenes content and increasing the solubility blending number. While, Sollaimany and Bayandori studied the influence of different factors on the asphaltene solubility such as composition and structure, to find a correlation between these properties and asphaltenes deposition behavior. According to their results, the stability behavior of asphaltenes was strongly influenced by the structural characteristics.

Several tests based on crude oil are available in the scientific literature to predict asphaltenes precipitation. Some studies indicate that crude oil stability does not depend totally on asphaltenes precipitation, but also on physicochemical properties of disperse and continuous phase. In addition, solubility of asphaltenes depends also on the maltenes fraction. Sometimes it could happen that blends of crude oil are less stable than parent crude oils as a consequence of interaction between them and destabilization of fractions.

Different ways and index are used to describe the stability of crude oils and their blends, like the CII the colloidal instability index or the CSI the colloidal stability index [8].

Fractions obtained by SARA fraction indicates that asphaltenes stability in crude oils depends on different factors. It is possible to say that the methods for predicting the stability have very low efficacy.

- *Parameters of the asphaltenes and model to describe the behavior*

In general, the parameters and the properties that are reported to affect asphaltenes deposition and/or flocculation include: pressure, temperature, chemical composition, asphaltenes and resins concentration in the reservoir fluid, electrokinetic effects induced by streaming potential generation during reservoir fluid flow and water-cut.

Over the last 30 years, several different models have been proposed to predict and to describe asphaltenes precipitation and, also the amount of precipitated asphaltenes [9].

The *solubility models* are the most commonly used for predicting asphaltenes precipitation. The model uses the concept of solubility parameter and assumes that petroleum consists of two phases: asphaltenes and de-asphalted oils.
In 1984, Hirschberg et Al. developed a thermodynamic model to describe the flocculation tendency of asphaltenes in light crudes. They used the Flory-Huggins's theory to calculate the amount of asphaltene precipitate from the liquid phase based on the assumption that the precipitate asphaltene do not change the vapor/liquid equilibrium. Flory-Huggins's theory is based on the assumption that asphaltenes have homogeneous structures and properties.

The *thermodynamic colloidal models* for the asphaltene precipitation are based on the assumption that the asphaltenes exist in the colloidal state stabilize by the resin molecules adsorbed at the asphaltene surface. This theory assumes that the precipitation of asphaltenes is an irreversible phenomenon and that a certain amount of resins is necessary for asphaltenes to be completely peptized in crude oil.

The solubility and thermodynamic models will be better to investigate in the paragraph 2.3.1, where the mixing rule for the sediment content will be better explained.

2.1.4 Residue upgrading process and sediments formation

Concerning the refining process, the decrease of the consumption of fuel oil and the increase in the demand of gasoline and middle distillates necessitate the conversion of atmospheric or vacuum residues into lighter cuts.

Upgrading processes are important for residues to break their long hydrocarbon chains into smaller ones, approaching gasoline or gasoil products, in this way it is possible to increase the yield of the light refined products which are the most requested by the market.

The bottom of the barrel fraction obtained after the vacuum distillation of heavy crude oil has propensity to form cock, or a substance similar to coke, that is called *sediment*. Sediment is formed due to the demand for high temperature needed to break the long chains, it is possible to say that both temperature and residence time are significant parameters that have impact on the process. Furthermore, the sediment limits the conversion of the process because they accumulate in downstream separators, heat exchangers and other equipment [8].

Thermal and hydrocracking processes have been largely studied for upgrading the asphaltenes, present in heavy oil, into useful oil. Chemically speaking, the conversion of asphaltenes to lighter fractions may involve the following combination: hydrogenation of aromatics, transalkylation, cracking, hydrogen transfer or hydrogenolysis. Thermal cracking gives lighter products while catalytic cracking which could be with or without hydrogen (fluid catalytic bed and hydrocracking, respectively) allows the conversion of vacuum distillates.

The main processes involved in the conversion of the asphaltenes are *thermal cracking* and *hydrocracking* [10].

- *Thermal cracking*

At the end of XIX century gasoline produced from crude oil was not used and often was discarded an accumulation of it. However, because of both the demand of gasoline increased with World War I and the increased production of cars during 1920s, more fuels had to be produced in order to respond to market demand. The problem was how to produce lower boiling fractions from crude oil, and the issue was solved in 1913 when the cracking unit were joined into refinery operations and the fractions, which usually were heavier than gasoline, started to be converted into gasoline by thermal decomposition.

Thermal processes comprehend all those operations that are able to break, decompose and rearrange heavy hydrocarbon molecules into smaller fractions, thanks to the heat provided to the solution. The range of the temperature varies between 455°C and 540°C, operating at a relatively low pressure (10 bar).

The feedstocks of the thermal cracking could be both from atmospheric or from vacuum distillation. The major processes used nowadays are:

- Visbreaking: is a cracking operation used to reduce the viscosity of residual fuel oils and residua. The feedstock of visbreaker is the product that arrives from the bottom of the vacuum unit, which is extremely viscous. To reduce the viscosity and to produce a marketable product, a relatively gentle thermal cracking operation is performed. The light product yield of the visbreaking reaches about 30% of the residue and increases the blendstock pool for gasoil. The operative conditions are temperature from 455°C to 510°C and pressure between 3,5 and 13,8 bar.

- Coking: comprehends a series of thermal processes used for the conversion of no volatile heavy feedstocks into lighter and distillable products. It is a severe thermal cracking process and, destroys the residual fuel fraction.

- *Hydrocracking*

The hydro-processes use the principle that if there is hydrogen during the thermal reaction of petroleum feedstocks then, the presence of it will interrupt the reaction which lead to the formation of coke and enhance the yields of some components such as gasoline or kerosene. Most of the time hydro-processes are used to improve the quality of the products.

The feedstock is heated and it is added hydrogen under pressure and using some catalysts. Initially this process was developed for removing the contaminants from atmospheric residue, but the cracking process has been also developed and it gives better results. Hydro-processes are divided into:

- Hydrocracking: is performed at high pressure and the main results is the conversion of the feedstocks into lower boiling products. There is a very low yields of gaseous products.

- Hydrotreating is catalyst process which converts sulfur and/or nitrogen into low sulfur and low nitrogen liquids.

The main difficulty is that in residue upgrading processes all the operative conditions such as temperature, pressure or residence time must be closely checked to avoid the flocculation or precipitation of asphaltenes. During upgrading processes both asphaltenes and maltenes phases change from a chemical point of view, in fact a coke-like substance often forms in the liquid product. This material limits the conversion of the process because it accumulates in the downstream equipment. Moreover, the amount of such materials is not possible to predict or to correlate to the characteristic of the vacuum residue.

The formation of sediment can be related to the presence of heptane insoluble asphaltenes in the residue. It has been suggested that the reason why sediment is formed is because of the precipitation of asphaltenes during the processing. The exact mechanism that occurs is undoubtedly complicated and several explanations have been proposed by literature authors. For example, it has been proposed that asphaltenes are less soluble in the non asphaltenic fraction because of the chemical transformations that occur. Another explication is that the non asphaltenic fraction becomes less able to solubilize asphaltenes due to the chemical transformations that occur or another one more is that lots of asphaltenes are created during the conversion from no asphaltenes, and they eventually precipitate because the solubility limit is exceeded.

Upgrading treatments are used to avoid or at least to limit the sediment formation.

2.1.5 Blending process

Blending is the process which transform less desirable oil cuts into more applicable fuels through the mixing two compounds. The process acts by adding a light distillate fraction, called cutter stocks, to a heavier fuel fraction. The main purpose is to produce an intermediate-viscosity fuel suitable for use it, in this way the final product responds to specific requests and it is possible do not waste the heavy fuel, which use is difficult [11]. The operation is extremely complicated because it must follow certain composition specifications and defined conditions, but nevertheless the fuel cost savings for an intermediate fuel grade are good enough to justify the cost of the blending plant.

The main problem in blending process is that petroleum crude oils and asphaltenes contain oils which derive from petroleum crude oils that have the tendency to precipitate and to deposit organic solid, called *coke* or *foulant*. Even just a small amount results not healthy for the process. Furthermore, the compatibility between two or more fuels could be an issue, for this reason several tests must be leaded for any new fuel before using it indeed, incompatible fuels may produce sludge or sediment. The different compounds that it is possible to use depend on the refinery product, so blending depends on the refinery and on the light/heavy oil composition.

A blending unit is located to mix the two (or more) fuels in the appropriate proportion before to feed them to a blended fuel supply tank.

Because of the cuts present different chemical compositions, incompatibility problems may occur during the blending process, which is considered one of the main sources of sediments in fuels. Some cutter stocks could have stabilization effects while other lead to destabilization.

The aim of this internship is very important, it will be possible to use also the heavy fuel and do not waste them, but before that it is necessary understand the behavior of the blends and their properties, moreover the sediment contents which cause problems to the equipment .

2.2 Residual heavy fuels composition and properties

The classification of the fuels is based on their applications and their physicochemical properties. The general oil classification is related to crude oil's ease to flow and consequently it denotes specific technical characteristic of their production, transportation and refining. Nowadays it is possible to find different definition for fuels, for example oil companies gives an economical meaning while refineries adopt criteria based on the properties, such as density or viscosity.

Due to the high variability in composition, heavy fuels have different physicochemical property and, for this reason, it is difficult to describe them as a unique species, also an elemental characterization is extremely hard, precisely because of its complex nature. Because of the big amount of several properties it is possible to give different definitions for the heavy oils.

Specifications concern global properties that every kind of fuels have. The most important properties are the following:

- *Density* is considered as an input variable for describing many other fuel properties and most important is unique for each component and it needs an exact measurement. Density is temperature-dependent and in some cases it is also time-dependent. In fact, the density of spilled oil will also increase with time, as the more volatile (and less dense) component are lost.

- *Viscosity* is an intrinsic property defined as the resistance of a material to flow, the lower the viscosity of a fluid, the more easily it flows. Such as for density, viscosity is related to temperature. It is very important property because it affects the rate at which spilled oil will spread, the degree to which it penetrates in the substrates. The importance of the viscosity plays an important role about the transferring of oil in pipes. Sometimes viscous and gel-like heavy fuel must be heated before their transport because of the difficult in flowing. Furthermore, it is important to specify that various studies confirm that viscosity has a molecular origin and so, it can be an indication for molecular interaction.

- *Reflex Index* is easily to be measured and it is correlates to density. It is also been used to determine solubility parameters of crude oils for asphaltenes stability modeling.

- *CCR* is the fuel tendency to form carbon residue during a combustion and it indicates the formation of the coke. It has also abrasive effects which could be presented on the engines. The amount of carbon residue is correlated to the asphaltenes content, if there is an increase of the CCR it is been observed an increment of the asphalthenes content.

- *Sulfur content* is important moreover for the downstream processes such as catalytic reforming. During the spill, the sulfur content becomes a health and safety concern for people who works there.

- *Surface tension and Interfacial tension* is the force of attraction between the molecules at the interface of two fluids. The surface tension of an oil, together with its viscosity, affects the rate at which an oil spill spreads. Air/oil and oil/water interfacial tension can be used to calculate a spreading coefficient which gives an indication of the tendency for the oil to spread.

2.3 Mixing rules

Research into the properties of mixed crude oils has been one of the most important and researched topics both for refineries and for oil transportation of the last decades.

A mixing rule defines mathematically the evolution of a certain property based on the composition of the mixture. Properties are difficult to calculate, especially when it is a mixture. It is possible to have two different type of mixing rule which depends on the specific property considered: it could be linear or non-liner. In chemistry the linear property could be based both on the weight or on the volume, it depends on the property. For a certain property, denominated X, a linear mixing rule is described by equation (2.1) and (2.2):

$$X_m = \sum_i w_i X_i \tag{2.1}$$

$$X_m = \sum_i V_i X_i \tag{2.2}$$

Where X represents the property, W the weight proportion, V the volume, m indicates the mixture while I the component.

To deal with nonlinearities, industry started to rely an “index number” or “factors”. The intention was to use a linear relationship in calculations, even if in the latter part of the last century several no linear models have been developed.

2.3.1 Sediments contents mixing rule

In the scientific literature, no mixing rule have been tested or found for sediments content. Some studies tried to correlate the heavy fuel sediments contents to petroleum properties such as nitrogen or sulfur.

Since the demand of light oil is increasing by the time, in the last decades it was important try to use also the heavy part of the petroleum by adding light oil as diluents, like said previously. The problem is about the sediment deposition [2]. For this reason, it was and still be important to understand the mechanism. The sediment deposition has effect on the power plant. Figure2.4 represents a scheme of a plant, the circled area indicates the location of sediment the deposition.

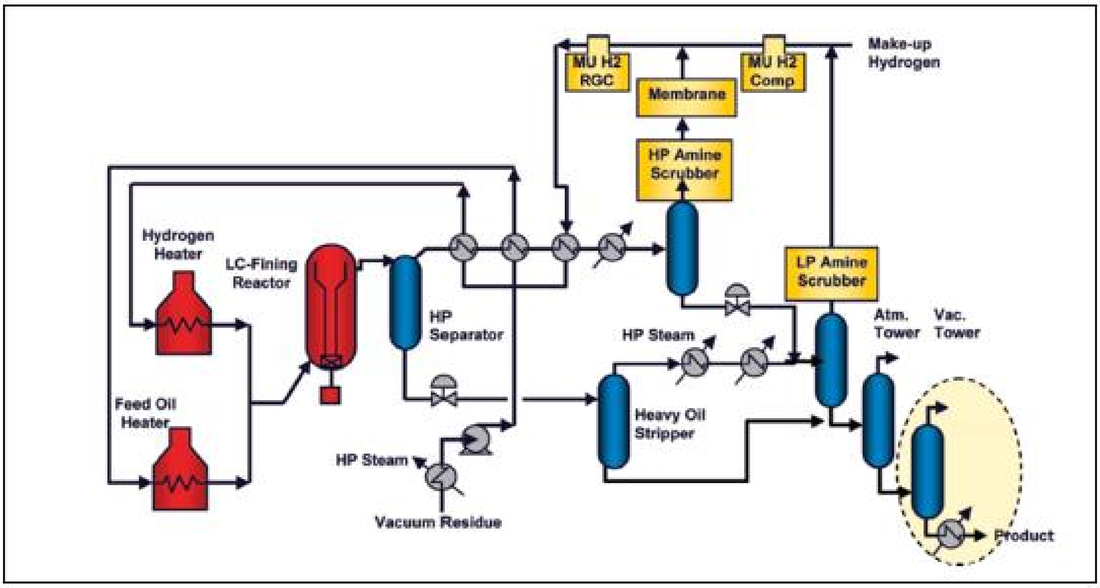


Figure 2.4. Typical LC-FINING process flow diagram. The circles area indicates the location of the sediment deposition.

Sedimentation is still difficult to define, and regardless of the progress in understanding the foundation of the sediment formation during residue hydroconversion, it is still difficult to predict quantitatively it in a commercial scale. It is known that the hydroconversion process modifies the solvent power of the residual oil maltenes fraction while the unconverted asphaltene cores after the cracking become more aromatic and condensed. All these changes induce the precipitation of the most aromatic and condensed molecules in the solution.

Many people, since 40 or 50 years, have worked to find a theoretical correlation but without achievement for the sediment deposition. It is possible to find a theoretical correlation, the problem concerns the physical properties which play an important role, because sometimes some properties are difficult to be measured, such as the solubility of the asphaltenes.

In the past, empirical and semi-empirical correlations have been developed for predicting the sediment deposition. A large amount of date in the literature indicates that the thermodynamic models are superior to the empirical models. Another difficult thing that must be reached is a correlation of a ternary blends, also in this case the scientific literature is not able to help, because from a theoretical point of view it is extremely difficult. It is presented below the comparison of two works: the first one pursues a theoretical approach while the second one follows an empirical method.

Theoretical approach

In 2008 Sundaram et Al.[12] worked on a thermodynamic model able to predict the sediment deposition, because of sediment deposition in the downstream equipment sometimes affects the overall economics by limiting the operating conversion.

In their work, the sediment was measured by SHFT value (Shell Hot Filtration Test method). The SHFT value approximately measures that portion of the asphaltenes which are insoluble in the heavy oil. A portion of the asphaltenes deposit in the separation section of the power plant and cause an increase of the pressure drop across the equipment.

Sundaram et Al., affirm that asphaltenes is not a simple molecule such as benzene or naphthalene. Because of its complexity, it must be defined by its *solubility*. It is measured by the SARA analysis, which measures the residue in terms of SARA fraction, which are soluble in a particular solvent. Therefore, physical properties like the molecular weight or the hydrogen content can vary from feed to feed.

To better understand the sediment deposition it was important to understand the structure of the asphaltenes, and some hypothetical chemical structures had been proposed. It is important to underline that the structure is only used to explain the basis of the model they proposed, it does not necessarily represent the structures proposed by other authors. It contains five and six member rings with heteroatoms, small and long aliphatic side chains are attached to the ring carbons. The number of rings, H/C atomic ratio and molecular weight are feed source dependent.

Solubility Approach

Asphaltenes are considered in solid form and the solubility model is developed assuming that it is in equilibrium with the fluid which is surrounding.

The solubility model is based on a thermodynamic approach and it has two parameters related to asphaltene: solubility and molecular weight. All the other parameters are related to the surrounding fluid, and they are not considered. For the model proposed in this work, asphaltene (the solute) is in equilibrium with the heavy oil (the solvent) and it is possible to apply equation 2.3:

$$K_i = \frac{X_s}{X_l} \tag{2.3}$$

Where X_s and X_l are the mole fraction of the asphaltene in the solid and liquid phases, respectively, and the K_i represents the equilibrium constant for the i-th phase.

The equilibrium condition between asphaltenes phase A and solvent phase B is correlated by equation 2.4:

$$\mu_i^A = \mu_i^B \tag{2.4}$$

The activity coefficient of asphaltenes (a_s) can be written as the equation 2.5:

$$\ln(a_s) = 1 - \frac{V_s}{V_l} + ln\left(\frac{V_s}{V_l}\right) + \frac{V_s}{RT\,(\delta_1 - \delta_s)^2} \tag{2.5}$$

In this model the solubility parameter is treated as an optimizer parameter. For this reason, the solubility parameter was calculated by considering the asphaltenes activity coefficient as unity, it means that only asphaltenes is presented in the asphaltenes phase, the asphaltenes equilibrium is given by equation 2.6:

$$\ln(K_s) = 1 - \frac{V_s}{V_l} + ln\left(\frac{V_s}{V_l}\right) + \frac{V_s}{RT\ (\delta_1 - \delta_s)^2} \tag{2.6}$$

Equation 2.6 predicts the maximum amount of asphaltenes deposited, where the molar volume V and the solubility parameter are unknown, because R is the universal gas constant and T is the absolute temperature.

The solubility parameter (δ), for the liquid phase is calculated by equation 2.7 according to Hildebrand’s definition:

$$\delta = \left(\frac{\Delta E}{V}\right)^{0,5} = \left(\frac{\Delta H_v - RT}{RT}\right)^{0,5} \tag{2.7}$$

Where ΔE is the internal energy of vaporization and ΔH_v is the heat of vaporization. When the phase assumed for asphaltenes is solid, the solubility parameter has to be read as equation 2.8:

$$\delta_{solid}^2 = \delta_{liquid}^2 + \frac{\Delta H_f}{V} \tag{2.8}$$

Where ΔH_f is the heat of fusion. Heat of vaporization and heat of fusion are extremely difficult to calculate for asphaltenes, this is the main problem for the solubility method. The molar volume is related to the molecular weight.

For the solubility parameter Rogel concluded it is linked to the H/C atomic ratio and he found a correlation:

$$\delta = 35{,}87 - 10{,}477\ (H/C) \tag{2.9}$$

Sundaram et Al, studied also the effects of different diluents, Figure 2.5 shows it.

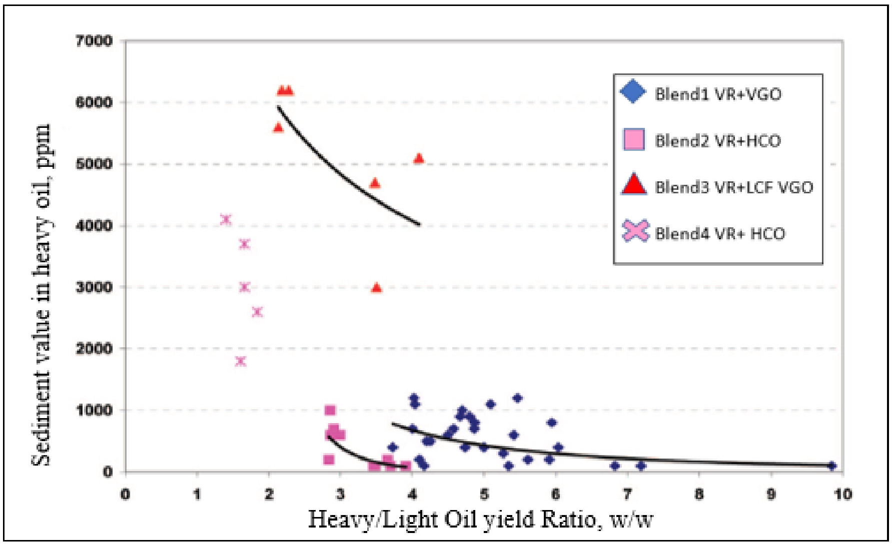


Figure 2.5. Effect of adding different diluents on sediment value for processing Arabian heavy vacuum residue.

The Arabian heavy vacuum residue was processed with two different diluents: VGO and heavy cycle oil. In this case the blend with VGO has the highest sediment level. Their study concluded that the molecular weight of asphaltenes decreased with the increasing of the aromaticity and the decreasing of H/C atomic ratio, and this depends on the diluent.

The solubility model based on the thermodynamic theory has as key parameters the molecular weight and the solubility parameter of the asphaltenes. These parameters were not measured directly, but simply estimated from the data. This is what makes the thermodynamic model inefficient from a practical point of view, it would not give an accurate industrial estimate.

Empirical approach

Most of the thermodynamic approaches were not able to give precise information about the sediment deposition. Empirical approaches have been developed to find the behavior of the sediments. In this report the work of Stratiev et Al. have been reported.

Stratiev et Al.'s approach

The study of Stratiev et Al.[2], made in 2016, was based on the effect of vacuum residual oil feed source on the process of sedimentation in the H-Oil hydrocracker (which it was a new residue for the plant).

In their studies, eight vacuum residual oils (VRO) were processed in the LNB H-Oil hydrocracker. The evolution of the sediment content was studied in blends of hydro-converted residues and fluid catalytic cracking gas oil (LCO and HCO) which were used as diluents. It was important knowing physical and chemical properties of the vacuum residual oils and of the fluid catalityc cracking (FCC).

The study had been focused on the TSE content and it was proposed a linear correlation between the Total Sediment Existent (TSE) and the Total Sediment Potential (TSP). TSE is equivalent to the hot filtration test of the residue sample. The hot filtration test means that the residual oil sample is filtered through an apparatus (the procedure is described in paragraph 3.3.2). TSP is equivalent to the hot filtration test of the residue sample that has previously stayed at 100°C for 24 hours.

In first analysis, the asphaltenes content and the stability had been demonstrated to be the best parameters that correlate the tendency of a specific residual feedstock to form sediments during the hydro-conversion.

Some "rules" have been understood during this period. The VRO processed differ significantly in their asphaltenes content and the stability of the asphaltene fractions of the VRO considered could be judged by the colloidal stability parameters. The VCO feedstocks have been characterized by a very high colloidal stability and by the absence of any kind of sediments. It was noticed a correlation between the colloidal stability and the asphaltenes solubility and, it was also observed that, the lower is the ratio H/C the higher is the solubility parameter, and of course the lower is the solubility. Based on this perception it would be possible to try to estimate the trend of the mixtures.

It was studied the relationship between H-Oil and the VTB (vacuum tower bottom) sediment content. Even in this work has been confirmed that sediments were mainly formed from aggregation of the asphaltenes contained in the H-Oil residual oils, since the asphaltenes are concentrated in the VTB after evaporating the VGO from the ATB (atmospheric tower bottom) in the vacuum distillation column. The previous experience with EBR (ebullated bed residue, used to hydrocrack residuum) hydrocracking ATB and VTB products sampled from a pilot EBR H-Oil hydrocracker showed that VTB product had a lower sediment level than ATB product. Contrary to this expectation the LNB H-Oil commercial unit exhibited that the VTB product had a higher sediment level than the ATB product.

Another thing was noticed, and maybe is the most important one. Because of the asphaltenes are the most aromatic compounds, authors followed the rule "*like dissolves like*", and several samples of VCO having different sediment content have been blended with the same cutter stock. Figure 2.6 presents the result of their work.

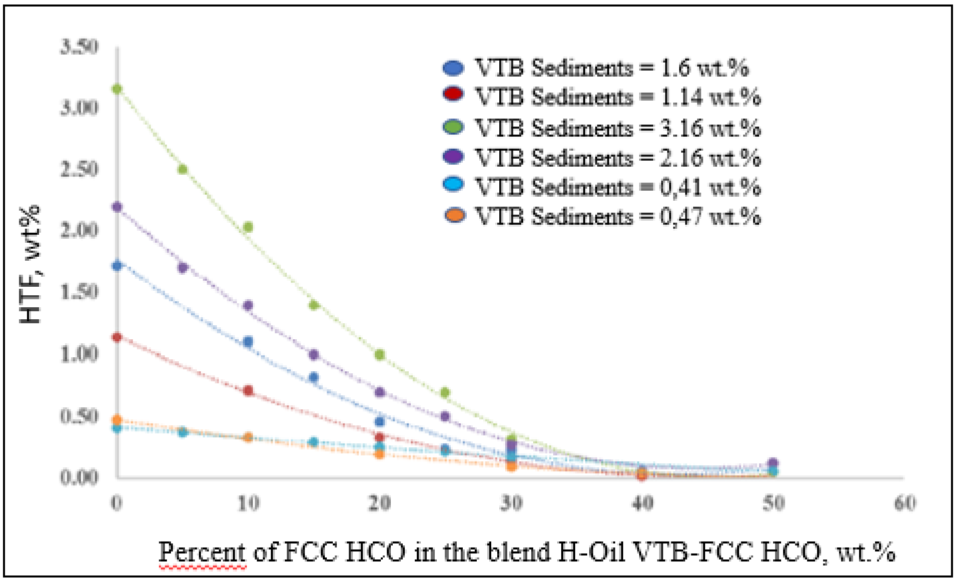


Figure 2.6. Sediments content evolution in blends of different hydroconverted residues mixed with different amount of HCO.

Figure 2.6 shows that the addition of the high aromatic FCC HCO (the cutter stocks) to the H-Oil-FCC VTB (heavy oil) samples leads to a reduction of the TSE, the figure shows also that the higher is the TSE, the higher is the reduction effect of the HCO on the blend. In the concentration range between 0-25%, the dependence of the blend on the FCC HCO could be seen in the neighborhood of a straight line. So, it is possible to say that, the sediments disappearance is relevant with the stabilization of the asphaltenes. The author suggested that the trend of the curves could be approximated by a third order polynomial equation, but they did not write any detail about the equation. Moreover, another cutter stock was taken into account to be compared with the effect respect the previous one, LCO was compared to HCO, but not significantly differences have been observed between the both cutter stocks. Of course, based on different cutter stocks the trend could be significantly different.

A correlation between the sediment content and precipitation of the asphaltene had been found. Although the mechanism of the precipitation has been objective of the last decades, no physical models is able to describe the sediments content in the petroleum products, even from asphaltenes precipitation behavior.

It was also studied the effect of the different feeds on the sediment level of the unconverted H-Oil VTB. Stratiev et Al. analyzed the operation of the LNB H-Oil hydrocracker during processing of three VRO feedstock blends. During the process the asphaltenes H/C ratio decreased, while the maltenes H/C ratio increased. That means that asphaltenes becomes more aromatic, while maltenes more saturated. This behavior was in common for all the three feedstocks. Based on this data it is possible to conclude that the sediment level depends on the asphaltenes solubility (H/C ratio) and on the maltene H/C ratio (solubility power). The lower is the difference between the two ratio and the lower the sediment content is.
It was important because it means that the origin of the feedstocks plays a role in the sediment contents.

Sanaz Hajjami's approach

The objective of the study, made in 2018 at the IFPE, was to determine mixing rules for specified properties of heavy fuels. Hajjami followed an empirical approach, based on Stratiev et Al.'s work, in order to develop an original model able to predict sediments content. The date collected were taken from a previous database and from some new experiments made.

Several constraints had to be taken into account for the building of the mixing rule:

- Mixing rules had to be related to the properties and the proportions of pure components in the blends.
- Model should be applicable in the industry, therefore the parameters of the model had to be easily measures in each refinery from standard methods known.

In Hajjami's work [13], several residues (RS) have been used to build the sediment content mixing rule. The RS came from Ural, Cerro Negro, and AH (six in total). And several residues have been used after to validate the model found. Even many cutter stocks have been used: HVGO, Liqtot, GO, ARO, DAO, HAGO, HCGO, HCO, LCO, VGO, and SLO. Many binaries blends have been created mixing the RS and the cutter stocks in different proportion. To be able to look at the trend. Furthermore, ternary blends, mixed with different composition with residues, have been created to find a more general law.

The mixing rule was built to predict the sediment content in blends, using more than one hundred binary mixtures achieved between hydroconverted and several cutter stocks. In order to determine the equation.

The model was created by following the next steps:

1. In first approximation, the model was calibrated to predict TSE content in a wide range, this was to limit the effects of the measurement inaccuracy. For example, a residue was mixed with 8 different cutter stocks in different proportions. The results, presented in Figure 2.7, showed different trends. For the VGO is possible to notice a linear trend, which is related

to the dilution effect of the sediment. Whereas, two different trends can be seen: the GO and the aromatic (LCO, HCO, SLO) blends. For GO the TSE content in the blends are higher than the ones obtained by the pure residue. For the aromatic, the TSE content is weaker as the dilution is higher. It was notices, again, that the TSE effect of aromatic cutter stocks is in accordance with the study of Stratiev et Al. Respect to Stratiev et Al.'s work, more cutter cuts have been used. SLO is a stronger stabilizer than HCO and LCO.

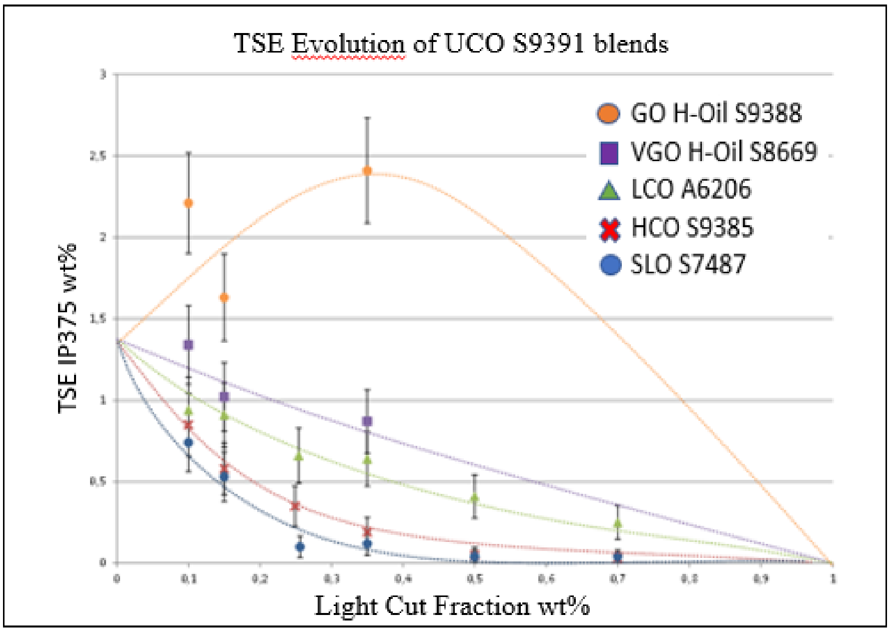


Figure 2.7. TSE content evolution of UCO S9391 mixed with different cutter stocks.

Stratiev et Al. proposed a polynomial model, while Hajjami's assumed an exponential equation (2.13) since it can describe the three observed trends with only one fitted parameter:

$$TS_m = W_R \cdot TS_{0,R} \cdot e^{-k\,W_{CS}} \tag{2.13}$$

Where TS represents the total sediment content, *k* the rate of cutter stocks power, W the weight proportion of the components, 0 is for the initial time. *m* is mixture, R residuum and CS cutter stocks.

The equation had to be able to describe the behavior both of the cutter stocks and of the residuum in the blends. Several types of equation have been tested and the equation found was formed by two part: the linear trend which describes the sediment dilution effect of the cutter stock, while the curve one, which is exponential, describes the sediment stabilization or destabilization effect.

Stabilization effect leads to dissolution of some sediments and consequently the sediment content of blends is lower than what was expected with the dilution effect. While destabilization effect means the creation of some sediments in the mixture and consequently a higher sediments content than the one expected with the dilution effect. The main problem is that both dilution and stabilization/destabilization phenomena occur at the same time during blending, but the intensity of each phenomena depends on the cutter stocks used and on the concentration.

2. Then, it had to be understood the physical/chemical meaning of the parameter *k*. It was clear that *k* depended on the cutter stocks used. Since it was assumed that residue did not play any important rule in the stabilization/destabilization effects, *k* could be related only to the properties of the cutter stocks. The stabilization power of each cutter stock had been considered unique. This value had been correlated to cutter stock properties using the mean square method to fit the experimental data.
   Several filtrations have been leading in order to see what the trend of the blends was. Figure 16 shows the normalized TSE content values according to the initial TSE content of residue (RS U217-3013-8). Results show that, although the TSE measurement are inaccurate, the global trends of each cutter stocks have been satisfactory predicted by the model.

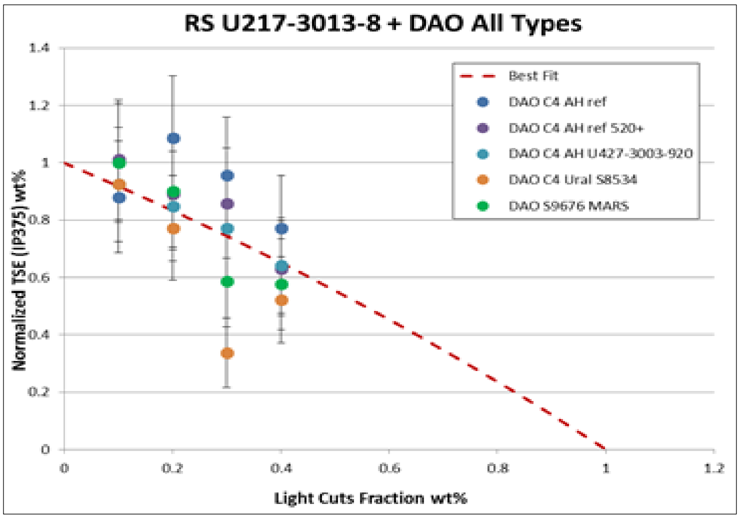


Figure 2.8. TSE content evolution for RS U217-3013-8 mixed with 8 types of DAO

The relation between *k* and the properties. Due to the fact that the more the cutter stocks are aromatic and the more the stabilization effect is noticed, one of the properties of the cutter stocks took into account was the carbon aromatic content and the equation which describe it is:

$$k = \mathrm{a}\, C_{aromatic} - \mathrm{b} \tag{2.14}$$

For equation 2.14 the coefficient a and b are known, but they are reserved information.

The most common property related to the aromaticity of petroleum products is the *density*. The result showed it was difficult estimate an average for *k* using these two properties. In fact, using both parameter some cutter stocks had to be excluded because their density was quite similar but a significant effect on the sediment (such as HCGO and LCO) due to the difference in their aromaticity. For this reason, another *k* was assumed able to correlate boiling temperature, which was measured by simulated distillation, and density, without considering the aromaticity. It is given by equation 2.15:

$$k = a\,T_{SD} + b\,\rho + c \tag{2.15}$$

Unfortunately, it is not possible to know the exact values of the coefficient because the information is confidential.

3. Then, the following step of the study was the evaluation of the model performance in the prediction of sediment content in heavy fuels using a set of blends that were not included in the database.

The model found is able to describe well enough the behavior of the cutter cuts, because it considers both the properties of the cutter stocks and of the residue.

This internship starts from the knowledge that Stratiev et Al. have left about the using of an empirical approach and reach Hajjami's work, considering properties of cutter stocks and residues.

2.5 Conclusion of the literature review

Heavy fuels are mixtures composed of refined petroleum cuts such as distillation residues and lighter cuts, better known as cutter stocks. With the increasing demand for light oils, refiners have taken a keen interest in converting vacuum residuum into distillates. The problem is that during the conversion process there is the creation of sediments. In commercial application, sediment deposition affects heat transfer and pressure drop. Sediments come in different form: it can be hard like coke or in a gelatinous, gummy form. It is important to understand the mechanism of the deposition, the common opinion is that sediments are primarily caused by the precipitation of asphaltenes following complex incompatibility phenomena. For this reason, the chemistry of asphaltenes have been studied and analyzed to better understand the origin and the cause of the sedimentation. The importance of this part of the work is to understand the molecular origin of the deposition due to the structure of asphaltenes.

Every property can be described by a mathematical law. Mixing rule is a mathematical law able to predict properties of the mixtures knowing the proportion and the properties of the pure components. The main problem is that most of the time there is no a linear correlation between the property and the concentration, for this reason building a mixing rule for all the properties is very complex and it takes many times. During the years, a big quantity of mixing rules has been built for the more common and used properties of heavy fuels, except for the sediment contents. The aim of the internship is to find the equation able to describe the behavior of the sediment deposition, the approach used is empirical.

Based on the knowledge of the literature, it is now evident that the use of a theoretical approach it is possible and mostly preferable but, is very difficult to follow it because of the physical and chemical characteristics of the asphaltenes. Many thermodynamic laws have been found but it is still difficult to correlate the mathematical parameters to a physical meaning, and many scientists are not able to find the correlation, since they are working on this topic since long time. Moreover, it is particularly difficult to find some of the properties of the heavy oil, such as the solubility of the asphaltenes.

The study of Stratiev et Al. was based on an empirical approach and was able to build a polynomial equation, it was noticed that the decreasing of sedimentation increased with the aromaticity of the cutter stocks, following the common chemical law “like dissolves like”. Another thing found was that the origin of the residues is important.

Hajjami discovered an exponential equation able to describe the sediment deposition, taking into account properties of cutter stocks and of residues, and trying to understand what where the important properties. Stratiev et Al.’s work has been followed and the properties of cutter stocks considered was the carbon aromatic.
Based on these considerations an empirical approach has been followed.

Following the empirical model means that lots of experiment must be done to find the mathematical correlation. The difficulty is on the relation between the physical property of the model and the mathematical model found. It is necessary to find a relationship between the mathematical and chemistry/physics using the empirical approach.

Chapter 3 will present the methodology and the experiments realized to reach the purpose of the study.

3. Methodology and experiments

The chapter presents the experimental methodology of the work done in IFPE during the internship lasted 6 months and it is a continuation of the work done by Sanaz Hajjami in 2018.

The general form of Hajjami's equation is corrected, but it needs some improvement. In order to get it better, more experiments (or rather more filtration) on sediments content are necessary to know the sediment deposition of many blends. Having a bigger database about sediment content will be helpful to find a general equation that can be utilize for every mixture and not only for the ones studied.
Obviously, not only sediments content is necessary, but also new and more properties than the ones used previously are necessary to be considered. For this reason, many properties of the pure components and of the blends will be measured. Different methods are used to measure the properties of heavy fuel that have an influence on the behavior of sedimentation.

3.1 Mixing rule

In scientific literature is possible to find mixing rules proposed for several properties of the heavy crude oil, such as density or viscosity, but one of the exceptions is represented by the Total Sediment content (TS) or surface tension for example. The main objective of the internship is to find the Total Sediment content mixing rule and for doing that it is necessary to have available a huge quantity of blends. Studying the deposition of their sediment, in order to be able to plot how the sediment change while the increasing of the concentration of the cutter stocks, and measuring the properties of residues and cutter stocks, because as Hajjami understood: the deposition of the sediment particles depends on both of them.

As said in paragraph 2.3, it is possible to have two types of mixing rule: linear or no linear. Linear mixing rules are able to predict the property of a mixtures which is directly proportional to his weight or his volume. Weight dependency is easier to use in this specific case where components are weighed before making the blend of interest. On the other hand, the no linear mixing rules are no directly proportional and it is much more complicated to study the relationship. Sometimes it could happen, like for sediments content, that the deposition is linked to other properties and many properties must be considered.

As said, mixing rule for sediment content is not simple to be found: sediment deposition depends on many factors and many properties. Density, viscosity, SARA fractions, elemental composition, AC7 (Asphaltenes precipitated by heptane), surface tension, carbon aromatic and simulated distillation are properties which play an important role and they are measured.

The properties are measured by the candidate or by the expert technicians. Only the surface tension was measured in a laboratory located next to Paris and not in IFPE.

3.1.1 Mixing rule quality

The equation found by Hajjami must be improved, it is tested comparing it with new equations developed during the internship.

The quality of the prediction can be estimated by four different criteria. At the end of the internship the criteria will be applied to confirm or to not confirm the validation of the model found, and also to say if the new equation found will be better or not respect to the equation proposed by Hajjami.

1. The proportions of predicted values which were in the experimental confidence interval of the measured method.

2. The RMSE (root mean square root) evaluate the standard deviation of predictions.

   There are two different types of RMSE, the RMSEc obtained during the calibration step for the building of the model, and the RMSEp obtained during the validation of the model. They are two values which are different because the mixtures considered are different, in fact for the validation of the model the mixtures used for the creation are not considered.

   The general result for the root min square root is given by equation:

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(\hat{y}_i - y_i)^2} \tag{3.1}$$

3. The average relative error (ε) is given by equation:

$$\varepsilon = \frac{1}{n}\sum_{1}^{n}\frac{|\hat{y}_i - y_i|}{y_i} \tag{3.2}$$

4. The β in order to evaluate if the predictions are globally under or over-estimated and it is given by equation:

$$\beta = \frac{1}{n}\sum_{1}^{n}(\hat{y}_i - y_i) \tag{3.3}$$

Where:

n represents the number of measurements,

ŷ is the predicted value,

y is the measured value.

3.2 Internship and experiments

A first approximation of the equation able to describe the sediment deposition (equation 2.13 showed in paragraph 2.3.1) had been found previously by Hajjami and the structure is maintained also in this internship, even though more information are added. In fact, previously as it has been explained in paragraph 2.3.1, the model was formed by a curve and by a linear trend, while now it is composed by three part: the linear trend, the residue effect and the cutter stocks effects.

The linear trend takes into account the dilution effect, the parameter α (which is added to the equation) considers the residue effect (which means the properties of the residue) and the exponential trend concerns the stabilization or destabilization effect of the sediment, which depends on both the residue and the cutter stocks. The three phenomena occur at the same time during blending, but the intensity of each phenomena depends on the properties of the cutter stocks.

The main work followed during the internship is divided into three principal parts and it explains what the procedure to build the model is:

1. The first step of the internship concerns the understanding of the general form of the model. To reach that knowledge several new blends are created. Firstly, 60 binary mixtures using three residues and four cutter stocks used also by Hajjami in her internship. The importance of the using the cutter stocks utilized also previously is because the values of the parameter *k* for that cutter stocks are known, otherwise would not be possible. Of course, the parameter *k* found by Hajjami and used by me is only a first approximation, a better value will be determined. In the first step not only the mixtures created by me are taken into account to determine the model but also he mixtures of Hajjami.

   Firstly, the blends are created to study the effect of the residue, in fact the new parameter, α, concerns the properties of the residues. Several new equations are tested which contain the α parameter. The least square method is used between each new equation and the one of Hajjami, using a solver on Excell the value of the new parameter of the equation is found, minimizing the different between the new and the old equation.

   In a second moment, the focus was on the importance of the cutter stocks and on the parameter *k*. Many new blends are created with only one residue and 26 different cutter stocks. It is been though to use only one residue because the effect that many residues have with the same cutter stocks does not change. Another important reason was based on the time available. In fact, because of the number of experiments is very large, it has been necessary to make a compromise.

   In this way it is possible to assume the form of the model and know a first approximation of the values of the parameters α and *k*.

2. The second step concerns the knowledge of parameters α and *k*. In the first step, only a numerical value of α and *k* is known but not the mathematical equation which describes the parameters, which are both function of the properties of the residue for α and of the cutter stocks for *k*. To solve this question, all the properties of cutter stocks and residues must be known, and many experiments for the measurement of the properties must be done. Thanks to the knowledge of many properties of the pure component it is possible the use a Software which is able to correlate the chemical and physical properties to the two parameters.

3. The final step is the validation of the model found. At this point the form of the model is known and also the form of the equation for α and *k*. For the validation part, ternaries mixtures are considered, in this way it possible to say if the model is better than the one that Hajjami built and if it works also for ternaries mixtures.

3.3 Database

In order to develop the mixing rule an extremely huge database it necessary, taking into account several different kind of mixtures, binaries and ternaries, and the properties of the mixtures or of the pure components used.

3.3.1 Blends and components

The production of heavy fuel from residual hydro-processing effluents has been studied in IFPEn since many years. Different mixtures were made in different proportion through the mixing of residues and of cutter stocks. Some properties have been measured for pure component but not collected into a general database: the first step of the previously internship had been to complete the database with all the information obtained from the experiments about the properties of residues and cutter stocks, the database is increased also with the blends created by the candidate.

In the previous work the database contained 92 different residues and 88 different cutter stocks. In total there was 416 binaries and 79 ternaries combination. In this internship 4 different residues and 27 cutter stocks are added and studied, for a total of 114 binaries and 96 ternaries added to the previous database. For every new sample created, all the properties have to be known and added to complete the database.

Tables 3.1 and 3.2 indicate the residue and the cutter stocks used to understand the parameter α. It is not possible to show the origin of the components used since it is a reserved information.

Tables 3.3 and 3.4 indicate the residue and the cutter stocks used to understand the parameter *k*. Even in this case it is not possible to show the origin of the components used.

Table 3.5 shows the ternary mixtures created for the validation of the model, since it is extremely important that the validation is done on blends did not use for the building of the model.

Table 3.1. Residues used for the linear trend.

Cut	*Ref. (unity test period)*	*Origin*	*Initial TSE just before blending*
RS	U217 3007 7B	-	0,80
RS	U217 3018 25	-	0,77
RS	U217 3009 16	-	0,51

Table 3.2. Cutter stocks used for the linear trend.

Cut	*Reference ID*	*Origin*
LCO	LCO S6206	-
LCO	LCO Burgas S9387	-
HCO	HCO Burgas S9385	-
VGO	VGO H-Oil S7485	-

Table 3.3. Residues used for the curve trend.

Cut	*Ref. (unity test period)*	*Origin*	*Initial TSE just before blending*
RS	U217 3023	-	0,80

Table 3.4. Cutter stocks used for the curve trend

Cut	*Reference ID*	*Origin*
HCO	HCO S9358	-
	HCO S3001-8	-
	HCO S8834	-
	HCO S9702	-
	HCO S9702-3	-
	HCO S9385	-
VGO	VGO S7124	-
	VGO S9384	-
	VGO S9149	-
	VGO S5469	-
	VGO S7485	-
SLO	SLO S9386	-
	SLO S8836	-
DAO	DAO S9012	-
	DAO S9013	-
	DAO S9676	-

LCO	LCO S6206	-
	LCO S9387	-
	LCO S5832	-
	LCO S8322	-
	S7351	-
	S5806	-
	S5325	-
	S9388	-
	S5177	-
	HCO/SLO S7487	-

Table 3.5. Ternary mixtures

Component 1	*Component 2*	*Component 3*
RS U217 3007 7B	RS U217 3009 16	LCO S6206
RS U217 3007 7B	RS U217 3009 16	LCO S9387
RS U217 3007 7B	RS U217 3009 16	VGO S7485
RS U217 3007 7B	RS U217 3009 16	HCO S7487
RS U217 3007 7B	RS U217 3018 25	LCO S6206
RS U217 3007 7B	RS U217 3018 25	LCO S9387
RS U217 3007 7B	RS U217 3018 25	VGO S7485
RS U217 3007 7B	RS U217 3018 25	HCO S7487
RS U217 3009 16	RS U217 3018 25	LCO S6206
RS U217 3009 16	RS U217 3018 25	LCO S9387
RS U217 3009 16	RS U217 3018 25	VGO S7485
RS U217 3009 16	RS U217 3018 25	HCO S7487
RS U217 3023 14-16	Hyval S5177	SLO S93896
RS U217 3023 14-16	Hyval S5177	VGO S7485
RS U217 3023 14-16	Hyval S5177	DAO S9012

3.3.2 Analytical methods for the measurement of the properties

It is now presented the different analytical methods used to measure the properties of the samples that are present in the database. After the measurement each property is added to the database.

The principle of the methods, the scope and the accuracy are given in the table below for each property. The accuracy of the methods is estimated by the reproducibility (R) or the repeatability (r) values which have been determined during ring test evaluation or laboratory statistical validation.

Table 3.6 summarize the analytical methods used, with the scope and the accuracy for each method.

Table 3.6. Analytical methods

Property	*Method*	*Scope*	*Accuracy*
Sediment content	IP375	0,1-0,5 wt%	R= 0,294 x^2
Density	ISO 128145	0,680 < ρ < 0,9700 ρ > 0,970	R= $5 * 10^{-4}$ R= $2{,}7 * 10^{-3}$
Viscosity	ISO 3104	50°C 80-100°c	R = 0,074 υ R = 0,04 (υ + 8)
SARA fraction	IFPEN 9305	5 < Saturates < 60 wt% 30 < Aromatics < 65 wt% 3 < Resins < 40 wt%	R = 1 + 0,8 A R = 2 * r
AC7	IFPEN 9305	AC7 < 30 WT%	r = 0,14 AC7
S, Ni, V content	IFPEN 9910 IFPEN 9422	0,03 < S < 6 wt% 2 < Ni < 600 ppm 2 < V < 1200 ppm	$r = \left(\frac{8 + 0{,}005 * 1000\,S}{10000}\right)$ r = 0,35 $Ni^{0,25}$ r = 0,35 $V^{0,25}$
Simulated distillation	IFPEN 1202	35 < Teb < 720°C	R = f (% distilled)
Carbon aromatic	IFPEN 9410	Caro > 1 wt%	R = 0,021 Caro

The scope indicates the range of validity of the measurement and the accuracy indicates the proximity of the value found to the real one. It is a qualitative concept that depend on both random and systematic errors.

The *accuracy* can be given by two different value repeatability and reproducibility.

The *repeatability* is the value obtained from several experimental trials conducted with:

- Same experiment tools
- Same observer
- Same measuring instrument, used under the same conditions
- Same location
- Repetition over a short period of time

The *reproducibility* is a value obtained from distinct experiments conducted by different people, in different laboratories, and with long distance in time between them.

R is the difference between two single and independent results, obtained by different operators working in different laboratories on the same test material.
The confidence interval (CI) of the methods is calculated according to equation (21):

$$CI = \frac{R}{\sqrt{2n}} = 2\,\frac{r}{\sqrt{2n}} \tag{3.4}$$

Where n represents the number of measurement repetitions.

a. Sediment contents

Sediments content evolves during time and three types of sediments can be defined:

- TSE: Total Sediment Existent which corresponds to the sediment existent in a sample at a certain time.
- TSP: Total Sediment Potential which correspond to the sediment measured in the sample after a thermal aging at 100 °C during 24 hours.
- TSA: Total Sediments Accelerated which correspond to the sediments measured in the sample after a chemical accelerated ageing at 100°C during 1 hour with the adding of 10 % of cetane (n-hexadecane).

In this internship, to reach the main aim, only the Total Sediment Content is calculated according to the IP375 method.

Looking back at the method used in the last years [14], the measurement of sediment content was extremely different: it was conducted by *extraction*. The extraction method was commonly applied to bunker fuel oil and apparently gives protection against the excessive deposition of the sludge in the storage, thought it does not always value in a correctly way the rate oils.

The new method avoids certain theoretically objectionable features of the sediment by extraction test and has been found to correlate accurately with the actual tendency of the fuel oil. The method has also as a tool for use in conducting tests for predicting the tendency of fuels to clog preheaters, in fact it can be carry out in a shorter time then the sediment by extraction test.

The IP375 method for TSE is carried for each new blends created, both the binaries and the ternaries.

Preparation of the blend

The sample has been created using one residuum (or two in the cases of ternary mixtures) adding one cutter stock (or two in the cases of ternary mixtures), respecting the composition 90%-10%, 80%-20%, 70%-30%, 60%-20%, respectively for residue and cutter stock. While for the ternary mixtures the proportion was different, for the blends with two residue and one cutter stocks the composition is 10%-36%-54%, 20%-32%-48%, 30%-28%-42%, 40%-24%-36%, cutter stock, residue number one, residue number two, respectively. While for the blends with one residue and two cutter stocks the proportion is 90%-7%-3%, 90%-5%-5%, 90%-3%-7%, 70%-21%-9%, 70%-15%-15%, 70%-9%-21%, residue, cutter stocks number one and cutter stocks number two respectively.

After the creation, the mixture had to be homogenized, a magnetic stirrer is used with a rotation rate of 300 rpm and a temperature set at 70°C, it may last one hour for minimum. This passage is extremely important in order to avoid the deposition of solid material. Then, the blend is put in an oven for about 20 minutes at the temperature of 110°C to reduce the viscosity of heavy blends and to conduct the experiment easily, in this way the filtration of the compound it is facilitate to the fact that the mixture is more like a solid.

Before starting the filtration test, the sample must be shaken, to make it more homogeneous as possible and to avoid the sediment deposition on the bottom or on the walls of the bottle. Now, it is possible to consider it homogeneous now.

Filtration test

10 g of sample passes through a dry filter of 1,6 μm

of porosity. The time of the filtration depends on the components, for some blends it is necessary more than 15 minute for others only 1 minutes is enough. But, it is important to pay attention on the duration of the experiment: the filtration should not exceed 25 minutes, in fact, the blends could return to their original viscosity. The aim of this passage is to trap the sediment on the filter, while the maltenes components pass through the filter. Figure 3.1 represent a scheme of the equipment used for the filtration.

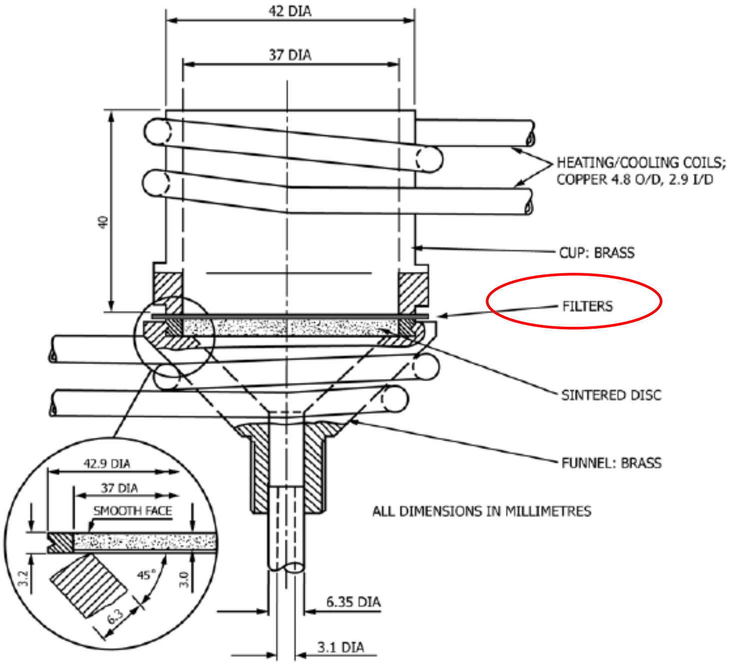


Figure 3.1. Sediments content measurement apparatus for IP375 method.

During the filtration phase, heat is sent in form of steam to maintain at low viscosity the blend and helps the filtration of it.

When the filtration is finished, it is necessary to send cold water for at least 5 minutes to cool the entire equipment. Once everything is colder, the filter must be washed by a solution of 60 ml of heptane/toluene (with a proportion respectively of 85/15) and then by a solution of 10 ml of pure heptane, to dry filter paper better. Due to the presence of a pump which help the filtration, it is important not to send to it the heptane or the toluene in form of steam. The solvents must be at the liquid state, in this way is possible to recover them. This is the reason why it is very important to wait at least 5 minutes to cool the entire equipment: solvents do not have to reach the pump.

The filter is then put in an oven for 1 hour: the filtration cake remaining on the filter and it is weighted, it represents the sediment content deposition.

Figure 3.2 represents the result of the filtration, the sample has been for 1 hour in the oven and all the solvents are evaporated, leaving the sample dry. Because of two filters at the same time are used (one over the other) there are two filters, the one on the left is the filter under the first one, and for this reason it is lighter in the color, because on it the amount of sediment is less.

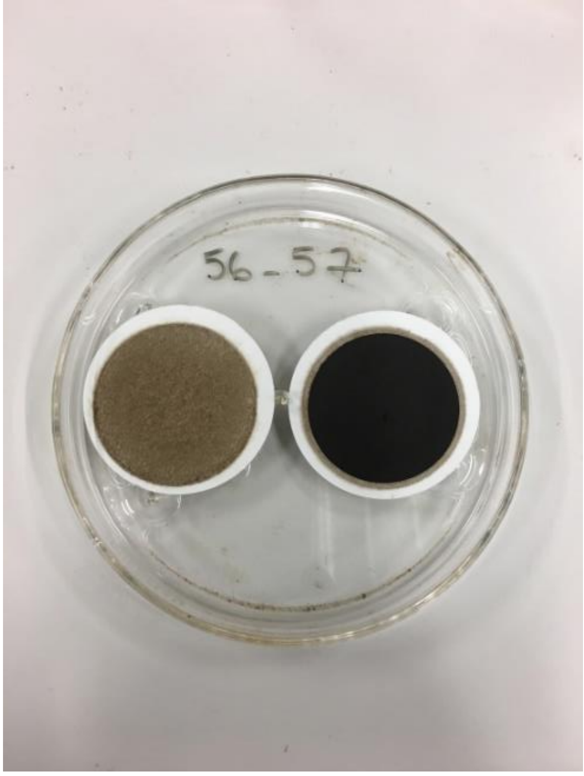


Figure 3.2. Sample after 1 hour in the oven.

The experiment is lead before for the residue in order to know the initial sediment content (TSE) and then for all the blends, with the same cutter stocks in different proportion. It was conducted for binaries to build a robust model and for ternaries to validate the model.

b. Density

Density has been measured using the ISO 12815 method in IFE by the candidate, it covers determination of the density or relative density of petroleum distillates and viscous oils.

Density measure

The sample, before starting the test, must be heated at a temperature of 70°C for at least 40 minutes, in order to reduce the viscosity.

The method is based on an oscillating U-tube, where approximately 0,70 mL of the liquid sample is introduced. The U-shaped borosilicate glass tube containing the sample is excited to vibrate at its characteristic frequency. The characteristic frequency changes depending on the density of the sample and the density is calculated from quotient of the period of oscillation of the U-tube and the reference oscillator according to equation 3.5:

$$\rho = KA * Q^2 * f_1 - KB * f_2 \tag{3.5}$$

Where:
KA, KB: apparatus constants

Q: quotient of the period of oscillation on the U-tube divided by the period of oscillation of the reference oscillator.
f_1, f_2 : corrections terms for the temperature, the viscosity and the non-linearity.

Figure 3.3 represents the equipment used for the measure of the viscosity, it is not possible to notice the U tube because it is located inside the equipment itself.

Figure 3.3. Apparatus which measure the density.

This method is used for bitumens and heavy oil by first heating at 70°C the sample,but the result is given back at 15°C.

The value of the density is an important index to understand if the mixture is created in the correct proportions, for this reason this measure must be done on each and every sample preparaed. Since it is possible to predict the density of a blend using the mixing rule (knowing the density of the pure component and the proportion), then this value is compared with the value measured by the densimeter. If the absolute difference of the two is higher than 0,002 the mixture should be created again.

c. Refractive Index

The refractive index is measured in IFPE by using the same machine used for the measurement of the density.

A little drop of the sample, around 1,5 mg, is placed on a refractive prism and covered because darkness conditions are requested. Then the measure of the refractive index is given immediately on the screen, it needs only 10 seconds to be done.

It is not necessary to pay attention on the temperature, since it does not have relevance on the refractive index.

Figure 3.4 represents the equipment used for the measurement of the refractive index.

Figure 3.4. Apparatus for the measurement of the refractive index.

d. Viscosity

Viscosity measurement can be divided into kinematic and dynamic methods. The kinematic method measures the flow rate, driven by gravity through a capillary tube. On the other hand, dynamic method measures the shear stress resulting from mechanical application of a shear on the fluid between a stationary body and a sliding body. The shear applied could be static or variable. In IFPE the one measured is the kinematic viscosity since it is possible to relate them by equation 3.6

$$Cinematic\ viscosity = \frac{Dynamic\ viscosity}{\rho_{fluid}} \quad \left[\frac{m^2}{s}\right] \tag{3.6}$$

Where ρ_{fluid} represents the density of the fluid considered.

Viscosity measurement

It is measured using the ISO 3104 method. Kinematic viscosity (υ) is measure knowing the time needed for a volume of a sample to flow under gravity through a calibrated glass capillary viscometer at a given temperature.

Before starting the experiment, it is necessary to understand, just from a visual point of view, if the cutter stock is too viscous. When cutter stocks are too viscous, it is necessary to heat them at 70°C for 20 minutes, in order to reduce the viscosity: in this way the measurement will be to be conducted.

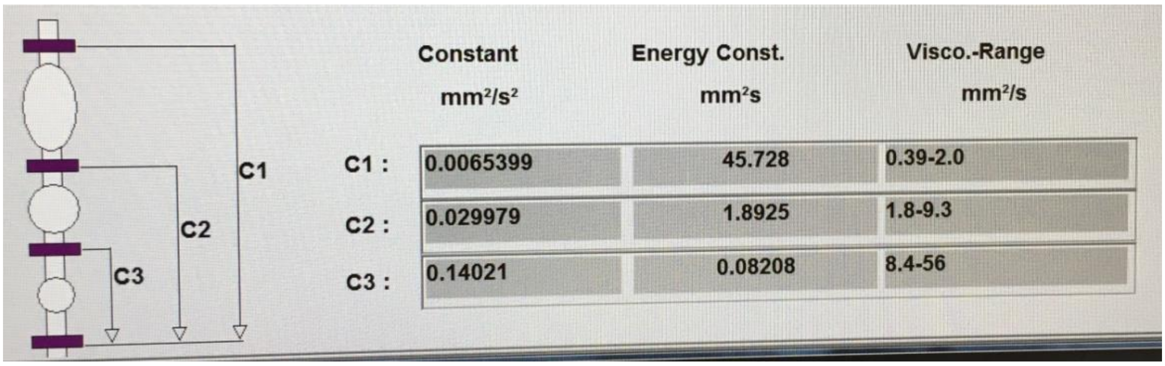
About 20 gr of sample are used to make the measurement. The sample is added in the viscosimeter and the first phase is about a pre-heating (again) of the sample for 15 minutes at the temperature the measurement is requested. After, the fluid goes up the capillary tube. The capillary tube is located inside a column, which inside there is thermic oil which aim is to maintain the temperature in the capillary tube homogeneous.

Figure 3.5 represents the tube with inside the other tube in which the fluid rises.

Figure 3.5. Viscosity measurement apparatus for ISO3104 method.

The capillary tube is very long and at the top there are sequentially three spheres, which are possible to be notice in Figure 3.5, that the fluid has to pass. In first approximation the fluid choses one on the glass sphere. Based on the sphere chosen it is possible to have a first approximation range for the viscosity. Figure 3.6 shows a scheme of the top of the capillary tube, it is possible now to better understand where the three spheres are located inside the capillary tube.

The fluid will choose a position between two spheres and only in a second moment will be possible to understand the real position of the fluid inside.



	Constant mm²/s²	Energy Const. mm²s	Visco.-Range mm²/s
C1 :	0.0065399	45.728	0.39-2.0
C2 :	0.029979	1.8925	1.8-9.3
C3 :	0.14021	0.08208	8.4-56

Figure 3.6. Sphere glasses for the measurement of the viscosity with the appropriate calibration constant.

After the fluid is located between two sphere, it goes down, and based on the time it needs to reach the right sphere glass, the viscosity is calculated as the product of the flow time (τ) and of the calibration constant (C, which depends on the sphere chosen by the liquid and it is a numerical value given by the producers of the machines).

Viscosity is given according to equation 3.7:

$$\upsilon = C * \tau \ \left[\frac{m^2}{s}\right] \qquad (3.7)$$

Where υ represents the average value of the kinematic viscosity measurement.

Due to the high viscosity of the heavy oil, viscosity is mostly measured at a temperature higher than 100°C and then converted to the standard temperature that is 50°C, according to equation (3.8):

$$\upsilon_T = exp\left\{ exp \left\{ln \left[ln(\upsilon_T - 0,7)\right] * B * \ ln\left(\frac{T}{T_1}\right)\right\}\right\} - 0,7 \qquad (3.8)$$

Where the parameter B is represented by:

$$B = \frac{ln\left[\frac{ln\left(\upsilon_{T_1}+0,7\right)}{ln\left(\upsilon_{T_2}+0,7\right)}\right]}{\ln\left(\frac{T_2}{T_1}\right)} \qquad (3.9)$$

It is important to focus on the fact that the parameter *B* contains two different values of viscosity: in fact, for each sample two viscosity mustbe measured. The two temperatures chosen for the measurement of each cutter stocks depends on their initial viscosity. In fact, if the sample is hardly viscous the temperatures chosen could be probably 70°C and 100°C, while if it is not viscous the temperatures could be 20°C and 40°C. Both temperatures must be considered in absolute temperature (Kelvin degree).

After the measurement the sample is completed recovered and the capillary tube is washed by heptane and toluene.

The measurement of the viscosity is conducted on each cutter stocks.

e. SARA fractions

The SARA fraction method is used for the separation of the four generic fractions of the heavy fuel: Saturated, Aromatics, Resins, and Asphaltenes. The method used in IFPE is the IFPEN 9305. The candidate makes the first part of the experiment: the separation of the asphaltenes from the maltenes, while an expert technician makes the second part: the separation of the maltenes fraction.

The SARA fraction is conducted on the residues utilized by the candidate and on the ones used by Hajjami, which are shown in table 3.7:

Table 3.7. Residues used for the SARA fraction test.

Cut	*Ref. (unity test period)*
RS	U217 3007 7B
RS	U217 3018 25
RS	U217 3009 16
RS	U217 3016 2
RS	U217 3013 9
RS	U217 3016 16 AH
RS	U217 3009 18
RS	U217 3021 11/13
RS	U217 3012 6
RS	U217 3023 14-15-16

The method divides crude oil components according to their polarity.

The first step consists in the division of the asphaltenes fraction from the maltenes fraction by adding n-heptane, this step is followed by the filtration: in this way asphaltenes precipitate. Asphaltenes is the fraction of the sample that precipitate when it is diluted with n-heptane, while maltenes is soluble in n-heptane.

Then the maltenes fraction is weighed and injected into a chromatographic column packed with activate alumina and silica gel. N-heptane circulate and cause the separation of the Saturate fraction, which consist of nonpolar material including linear, branched, and cyclic saturated hydrocarbons (paraffins). Then, aromatic fraction, which contains one or more aromatic rings, is eluted with a mixture of heptane and toluene. Finally, the Resin fraction, which contain polar substituents, is eluted with a mixtures of methylene chloride, toluene, and methanol.

As last step, the solvents are removed from each fraction which now are known as Saturated, Aromatics, and Resins and they can be weighed.

Figure 3.7 shows a scheme of the SARA fraction.

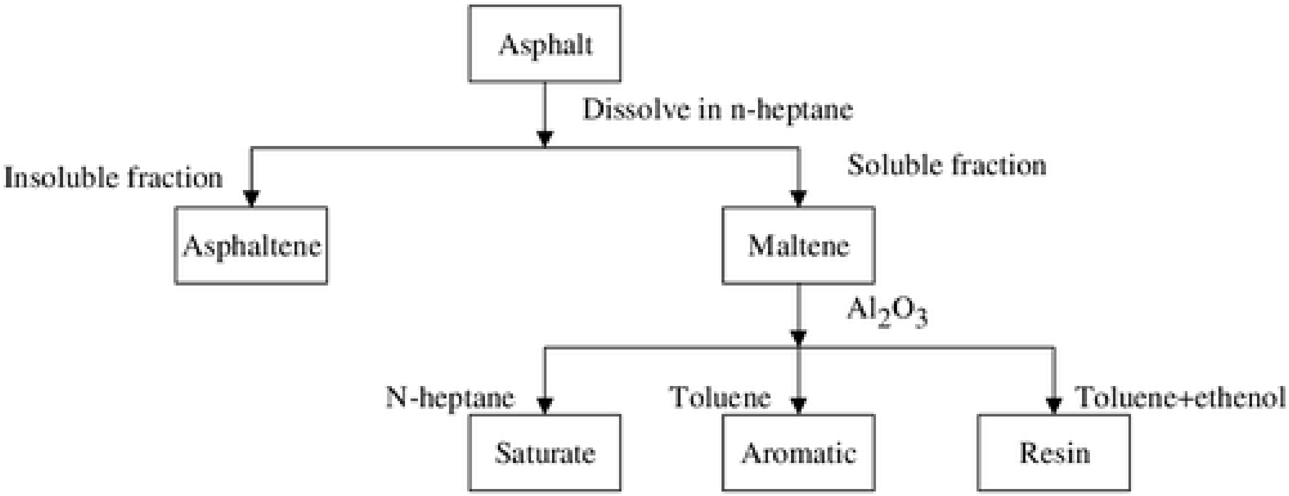


Figure 3.7. SARA fraction: scheme of the process.

First step: asphaltenes – maltenes separation

Preparation of the sample

Weight between 1 and 50 g of the residue in a round bottom flask of 2 L. For some sample it is necessary to heat them, before to put them in the round bottom flask, due to their high viscosity and another reason is to make them more homogenous.

Then a volume of n-heptane, bigger than 30 times the volume of the sample, is added inside the glass sphere. The n-heptane is fundamental because is the factor which allows the precipitation of the asphaltenes, due to its insolubility in it.

Preparation of the equipment

The equipment is composed by a heating magnetic plate controlled by a thermometer that can heat up to 150° C and stir up to 1000 rpm, a heating balloon, a refrigerant and a cryostat, Figure 3.8 shows it.

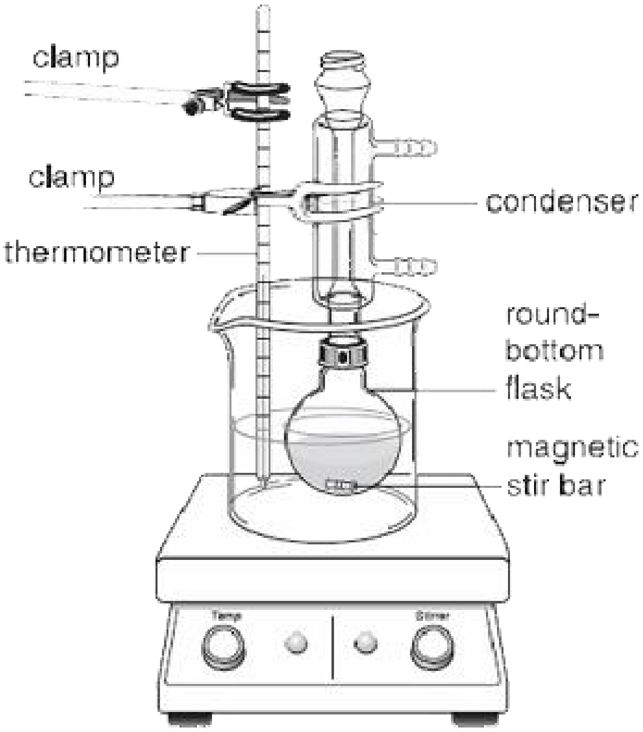


Figure 3.8. Apparatus for heating the mixture.

Experiment

The round bottom flask, which now contains the residue and the n-heptane, is located, with a magnetic stir inside, on the heating magnetic plate. The temperature is set at 122°C while the stirring at 800 rpm to reflux (one condense droplet for second). The heating magnetic plate works for 1 hour ± 10 minutes. After, the mixture has to rest for 1,5 hour ± 30 minutes, in dark condition (light can alter the precipitation of the asphaltenes) and at room temperature in order to decrease the temperature.

After, the mixtures must pass through a filter system. The mixture (residue + cutter stocks and the 30 times volume of heptane) is washed with more heptane, which has been heated separately. The excess of hot heptane is requested because it helps a better precipitation of the asphaltenes and their separation from the maltenes fraction.

At this point it is possible to notice the division of the two phases: asphaltenes and maltenes.

The asphaltenes, which remain on the filter, must be dry at a temperature of 60°C , the round bottom flask which contain a bit of asphaltenes and the filter which contain the bigger amount of asphaltenes are located in an oven for a minimum time of 40 minutes and then weighed. Figure 3.9 shows the filter with the asphaltenes which remains on it after the separation from the maltenes component, in the figure the filter was dried yet.

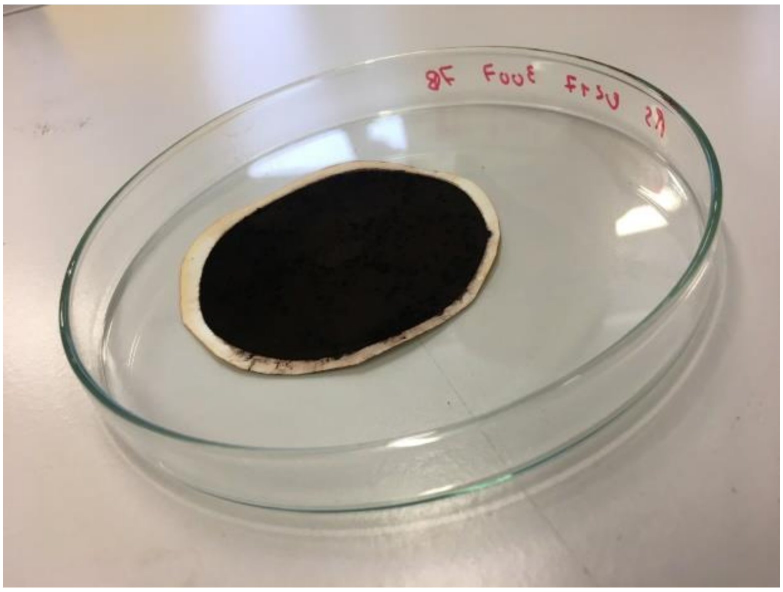


Figure 3.9. Sample of asphaltenes using the SARA fraction method.

While, the n-heptane in the solution (now presented only in the maltenes phase) has to evaporate. The evaporation is conducted in vacuum condition, at a pressure of 250 mbar. The round bottom flask is put in a bath of water at 70° C. This helps the maltenes to remain inside the glass sphere, while the n-heptane goes to a steam form and it is recovered back in liquid form thanks to the column of true boiling temperature. This part of the experiment lasts for 20 minutes, depends on the amount of n-heptane.

Figure 3.10 shows the equipment used for the evaporation of the n-heptane in the mixtures.

Figure 3.10. Apparatus for the concentration of the maltenes

After the solution is concentrated. In fact, it has to be completely dry, eliminating entirely the excess of n-heptane, using another machine. Now, it is possible to weigh them.

Result

Asphaltenes content is determined by equation 3.10:

$$content_{AC7} = \left(\frac{m_{AC7_{membrane}} + m_{AC7_{round\ bottom\ flask}}}{m_{pe}}\right) * 100 \qquad (3.10)$$

Where:

$m_{AC7_{membrane}}$: mass of asphaltenes on the membrane (g)

$m_{AC7_{round\ bottom\ flask}}$: mass of asphaltenes on the wall of the round bottom flask (g)

m_{pe}: mass of the part of the sample analyzed (g)

The method can be applied only to samples that have an initial boiling point higher than 350°C due to the solvent evaporation step before to be weighed.

Second step: Maltenes separation into Saturates, Aromatics, and Resins

After the separation from the Asphaltenes, a little quantity of maltenes (which has to contain less than 1% in weight of asphaltenes) is injected into a column, which is filled with a mixture of silica and alumina. The fraction of saturates are eluted by n-heptane, the aromatics by n-heptane and toluene while the resins by a mixture of dichloromethane, toluene and methanol. At the exit of the column the different contents are separated and successively weighed.

The column has different entrance to inject the different solvents.

Preparation of the sample

To perform a homogeneous sampling of the sample, it has to put in an oven at the temperature of about 60°C for at least 15 minutes. Temperature and time can vary, based on the quality of the sample and the viscosity it seems to have.

Also, the amount of the sample used for the measurement can be different based on the amount of asphaltenes presents inside.

Preparation of the equipment

Every bottle must be filled with the solvent respecting the right ways: in A there is the n-heptane, in B the toluene, in C the dichloromethane and in D the methanol. Purge each channel separately at 40 ml/min, taking care not to switch from channel to channel without cleaning them with dichloromethane, to avoid create two immiscible phases in the system. Then, it is necessary to clean the system with n-heptane at 40 ml/min.

Some bottles at the bottom of the column are located to collect the fractions separated of maltenes.

Experiment

It is extremely important to heat the sample to facilitate the solubilization. The sample must be transferred in a bottle of 20 ml and take 10 ml to inject into the column, paying attention on avoid push also air inside the column.

After the injection of the sample the elution must start and the way there is the separation of the fraction is based on the chemical and physics characteristic. In fact, the operative conditions and the duration of the analysis depends on the type of sample.

Then, the fraction obtained must be dried by a rotatory evaporator under vacuum conditions.

After the evaporation the bottle have to rest for at least 4 hours at room temperature.

To be sure all the experiment was conducted in an appropriate way it is necessary to make a mass balance, in which the losses must be less than 3,5%. If there should be a gain in the balance, the evaporation is requested again.

f. Elemental compositions – sulfur, nickel and vanadium

The method used for the determination of the sulfur, nickel and vanadium contents in heavy fuel is IFPEN 9910 and IFPEN 9422, and in this case the measurement is not done by the candidate. The elemental composition is lead on the sample of maltenes that derives from the separation of asphaltenes from maltenes (the first part of the SARA fraction experiment).

X-ray fluorescence spectrometry measures the intensity of a specific peak emission by the three atoms. The sample is excited by an X-ray beam and the fluorescence intensity is measured.

The methods are extremely fast, they need less than 5 minutes for each sample. Obviously, it is better if more than one measure is done in order to have a better and a more precise result.

Several precautions have to be considered that one may to achieve an accurate measure, such as the H/C ratio and the oxygen content of the sample.

g. AC7 (Asphaltenes precipitated by heptane)

Asphaltenes content is measured according to NFT 60-115 method. This method has been developed to determine the asphaltenes n-C7 in petroleum samples. It is completely different from the SARA fraction method.

Experiment

The sample is put in an oven at a temperature than can be from 70°C to 150°C, it depends on the viscosity of the heavy oil, then it is weighed and put into a round bottom flask. Before the experiment started, 10 mL of toluene are added to solubilize better the product and if the heavy oil still be in solid form, the round bottom flask is located on a sandbar at 100°C for 15 minutes.

250 mL of n-C7 are added in the round bottom flask with the sample and a little piece of porcelain is added to simulate the agitation. The sample then is brought to a boil and reflux is necessary for 1 hour. After this period, the heater is turned off and the round bottom flask can get cold and is put in dark conditions for at least 2 hours.

Once the dark conditions are finished, the content of the round bottom flask is passed through a filter that trapped the asphaltenes particles. The round bottom flask now contains only asphaltenes particles and a little amount of toluene is added to solubilize it better.

After, the filter is put above another round bottom flask that contains 100 mL of n-C7. Again, it is necessary to brought to a boil and reflux for 45 minutes. It needs to wash the filter ad remove all the maltenes could be present.

It is now necessary to put together all the asphaltenes particles present. The round bottom flask, with asphaltenes and toluene, is put under the filter, brought to a boil and reflux for 45 minutes in order to dissolve the asphaltenes particles presented on the filter and that enter the round bottom flask and remain there.

All the product present in round bottom flask, which is asphaltenes more toluene, is transferred to a bowl. The bowl is put in an oven at 100°C for the necessary time in order to evaporate toluene. Finally, the flask is weighed to see the amount of asphaltenes in the sample.

The asphaltenes content is calculated thanks to equation (3.11):

$$\textbf{Rate of Asphaltenes}\ \% = \frac{(\textbf{weight of the flask} + \textbf{asphaltenes}) - (\textbf{weight of the empty flask})}{\textbf{initial weight of the sample}} \tag{3.11}$$

h. Simulated distillation

Simulated distillation employs gas chromatography (GC) to separate compounds by boiling point to produce a boiling curve.

It is based on the principle that hydrocarbon elutes from nonpolar column in order of their boiling points. It is a very precise method, in fact it produces a precise boiling curve and can extend to a final boiling temperature of 750°C.

The column is no polar because in this way compounds are separated by their volatility: the lighters are the first that go out, while the heaviest after, with the increasing of their no polarity.

IFPE 1012 method is very similar to ASTM D7269, it is used to cover the boiling range distribution of crude oils and residues.

The method uses:

- capillary column from which the amount of sample eluted may be calculated.
- helium as mobile phase.
- flame ionization detector.

Figure 3.11 shows the equipment which can be used for the measurement of the simulated distillation temperature.

Figure 3.11. Apparatus for simulated distillation

In simulated distillation three basic steps are involved:

- injecting the sample into the GC.
- The column separates the sample into individual components in order of their boiling points.
- Detecting the component as they elute from the column.

Figure 3.12 shows a scheme of the two column, one polar while the other one not. In this caseIt is possible to notice the inlet, first the fluid enter column 1, then column 2 and finally it goes to dectector module, which every molecule will be recognize. It is a little bit difference respect the one used in IFPE, but the principle is the same, because the separation of the component it is also based on time.

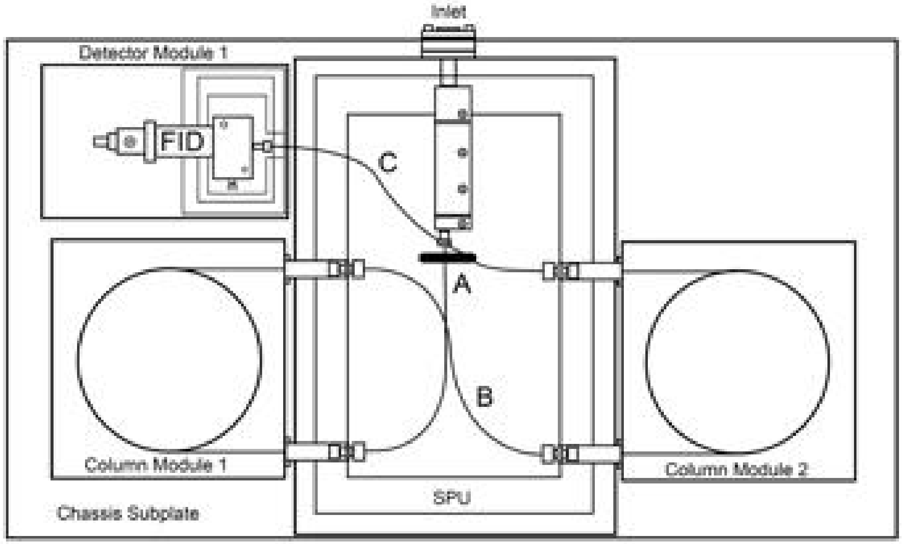


Figure 3.12. Scheme of the columns

Figure 3.13 shows the boiling-point-temperature distribution versus temperature. Integrating the area under the peaks, the total distillation portion of the sample is quantified according to the temperature. The method is valid in the temperature range 35°C / 720°C.

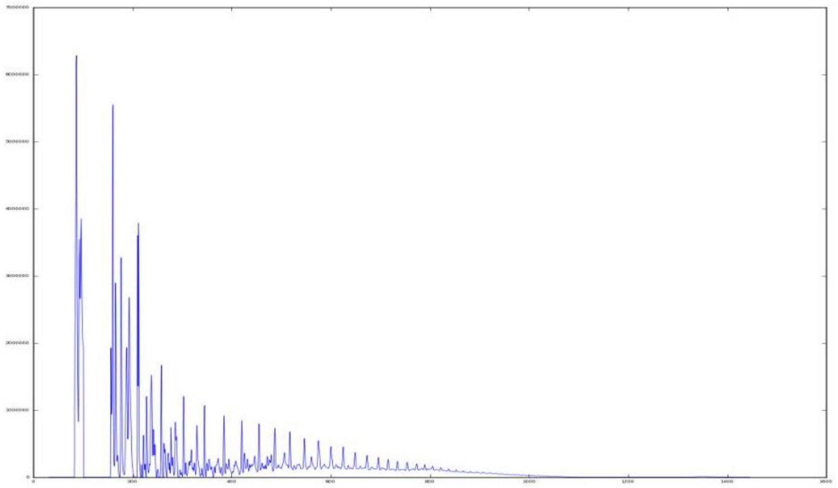


Figure 3.13. Simulated distillation cromatograph of a sample

i. Carbon aromatic

The carbon aromatic was measured according to IFPEN 9410 method.

The sample is solubilized in CD_3Cl. The ratio between unsaturated and saturated carbons is measured by NMR (Nuclear Magnetic Resonance). It was assumed that in heavy oil product, the unsaturated carbon can be considered as aromatics carbon.

j. Surface tension

The measurement of the surface tension is not conducted in the laboratories of IFPE but in another one next to Paris.

4. Result and Discussion

The following chapter explains the results obtained during the internship step by step and it analyzes them, in order to explain if they can be considered good or not.

As explained in the previous Chapters, the aim of the sediment content (TSE) mixing rule is to predict their amount in mixtures composed by heavy fuels and by light oils. In this way it will be possible to use also the heavy oils available but with intermediate properties thanks to their mixtures with the light oils.

The scientific literature does not have a model able to predict the sediments content in blend achieved with a huge variety of residues and cutter stocks. The model found in the internship is built by following an empirical approach since it must be utilized at industrial scale, the theoretical approach would not have been satisfactory enough, because the great amount of data and the property are difficult to be measured and another reason is the huge amount of time that should be requested.

4.1 Modeling of the Sediment Contents

It is extremely important to investigate the sediments content evolution in blends, considering some new residues but also the residues Hajjami used in the previous internship. As it has been previously described the equation found by Hajjami consists in two part: a linear trend and a curve trend, while the equation found in this internship can be divided into three: linear trend, the α parameter which contain the properties of the residues and the exponential trend containing the k parameter, which describes the properties of the cutter stocks.

The main steps followed, to find the mathematical model, are here briefly explained.

1. The first step considers the residuum effect, all the mixtures created (by Hajjami and by the candidate) are used to analyze the sediment content, but only due to the residuum. In this first part a new parameter is added, respect to Hajjami's equation, which is called "α" and which describe the properties of the residue that, is recognized, play a very important role in the sediment deposition in the blends. The equation that describes the parameter α will be better investigate later.

   After, some more others filtration experiments are requested, but this time executed to understand the value of k, which is a specific value for each cutter stocks and which is related to the properties of the light component. Even in this case, the equation that describes the parameter k will be studied later.

2. Finally, an implementation software is used to find the mathematical correlation for the α and k parameters, where several properties of the residuum and of the cutter stocks are used. In this way it is possible to find the correlation between a mathematical parameter and the chemical or physical properties. For the execution of this step has

been necessary to measure a great number of properties both for the residue and for the cutter stocks.

3. As last step, ternaries mixtures are used to validate the model. It is important to pay attention on the fact that the mixtures used for the validation of the model are different from the mixtures used for the building of the model, this is necessary to be able to understand if it is possible to apply the model to cutter stocks and to residues completely different.

The steps to find the value of α and *k,* and also the part for the validation of the model are divided into two part. The first part is the experimental one with the result of the filtration conducted in which also the behavior of blends will be explained, while the second part is about the modeling part.

4.1.1 Study of the residue effect

The first part of the internship is important to find a new parameter that gives more information about the properties of the residue. This step is even more important than the evaluation of the parameter *k,* because the properties of the residues were not considered in the internship lead by Hajjami.

To find a better correlation many filtrations must be done in order to have a bigger database respect to the one used before, in this way in fact it is possible to find a correlation for the properties of the residues.

4.4.1.1 Experimental part

Figure 4.1 represents the amount of sediment contents for each residue used to study their property.

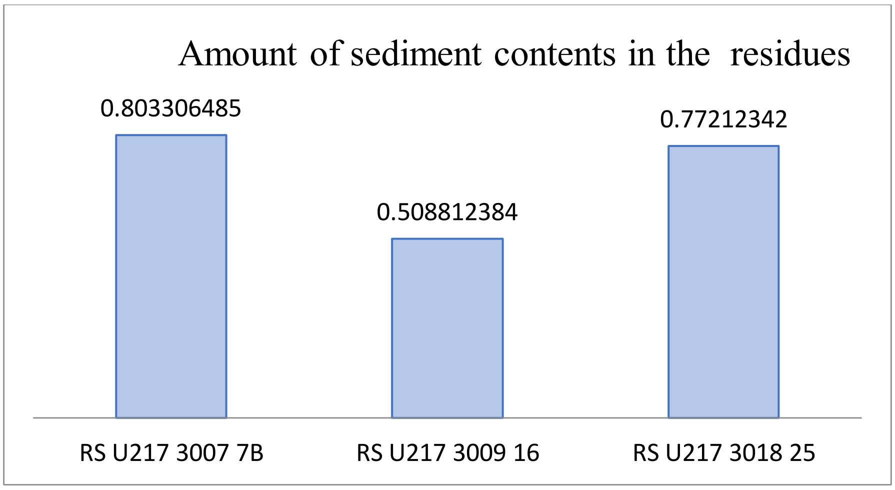


Figure 4.1. Amount of sediment content in the residues studied

Table 4.1, 4.2, 4.3 show the value of the sediment content while Figures 4.2, 4.3, 4.4 represent the behavior of the sediments content of a single residue with the several cutter stocks used.

Table 4.1. Value of the sediment content using RS U217 3007 7B

RS U217 3007 7B	Proportion of the Cutter stocks					
	0	0,1	0,2	0,3	0,4	1
HCO S9385	0,8	0,53	0,44	0,21	0,08	0
LCO S9387	0,8	0,62	0,4	0,29	0,22	0
LCO S6206	0,8	0,61	0,44	0,44	0,24	0
VGO S7485	0,8	0,71	0,62	0,51	0,41	0
HCO/LCO	0,8	0,68	0,53	0,34	0,25	0

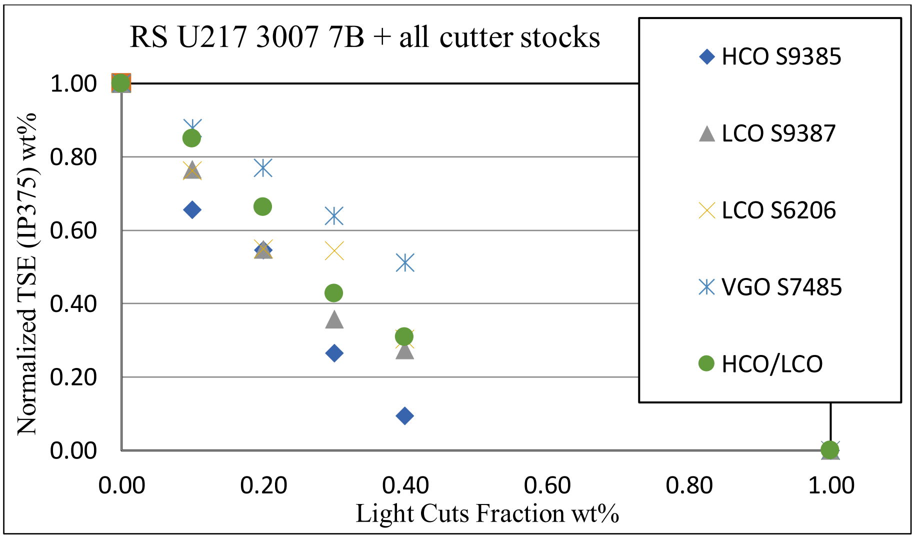


Figure 4.2. TSE content evolution for RS U217 3007 7B mixed with all the cutter stocks.

Table 4.2 Value of the sediment content using RS U217 3009 16

RS U217 3009 16	Proportion of the Cutter stocks					
	0	0,1	0,2	0,3	0,4	1
HCO S9385	0,51	0,37	0,33	0,24	0,20	0
LCO S9387	0,51	0,43	0,30	0,20	0,14	0
LCO S6206	0,51	0,41	0,4	0,32	0,17	0
VGO S7485	0,51	0,43	0,38	0,35	0,28	0
HCO/LCO	0,51	0,46	0,45	0,32	0,30	0

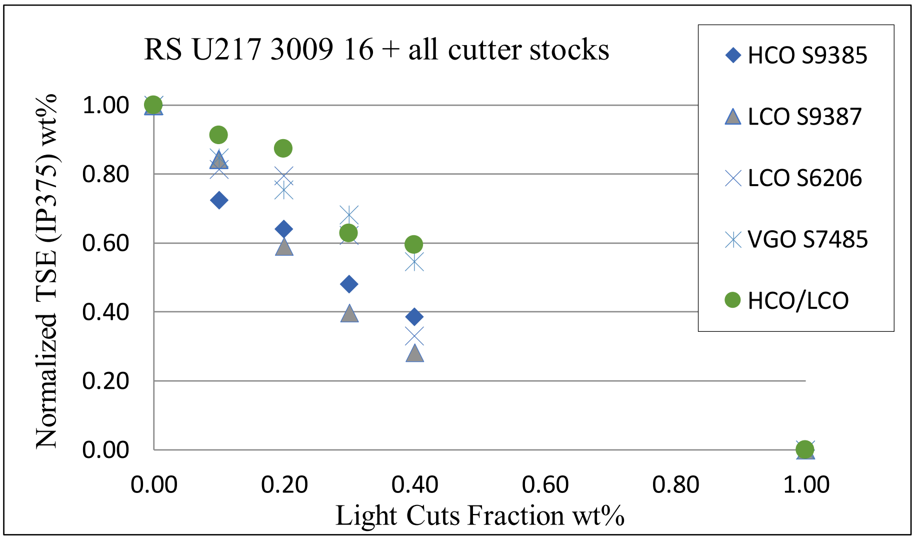


Figure 4.3. TSE content evolution for RS U217 3009 16 mixed with all the cutter stocks

Table 4.3. Value of the sediment content using RS U217 3018 25

RS U217 3018 25	Proportion of the Cutter stocks					
	0	0,1	0,2	0,3	0,4	1
HCO S9385	0,77	0,60	0,43	0,39	0,19	0
LCO S9387	0,77	0,57	0,26	0,22	0,15	0
LCO S6206	0,77	0,76	0,66	0,54	0,60	0
VGO S7485	0,77	0,88	0,70	0,72	0,63	0
HCO/LCO	0,77	0,90	0,54	0,35	0,20	0

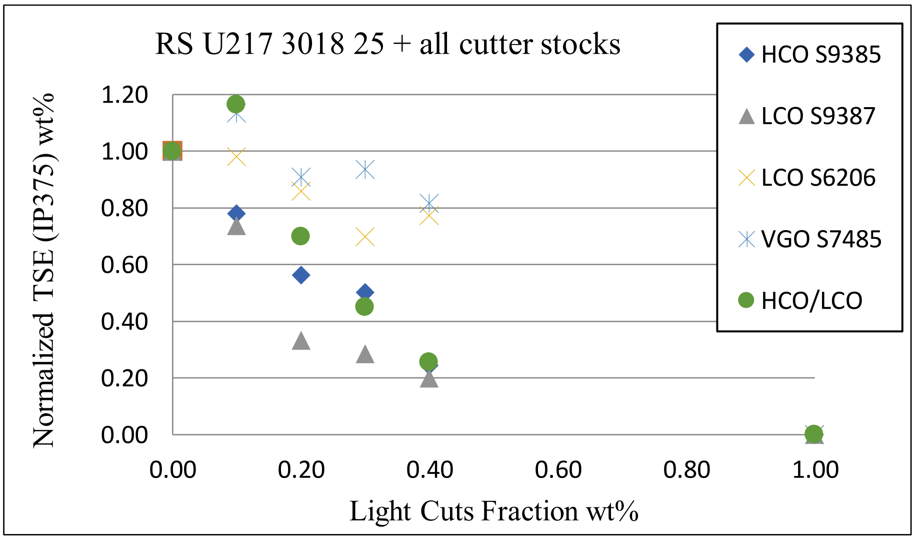


Figure 4.4. TSE content evolution for RS U217 3018 25 mixed with all the cutter stocks.

Firstly, it is extremely important to specify that each graphics represent the normalized TSE content values according to the initial TSE contents of residues.

As understood by Stratiet et Al. and subsequently confirmed by the work lead by Hajjami in IFPE, different behaviors are noticed when the same residue is mixed with different cutter stocks, in fact the properties of the light oils play an important role on the sediment deposition, and this is why the second step is important in the same way.

In paragraph 2.3.1 Figure 2.7 shows that a linear trend can be observed for the VGO S7485, and the same behavior can be noticed also in Figures 4.2, 4.3, and 4.4. The linear trend of the VGO S7485 is more regular for the residues RS U217 3007 7B and RS U217 3009 16, while for the RS U217 3018 25 there is firstly an increasing in the sediment content, this behavior could, probably, be caused by experimental errors.

On the other hand, it is possible to notice a curve (exponential decreasing) trend, when the cutter stocks used are aromatics, such as LCO and HCO. This trend is linked to the stabilization effect of the cutter stock due to a sediment content dissolution. The rule "*like dissolves like*" is here confirmed, and the bigger is the amount of cutter stocks used the bigger is the decreasing of the sediment content. Of course, also the properties of the residues play a role in sediment deposition: RS U217 3007 7B and RS U217 3009 16 show a similar trend among them, while RS U217 3018 25 shows a different trend.

Obviously, as said before, the data collected derive from experimental tests and some errors can be committed during the preparation of the blends or also during the filtration test. The important is that the general behavior respects the mathematical law found previously by Hajjami. For example, it is clear that for LCO S6206 and VGO S7485 mixed with RS U217 3018 25, which Figure 4.4 shows, the behavior is not really exponential like the mathematical model described, but it can be due, without any doubt, to human errors.

4.4.1.2 Modelling part

Stratiev et Al. used a polynomial equation, while Hajjami though about an exponential one since it can portray the observed trend with only one fitted parameter to describe the sedimentation. In this work one more parameter is added to the equation of Hajjami and it is called "α", which is a parameter related specifically to the properties of the residues.

In the first part of the internship it is not possible to know what the chemical or physical properties related to α are. At the beginning, the important is to understand a mathematical and general law for the equation of the sediment content, the chemical properties related are studied and understood in a second moment, thanks to the use of a software.

Many equations are tested and the α parameter is added to them in several ways. Since it is only the first part of the experiments it is not possible having a good value of the k parameter, and the values of k found in the work of Hajjami are used to find the α parameter for this first step of the internship, for this reason it is extremely important to use cutter stocks used by Hajjami, otherwise would not be possible to have any kind of idea on the value of the parameter k.

It is important to remember that α is only a numerical value in this first step.

Initially, to find the value of α it is fundamental to know:

- the initial sediment content,
- the concentration of the residues and of the cutter stocks for each blend created,
- the k parameter of the cutter stocks used to create the mixtures.

Choose of the equation

Several equations are considered and tested, and they are all present in Appendix 1.
For all the equations proposed an Excel solver is used, in this way it is possible to find the value of α which minimize the sum of the square root of the difference between the new equation proposed and the experimental value measured. This procedure has to be done for each different residue used, in this way it is possible to find a parameter α which contain a specific property for it.

Equation 4.1 represents only an example to better understand the use of the solver. The method of the minimum RSME, given by equation 3.1 presents in paragraph 3.1.1, has been applied.

$$\min square\ root = \sum_{i=1}^{n} \sqrt{(\hat{y}_l - y_i)^2} \tag{4.1}$$

Where:

$\hat{y}_l$ represents the real value of the sediment content, the measure obtained by the experiments

y_i represent the value of the sediment content which is given by the proposed equations.

The parameter found was calculated for each residue mixed with different cutter stocks in different proportion, in this way there was a kind of security that the parameter was only about the properties of the residue.

Most of the equations tested had a parameter which were not a finished value, this is was the first criteria to choose the correct equation, given by equation 4.2:

$$y = W_R * \left(\frac{1}{\alpha} - TS_{0,R}\right) e^{-k\, W_{CS}} \tag{4.2}$$

Secondly, many plots have been performed to notice the correlation between the value measured by the experiment of the sediment content and the value of the sediment content obtained by the different equation proposed, and using equation 4.2 there was the best linear correlation.

Figure 4.5 shows only a first approximation of the correlation between the two values, because it is necessary to do an iterative calculation, which will be better explained in paragraph 4.1.3.

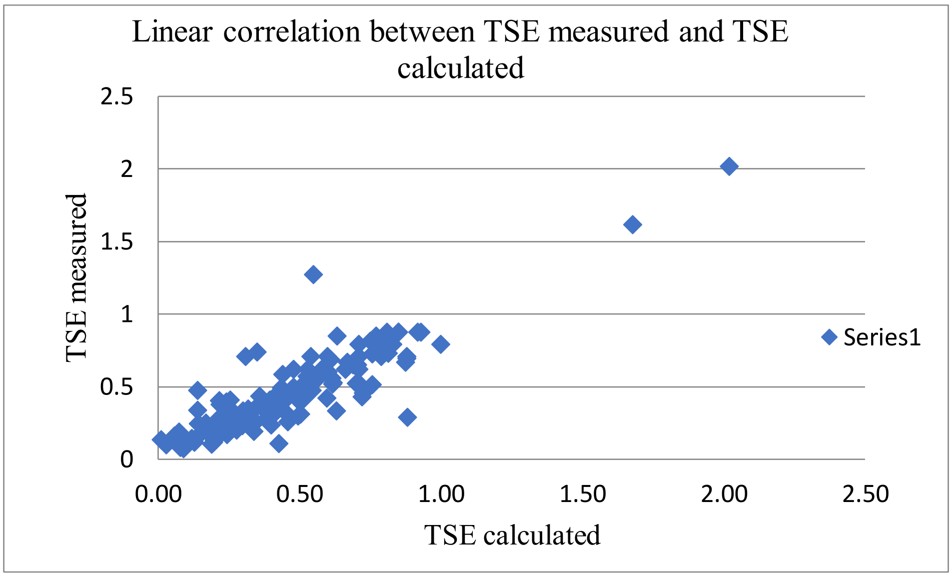


Figure 4.5. Correlation between TSE measured and TSE calculated.

The first part was important to find a model and it is followed by the research of the right value of α, which is not only for the new mixtures created since also for the mixtures of Hajjami, in this way a more precise value of α could be found.

It is not possible to write the value of α found for equation 4.2 and neither for all the other equation tested, due to the confidential information.

After finding α, it is important to compare the equation with the one proposed by Hajjami, equation 2.13, to understand if the new model is better or not respect to the previous one.

To do the comparison the definition of RMSE, equation 3.1, has been applied. The RMSE has been conducted on each residue and also on the total sum to analyze the overall effect. Table 4.4 summarizes the overall effect of the model.

Table 4.4. Error of the model

Hajjami equation	*New equation*
0,1961	0,1392

4.1.2 Study of the cutter stocks effect

The aim of the second part is to correlate the properties of the cutter stocks to the sediment deposition. The cutter stocks effect is related to the exponential part of the equation where a parameter, *k,* is related to the properties of the light oils. To have a better knowledge it is necessary to increase the database, for this reason, 52 more filtrations are executed.

The filtrations are conducted using only a single residue and 26 different cutter stocks. The choice of the use only one residue is because the effect it has on the cutter stocks is always the same. And, most important there was no enough time to be able to make more than that number of experiments.

To find the value of *k* it is fundamental, as it happened for the filtration experiments for the residue parameter, to know:

- the initial sediment content,
- the concentration of the residues and of the cutter stocks for each blend created,
- the α parameter calculated in the first step.

Before starting the experiment of filtration for the mixtures was necessary to know the initial sediment content of the residue RS U217 3023 14-15-16, which is 0,71.

4.1.2.1 Experimental part

Table 4.5 shows the value of the sediment content, with all the different cutter stocks used for the creation of the blends. The residue used in this case is RS U217 3023 14-15-16.

Table 4.5. Value of the sediment content using RS U217 3023 14-15-16.

Cutter stocks	Concentration of the light w%			
	0	0,1	0,3	1
HCO S3001-8	0,71	0,29	0,11	0
HCO S9702-3	0,71	1,08	1,31	0
HCO S5358-963	0,71	0,26	0,12	0
HCO S8834	0,71	0,33	0,15	0
HCO S5325	0,71	2,08	1,46	0
HCO S9702	0,71	0,19	0,21	0
HCO S9385	0,71	0,43	0,17	0
VGO S9384	0,71	0,70	0,79	0
VGO S7124	0,71	1,02	1,42	0
VGO S9149	0,71	0,62	0,61	0
VGO S5469	0,71	0,66	0,91	0
VGO S7485	0,71	0,73	0,88	0
SLO S9386	0,71	0,40	0,16	0
SLO S8836	0,71	0,48	0,14	0
DAO S9012	0,71	0,52	0,22	0
DAO S9013	0,71	0,72	0,40	0
LCO S5832	0,71	0,55	0,47	0
LCO S6202	0,71	0,12	0,02	0
S7351	0,71	0,49	0,30	0
S5806	0,71	1,52	1,24	0
S5177	0,71	0,70	1,62	0
S9388	0,71	1,21	1,39	0

The plots, shown in Figures 4.6, 4.7, 4.8, 4.9, 4.10, and 4.11, represent the normalized TSE content values according to the initial TSE contents of residues.

The results could be not extremely correct due to the human error in the preparation of the blends or during the filtration test, but the important is that the global trend of every cutter stocks have been predicted in a satisfactory way.

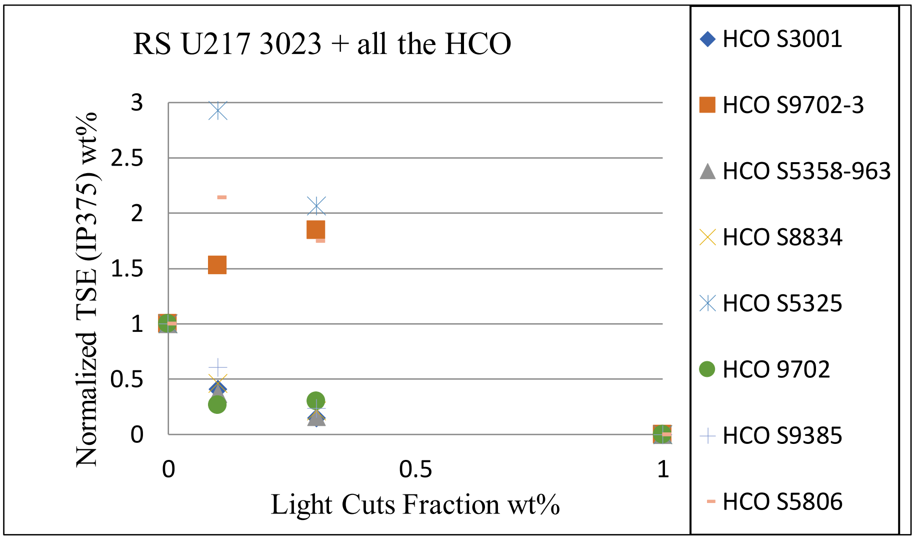


Figure 4.6. TSE content evolution for RS U217 3023 mixed with all the HCO

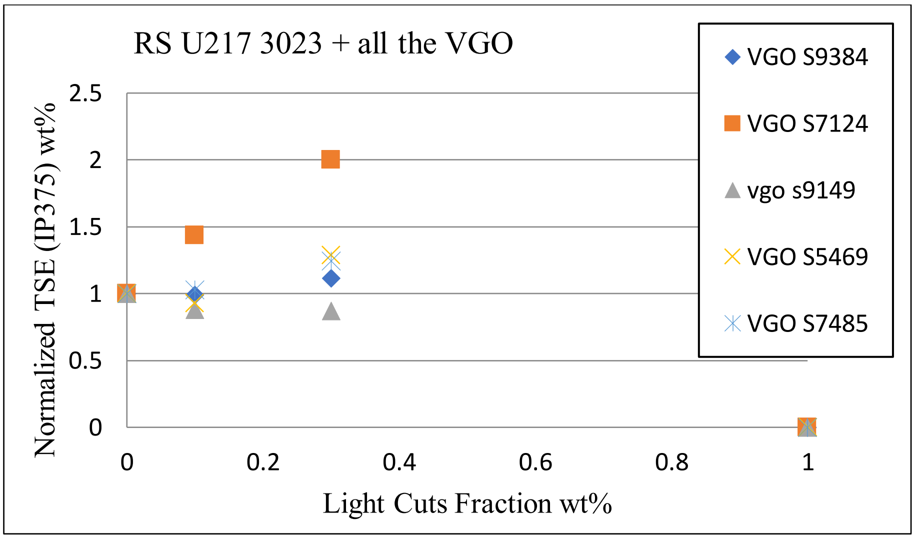


Figure 4.7. TSE content evolution for RS U217 3023 mixed with all the VGO

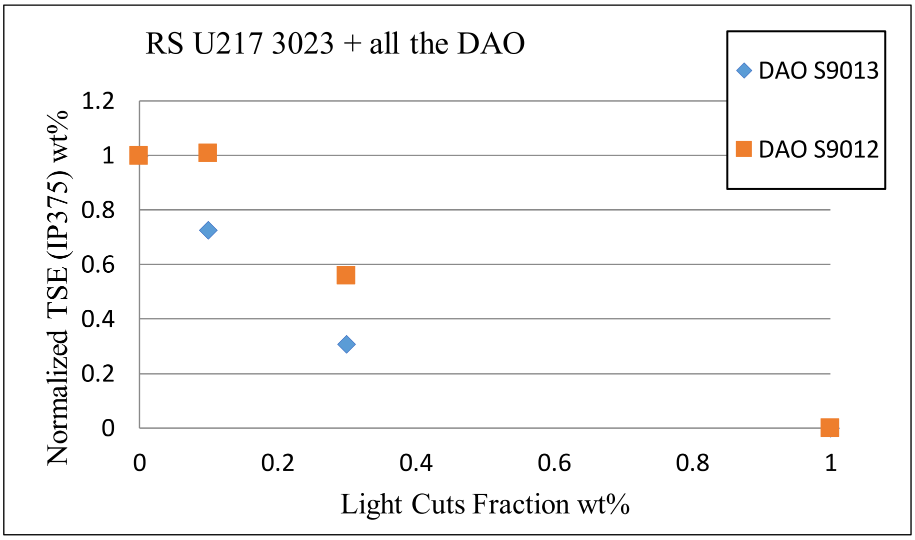


Figure 4.8. TSE content evolution for RS U217 3023 mixed with all the DAO

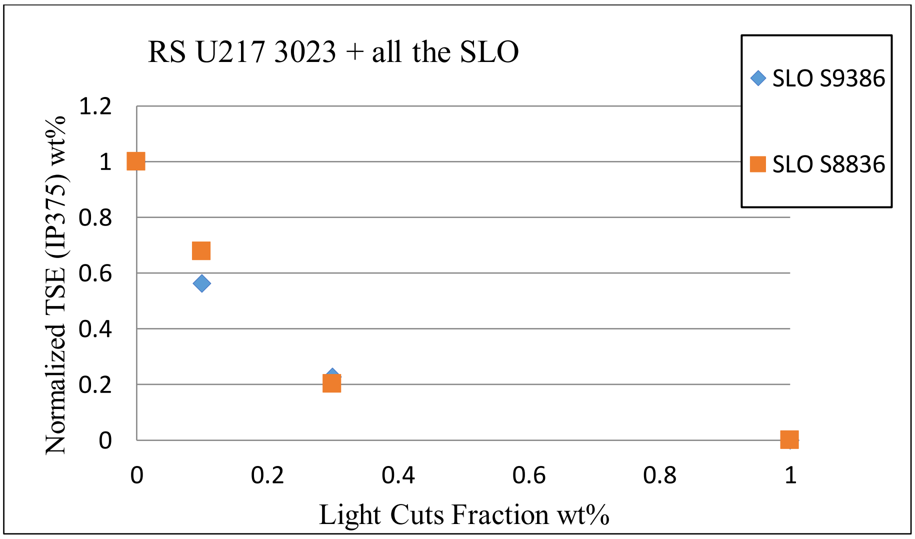


Figure 4.9. TSE content evolution for RS U217 3023 mixed with all the SLO

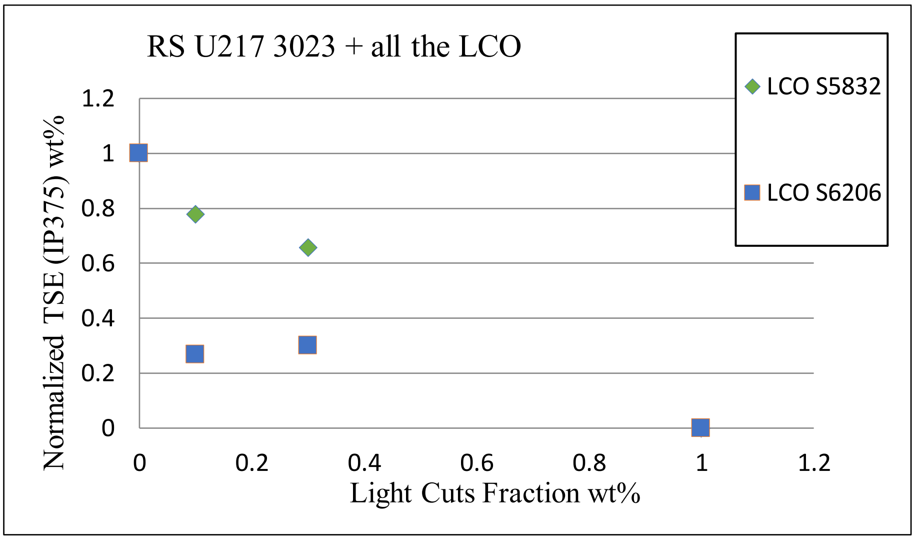


Figure 4.10. TSE content evolution for RS U217 3023 mixed with all the LCO.

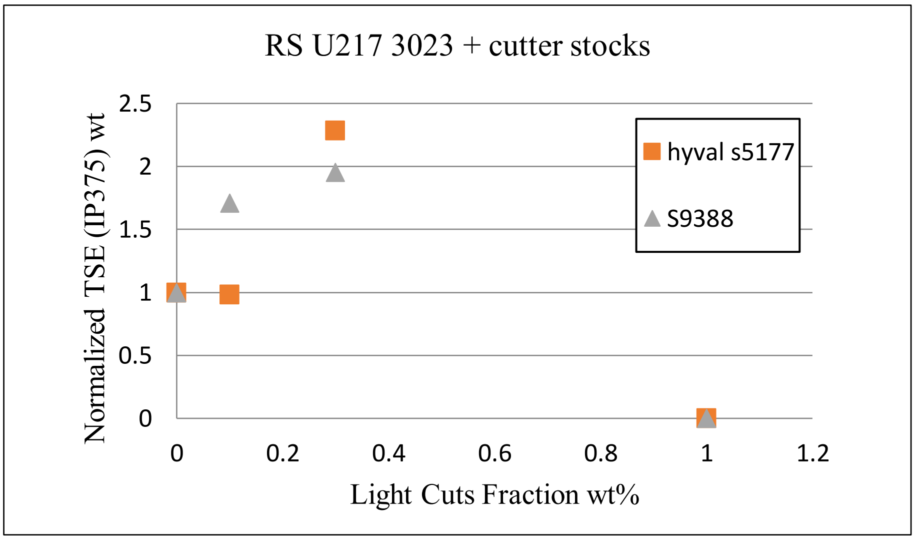


Figure 4.11 TSE content evolution for RS U217 3023 mixed with some other cutter stocks.

Figure 4.6 shows an abnormal behavior for two of the HCO, which normally has an exponential decreasing trend. In fact, HCO S5325, HCO S9702-3 and HCO S5806 increase the content of the sediment content, which is extremely strange for this type of cutter stocks.

Regarding the VGOs, plotted in Figure 4.7, they have a peculiar behavior, also VGO S7124 increase the amount of sediment deposition, while the sediment content for this type of cutter stocks should be decreasing following a linear behavior.

Figure 4.8, 4.9, and 4.10 show the behavior expected: an exponential decreasing trend for the DAOs, the SLOs, and the LCOs.

Figure 4.11 shows different types of cutter stocks, among which there is the HYVAL S5177 which is a diesel. As discussed in Chapter 2, paragraph 2.3.1, diesel does not have a great amount of carbon aromatic, for this reason the sediment content does not decrease with the increasing of the amount of the cutter stocks.

4.1.2.2 Modelling part

To find a better value of the parameter k for each cutter stocks, the same method used to find the parameter α is utilized. Even in this case, in fact, the knowledge of the initial sediment content, the concentration of residue and of cutter stocks, the α found in the first step, allows to find the correct numerical value of k.

It is possible to use the Excel solver which is able to find the minimum value of k. The parameter k must minimize the sum of the square root of the difference between the new equation proposed and the value obtained by the filtrations.

The procedure has done for each cutter stocks. Following the same procedure used previously (the least square method used with the Excel solver) the value of k has been found for each cutter stocks.

Even in this case it is possible to show if the equation proposed can be defined correct respecting the experimental results. As shown in Figure 4.12, it is possible to confirm it, in fact there is a quite linear correlation between the experimental value and the one calculated. It is important to remember that in this case only two measured for each residue have been executed, this is why this correlation can appear less correct than the one done for the parameter α, but it is enough correct to confirm that the equation proposed could be truly.

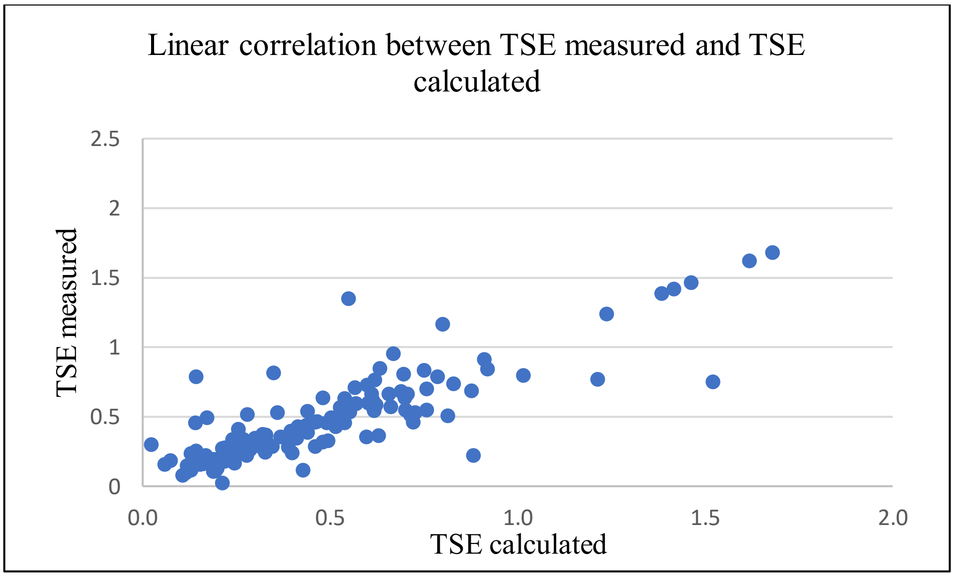


Figure 4.12. Correlation between TSE measured and TSE calculated.

4.1.3 Iterative calculation

In order to find a value of the parameters α and *k* as precise as possible, it is necessary to repeat again the evaluation of the parameter α, using the new values of *k* found in the second step. And to repeat the calculation for the parameter *k* using the new values of α. It is important to execute the iterations until the difference between the new value and the previous one is extremely reduced.

In the report all the iterations executed are not reported, since it would be highly copious but without adding interesting information.

Figure 4.13 shows the correlation between the value measured by experiment of the sediment content and the value of the sediment content obtained by the new equation proposed.

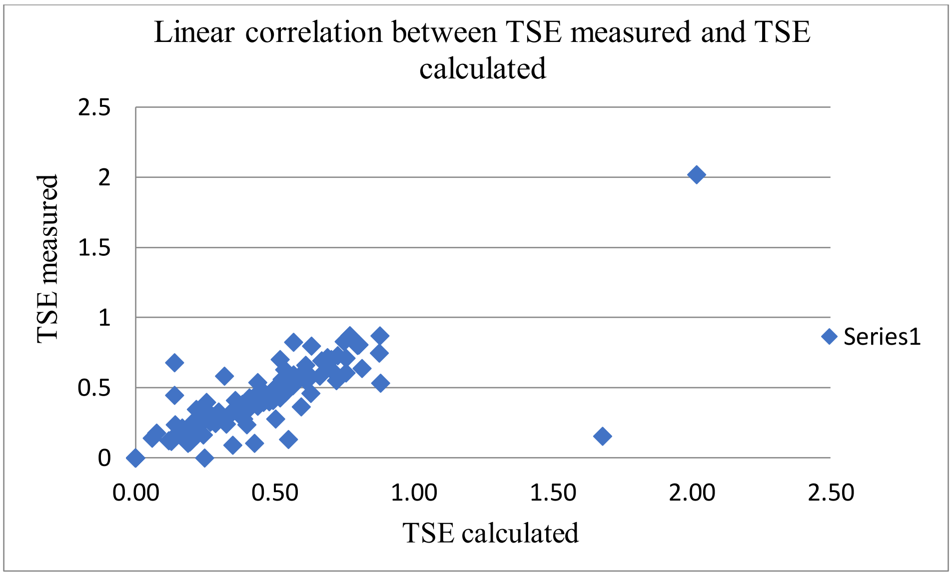


Figure 4.13. Final correlation obtained with several iterations.

It is not possible to show the final corret values for the parameters α and *k* since the information is reserved by IFPE.

4.1.4 Software implementation for the both parameters related to the properties

An IFPE software named "visu3D" is used to find a correlation between the mathematical parameter and the chemical or physical properties of the residue and of the cutter stock. Even in this case some steps must be followed.

Creation of the matrix

First of all, it is necessary to have a database with several properties both for the residues and for the cutter stocks, even though it could be possible that not all the properties considered play an important role in the sediment content deposition. The properties used to build the model are:

- *For the residue*
  Initial sediment content, density at 15°C, aromaticity, simulated distillation temperature (from the initial to the final value), SARA fraction, elemental composition (carbon, hydrogen, oxygen, nitrogen, sulfur, nickel and vanadium), AC7, and AC5.

- *For the asphaltenes contained in the residue*
  Aromaticity, elemental composition (carbon, hydrogen, oxygen, nitrogen, sulfur, nickel and vanadium), and molecular weight.

- *For the maltenes contained in the residue*
  Surface tension at 70°C, density at 15°C, and viscosity at 70°C.

- *For the cutter stocks*
  Initial sediment content, density at 15°C, kinematic viscosity at 40°C and 70°C, refractive index at 70°C, SARA fractions, pour point, flash point, AC7, surface tension at 70°C, elemental composition (carbon, hydrogen, oxygen, nitrogen, sulfur, nickel and vanadium), carbon insaturated by using the NMR technique, and the simulated distillation temperature (from the initial to the final value).

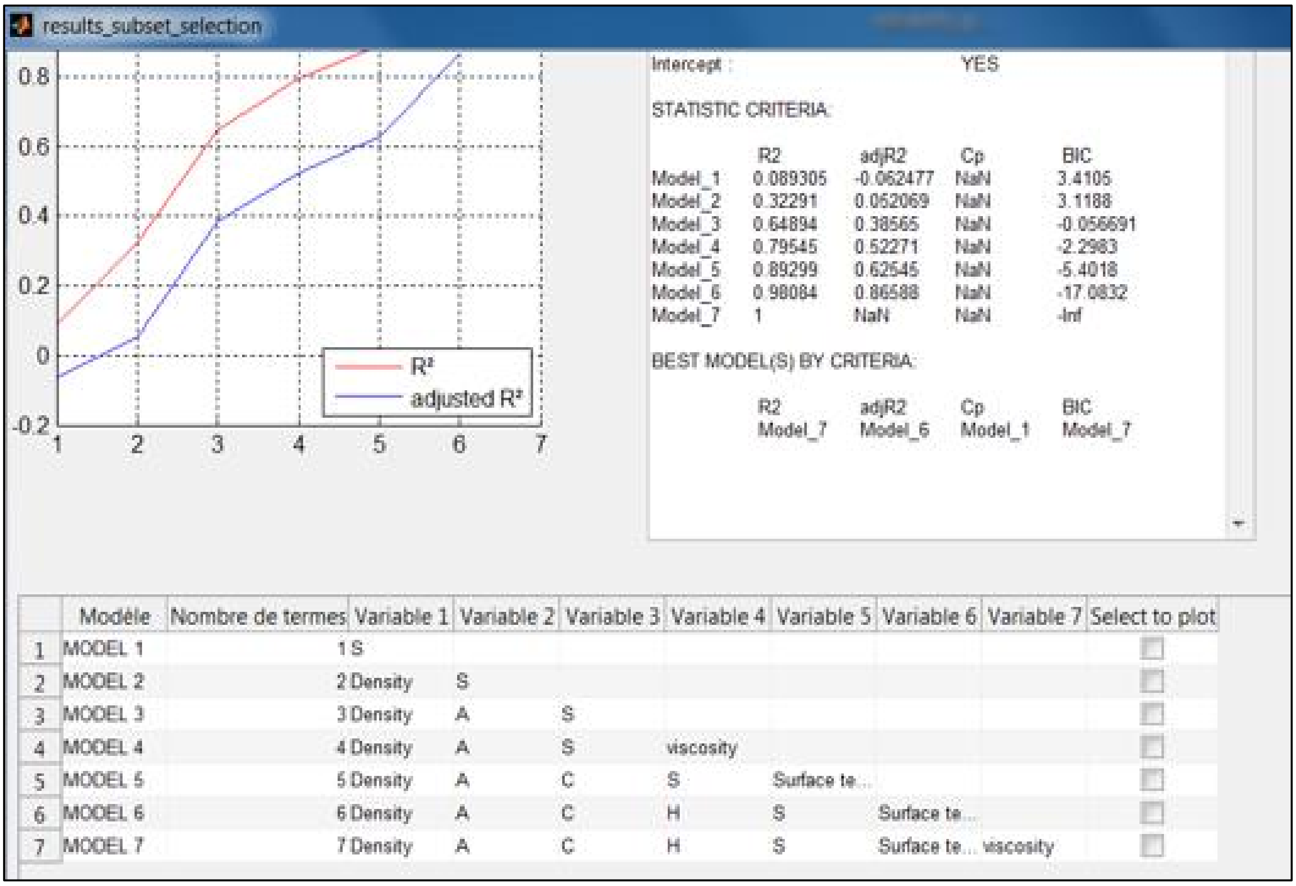
Relation of the chemical properties to the mathematical parameters.

The possibility to find properties which describe α or *k* are infinite, in fact all the properties gives some information on the behavior of the sediment deposition. Of course, it is not appropriate to use all the properties, in fact now it is the moment to remember that the model must be utilized at an industrial level, and at industrial level it is not possible to know or it is no possible to measure some of the properties. This is the reason why a selection of them must be done.

The software visu3D gives the possibility to understand also if the properties are related among them, in this way it is better to use just one property (maybe the one which is easier to be measured) and exploit the correlation among the properties that are possible to find in the scientific literature. In this case all the properties which are thought to be extremely important are used at the same time to find the correlations.

Visu3D allows to find different model based on the properties selected and it gives information about the error, of course an equation which contains several properties will have an error that is smaller than another equation which contain less properties. Mostly, increasing a lot the number of the properties does not decrease the error as well.

Figure 4.14 shows the result with all the model proposed by visu3D. In the screen it is possible also to notice on the top the error that each model gives, and as explained, it is possible to choose the best model also considering the error. To choose the model the reference was only the value of R2 but also the properties considered in the model.



```
Intercept :                          YES

STATISTIC CRITERIA:

           R2          adjR2       Cp     BIC
Model_1    0.089305    -0.062477   NaN    3.4105
Model_2    0.32291     0.052069    NaN    3.1188
Model_3    0.64894     0.38565     NaN    -0.056691
Model_4    0.79545     0.52271     NaN    -2.2983
Model_5    0.89299     0.62545     NaN    -5.4018
Model_6    0.98084     0.86588     NaN    -17.0832
Model_7    1           NaN         NaN    -Inf

BEST MODEL(S) BY CRITERIA:

           R2          adjR2       Cp         BIC
           Model_7     Model_6     Model_1    Model_7
```

	Modèle	Nombre de termes	Variable 1	Variable 2	Variable 3	Variable 4	Variable 5	Variable 6	Variable 7	Select to plot
1	MODEL 1	1	S							☐
2	MODEL 2	2	Density	S						☐
3	MODEL 3	3	Density	A	S					☐
4	MODEL 4	4	Density	A	S	viscosity				☐
5	MODEL 5	5	Density	A	C	S	Surface te...			☐
6	MODEL 6	6	Density	A	C	H	S	Surface te...		☐
7	MODEL 7	7	Density	A	C	H	S	Surface te...	viscosity	☐

Figure 4.14. Screen of the program visu3D for the parameter α.

For example, in this case the model chose is MODEL 6, R2 indicates the mean square root, and for this particular case it is possible to notice that there is a huge different with MODEL 5, while MODEL 7 is completely wrong.

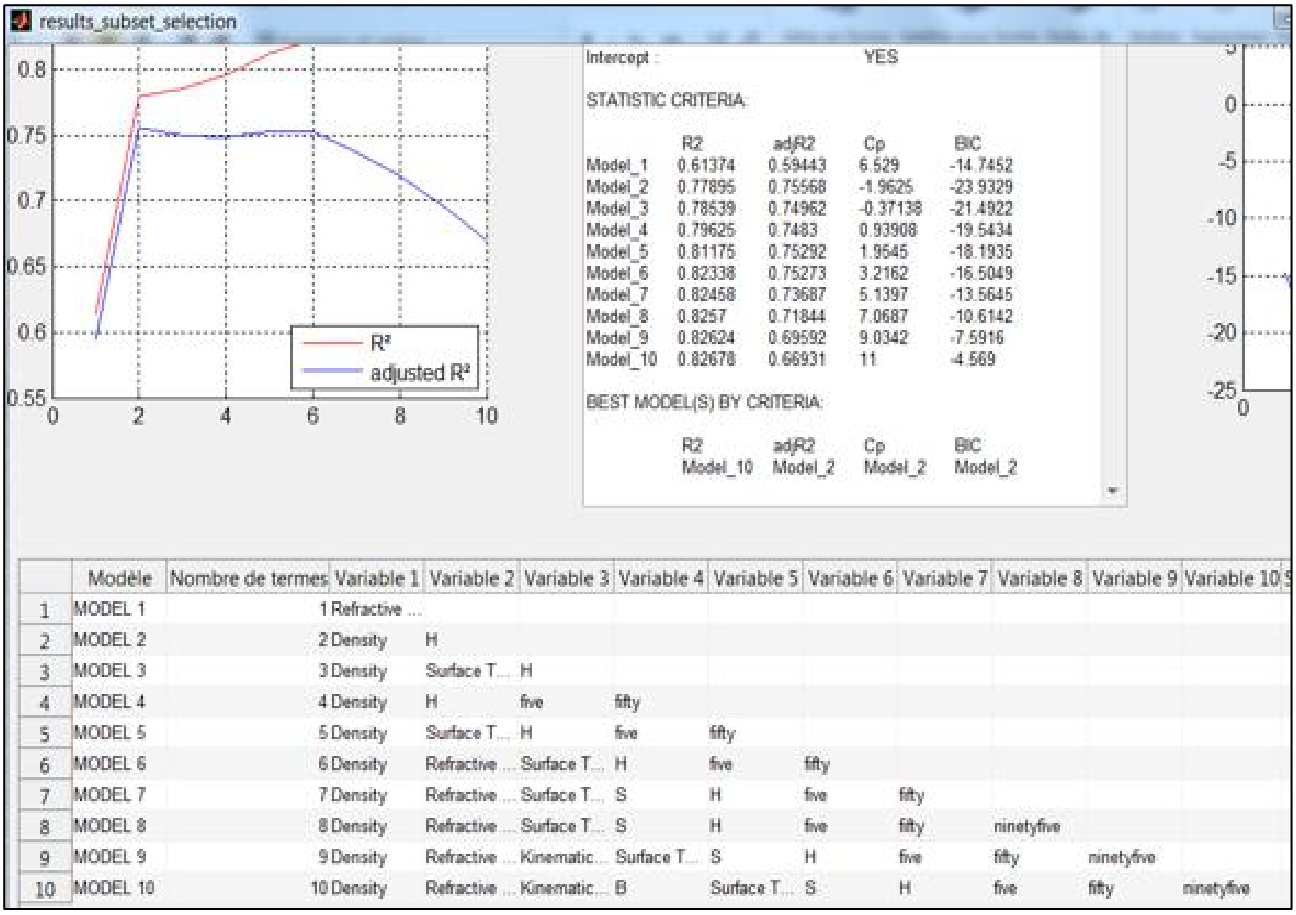
Equation 4.3 gives the form for the parameter α:

$$\alpha = a + b * \rho + c * A + d * C + e * S + f * \gamma \tag{4.3}$$

Where:

ρ is the density,
A the Aromatic content (from SARA fraction),
C is the amount of carbon,
S is the amount of sulfur,
γ is the surface tension of the maltenes.

While for the parameter *k*, two equations have been considered important, they take into account different properties. Figure 4.15 shows the result of visu3D for the parameter *k*.



```
Intercept :                    YES

STATISTIC CRITERIA:

            R2        adjR2      Cp         BIC
Model_1     0.61374   0.59443    6.529      -14.7452
Model_2     0.77895   0.75568    -1.9625    -23.9329
Model_3     0.78539   0.74962    -0.37138   -21.4922
Model_4     0.79625   0.7483     0.93908    -19.5434
Model_5     0.81175   0.75292    1.9545     -18.1935
Model_6     0.82338   0.75273    3.2162     -16.5049
Model_7     0.82458   0.73687    5.1397     -13.5645
Model_8     0.8257    0.71844    7.0687     -10.6142
Model_9     0.82624   0.69592    9.0342     -7.5916
Model_10    0.82678   0.66931    11         -4.569

BEST MODEL(S) BY CRITERIA:

            R2        adjR2      Cp         BIC
            Model_10  Model_2    Model_2    Model_2
```

	Modèle	Nombre de termes	Variable 1	Variable 2	Variable 3	Variable 4	Variable 5	Variable 6	Variable 7	Variable 8	Variable 9	Variable 10
1	MODEL 1	1	Refractive ...									
2	MODEL 2	2	Density	H								
3	MODEL 3	3	Density	Surface T...	H							
4	MODEL 4	4	Density	H	five	fifty						
5	MODEL 5	5	Density	Surface T...	H	five	fifty					
6	MODEL 6	6	Density	Refractive ...	Surface T...	H	five	fifty				
7	MODEL 7	7	Density	Refractive ...	Surface T...	S	H	five	fifty			
8	MODEL 8	8	Density	Refractive ...	Surface T...	S	H	five	fifty	ninetyfive		
9	MODEL 9	9	Density	Refractive ...	Kinematic...	Surface T...	S	H	five	fifty	ninetyfive	
10	MODEL 10	10	Density	Refractive ...	Kinematic...	B	Surface T...	S	H	five	fifty	ninetyfive

Figure 4.15. Screen of the program visu3D for the parameter *k*.

In this case two equation have been considered for the parameter *k*, in fact MODEL 3 and MODEL 4 give back an error that is not so different from that model which take into account ten properties, for this reason in this case it possible to consider a model which of course it is less “precise”, but considers also less properties.

Equation 4.4:

$$k_1 = a + b * \rho + c * \gamma + d * H \tag{4.4}$$

Where:

ρ represents the density,
γ is the surface tension,
H represent the amount of hydrogen.

The other equation proposed by the software is given by equation 4.5:

$$k_2 = a + b * \rho + c * H + d * DS5 + e * DS50 \quad (4.5)$$

Where:

ρ represents the density,
H represent the amount of hydrogen,
DS5 is the temperature which leads to a distillation of the 5 wt% of the sample,
DS50 is the Temperature which leads to a distillation of the 50 wt% of the sample.

Unfortunately, for both equation it is not possible to share the information about the numerical value of the coefficients, due to the confidentiality of the information.

It possible to use both equations and the choice can be done based on the refinery and on the properties they are able to measure in loco. Of course, the knowledge and the facility to measure the properties has been the major factor to be considered for the building of the equation that give the parameters. Equation 4.4 which contain one parameter more, describe better the relationship between the properties and the *k*, but both equations are corrected and can be used. Now that the mathemathical relations are found, it is possible to summarize the values of the parameters and to show if the new values, found thanks to visu3D are better than the values found simply using the Excell software.

Figure 4.16, 4.17, and 4.18 show the correlation between the values calculated thanks to visu3D and the values calculated thanks to Excel, it is possible to notice it is almost linear.

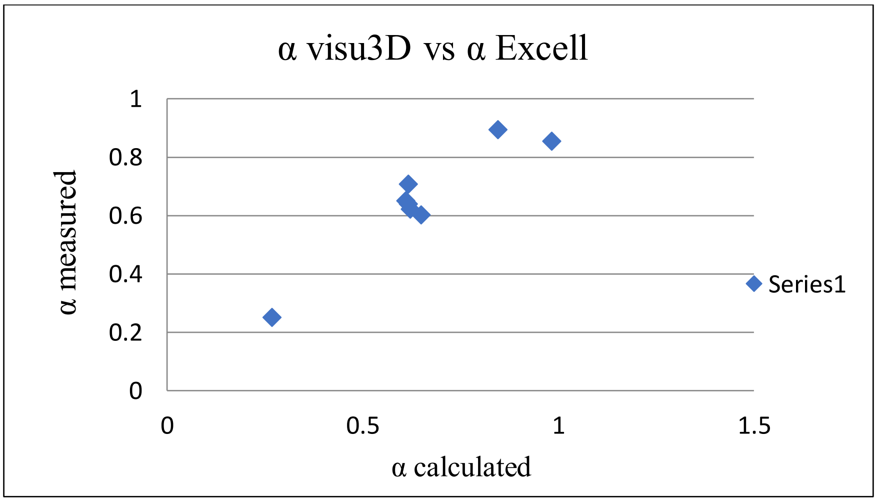


Figure 4.16. α calculated thanks to visu 3D vs α calculated thanks Excell

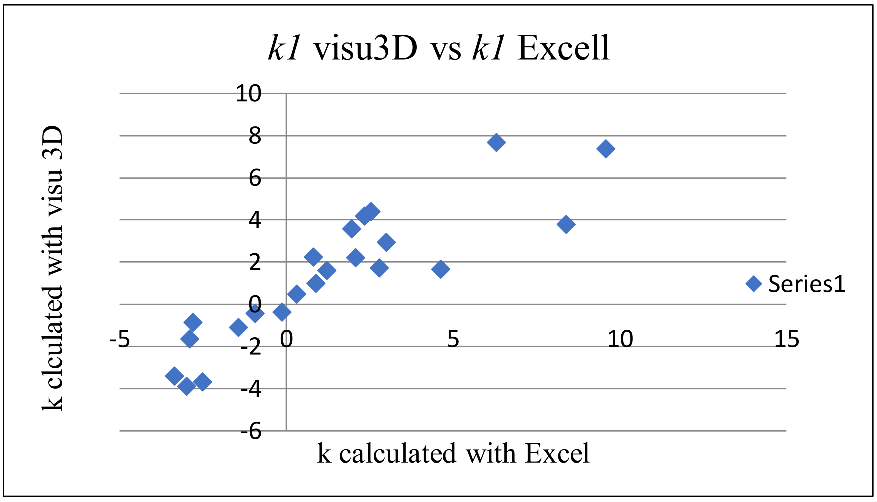


Figure 4.17. $\boldsymbol{k_1}$ calculated thanks to visu 3D vs $\boldsymbol{k_1}$ calculated thanks Excel.

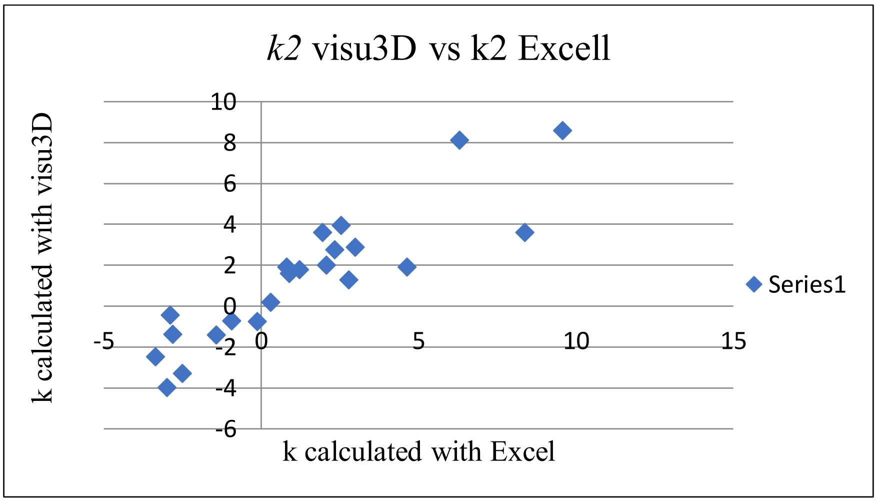


Figure 4.18. $\boldsymbol{k_2}$ calculated thanks to visu 3D vs $\boldsymbol{k_2}$ calculated thanks Excel.

4.1.5 Validation of the model

4.1.5.1 Experimental part

Several ternaries mixtures both with two residues and a cutter stock, or the opposite, it means two cutter stocks and only one residue, are created in order to validate the model. All the ternaries mixtures were not considered for the building of the model. The model found, in fact, is tested to predict the sediment content of the new blends.

Table 4.6 shows the concentration of the general blends created for the validation of the model.

Table 4.6. Concentration of the general blends created for the validation of the model.

Concentration of the cutter stocks	*Concentration of Residuo 1*	*Concentration of Residuo 2*
0,1	0,54	0,36
0,2	0,48	0,32
0,3	0,42	0,28
0,4	0,36	0,24

Figures 4.19, 4.20, 4.21, 4.22, 4.23, and 4.24 show the behavior of each blends created with two different residue and only one cutter stocks.

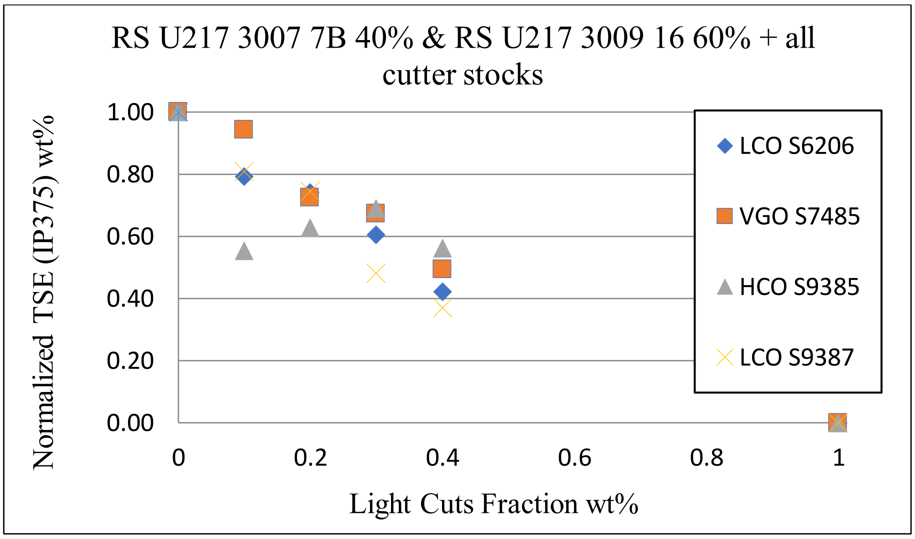


Figure 4.19. TSE content evolution of a ternary mixture

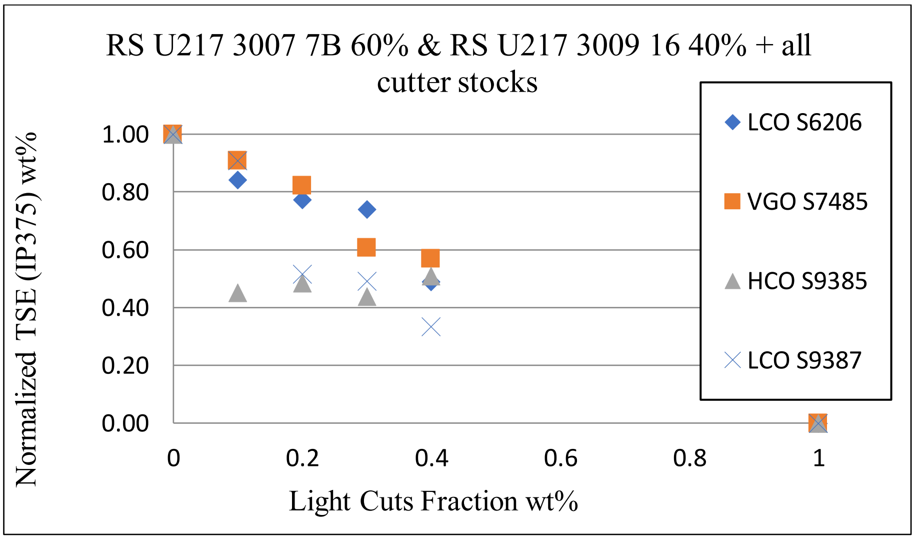


Figure 4.20. TSE content evolution of a ternary mixture

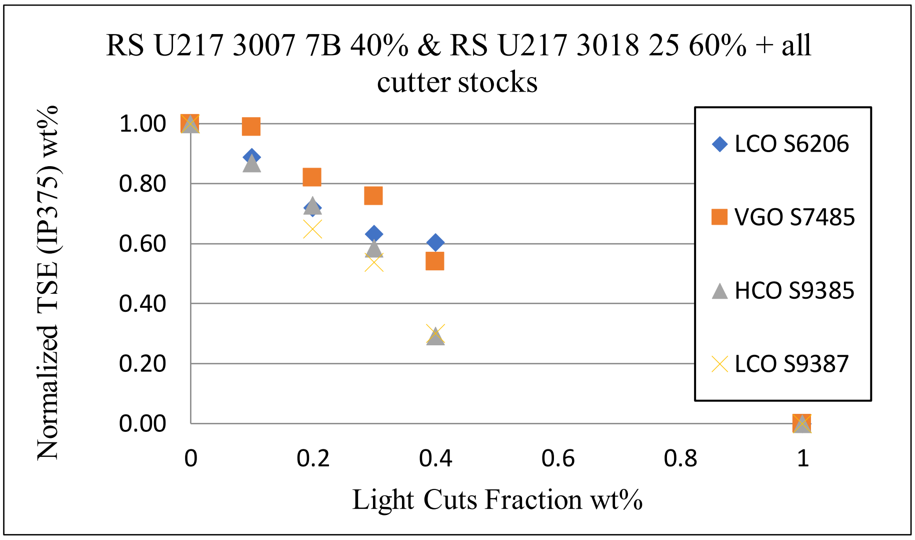


Figure 4.21. TSE content evolution of a ternary mixture

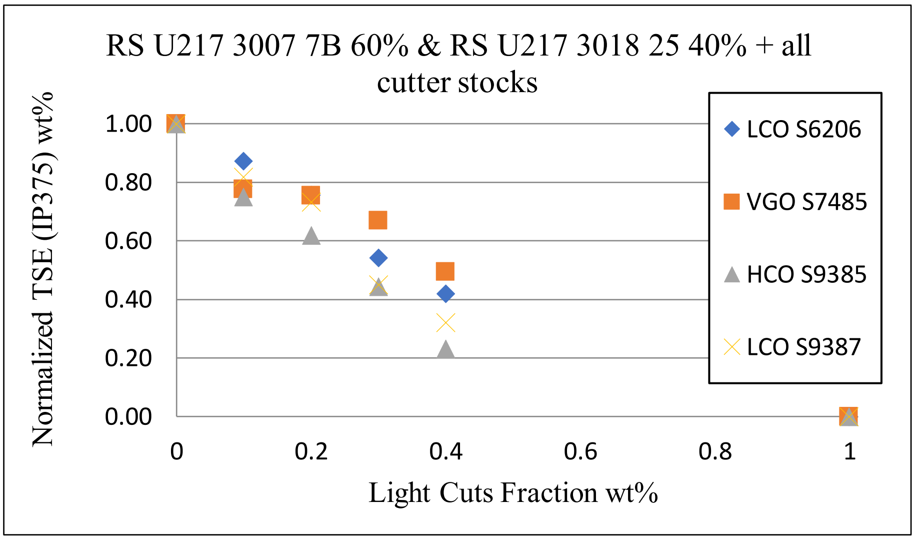


Figure 4.22. TSE content evolution of a ternary mixture

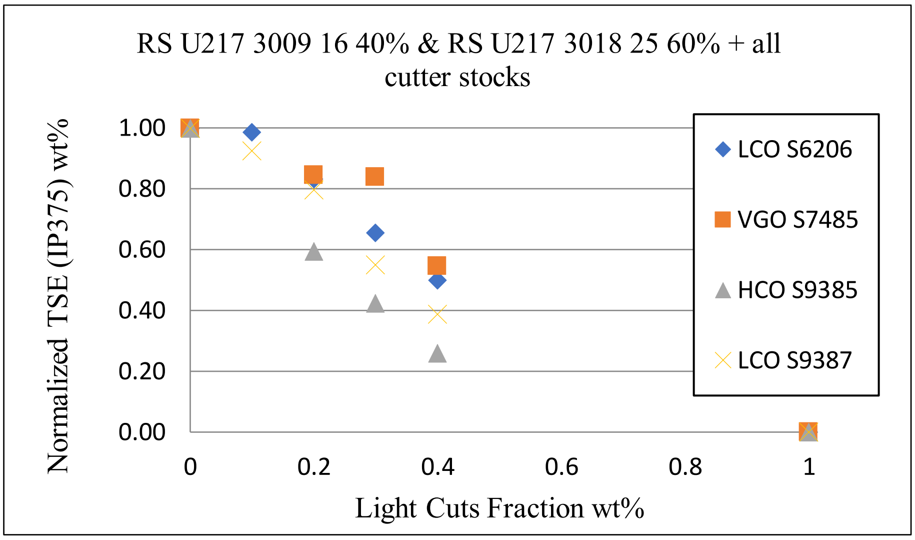


Figure 4.23. TSE content evolution of a ternary mixture

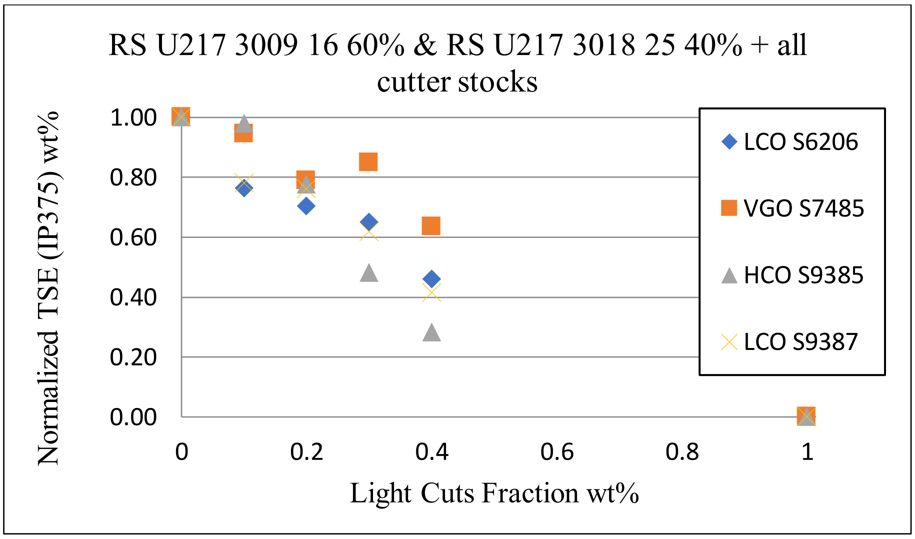


Figure 4.24. TSE content evolution of a ternary mixture

Concerning the mixtures which consider two residues have a behavior very similar to the binary mixtures. This is due to the fact that mixtures between residues can be considered as a single residue. The behavior of the sediment deposition is the same that occours when binaries mixtures are considered, which means a quite linear trend for the VGO S7485, while a more curve trend for the other cutter stocks. The mixtures that gives worst behavior seems to be the two binaries of the RS U217 3007 7B and RS U217 3009 16, for both compositions. This could be because of the initial sediment content which is very different for the two residues but it can be also because of an error due to the experiment.

Table 4.7 shows the concentration of the general blends created for the validation of the model.

Table 4.7. Concentration of the general blends created for the validation of the model

Concentration of Residuo	*Concentration of Cutter Stocks 1*	*Concentration of Cutter Stocks 2*
0,9	0,07	0,03
0,9	0,05	0,05
0,9	0,03	0,07
0,7	0,21	0,09
0,7	0,15	0,15
0,7	0,09	0,21

Figures 4.25, 4.26, and 4.27 show the behavior of blends created with one residue and two different cutter stocks.

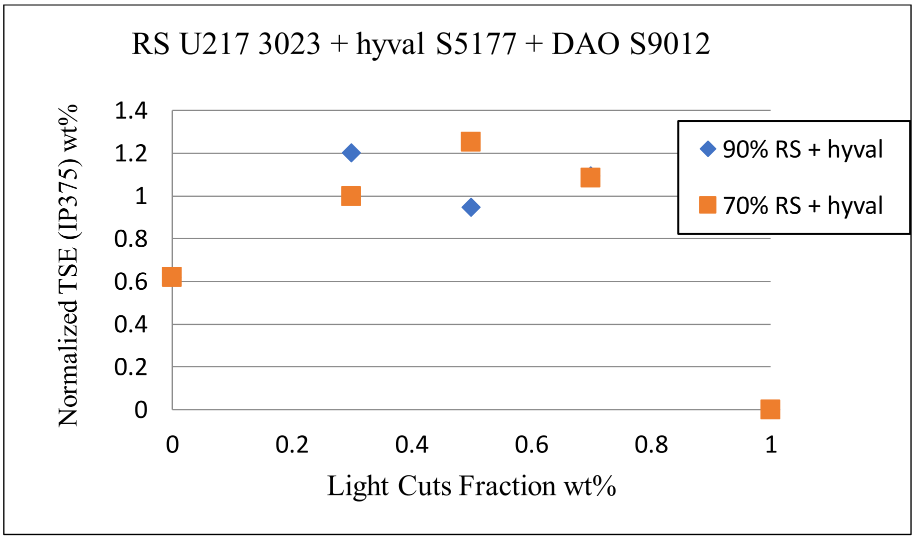


Figure 4.25. TSE content evolution of a ternary mixture

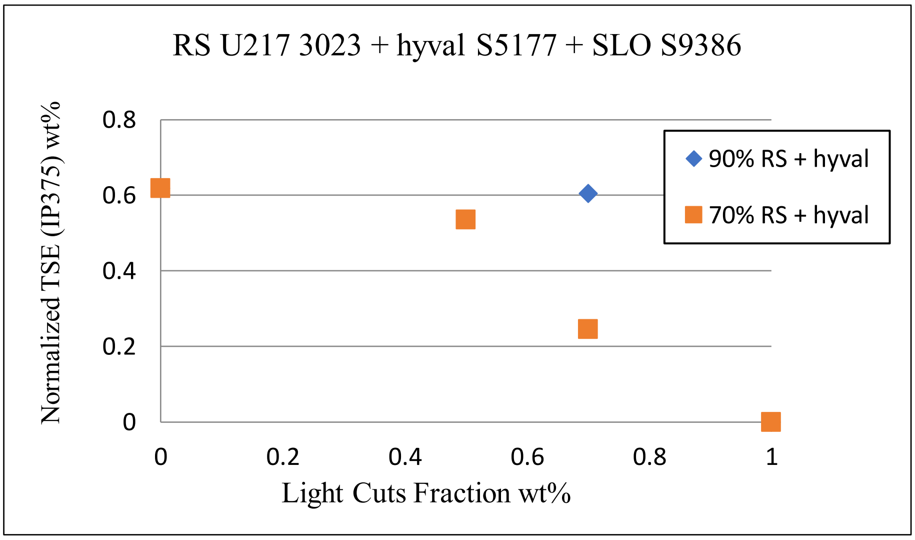


Figure 4.26. TSE content evolution of a ternary mixture.

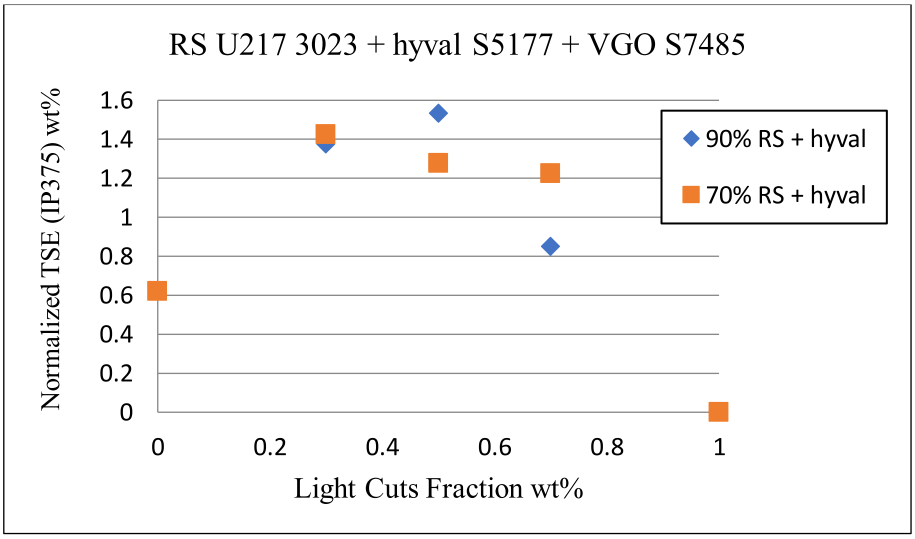


Figure 4.27. TSE content evolution of a ternary mixture.

In these cases the behavior is completely unexpected. In fact, it could appear very strange that the sediment content increase if there is the dilution with cutter stocks, but the fact is that one of the cutter used is the HYVAL S5177 which is a diesel and that is not very aromatic, for this reason there is the increasing of the sediment content. It seems that the effect of the aromaticity is very important in these cases, because the other cutter stocks is not very able to stabilize a lot the mixtures.

It appears, in first analysis, that the choice to have also aromatics characteristics in the parameter *k* is correct, where for both equations found is given by the hydrogen content in the cutter stocks.

4.1.5.2 Modelling part

For this last part it is necessary to validate the model, which means to understand if the model found is a good approximation of the real value of the sediment contents obtained by the filtration experiments, and in this case it should give better values respect to Hajjami's equation. On the other hand, the model found is not correct enough and for this reason a bigger database it is necessary, and more filtrations will be necessary or maybe more physical and chemical properties will be necessary.

It is necessary to validate the model with blends which were not used for the building of the model itself, for several reasons. For of all it necessary to understand if the model found can be used with all the mixtures that are possible to be created, using any kind of residue and of cutter stocks. And secondly, because another aim of the internship was to understand also a mixing rule for ternaries mixtures, and for this reason it necessary to validate the model with ternaries.

Because of ternaries mixtures have been created, to calculate the final value of the sediment content it was necessary to calculate the average value of the α and k parameters, the mathematical equation of α and k are known. Also, the average value of the initial sediment contents, for the cases where the ternaries mixtures was created with two different residues.
And of course, because of two different parameters for the cutter stocks have been found, the validation is conducted using the both values.

As always, by knowing the initial sediment content or the average sediment content, the composition of the mixtures, the value of the α and k parameters, it was possible to calculate that value of sediment content that the model found gives back.

For the blend where the ternary mixtures were created with two different residues, Figure 4.28 and Figure 4.29 show the correlation between the prediction with the equation proposed and the measured values. 4.28 using the correlation of k_1 while 4.29 using k_2.

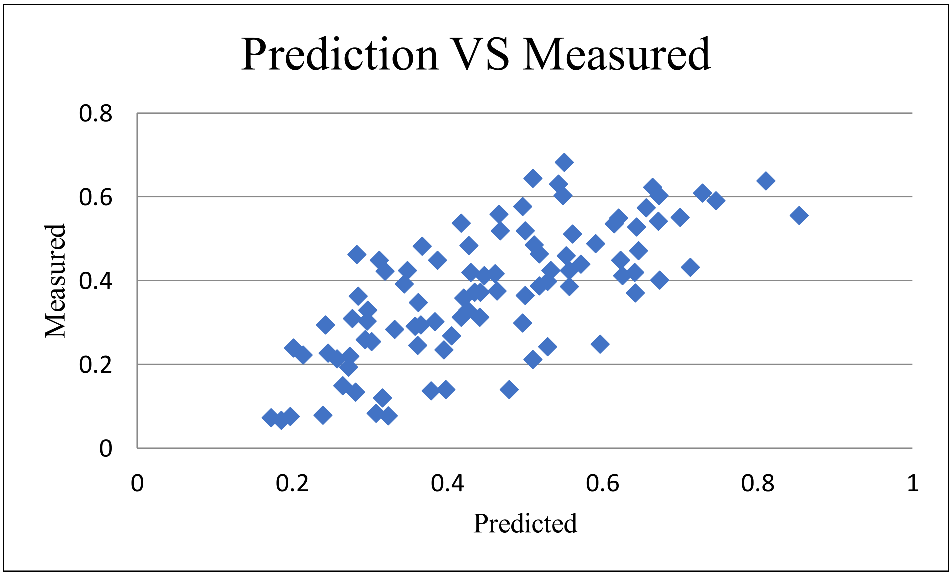


Figure 4.28 Correlation between the prediction with the equation proposed and the measured values (two residues and one cutter stock). Using k_1.

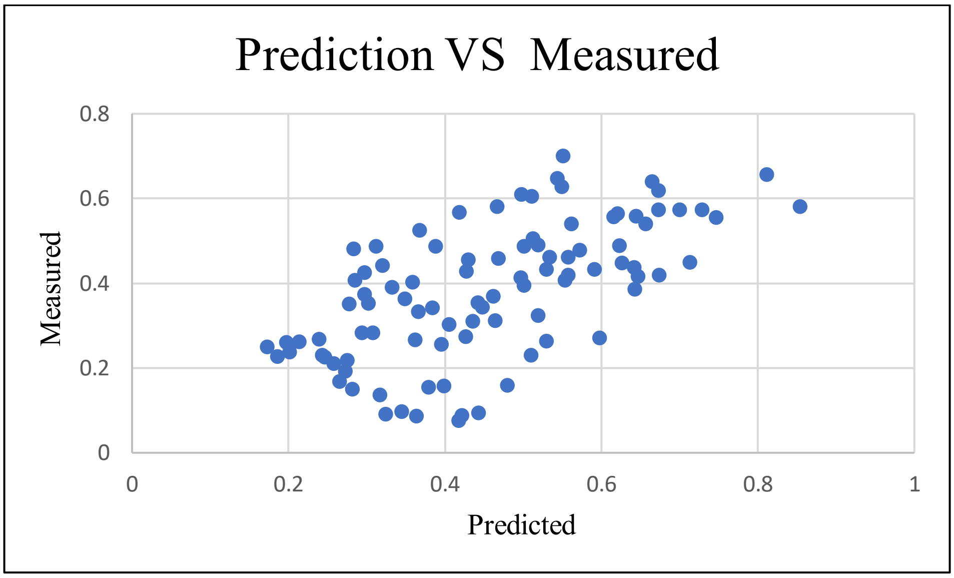


Figure 4.29. Correlation between the prediction with the equation proposed and the measured values (two residues and one cutter stock). Using k_2.

It is possible to notice that the correlation it not perfectly linear, but it is not completely bad. This simply means that a bigger database it is necessary and some little improvement must be done.

While, for the blend where the ternary mixtures were created with two different cutter stocks, figure shows the correlation between the prediction and the measured values. Figure 4.30 shows the prediction using k_1.

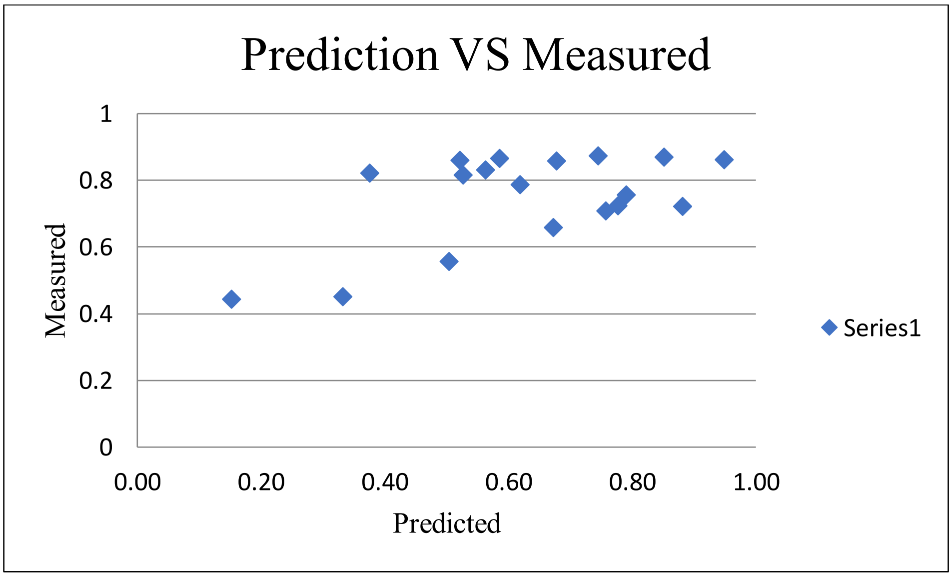


Figure 4.30. Correlation between the prediction with the equation proposed and the measured values (one residue and two cutter stocks). Using k_1.

While Figure 4.31 shows the prediction using k_2.

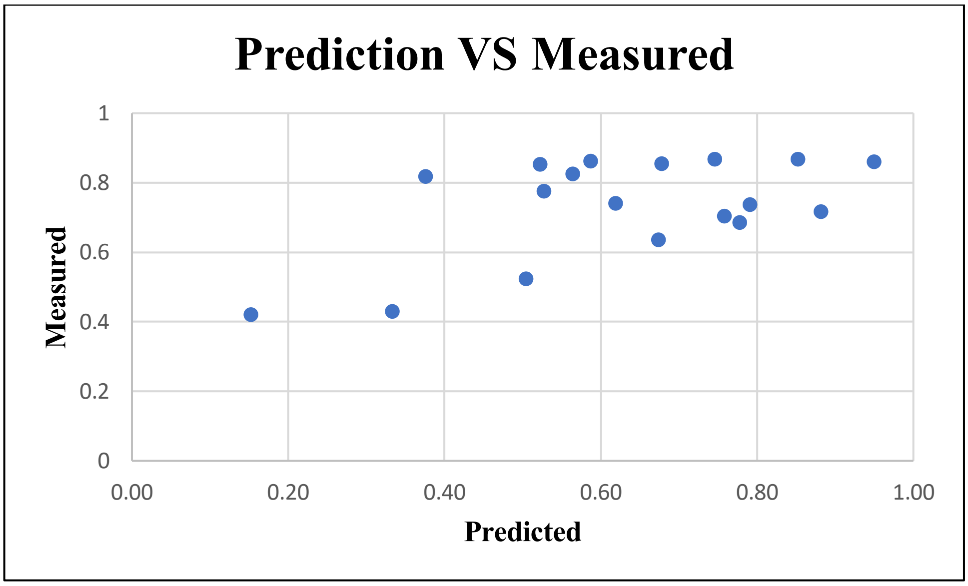


Figure 4.31. Correlation between the prediction with the equation proposed and the measured values (one residue and two cutter stocks). Using k_2.

In this case the prediction it is not very good for both the parameter k, but it is necessary to remember that for this kind of ternaries the cutter stock used was a diesel, the HYVAL S5177. The problem with diesel, as said before, is that it is not very aromatic and this create problem for the parameter k. It looks like obvious that the average of the parameter k was not good to calculate in an appropriate way the value of the sediment content.

4.1.5.3 Performance of the prediction

As said in chapter 3.1.1 it is necessary to calculate the error committed with the using of this kind of model.

Different kind of error are calculated, the equations are presented in Chapter 3, and are presented in table 4.8 for the mixtures with two residues, while table 4.9 is for the mixtures with two cutter stocks.

Table 4.8. Error of the blends with two residues and one cutter stock.

Kind of error	*Numerical value of the error using* $\boldsymbol{k_1}$	*Numerical value of the error using* $\boldsymbol{k_2}$
RMSE	0,1471	0,1516
ε	0,2867	0,2815
β	0,1256	0,1234

Table 4.9 Error of theblends with two cutter stocks and one residue.

Kind of error	*Numerical value of the error for* $\boldsymbol{k_1}$	*Numerical value of the error for* $\boldsymbol{k_2}$
RMSE	0,2062	0,1977
ε	0,3841	0,3633
β	0,1653	0,1594

There is no a big difference the error, but the prediction for the ternaries which contain only one cutter stock results to be better.

The error can be considered small enough when it is minor than a certain value. Table 4.10 shows the acceptable values of the error.

Table 4.10 Value acceptable of the error.

Kind of error	
RMSE	< 0,20
ε	< 0,20
β	0,15 - 0,20

For this reason, it is, probably, necessary to improve the parameter k adding more properties information. In fact, the error is bigger for the case of ternaries mixtures composed by two different cutter stocks. Probably, the reason why the results are not good enough is because the use of a diesel, which is not aromatics and it increases the sediment content.

5. Conclusion

The following chapter reports the final results which have been achievied during the internship. In accordance with the initial premises that set the objectives of the application, the intent is to present that obtained success. The work done during the internship should not be considered an end itself, since it is possible to have better and better results increasing the database. For this reason, it will be presented a way to better improve the results obtained and an overview of future developments.

5.1 Conclusion

The aim of the study is to determine a mixing rule able to describe the behavior of the sediment deposition of the asphaltene particles. The importance of this type of mixing rule is due to the wish to understand and to be able to predict what happens in a mixture between light and heavy oil. The importance of the mixture is due to the fact that in this way not only light petroleum is utilized, since also the heavy oil, called residue, is used, in this way it is not wasted.

The problem is that any time there is a blend of heavy and light, the asphaltenes contained in the residue can form agglomerate and deposit, causing problems in the pipes of the power plant or problems in the equipment. For this reason, it is extremely important to predict the sediment content deposition, in order to avoid it and to be able to choose the correct light oil which better stabilize the mixture.

At the beginning it was thought that a thermodynamic and theoretical approach was the best to describe the sediment content deposition. It was quite easy to demonstrate and to find a mathematical model, the major problem was about the properties took into account: most of them are really hard to be measured. Due to this, an empirical approach has been followed in this internship. Using an empirical approach, instead of the thermodynamic one, allows to save time and to be able to find a model that truly describes the sediment deposition in a correct way, even though it is not extremely precise.

The model found in IPFE must be utilized at industrial level, it is importance obviously the correctness but most importance is that the model must be adapted to the largest number of residue and cutter stocks.

The internship, lasted six months, took into account more than two hundred binary mixtures between hydro-converted residues and several cutter stocks in order to build a stronger model than the one found in the previous internship done by Hajjami. Several properties related to residue, to the asphaltenes, to the maltenes, and to cutter stocks were measured. In fact, the model was linked to the properties both of cutter stocks and of residues. After the discovery of the model, ternary mixtures were considered to validate it.

The importance in using new mixtures for the validation of the model is crucial: in this way it possible to understand if the model can be applied to other mixtures. The ternary mixtures created were of two types: ternary created with two residues and one cutter stocks, and ternary created with two cutter stocks and only one residue. It is easily to notice that the blends containing two residues gives better results than the mixtures obtained by the blending of two cutter stocks. In fact, one of the cutter stocks used was a diesel, the HYVAL S5177 which is not aromatic and that destabilizes the mixtures a lot.

5.2 Future development

The developed model could be better and better exhaustive by increasing the data collected, maybe in the next years with the future internships. With more experiments will increase the data to find a better model. Having more properties for all the residue and the cutter stocks considered will give better opportunities to find a better approximation for the parameters α and k.

Another way to better improve the model could be to consider in the equation the variable of the time, which is also an important factor which play a role in the sediment deposition. It is common opinion that sediment content increases during the time, and this fact has been found during the internship. In fact, one of the residues was filtered a second time a month after the first filtration and the discovered was an improvement of the sediment deposition. The sediment content evolution in time should be modeled mostly in order to prevent the instability, in this way should be easy to predict the (exactly) moment in which the sediment is too high.

Appendix

Appendix 1 – Other equations tested

$$y = \left[W_R * TS_{0,R} * \alpha\right] * e^{-k\,W_{CS}} \tag{1}$$

$$y = \left[\left(W_R * TS_{0,R}\right) + \alpha\right] * e^{-k\,W_{CS}} \tag{2}$$

$$y = \ (W_R + \alpha) * TS_{0,R} * e^{-k\,W_{CS}} \tag{3}$$

$$y = \ \left(TS_{0,R} + W_R\ \right) * \alpha * e^{-k\,W_{CS}} \tag{4}$$

$$y = \ \left(TS_{0,R} + \ \alpha\right) * W_R * e^{-k\,W_{CS}} \tag{5}$$

$$y = \ \frac{W_R * TS_{0,R}}{\alpha} * e^{-k\,W_{CS}} \tag{6}$$

$$y = \ (W_R - \alpha) * TS_{0,R} * e^{-k\,W_{CS}} \tag{7}$$

$$y = \ \left(TS_{0,R} - \ \alpha\right) * W_R * e^{-k\,W_{CS}} \tag{8}$$

$$y = \ (\alpha - \ W_R) * TS_{0,R} * e^{-k\,W_{CS}} \tag{9}$$

$$y = \ \left(\ \alpha - \ TS_{0,R}\right) * W_R * e^{-k\,W_{CS}} \tag{10}$$

$$y = \ \frac{W_R + TS_{0,R}}{\alpha} * e^{-k\,W_{CS}} \tag{11}$$

$$y = W_R * \left(TS_{0,R} + \ \frac{1}{\alpha}\right) e^{-k\,W_{CS}} \tag{12}$$

$$y = TS_{0,R} * \left(W_R - \ \frac{1}{\alpha}\right) e^{-k\,W_{CS}} \tag{13}$$

$$y = W_R * \left(TS_{0,R} - \ \frac{1}{\alpha}\right) e^{-k\,W_{CS}} \tag{14}$$

$$y = TS_{0,R} * \left(\ \frac{1}{\alpha} - \ W_R\ \right) e^{-k\,W_{CS}} \tag{15}$$

$$y = \left(W_R + TS_{0,R}\right) * e^{-\alpha} * e^{-k\,W_{CS}} \tag{16}$$

$$y = \left(TS_{0,R} + e^{-\alpha}\right) * W_R * e^{-k\,W_{CS}} \tag{17}$$

$$y = (W_R - e^{-\alpha}) * TS_{0,R} * e^{-k\,W_{CS}} \tag{18}$$

$$y = \left(TS_{0,R} - e^{-\alpha}\right) * W_R * e^{-k\,W_{CS}} \tag{19}$$

$$y = (e^{-\alpha} - W_R) * TS_{0,R} * e^{-k\,W_{CS}} \tag{20}$$

$$y = \left(e^{-\alpha} - TS_{0,R}\right) * W_R * e^{-k\,W_{CS}} \tag{21}$$

Appendix 2

Abbreviations

5%T	Temperature which leads to a distillation of the 5 wt% of the sample
AC7	Asphaltenes precipitated by heptane
AH	Arabian Heavy
AR	Atmospheric Residue
Caro	Carbon Aromatic
GO	Gasoil
HCO	Heavy Gas Oil
k	Cutter stocks effect rate on sediments content
LCO	Light Cycle Oil
n_D	Refractive Index
RS	Residue of Stripping
SLO	Slurry Oil
SR	Straight Run
TSE	Total Sediment Existent
TSP	Total Sediment Potential
VGO	Vacuum Gas Oil
VR	Vacuum Residue

List of symbols

α	Residue effect rate on sediment content
β	Bias
ε	Error
μ	Activity coefficient

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