OPTIMISATION OF DIESEL AND GASOLINE BLENDING OPERATIONS

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Abstract

Diesel, one of the main petroleum products, is widely used in industry and transportation. Only high quality diesel product can survive in the more and more competitive market. The optimization methodology for diesel production and management is critical to refineries' profitability.

LP/MIP models have been applied in diesel blending planning and scheduling in the last decades. With the benefits of reducing the model scale and computing efforts, LP/MIP models lead to operation results with inaccurate property estimation and profit loss due to the accuracy loss in the linearisation of blending models. To improve model accuracy, more accurate property prediction models for diesel blending should be incorporated into the refinery planning and schedule methods to improve decision making procedure in the case of scheduling for diesel blending, where academic effort is almost absent.

A model for planning of refinery diesel streams is developed to optimise the diesel production of a refinery. Nonlinear blending models are applied to calculate blending properties more precisely than conventional linear models. Due to the large number of equations and variables, it may be generated to an infeasible solution if the given initial points are not good enough. To avoid this situation, a solution algorithm is proposed. Based on the NLP planning model, a model for scheduling diesel blending is developed. In order to improve the model accuracy, nonlinear blending correlations are used, which lead to a complicated MINLP problem that cannot be solved by existing MINLP solver directly. A robust solution algorithm is proposed in this thesis to help optimizing the MINLP problem. A case study of diesel production blending scheduling is introduced to illustrate how to model a diesel blending scheduling problem and the efficient and reliability of the solution algorithm.

Besides, the proposed MINLP model and the solution algorithm can be extensively applied to other processes in a refinery, such as gasoline blending. Once gasoline blending models are taken into account, the model can be modified to optimize the gasoline blending scheduling problem.

DECLARATION

No portion of the work referred to in the thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

Shixun Jiang Manchester, 2016

Copyright Statement

Dedicated to my dearest parents and wife

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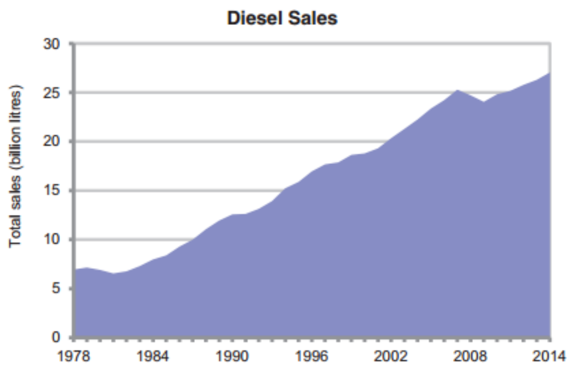
Chapter 1 Introduction

1.1 Diesel

The name ‘diesel’ comes from the German inventor and mechanical engineer who invented diesel engine. Today, diesel engines are used worldwide for transportation, manufacturing, power generation, construction, and farming. Their success comes from their efficiency, economy, and reliability. Sales of on-road diesel fuel in the U.S. rose from 32 billion gallons in 1999 to over 37 billion gallons in 2004, an increase of nearly three percent annually. In UK, road diesel fuel sales increase from 11 billion litres in 1988 to 28 billion litres in 2013 (Vandervell, 2015). Over the period to 2030, energy analysts forecast that diesel demand will continue to grow and petrol demand to decline, albeit both at a much slower rate than that seen in the last decade (IHS, 2013).

Diesel fuel is a mixture of hydrocarbons obtained from oil petroleum. Its boiling points are normally in the range of 150 to 380 ℃. It is produced from oil refineries by refining and converting crude oil into various hydrocarbon fractions. The beginnings of the oil refining industry date back to 1859, when crude oil was discovered in Pennsylvania. The first product refined from crude was kerosene, which was used as lamp oil (Chevron 1998). Since only a fraction of the crude could be refined into kerosene, quantities of petroleum by-products were wasted. These petroleum by-products attracted the attention of Rudolf Diesel, the inventor of compression ignition reciprocating engine. Although the original design by Rudolf didn’t work, the engine concept was re-designed by other engineers, resulting in a successful prototype in 1895. Both the engine and the fuel still bear the name of Diesel.

Nowadays, diesel has become one of the most important petrol products due to its high and increasing demand globally. From Figure 1.1, sales of diesel in UK have been steadily increasing for the last twenty years, with demand exceeding 27 billion litres in 2014. Meanwhile, Sales of petrol have been falling since reaching a peak of 33 billion litres in 1990, which was equivalent to 73% market share of transport fuels. Till the end of 2014, sales of petrol have fallen to below 17 billion litres. However, after barring a short decline period in 2008 and 2009 due to the economic recession, sales of diesel has increased to around 27 billion litres till the end of 2014.



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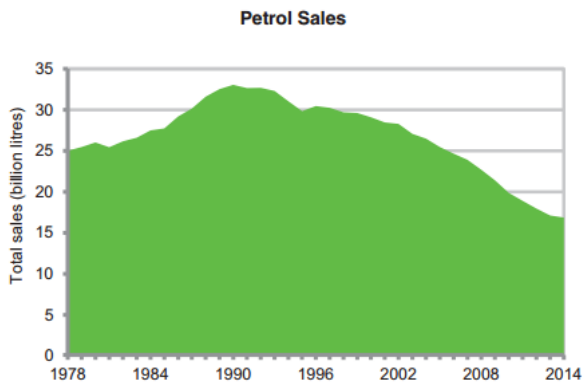

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Figure 1.1 Diesel and Petrol Sales in UK (UKPIA, 2015)

The increasing in diesel sales in UK is part of a Europe-wide trend, which has largely been fiscally driven for over two decades (UKPIA, 2015). In 2004, petrol sales were 4 billion litres greater than those of diesel, whilst annual registration of new diesel vehicles was still only one third of the total vehicle fleet. A key reason for this relatively slow uptake had been the lack of any tax advantage for diesel, which is taxed at the same rate as petrol. However, with the advances achieved in diesel engine performance leading to improved fuel efficiency relative to petrol, combined with changes in company car personal tax policy and VED (Vehicle Excise Duty) rates, consumers in recent years have increasingly favoured diesel cars. Today, approximately 53% of new registered vehicles in the UK are diesel fuelled (up from 49% in 2013), and over 61% of the 44 billion litres of road fuels sold in 2014 was diesel.

For diesel engine technical and environmental reasons, there are strict diesel fuel specifications including many property requirements. In U.S., the ASTM D975 standard covers seven grades of diesel. The specifications are presented in Table 1.1. Grade No.1 –D and No.2 –D both are consisted of 3 sub-grades: S5000, S500 and S15. The ASTM D975-04 edition of the standard first adopted the ‘Sxxx’ designation to distinguish grades by sulfer content. The S5000 grades correspond to the “regular” sulfer grades, the previous No. 1-D and No. 2-D. S500 grades correspond to the previous “Low Sulfer” grades (D975-03). S15 grades are commonly referred to as “Ultra-Low Sulfer” grades or ULSD in which the maximum requirement for sulfur content 15 ppm.

European Union Directive sets specifications for fuels to be used in Europe. For compression ignition engine fuels, the technical properties regulated by this directive include: cetane number, sulfer content, polycyclic aromatic hydrocarbons, density and some distillation characteristics, which are presented in Table 1.2.

Table 1.1 U.S. requirements for diesel fuel oils

Property	Test Method	No.1-D	No.2-D	No.4-D
Flash Point, °C , min	D 93	38	52	55
Water and sediment, % vol, max.	D 2709 D 1796	0.05	0.05	- 0.5
Distillation temperature, °C, 90% Volume Recovered: min max	D 86	 288	 282 338	
Kinematic Viscosity, mm^2/s at 40°C min max	D 445	 1.3 2.4	 1.9 4.1	 5.5 24.0
Ash, % mass, max.	D 482	0.01	0.01	0.1
Sulphur, ppm ,max	D 5453	15	15	-
Copper Strip Corrosion Rating	D 130	No.3	No.3	-
Cetane Number, min	D 613	40	40	30
Cloud Point, °C, max	D 2500	Varies	Varies	-
Ramsbottom carbon residue, max	D 524	0.15	0.35	-
Lubricity, 60°C,max	D 6079	520	520	-

Table 1.2 Diesel Fuel Requirements in Europe

Diesel Specification Parameter	Units	Limits	Test Method
Cetane Number		51.0 minimum	EN ISO 5165
Cetane Index		46.0 minimum	EN ISO 4264
Density at 15°C	kg/m^3	820 minimum to 845 maximum	EN ISO 3675 EN ISO 12185
Polycyclic Aromatic Hydrocarbons	% (m/m)	11 maximum	EN 12916
Sulphur Content	mg/kg	10.0 maximum	EN ISO 20846 EN ISO 20847 EN ISO 20884
Flash Point	°C	>55	EN ISO 2719
Carbon Residue (on 10% Dist. Residue)	% (m/m)	0.30 maximum	EN ISO 10370
Ash Content	% (m/m)	0.01 maximum	EN ISO 6245
Water Content	mg/kg	200 maximum	EN ISO 12937
Total Contamination	mg/kg	24 maximum	EN 12662
Copper Strip Corrosion (3 Hours at 50°C)		class 1	EN ISO 2160
Oxidation Stability	g/m3	25 maximum	EN ISO 12205
Lubricity, WSD at 60°C	µm	460 maximum	EN ISO 12156-1
Viscosity at 40°C	mm^2/sec	2.00 minimum to 4.50 maximum	EN ISO 3104
Fatty Acid Methyl Esters (FAME) Content	% V/V	5 maximum	EN 14078

Besides, to provide options for different climates, the EN 590 standard specifies six Temperature Climate Grades of diesel fuel (Grade A...F) which differ in the Cold Filter Plugging Point (CFPP) value (Table 1.3). In addition, there are five Arctic

Classes of diesel fuel (Class 0...4) characterized by different properties (Table 1.4). Each country shall detail requirements for a summer and winter grade, and may also include intermediate or regional grades as justified by national climate conditions.

Table 1.3 Temperate climate grades of diesel fuel in Europe

Characteristics	Class A	Class B	Class C	Class D	Class E	Class F	Units
CFPP	5	0	-5	-10	-15	-20	℃
Density at 15 ℃	820 - 860	820 - 860	820 - 860	820 - 860	820 - 860	820 - 860	kg/m³
Viscosity at 40 ℃	2 - 4.5	2 - 4.5	2 - 4.5	2 - 4.5	2 - 4.5	2 - 4.5	mm^2/s
Cetane index	46	46	46	46	46	46	
Cetane number	49	49	49	49	49	49	

Table 1.4 Arctic climate grades of diesel fuel in Europe

Characteristics	Class 0	Class 1	Class 2	Class 3	Class 4	Unit
CFPP	-20	-26	-32	-38	-44	℃
Cloud point	-10	-16	-22	-28	-34	℃
Density at 15 ℃	800 - 845	800 - 845	800 - 845	800 - 840	800 - 840	kg/m³
Viscosity at 40 ℃	1.5 - 4.0	1.5 - 4.0	1.5 - 4.0	1.4 - 4.0	1.2 - 4.0	mm^2/s
Cetane index	46	46	45	43	43	
Cetane number	47	47	46	45	45	

In China, different specifications have been allocated to different regions due to climate varying and economic reasons. Regulation GB 17691-2005 specified emission limits for China III-V stages, but included fuel specifications for the China III stage only. Faced with the lack of official fuel standards to ensure availability of ultra-low sulphur fuels that were necessary to enable emission technologies at the China IV/V stages, the Ministry of Environmental Protection adopted regulation GWKB 1.2-2011 which regulated sulphur and polyaromatics as toxics. Selected specifications are shown in Table1.5.

Table 1.5 Selected specifications of diesel fuel for motor vehicles

	China III	China IV	China V
Sulfur content, mg/kg	≤ 350	≤ 50	≤ 10
Cetane number, min-max	50-53	47-51	
Polyaromatic hydrocarbons, % (m/m)	⩽ 11	⩽ 11	≤ 11

For sulfer content, the limit was set as 50 ppm in several cities in 2008. From 2013, the State Council issued a timetable for upgrading fuel quality nationwide. . By the end of 2014, automotive diesel fuel sulfer will be set at 50 ppm (China IV) and by the end of 2017, sulfer limits for automotive gasoline and automotive diesel will be 10 ppm maximum (China V). Diesel fuel standards for China V were required to be issued by July 2013. In April 2015, the State Council advanced timeline for 10 ppm gasoline and diesel fuel by one year making it nationwide available by January 2017.

In the globalized world today，the products form a refinery may serve several regions. Refiners need to acquaint the varying specifications in different regions. For instant, the cetane number limit in U.S. is 40, but in Europe it is 51, which is similar in China. The specification differences in various regions may influence the diesel process and marketing decisions for a refinery.

1.2 Diesel production

Refining is the process of converting crude oil into high value products. The main processes adopted in a refinery are the following:

Separation processes: Crude oil is separated into hydrocarbon streams boiling at different temperatures by a process of distillation in the Crude Distillation Unit (CDU).

The products that are obtained directly from CDU are called straight-run products (e.g., straight-run diesel). The material that is too heavy to vaporize under atmospheric distillation is removed from the bottom of the column (atmospheric bottoms). The atmospheric bottoms can be fractionated further by a second distillation carried out under reduced pressure. The lower pressure in the distillation column allows some of the heavier components to be vaporized and collected. This process is called vacuum distillation; the distillated product is called vacuum gas oil (VGO), and the bottoms product is called vacuum residue.

Upgrading processes: These processes improve the quality of selected component streams depending on their use, by using chemical reactions to remove compounds present in trace amounts that give the material an undesirable quality, such as hydrotreating to remove sulfer. Otherwise the bulk properties of the streams are not changed.

Conversion processes: These processes fundamentally change the molecular structure of the feedstock streams, usually by “cracking” large molecules into small ones. Examples of these process units are Fluidized Catalytic Cracking Unit (FCCU), Hydrocracking unit (HC) and Delayed Coking Unit (DCU).

The primary aim of the FCCU is to convert streams suitable for the gasoline pool; however, one product stream, light cycle oil (LCO), is often blended into diesel fuel. Before blending, LCO undergoes subsequent hydrotreating to lower sulfer content which makes the LCO more stable and suitable for adding to diesel fuel. To meet the 15 ppm sulfer requirement in Euro 5 , LCO undergoes subsequent hydrotreating to lower sulfer content.

Hydrocracking is another major conversion process. It is similar to catalytic cracking because it uses a catalyst, but the reactions take place under a high pressure of hydrogen. The primary feed to the hydrocracking unit is VGO. During hydrocracking, large VGO molecules are cracked into smaller molecules by either cleaving carbon-carbon bonds or by plucking out sulfer and nitrogen atoms from -carbon-sulfer-carbon- and -carbon-nitrogen-carbon- molecular linkages. Because of the high hydrogen pressure used in hydrocracking, hydrogen is added to the fragmented molecular ends formed by either cleaving carbon-carbon bonds or by extracting sulfer and nitrogen linkage atoms; in addition, rings of some aromatic compounds are saturated with hydrogen during the hydrocracking process. Kerosene and diesel form a large percentage of the product from a hydrocracker. These products are nearly devoid of sulfer and nitrogen and are enriched in hydrogen.

The extent of conversion is the most significant difference between hydrotreating and hydrocracking. "Conversion" is defined as the difference in amount of unconverted oil between feed and product divided by the amount of unconverted oil in the feed. Unconverted oil is defined as material that boils above a specified temperature. For vacuum gas oil (VGO), a typical specified temperature is around 343℃. Conversion in hydrotreaters is less than 15 wt%, while conversion in hydrocrackers and mild hydrocrackers exceeds 20 wt%.

The vacuum residue can be processed in a Coker Unit that thermally cracks the long chain hydrocarbon molecules in the residual oil feed into shorter chain molecules that forms the Coker Light Gas Oil (CLGO), which can either be blended into diesel directly or be refined to be a diesel product.

In a modern refinery (Figure 1.2), diesel intermediates can be produced from various operating units such as CDU (crude oil distillation unit), catalytic cracking, hydro-treater, hydro-cracker and delayed coker etc. Various streams from different units with different specifications can be classified to diesel. However, not all streams within the required carbon atom numbers (C10-C23) and boiling ranges (150℃

-370℃) of diesel from the units can be blended to meet the quality requirements for market. Compared with the standard specifications, some of the diesel streams have superior properties and others have inferior properties.

According to particular blending ratios, the diesel streams with inferior properties can be blended to diesel products that meet standard specifications.

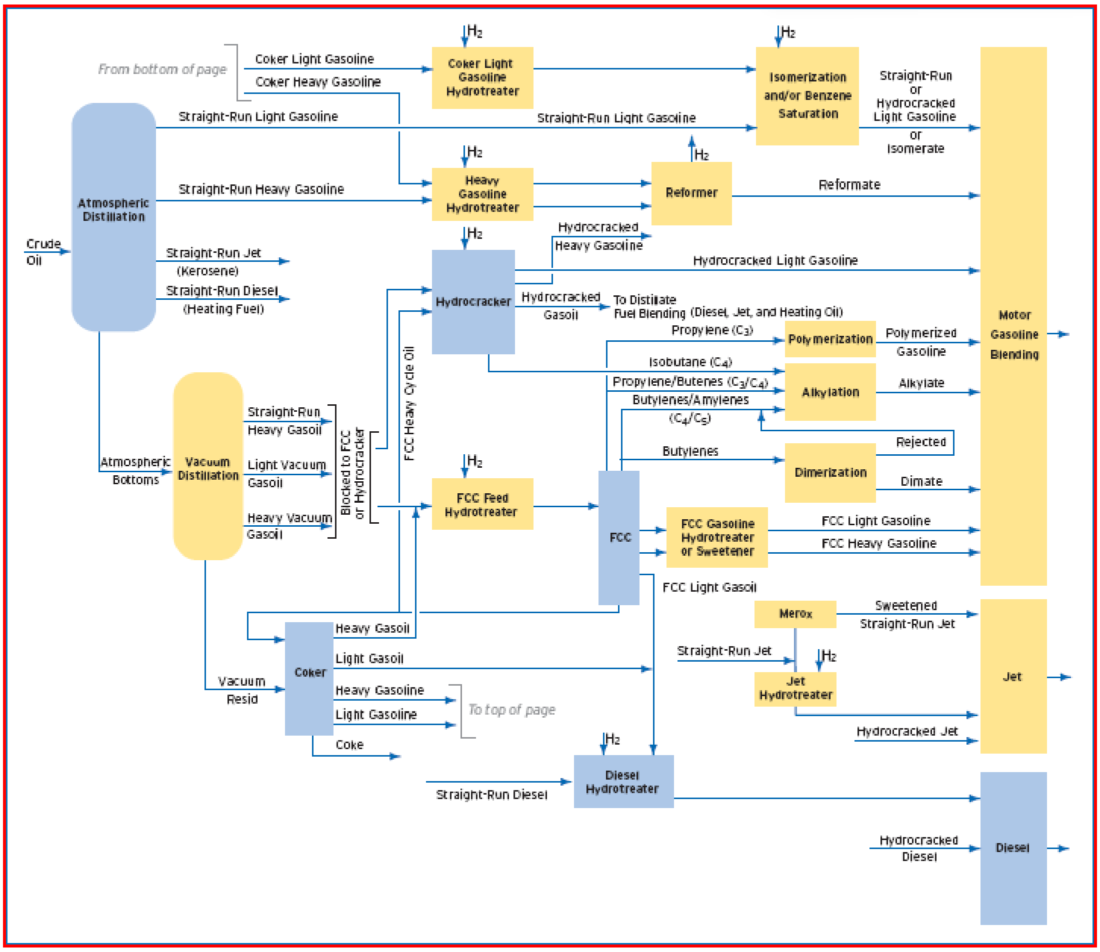

Figure 1.2 A modern Refinery (chevron, 1998)

1.3 Hierarchy of decision making for diesel production

Production of diesel in an oil refinery is a complicated process, due to a long processing chain with a large number of processes involved, various grades of diesel products, fluctuated market demands, and comprehensive quality requirement. Different operations could make significant influence in total profit. Therefore, decision making in refinery diesel production has a significant implication on its profitability.

The hierarchy of decision making mainly consists of three levels: planning for the higher level, scheduling at the intermediate level and advanced control at the lower level (Gupta, 2008). In a refinery, the planning level provides targets for the scheduling operations and the scheduling provides targets for the advanced control/regulatory control. Whereas, the advanced control sends feedback to the scheduling model and the scheduling sends feedback to the planning model. Feedbacks come from monitoring the results of processes and will reflect the effects of planning and scheduling operations. According to which, refiners change the recipes to optimize the operations for the maximum profit

1.3.1 Distinguishing between planning and scheduling

Planning is essential for successful scheduling as it provides the activities and targets required to be met in the scheduling operations. The result of scheduling operations could help refiners to modify planning. Planning is forecast driven to which scheduling is order driven with a further explanation presented in the definitions of each expression (Kelly and Mann, 2003).

1.3.2 Definition of planning

Planning is essential for successful scheduling as it provides the activities and targets required to be met in the scheduling operations. The result of scheduling operations could help refiners to modify planning. Planning is forecast driven to which scheduling is order driven with a further explanation presented in the definitions of each expression (Kelly and Mann, 2003).

1.3.3. Definition of scheduling

Planning of a refinery contains the long-term aspects, which normally takes months, in which refiners operate equipment, crude oils and products. It is the first step to run a refinery to maximize the process efficiency. In planning stage, specifications and quantities of demanded products are provided to refiners. Refiners process the product requirements with the refinery condition (feedstocks' properties and quantities, producing capacity, operation conditions etc.). By solving mathematical models, a feasible production plan (properties, quantities and compositions of products) is obtained.

1.3.4 Relation of planning and scheduling

The business area hierarchy in any industry consists of long-term planning, short-term scheduling and process control. The hierarchical management levels are shown in Figure 1.3 with the longest planning horizon at the top which shortens rapidly while moving down to the process control level. On the other hand, the reliability of information and their detail increases from the top to the bottom in the hierarchy. The complex planning and scheduling tasks are broken into simpler ones that can be solved at each stage separately. Three levels in the hierarchy are connected in a way that the results of each level are forwarded to the next level.

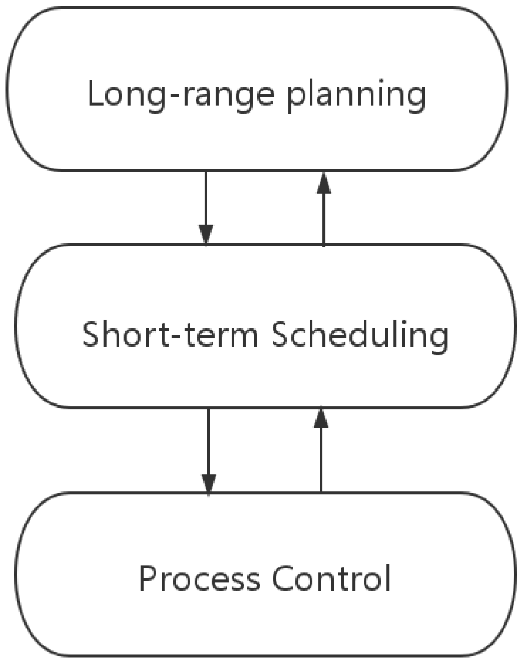

Figure 1.3 Hierarchical management levels

In long-range planning horizon, refiners deal with feedstocks and products according to the market demand and environmental regulations. A planning horizon normally lasts 1-3 months while a scheduling period is generally 1 week. The optimal process variable values are transferred to the short-term scheduling level in which the time horizon is counted by week, and the due date of each product should be met. Afterwards, parameters of each process are derived on the base of scheduling recipe. The processes can be operated with the help of the parameters, which comes to the process control level. To sum up, the operating instructions are based on the three levels. A design which is optimized in all the three levels can be called optimised.

1.4 Challenges in diesel production blending

The refining industry today has to comply with both higher product quality specifications and more stringent environmental regulations regarding emissions and waste productions. This means that refineries are now faced with the pressure of reducing emissions that arise from its operations. Product specifications are always a highly charged subject, due to the interests of environmental pressure groups, refiners, governments, consumers and engine manufacturers. However the interaction of these groups makes the predictions of future trends difficult. In old days, many refiners used to consider product blending as a linear problem but the need to comply with the environmental restrictions and the demand for higher grades of petroleum products enforce refiners to solve the scheduling problem in more accurate ways.

Table 1.2 shows diesel fuel standards in Europe. The minimum cetane number of diesel product has been driven up slowly due to the requirement of new technology in the engine designs, which in turn requires higher grade diesel to produce lower emissions. This is one of the major problems that refiners face as high cetane blend stocks are limited in conventional refineries.

Particulate emissions, as heavy diesels tend to produce higher particulate emissions, is the core reason for the need to reduce specific gravity and ASTM 95% temperature. This increases the problems that refiners face as this further put limitation on the use of catalytic cracker light cycle oil.

The need for reduction of PAH (Polycyclic aromatic hydrocarbons) is due to the possible formation of benzene, which is carcinogenic, from incomplete combustion. This in turn increases the use of straight run blend stocks as possible blending stock.

The quality improvements, emission reduction, performance improvement to facilitate the advanced engine design and fuel economy are the main reason behinds the pressures imposed on the specifications (Simon 2001). Refiners face difficulties in practically meeting the tight specifications with existing blend stocks and limiting the cut range of blend stocks. Hence, product yield and profit are reduced due to the increment in the production of lower valued products.

The planning and scheduling of diesel production blending are very important in diesel producing processes. The intermediate streams have different properties. They need to be processed before enter diesel product market because they cannot compliance with the requirements. Blending is one of the most commonly used processes in a refinery. Refiners simulate the blending process and predict the product properties to obtain a blending ratio. In previous works, researchers simplify the blending process by linearization the blending property correlations. Through linearization, the blending problem can be solved directly but linear correlations can lead to an inaccurate result, which will cause dissatisfying of product specifications and property loss.

Since 2000, diesel specification has become more and more strict. The minimum cetane number of diesel has been driven up slowly due to the requirement of new technology in the engine designs, which in turn requires higher grade diesel to produce lower emissions. This is one of the major problems that refiners face as high cetane blend stocks are limited in conventional refineries. Particulate emissions, as heavy diesels tend to produce higher particulate emissions, is the core reason for the need to reduce specific gravity and ASTM 95% temperature. This increases the problems that refiners face as this further put limitation on the use of catalytic cracker light cycle oil. The need for reduction of polynuclear aromatics is due to the possible formation of benzene, which is carcinogenic, on incomplete combustion. This in turn decreases the use of straight run blend stocks as possible blending stock.

Due to the stringent quality requirements, it is critical for refiners to improve the diesel blending operation to decrease property loss and increase profit.

In recent years, oil refineries are increasingly concerned with improving the planning of their operations. Many commercial software for refinery production planning, such as RPMS and PIMS, are based on linear models. It was interpreted as general trends that don't allow to use more complex models and nonlinear mixing rules (Moro el al. 1998). In the new century, due to the pressure from more stringent specifications and competitors, refiners and researchers started to put more emphasis on developing new nonlinear models which formulate refinery processes more precisely.

1.5 Objective of this work

As mentioned before, the diesel product specification has become more stringent. Therefore, refiners are pursuing more efficient operation by deploying mathematical models for higher accuracy and optimality that can reduce profit loss. Since the nature of diesel blending is nonlinear, linear models in property prediction will lead to inaccuracy. A model that applies nonlinear correlations to predict properties in diesel blending planning and scheduling is developed. On account of the complexity of diesel blending problem, the nonlinear model in planning and mixed-integer nonlinear model in scheduling are difficult to solve. To overcome the difficulty, a feasible solution algorithm to solve and optimise the MINLP planning and scheduling problems is proposed. Besides, this model can be extended to other process of a refinery. In this work, it will be modified to optimise a gasoline production blending scheduling problem to demonstrate the applicability of the model.

1.6 Structure of the thesis

In Chapter 2, current approaches for diesel planning, scheduling and blending are reviewed. The basic features for each approach, as well as its advantages and drawbacks, are briefly discussed.

In Chapter 3, an NLP model for diesel blending problem is introduced. Nonlinear correlations in property estimation for different properties which are limited in environmental regulations are applied.

In Chapter 4, a new MINLP model has be built for the scheduling problem of diesel blending, and a robust solving algorithm is proposed to optimize it.

In Chapter 5, the proposed model can also be extended to gasoline blending scheduling problem. The extending process and how the model works will be presented.

Finally in Chapter 6, conclusions are drawn for this research work together with recommendations for future research work.

Chapter 2 Existing Work on Diesel Blending Optimization

2.1 Introduction

In this chapter, existing researches on diesel fuel and production processes are discussed. As diesel production processes are attached to refineries, the planning and scheduling methods for refinery operations are reviewed, especially for those that are related to diesel blending.

2.2 Diesel fuel technology

2.2.1 Diesel engine

Diesel engines have become increasingly common as a power plant source for providing motive power both in highway and non-highway transportation systems and also for industrial applications. In the last two decades, diesels have expanded their preserve from traditional heavy duty applications such as buses and trucks to even light duty passenger cars, where their operation is almost indistinguishable when compared to traditionally used gasoline powered engines, while conferring their advantages of better thermal efficiency and fuel economy. This has led to a spurt in demand for diesel fuel globally, as a result of which increased middle distillate or diesel production is the main objective of most refineries

Diesel engines most commonly use a four-stroke operating cycle (see Figure 2.1). In the first stroke (intake stroke), the intake valve opens while the piston moves down from its highest position in the cylinder (closest to the cylinder head) to its lowest position. This draws air into the cylinder in the process. In the second stroke (compression stroke), the intake valve closes and the piston moves back up the cylinder. This compresses the air and, consequently, heats it to a high temperature, typically in excess of 540 ℃ (1,000 ℉). Near the end of the compression stroke, fuel is injected under high pressure up to 30,000 psi (200 MPa or 2,000 bar) into the combustion chamber through a fine nozzle. The injection system is designed to produce a fine spray of small fuel droplets that will evaporate quickly in order to facilitate rapid mixing of fuel vapour and air.

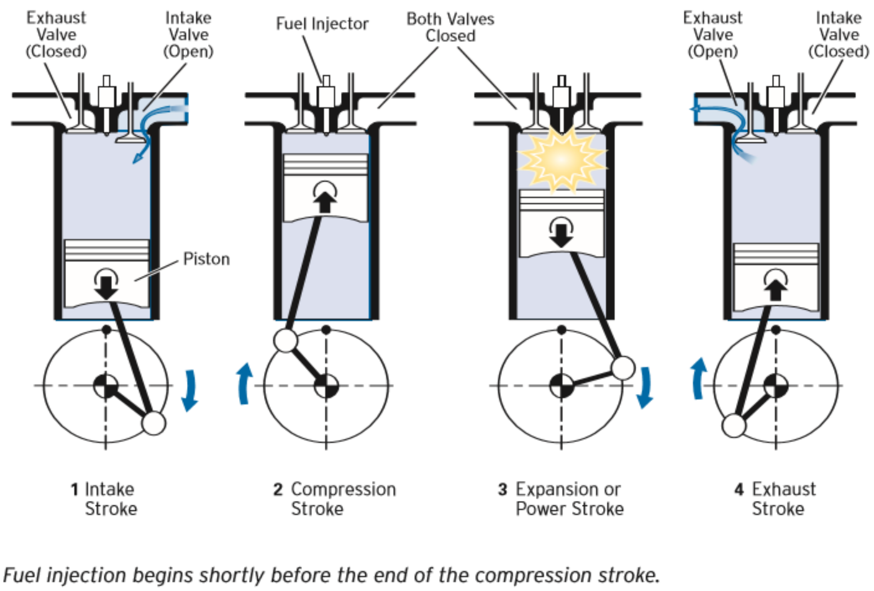

Figure 2.1 A typical diesel engine(Chevron,1998)

2.2.2. Diesel fuel properties

Since diesel fuel mostly serves diesel engine, the initial motivation of research on diesel fuel properties is to make diesel engine work in a safe and effective way. On the other hand, diesel, as a product of petroleum, could cause many environment problems if it is not produced or used in a proper way. The environmental regulation of diesel fuel has become more and more stringent in recent year. Researches on diesel properties would benefit more clean and environmental friendly diesel production.

1. Cetane number

The catane number is a measure of how readily the fuel starts to burn (auto-ignite) under diesel engine conditions. The ignition delay period can be evaluated by cetane number. To measure cetane number, its ignition performance is compared to two pure hydrocarbons: n-cetane which is given the number 100 and α -methynaphthalene which is given the number 0. If a diesel fuel behaves like a mixture of 60 volume % cetane and 40 volume% α -methynaphthalene, it is given a number of 60.

The cetane number of a diesel fuel can be measured by ASTM D 613 test method. A diesel fuel with a higher cetane number has a better performance in ignition by a shorter ignition delay. A diesel fuel with a higher cetane number can also reduce combustion noise and increase engine efficiency and power output (Riazi, 2005).

Cetane number also varies systematically with hydrocarbon structure. Normal paraffins have high cetane numbers that increase with molecular weight. Isoparaffins have a wide range of cetane numbers, from about 10 to 80. Molecules with many short side chains have low cetane numbers; whereas those with one side chain of four or more carbons have high cetane numbers.

Naphthenes generally have cetane numbers from 40 to 70. Higher molecular weight molecules with one long side chain have high cetane numbers; lower molecular weight molecules with short side chains have low cetane numbers.

Aromatics have cetane numbers ranging from zero to 60. A molecule with a single aromatic ring with a long side chain will be in the upper part of this range; a molecule with a single ring with several short side chains will be in the lower part. Molecules with two or three aromatic rings fused together have cetane numbers below 20.

2. Diesel Index or Cetane Index

The cetane method of expressing ignition quality presupposes the availability of a standard engine (Cooperative Fuel Research Engine), reference fuels and also tends to be somewhat time-consuming and expensive. Hence alternative tests, such as diesel index and cetane index, are often used for routine control purposes. ASTM D976 (IP 218) proposed a method of calculating cetane index as follows:

$$CI = 454.74 - 1641.416SG + 774.74SG^2 - 0.554T_{50} + 97.083(\log_{10} T50)^2 \tag{2.1}$$

where T_{50} is the ASTM D86 temperature at 50% point in ℃.

For diesel index, it is defined as :

$$DI = \frac{(API)(1.8AP+32)}{100} \tag{2.2}$$

which is the function of API gravity and aniline point in ℃. Cetane index is empirically correlated to DI and AP in the following calculation (Riazi, 2005):

$$\mathrm{CI}=0.72\mathrm{DI}+10 \tag{2.3}$$

$$\mathrm{CI}=\mathrm{AP}-15.5 \tag{2.4}$$

3. Viscosity

Viscosity is defined as the ratio of absolute viscosity to absolute density at the same temperature. In an easier way, viscosity means resistance to flow or movement and it’s sensitive to temperature. It can be measured by ASTM D 445 test method.

In the case of diesel fuels, low viscosity may give rise to:

(1) Leakage of fuel from pumps and injectors.

(2) Abnormal rate of wear of the moving parts of pumps and injectors owing to lack of lubricity.

(3) Too fine a degree of atomisation with the result that the fuel will not penetrate sufficiently far into the compressed air in the cylinder to give the food mixing essential for efficient combustion.

(i4) Overheating of the injector owing to the concentration of the fuel spray and hence the flame in a relatively small area around the injector nozzle.

However, if the viscosity of the fuel is too high, it will impede the flow of fuel to the pump, giving rise to poor atomisation and excessive penetration with inefficient combustion of fuel.

4. Carbon residue

Different fuels have different tendencies to crack and leave carbon deposits when heated under similar conditions. It measures coking tendency of a fuel and will affect the engine deposit. Heavier fractions with more aromatic contents have higher carbon residues while volatile and lighter fractions such as naphthas and gasolines have no car- bon residues. There are two older methods to measure carbon residue, Ramsbottom (ASTM D 524) and the Conradson (ASTM D 189). The relationship between these methods are also given by the ASTM D 189 method. There is a more recent test method (ASTM D 4530) that requires smaller sample amounts and is often referred as micro-carbon residue (MCR) and as a result it is less precise as a practical technique

5. Sulphur content

Sulphur content is significant because it governs the amount of sulphur oxides formed during combustion. Water from combustion of fuel collects on the cylinder walls, whenever the engine operates at low jacket temperatures. Under such conditions, sulphurous and sulphuric acids are formed, which attack the cylinder walls and piston rings, promote corrosion and thus cause increased engine wear and deposits. These effects can to some extent be overcome by the use of lubricants containing alkaline additives. If the diesel fuel is refined from a very high sulphur crude, it may become necessary to desulphurise it before marketing.

Sulphur content is also an important index for environmental organizations. In Europe, the sulphur content of diesel fuel specifications has decreased from 0.2 w% in 1993 to 0.001w% in 2009.

Sulphur content can be measured by ASTM D 129.

6. Ash content

Ash is a measure of the incombustible material present in a fuel and is expressed as a percentage of the weight of the fuel sample. In the case of distillate fuels, it usually consists of rust, tank scale or sand, which settles out readily. Blends of distillate and residual fuel, e.g. LDO may additionally contain metal oxide derived from oil soluble and insoluble metallic compounds. Ash is significant because it can give rise to deposit problems such as abrasion, malfunctioning of injectors and high temperature corrosion, particularly with residual fuels.

Ash content can be measured by ASTM D 482.

7. Pour Point

The pour point of a fuel is the lowest temperature at which it will pour or flow when chilled under prescribed conditions. It is a very rough indication of the lowest temperature at which a given fuel can be readily pumped. However, since practical conditions are quite different from those under which the laboratory test is conducted, many fuels can be pumped at temperatures well below their laboratory pour point.

Test procedures for measuring pour points of petroleum fractions are given under ASTM D 97 (ISO 3016 or IP 15) and ASTM D 5985 methods.

8. Cold Filter Plugging Point

The cold filter plugging point (CFPP) is defined as the highest temperature at which the fuel, when cooled under prescribed conditions, either will not flow through the filter (45 microns) or will require more than 60 seconds for 20 ml to pass through. This is the temperature at which wax crystals begin to cause blockage of filters.

CFPP can be tested by ASTM D 6371.

9. Freezing Point

The freezing point of diesel describes a temperature at which it changes state from liquid to solid. It can be tested by ASTM D 2386.

10. Cloud Point

The cloud point is the lowest temperature at which wax crystals begin to form by a gradual cooling under standard conditions. At this temperature the oil becomes cloudy and the first particles of wax crystals are observed. Cloud point is another cold characteristic of diesel under low temperature conditions. The standard procedure to measure the cloud point is described under ASTM D 2500.

The four properties above can all represent diesel performance in a cold weather. In Europe and China, CFPP is used to grading the diesel fuel products to indicate the suitable weather of a diesel fuel.

11. Aniline Point

Aniline point of a petroleum fraction is defined as the minimum temperature at which equal volumes of aniline and the oil are completely miscible. Method of determining aniline point of petroleum products is described under ASTM D 611 test method.

The value of aniline point gives an approximation for the content of aromatic compounds in the oil, since the miscibility of aniline, which is also an aromatic compound suggests the presence of similar (i.e. aromatic) compounds in the oil. The lower the aniline point, the greater is the content of aromatic compounds in the oil as obviously a lower temperature is needed to ensure miscibility.

12. Flash Point

The flash point of a diesel is the lowest temperature it will ignite. Therefore, the flash point of a fuel indicates the maximum temperature that it can be stored without serious fire hazard. This has no bearing on performance but is important largely from the point of view of safety in handling the fuel and minimum values are usually specified in the specification.

There are several methods of determining flash points of petroleum fractions. The Closed Tag method (ASTM D 56) is used for petroleum stocks with flash points below 80 ℃. The Pensky-Martens method (ASTM D 93) is used for all petroleum products except waxes, solvents, and asphalts.

As reviewed, a diesel fuel has a number of properties that measure ignition performance, environmental influence and safety. Since so many properties should be considered, it greatly increases the difficulty in optimizing diesel blending.

2.3 Predictions of diesel blending properties

Property estimation is the key part of diesel blending problem. Among the properties that we need to consider, many of them are not linear depend on the composition, which means quality loss and prediction error will occur if linear correlations are directly used. Researchers have done a quantity of works on predicting product property in a more accurate way.

For properties such as carbon residue, sulphur content, ash content, linear addition is suitable for property prediction of blending diesel oil. But for the calculation of cetane number, CFPP, freezing point, flash point, pour point, cloud point, viscosity, and distillation range, linear addition is not suitable. For these properties, the nonlinear blending models will be demonstrated in Chapter3.

2.4 Methods for diesel blending optimisation

Compared to gasoline blending problem, there is very few academic publication available for diesel blending. A planning model for refinery diesel production is addressed by Moro, Zanin and Pinto (1998). In order to achieve an optimal solution, this model applied nonlinear blending predictions methods to calculate production properties. However, it only concerns 5 properties in product specifications, including density, flash point, boiling range, cetane number and sulphur content.

Due to the more stringent environment regulations, it cannot meet the requirements of current diesel blending situations. On the other hand, since the Moro' model focuses on planning of diesel production, it didn't optimize the production blending process.

The common industrial perception for the diesel blending problem is that it is considered as simpler than the gasoline blending problem, with less nonlinear behavior in property mixing. Therefore, most research effort for refining product blending is focused on gasoline. As a common approach, the diesel blending problem is mostly treated as a linear problem, which can be dealt with in overall refinery LP optimization.

Therefore, the techniques for refinery diesel blending optimization are reviewed in the context of overall refinery planning and schedule in the next section.

2.5 Planning and scheduling methods in refineries

The configuration of a refinery is one of the most complicated industrial systems. There are a lot of processes including separation processes, upgrading processes and conversion processes. Every process has a number of equipment, such as reactors, distillation columns, heat exchangers, pumps, etc. Raw materials are turned into various higher value petroleum products. Refiners plan and schedule their operations according to income of crude oil and requirement of market with specifications satisfied.

2.5.1 Refinery planning

2.5.1.1 The objective of refinery planning

In the oil refining industry many products are produced from only one feedstock (crude oil) and the values of these products are in the same order of magnitude and this result as a complex economics of petroleum refining. Also cheaper products can be improved by upgradation processes. This makes it difficult to calculate the straightforward production cost. The aim of the optimization process is not only to achieve a single optimum operating point but also to understand the economics and price structure of a refinery. In simple mathematical terms, the refinery optimization can be expressed as:

Objective function:

Maximize profit = Product sale – Material cost – Operating cost

Subject to:

- Process operations (e.g. kinetics, temperatures, pressures, flowrates)
- Process connections
- Various limitations (e.g. throughput, storage, product specifications, market demand, raw material availability, environmental regulations)
- Resource utilisation (e.g. power, steam, hydrogen)
- Operation policy (e.g. allocation of the storage tanks, loading and unloading procedure of tanks, product grade transition policy in pipeline), etc.

Depending upon the amount of details incorporated, the formulations can generally be classified as planning or scheduling. The planning problem ignores some of the details such as inventories, operating policy, etc. and focuses on long-term goals such as production optimization, debottlenecking and retrofitting. On the other hand, the scheduling formulation considers inventory, dynamic markets conditions and detailed operating strategy; but the scope is limited to shorter time horizon.

2.5.1.2 Refinery planning models

Planning formulation can generally be classified as a linear programming (LP) and a nonlinear programming (NLP). If all the objective function and constraints are linear, it is an LP formulation whereas, if any of them are in a nonlinear form, it is an NLP formulation.

Linear programming is the most popular optimization techniques used by the refiners. LP formulation requires all relevant possible processing routes to be pre-considered. The linear programming algorithm calculates the optimum combination of supply, processing, blending and selling activities that generate the maximum profit. Besides, the linear programming output can also provide the marginal values of all refinery flows (that helps to understand the economics), marginal values of constraints such as product specification (to grasp the impact of the environmental regulation), marginal values of feedstock (feedstock selection decisions) & products (choice of product and deciding market) and marginal values of additional processing capacity (to make retrofitting and debottlenecking decisions). Interpreting the LP output requires skills and in order to evaluate different scenarios it is necessary to generate several cases and sub cases (Hartmann, 1999, 2003). By solving a large number of LPs systematically eliminating the options and providing and optimum solution, a mixed integer linear programming (MILP) can calculate these different scenarios. The linear programming techniques for overall refinery optimization are relatively well developed, represented by commercial software – PIMS from Aspen Technology (1993) and RPMS from Honeywell. In the meantime, many petroleum companies have developed their own LP tools in-house. The disadvantage of the linear programming is that it assumes linear combination of provided options. The refining process models are nonlinear and as a result, linear models cannot describe the nonlinear aspects accurately.

In order to overcome this defect of the linear programming methods, recursion techniques are employed. These methods use nonlinear simulation methods to complement linear programming. In recursion techniques, a number of sequential executions are required. The nonlinear simulation is performed after execution of LP and it provides the starting point for the next LP. Although recursion gives more accurate solutions, it not only increases computing time, but also reduces the transparency of LP's value structure and its economic driving forces, and therefore reduces users' confidence (Hartmann, 1997).

On the other hand, a rigorous nonlinear programming model for overall plant operation can be formulated by lumping all the rigorous process models together. Progress of nonlinear programming in 1990s (Viswanathan & Grossmann, 1993; Porn, Harjunkoski & Westerlund, 1999) allowed many researchers to use NLP models for optimization. However, most of the applications are limited to single unit optimization or a group of units. Moro, Zanin and Pinto (1998) optimized diesel production in RPBC refinery with considering density, flash point, boiling range, cetane number and sulphur content. Neiro and Pinto (2004) used NLP based method for the overall refinery optimization. Li et al. (2005) used integrated CDU, FCC and product blending models for refinery planning. However, researchers reported the need for decomposition method that would solve such a large size problem more efficiently.

Zhang (2000) provided a decomposition method to build a synergy between NLP based rigorous individual plant optimization and the overall refinery optimization. In his method, the optimization model has been decomposed into two levels: the site level (master model) and the process level (sub models). The site level optimization deals with the major refinery aspects such as flow arrangement and the process level optimization deals with process operating conditions for given flow arrangements. A feedback procedure is used with the help of marginal values derived from the site level optimization and iterations between both levels of optimization are performed until the convergence is achieved. This method provides good understanding of refinery price values and allows users to use in-house process models. The method is both mathematically solvable and computationally efficient. However, single period planning model has limits that it doesn't consider the time issue and storage element. It assumes that the refinery doesn't have a deadline of an order and unlimited capacity of processes.

2.5.2 Scheduling

The long-term and the plant wide planning problems in the petrochemical industry have been mainly addressed by mathematical programming techniques (Bodington, 1995). Pure linear programming methods have been used for long-term planning, but they are not suitable for the short-term scheduling and on-line optimization, since they are based on simplified correlations, without being able to deal with both continuous (and often nonlinear) processes and discrete decisions accurately (Zhang and Zhu, 2000). The mathematical formulation for scheduling problem can be classified as a mixed integer linear programming (MILP) and a mixed integer nonlinear programming (MINLP). If all the constraints and objective function are in linear form, it is an MILP formulation and if any of them is nonlinear, it is an MINLP formulation.

The combined crude allocation/pooling problem have been examined by Lee et al. (1996) with the development of a mixed integer linear programming multi-period model for proposing a short-term crude oil unloading, tank inventory management, and CDU charging schedule. Pinto et al. (2000) presented the results of the application of a mixed integer optimization model in a similar real world problem. In their model time is represented by variable length time slots, which corresponds to crude oil receiving operations (vessels unloading) as well as to periods between two receiving tasks. Shah (1996) proposed a mathematical programming approach, in which, tanks may store only one crude type and each CDU runs exactly one crude type from one tank at a time. In modelling of a refinery process, the calculation of crude oil mixing generates non-convex bilinear constraints. Some researchers have proposed techniques to linearise these bilinear constraints. Sherali and Alameddine (1992) proposed a new reformulation linearisation technique (RLT) and imbedded it within a provably convergent branch and bound algorithm. This RLT process yields a LP problem whose optimal value provides a tight lower bound on the optimal value of the bilinear programming problem. Quesada and Grossmann (1995) applied the technique proposed by Sherali and Alameddine (1992) to model process networks consisting of one or several splitters, mixers, and linear process units that involve multicomponent streams. Although the RLT constraints can sometimes replace bilinear constraints, this often leads to inconsistent solutions, in particular when handling storage of multiple oil types.

Glismann and Gruhn (2001) reported an MILP model to optimize recipe of short-term scheduling and blending process. The product recipe of each period is redefined by making use of a RTN representation. Although the long-term planning problem can be modified, the scheduling problem cannot be optimized. Mendez and Grossmann (2006) presented an approach that can optimize off-line blending and scheduling of oil refinery operations. Nonlinear correlations are applied for the property estimation. To avoid solving MINLP problem, an iterative procedure is used. The correlation factor ‘bias’ is introduced to modify the error between nonlinear and linear correlations and converge the solution in the iteration procedure. In this model, one of the most important assumptions is that the non-linear properties are a weak function of the compositions. However, in order to improve the accuracy, some correlations for non-linear properties are very complex. So the application of this model will be limited. .

In recent years, A number of review papers on scheduling have been written across different scientific communities, e.g. Floudas and Lin (2004), Méndez, Cerdá, Grossmann, Harjunkoski, and Fahl (2006), Li and Ierapetritou, 2008a and Li and Ierapetritou, 2008b, Maravelias (2012) and Iiro Harjunkoskia (2014).

Although there are little research in diesel blending scheduling can be found in literatures, researches on crude oil scheduling and production blending can be referred.

Many papers research scheduling methods based on crude oil operations. In crude oil scheduling problem, refinery operations involve three main segments: crude oil storage and processing, intermediate processing, and product blending and distribution. The crude oil needs to be blended before it arrives refining process, which is similar to diesel production blending. Li et al. (2011) proposed a novel unit-specific event-based continuous-time MINLP formation for crude oil operation scheduling. In which, realistic operational features such as single buoy mooring, multiple jetties, crude blending and etc. are incorporated. Several examples illustrated that better solutions are obtained. Li et al. (2012a) proposed a framework to optimise crude oil scheduling problem under uncertainty including demand fluctuations, ship arrival delays, equipment malfunction and tank unavailability. The novel MINLP formulation developed by Li et al. (2012b) and the robust optimisation frame work developed by Lin et al. (2004) and Janak (2007) are successfully utilized and applied to develop robust optimisation models. To solve the MINLP optimisation model, a robust optimisation approach and an extended branch and bound global optimisation algorithm for demand uncertainty are also proposed. Castro and Grossmann (2014) modelled crude oil operations by generate a Resouce-Task Network superstructure while extending the scope of a well-known continuous–time formation to variable recipe tasks with multiple input materials. In this mode, the objective is gross margin maximisation and can be solved close to global optimality. The advantage of this model is based on a new single time grid formulation, which is unlike previously proposed unit-specific and priority-slot specific based models. Cerdá et al. (2016) proposed a novel continuous-time mixed-integer linear programming (MILP) formulation based on floating time slots to simultaneously optimise blend recipes and the scheduling of blending and distribution operations. This MILP approach is able to find optimal solutions at much lower computational cost than previous contributions when applied to large gasoline blend problems. Dut to it features an integrality gap close to zero,

Cao and Gu (2014) proposed an online scheduling model for diesel production of a real-world refinery. They developed an MINLP model to optimise the operation of diesel production processes in a refinery. In their model, blending correlations of viscosity, flash point, and solidifying point are considered as nonlinear. For solidifying point, the equations are derived according to the experimental data.

Summarily, in the past literatures on blending and scheduling problems, most of the research regards oil blending as a linear problem. Some works proposed algorithm to make linear result more close to nonlinear result by correction model. These methods are more accurate than LP models. But there still are shortcomings. The modified linear result is still inaccurate comparing with nonlinear result. Besides, the application of the models is limited due to the assumptions made in the modelling process.

The difficulties in a diesel blending scheduling problem concerns primarily 1)the large number of property should be considered in the model due to product specifications, 2) the nature of blending model is nonlinear, which would make the scheduling MINLP, 3) the large number of constraints and variables including continuous and discrete ones, 4) complexity of nonlinear correlations, 5)the difficulty in solving MINLP.

2.5.3 Time Representation

Time representation is a preliminary major issue during the mathematical model formulation of a scheduling problem. Existing scheduling formulations can be classified into two main categories: discrete-time models and continuous-time models.

2.5.3.1 Discrete-time models

Early attempts in modelling the process scheduling problems relied on the discrete-time approach, in which the time horizon is divided into a number of time intervals of uniform durations and events such as the beginning and ending of a task are associated with the boundaries of these time intervals.

Discrete-time scheduling formulations make use of the concept of discretization. The time horizon is divided into a number of time intervals of uniform durations. The start/end of a task and other important events are associated with the boundaries of these time intervals. With such a common reference time grid for all the operations competing for shared resources, such as equipment items, the various relationships in a scheduling problem can be formulated as constraints of relatively simple forms. The basic concept of the discrete-time approach is illustrated in Fig. 2.3

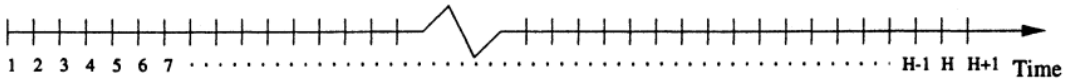

Figure 2.3 Discrete-time representation

The main advantage of the discrete-time representation is that it provides a reference grid of time for all operations competing for shared resources, such as equipment items. This renders the possibility of formulating the various constraints in the scheduling problem in a relatively straightforward and simple manner. In this research, discrete-time representation is applied due to the complexity of the blending correlations and the large number of equations and variables.

The discrete-time models provide a relatively simple way to represent time and program the processes, and, usually lead to a well-structured mathematical problem. Nevertheless, there are two main limitations in discrete-time models. First, as the nature of time is continuous, it is an assumption to model the problem in a discrete way, which would cause inaccuracy. Second, the duration of a time interval is a tradeoff problem between accuracy of the problem and difficulty of solving it. If the time interval is small, the problem can be modeled precisely while the scale of the model will be relatively large. It is difficult to obtain the solutions. However, if the time interval is too big, there is an incredible loss of model accuracy and the value and significance of the model can be very low.

2.5.3.2 Continuous-time models

To overcome the drawback of discrete-time model, continuous-time model have been researched in the past decade. From the literature, this model can be classified into two categories. One defines a set of events that are used for all the units and tasks. All units share same time slots which are continuous. The other one defines event point based on a unit, in which all units have different time points subject and allowing different tasks to start or end at different time instances in different units in the same event point.

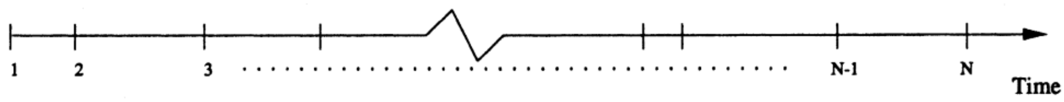

Figure 2.4: Continuous-time representation

All continuous-time approaches can be classified into two categories based on the type of processes. The first category of approaches focuses on sequential processes and the second category aims at the scheduling of general network-represented processes. The critical differences between these two types of processes is that sequential processes are order or batch oriented and do not require the explicit consideration of mass balances, which has important Compared to discrete-time model, continuous-time model is tougher to be built because of the flexibility in timing the events but requires less computation to be solved.

2.5.4 Process sequences

2.5.4.1 Sequential processes

In sequential processes, Different products follow the same processing sequence. It is usually possible to define processing stages, which can be single stage or multiple stages. There can be only one unit per stage or parallel units at each stage. For this type of process, batches are used to represent production and it is thus not necessary to consider mass balances explicitly. At each stage, there can be one or multiple parallel units. When multiple units are involved, time slots are defined for each unit.

2.5.4.2 Network-represented processes

When production recipes become more complex and/or different products have low recipe similarities, processing networks are used to represent the production sequences. This corresponds to the more general case in which batches can merge and/or split and material balances are required to be taken into account explicitly. It can be classified into state-task network (STN) (Kondili, Pantelides, and Sargent, 1993) and the resource task network (RTN) ((Pantelides, 1994).

- STN

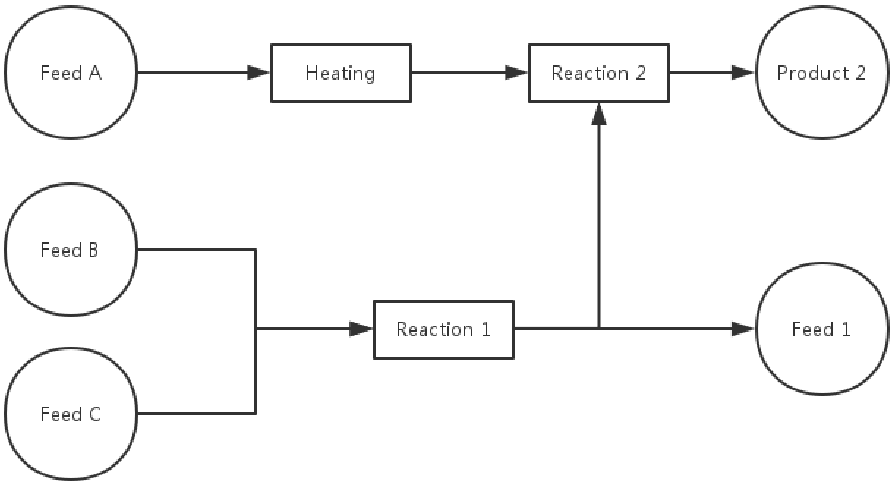

Figure 2.5 Example of State-Task Network

As Figure 2.5 shows, The STN representation of a chemical process is a directed graph with two types of distinctive nodes: the state nodes denoted by a circle, representing raw materials, intermediate materials or final products, and the task nodes denoted by a rectangle box, representing an operation. The fraction of a state consumed or produced by a task, if not equal to one, is given beside the arch linking the corresponding state and task nodes.

• RTN

RTN describes processing equipment, storage, material transfer and utilities as resources in a unified way. The RTN representation of the same process as in the STN example is provided in Fig.2.6. In addition to the resources of materials, denoted also by circles, the related four pieces of equipment, denoted by ellipses, are also included. Tasks taking place in different units are now treated as different tasks.

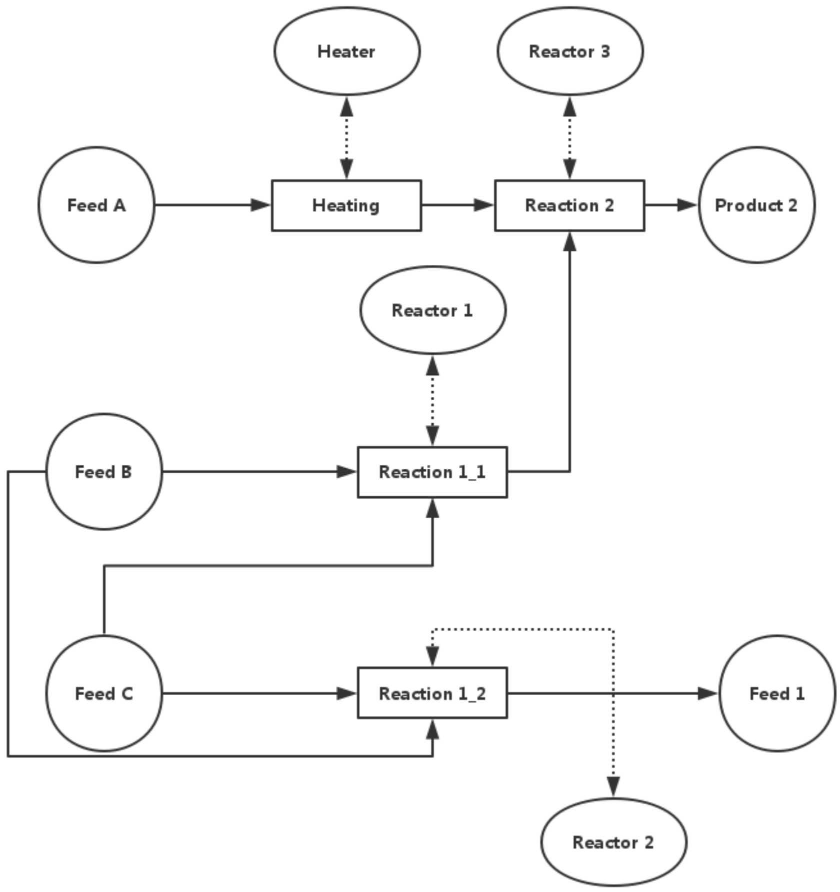

Figure 2.6 Example of State-Task Network

Both STN and RTN can be extended to represent storage vessels and alternative material locations, as well as different equipment states (e.g. clean, dirty, ready to process). Both STN and RTN representations were originally used for problems in network environments but have recently been used to address problems also in other environments (Sundaramoorthy and Maravelias, 2011 and Velez and Maravelias, 2013).

2.6 Summary

In this chapter, the basic information of diesel properties and the existing methods for diesel blending optimization are reviewed. The following areas of improvement are identified for optimizing refinery diesel blending operation:

- Even though diesel production from oil refineries plays a significant role of economic contribution in the refining business, the problem of diesel blending optimization has not received sufficient attention from the academic research so far.

- Contradictory to the common perception, the nonlinear property behavior of diesel blending is not trivial, which will be demonstrated in Chapter 3. More accurate property prediction methods should be adopted in diesel blending operation.

- More accurate property prediction models for diesel blending should also be incorporated into the refinery planning and schedule methods to improve the overall decision making procedure, especially in the case of scheduling for diesel blending, where academic effort is almost absent.

To address these shortcomings, a nonlinear diesel blending model is proposed in Chapter 3 to optimize the recipe of diesel blending problem, and further applied for refinery planning. In Chapter 4, the nonlinear blending model is incorporated into a diesel blending scheduling method, for which the overall problem becomes an MINLP problem. To overcome the difficulty in convergence and ensure the overall optimality, a solution algorithm is also developed. In Chapter 5, the developed methodology is applied to the gasoline blending problem, in order to further test its robustness and applicability.

Chapter 3 Modelling and Optimisation of Diesel Blending Planning

3.1 Introduction

Products blending tries to make use of available components for effective mixing in order to produce valuable products that meet demands and specifications to achieve maximum profit (Wu, 2010). Gasoline, diesel, aviation fuel, lubricating oils and heating fuels are the main products from refinery product blending. Since in normal conditions, the volumes of products sold by a refiner are very huge. As such, even savings of a fraction of 1% per unit will lead to a substantial increase in profit. Furthermore, the demand of refining products has been increasing gradually in the last years and the trends shows possibility of continuing increase in the foreseeable future. On the other hand, in recent years, modern refineries have been confronted with more stringent environment standards and strict requirements of quality specifications. These situations make the product blending strategy more crucial in a refinery in order to remain competitive in the global market.

3.1.1 Diesel blending

Diesel blending is a process of blending various refinery components from various refinery upstream units along with additives to produce different grades of diesel products. The blending ratio depends on the quality, the quantity and the cost of available blending streams, the demand and the price of the final products. Selection of blending components and their proportions in the blended product is a complex problem. In a refinery, the typical number of diesel blending component stream is between 6 and 8 (Riazi 2013). The diesel blending component streams are mainly as following:

- Straight Run Diesel from CDU

- Light Cycle Oil (LCO) from FCCU followed by Hydrotreating.

- Coker Light Gas Oil (CLGO) produced from the Coker Unit

- Hydrocracked diesel from HCU

The component properties vary since they come from different processes. For example, Straight Run Diesel usually has a high cetane number due to high composition of paraffin while the cetane number of Light Cycle Oil from FCCU is normally very low because of unsaturation.

Diesel blending is a process of blending various refinery streams produced from various refinery units along with additives to produce different grades of diesel products. The blending ratio depends on the quality, the quantity and the cost of available blending streams, the demand and the price of the final products. Selection of blending components and their proportions in the blended product is a complex problem. In a refinery, the typical number of diesel blending component stream is 6-8 (Riazi 2013). These component streams are mainly as following:

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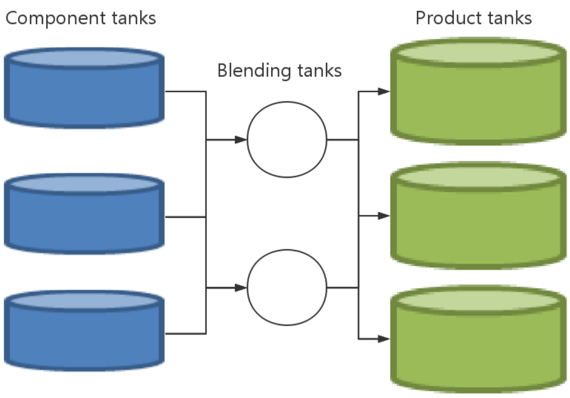


Figure 3.1 Diesel blending

As Figure 3.1 shows, in a blending process, intermediate diesel streams are delivered to several blending tanks. They are blended according to particular recipes in order to satisfy the product property requirement. After the blending complete (normally several hours), the diesel streams are delivered to product tanks, where they are stored and then transported to markets.

3.1.2 Diesel blending Methods

For diesel blending, there are two general blending methods: continuous blending and batch blending. Continuous blending, also named in-line blending, is a process of blending various component streams in a blender continuously, and supplying products to a product storage tank simultaneously. In continuous blending, samples of the blend are tested to obtain the sample properties periodically. The feedstock flow rate is adjusted to ensure the blend meets quality specifications. Continuous blending is beneficial due to a sequence of operations including: blending, quality analysis, loading and unloading, which can be accomplished in a single run.

In batch blending, various component streams are fed one after another into a blending tank, until product specifications of a particular grade are all met and the liquid level reaches the required value. The next run of blending can only be started after completing the offloading of previous product finishes. Storage tanks for both blending feedstocks and products are required. Compared to continuous blending, in batch blending the feed quality can be fairly constant over the time and the products can be more flexible. However, these benefits are obtained at the expense of higher storage costs and longer operation cycles.

Commercially, batch blending methods are commonly used that continuous blending for diesel production. Therefore, this work focuses on developing modelling and optimisation techniques for batch blending.

3.1.3 Motivation

To achieve a successful operation in most petroleum refineries, product blending is considered as a key process. As reviewed before, many refiners used to treat diesel blending as a linear problem. Linearization of blending correlations would simplify the problem by avoiding considering complex and massive nonlinear correlations. Therefore, the solution algorithm would be much easier than nonlinear problems. However, adopting linear blending correlations leads to accuracy loss of predicting the quality of diesel products. Even though a linear model contains the property specifications as constraints, it is still possible that the products are unqualified due to the errors of linear blending correlations, leading to a big profit loss.

On the other hand, diesel product specifications include many properties, such as density, viscosity, cetane number/cetan index, etc. In the literature, none of the existing diesel blending models considers all the properties specifications simultaneously. Such simplification could be applicable to some cases, but cannot be considered for general applications.

Therefore, a diesel blending model with more accurate nonlinear property prediction correlations and the full coverage of diesel property specifications is highly desirable to improve refining diesel blending operation.

3.2 Model development

3.2.1 Mathematical modelling

The objective of diesel product blending is to obtain a optimal blending recipe with maximum profit while satisfying product specifications and market demands.

The key elements in a diesel blending planning and scheduling problem:

Decision variables:

- Amount and type of products produced from different feedstocks.
- Blending recipe of each product.

Major parameters:

- Feedstock properties
- Standard specifications for different types of diesel products.

Major constraints:

- Quality limitation on each product must be satisfied.
- Demand of different grade of diesel must be satisfied.

- Mass balance.

Assumptions:

- The composition requirements of products are not considered in this research
- The input bounds of each components stream to each blender are neglected.
- The inventory limits are not considered in the planning model, but will be considered in the scheduling model in Chapter 4.

3.2.1.1 Objective function

The diesel product blending problem can be formulated as a Non-Linear-Programming (NLP) problem to maximise the profit. In the model, the profit is considered as the total price of all the diesel products that are sold to the market. Mathematical representation of the objective function is described as follows:

Maximise

$$Profit = \sum_{j=1}^{NP} P_j \cdot Price_j - \sum_{i=1}^{NF} F_i Cost_i \qquad (3.1)$$

where P_j is the production flow for product j, $Price_j$ is the market price for product j, $Cost_i$ is the cost of feedstock i.

3.2.1.2 Constraints

Material balance for component tanks

$$F_i = R_i + \sum_j FB_{i,j} \qquad \forall\ i \qquad (3.2)$$

$$F_i \leq F_{iup} \qquad \forall\, i \qquad (3.3)$$

Where F_i is feedstock of diesel component i that can be blended into diesel products before the blending process starts, R_i is residue amount of component i after the blending process, $FB_{i,j}$ is the amount of component i which is blended into product j during the blending process. F_{iup} is the available amount of component i

a) Material balance for product tanks

$$P_j = R_j + \sum_i FB_{i,j} \qquad \forall\, j \qquad (3.4)$$

Where P_j is the amount of diesel product j that can be sold to market after the blending process, R_i is residue amount of component j before the blending process starts, $FB_{i,j}$ is the amount of component i blended into product j during the blending process.

b) Market demand of each products

$$P_j \geq P_j^{min} \qquad \forall\, j \qquad (3.5)$$

where P_j^{min} is the market demand for product j

c) Other constraints

$$FB_{i,j} = P_j * x_{i,j} \qquad \forall\, i,j \qquad (3.6)$$

$$FB_{i,j} * den_i = xx_{i,j} \qquad \forall\, i,j \qquad (3.7)$$

where $xx_{i,j}$ is the mass amount of component i in product j.

$$P_j * dens_j = yy_j \qquad \forall\, j \qquad (3.8)$$

where yy_j is the mass amount of product j and $dens_j$ is density of product j

$$\sum_i x_{i,j} * den_i = dens_j \qquad \forall\, i,j \tag{3.9}$$

$$w_{i,j} * yy_j = xx_{i,j} \qquad \forall\, i,j \tag{3.10}$$

d) Product specification requirement

For properties that can be predicted by linear correlations

$$Pr_{j,z} = \sum_i x_{i,j} * \epsilon_z \qquad \forall\ j,z \tag{3.11}$$

$$Pr_{j,z} = \sum_i w_{i,j} * \epsilon_z \qquad \forall\ j,z \tag{3.12}$$

where $Pr_{j,z}$ is the value of property z of product j, $x_{i,j}$ is volume fraction of component i in product j, ϵ_z is the value of property z of component i. $w_{i,j}$ is mass fraction of component i in product j.

Common linear blending properties include

- Sulphur content based on weight fractions of blending components

- Ash content based on weight fractions of blending components

- Carbon residue based on weight fractions of blending components

- Polycyclic aromatic hydrocarbons based on weight fractions of blending components

For properties that can be predicted by different nonlinear correlations

$$Pr_{j,z} = f(x_{i,j},\ \epsilon_z) \qquad \forall\, i,j,z \tag{3.13}$$

On the other hand, a number of properties of interest to the refiners are not additives and need to be treated non-linearly. The correlations that are applied in this model are as follows:

- Pour point

Prem B.Semwal and Ram G. Varshney(1994) proposed a correlation to estimate pour point of blended diesel:

$$T_j^{1/y} = \sum_i \; V_i^A \, T_i^{1/y} \qquad \forall \, j \qquad (3.14)$$

Where V_i and T_i are volume fraction and pour point in degrees Rankine of stream i, respectively, $T_j^{1/y}$ is the blend pour point in Rankine. A and y are parameters to be estimated.

- Cold filter plugging point

Prem B.Semwal and Ram G. Varshney(1994) also proposed a correlation to estimate cold filter plugging point of blended diesel which is similar to the pour point correlation:

$$CFPP_j^{13.45} = \sum_i^n V_i^{1.03} \, CFPP_i^{13.45} \qquad \forall \, j \qquad (3.15)$$

Where $CFPP_i$ is the cold filter plugging point of the stream i, V_i is volume fraction of stream i, and $CFPP_j$ is that of the blend in Rankine.

- Viscosity

The viscosity of the blend of different component streams can be estimated using the

Refutas (2000) equation. In this method a Viscosity Blending Number (VBN) of each component is first calculated and then used to determine the VBN of the liquid mixture as shown below.

1) Calculate the Viscosity Blending Number (VBN)

$$VBN_i = 14.534 * \ln(\ln(v_i + 0.8)) + 10.975 \qquad \forall\, i \qquad (3.14)$$

where v_i is the kinematic viscosity at the stipulated temperature in diesel specifications.

2) Calculate the VBN of the blend

$$VBN_j = \sum_{i=1}^{N} x_i * VBN_i \qquad \forall\, j \qquad (3.15)$$

where x_i is the mass fraction of each component in the mixture

3) Calculate the viscosity

$$V_j = \exp\left(\exp\left(\frac{VBN_j - 10.975}{14.534}\right)\right) - 0.8 \qquad \forall\, j \qquad (3.16)$$

• Flash point

Wickey. R. O. and Chittenden, D. H (1963) suggested that the flash point of the blend should be determined from the flash point indexes of the components as given below:

$$log_{10} BI_F = -6.1188 + \frac{2414}{T_F - 42.6} \qquad (3.17)$$

where log_{10} is the logarithm of base 10, BI_F is the flash point blending index, and T_F is the flash point in kelvin. Once BI_F is determined for all components of a blend, the blend flash point index (BI_B) is determined from the following relation:

$$BI_j = \sum x_{vi} BI_i \qquad \forall\, j \qquad (3.18)$$

where x_{vi} is the volume fraction and BI_i is the flash point blending index of component i

- Cetane number

The relationship for calculation of cetane number blending index is more complicated than those for pour and cloud point (Riazi, 2005). In order to control the model scale and computing cost, in this work, the cetane number prediction of diesel blending uses linear correlation as follows:

$$Pr_{j,z} = x_{i,j} * \epsilon_z \qquad \forall\, i, j, z \qquad (3.19)$$

Where $x_{i,j}$ is volume fraction of component i in product j.

- Boiling range

AnASTM-D86 distillation point calculation by the ethyl equation is shown blow (Ethyl Corporation, 1981):

$$D86_{XB} = \sum_{i=1}^{n} v_i BV_{xi} \qquad (3.20)$$

$$\mathrm{BV}x_i = C0_x + C1_x A_i + C2_x A_i^2 + C3_x A_i^3 + C4_x A_i G_i + C5_x \frac{G_i}{A_i} + C6_x \frac{G_i}{A_i^2} + C7_x G_i \qquad (3.21)$$

Where $D86_{XB}$ stands for the predicted temperature at a given point X, BV_{xi} is the temperature blending value of components i at a desired point X, A_i is the average boiling temperature (℃) of component i, G_i is the components i ASTM severity

(T90-T10), and $C0x - C7x$ are the coefficients for each included D86 distillation point need to be regressed.

• Cetane Index

As Cetane Index is calculated by ASTM D 976 as follows

$$CI = 454.74 - 1641.416SG + 774.74SG^2 - 0.554T_{50} + 97.083(\log_{10} T50)^2 \tag{3.22}$$

where T_{50} is the ASTM D86 temperature at 50% point in ℃, SG is the special gravity.

As the product density is assumed blended by linear correlation and boiling range can be predicted by the models above, the cetane index of the product can be calculated by equation 3.22

3.2.1.3 Key variables

A diesel blending model should solve the following variables that are very significant for refiners.

1) Blending ratio

Blending ratio of a diesel blending problem describes how to blend feedstocks into diesel products. It determines composition and properties of a diesel product.

2) Productivity

The productivity needs to be optimised under the condition of market order requirements. It is vital to optimising the profit of the blending process.

3) Products properties

Products specifications are the key constraints of a diesel blending model. Properties should satisfy all the specifications. Otherwise, products cannot be delivered to diesel fuel market. Properties are also the key to optimise the profit of a diesel blending process. Imprecise property calculation leads to property loss and profit loss. That's the reason why more and more refiners make efforts to develop and apply nonlinear model of refining processes, including diesel product blending.

3.2.2 Model validation

A verification case from an Asian refinery is studied to show the accuracy of properties prediction of blending products. Five blending components are mixed together to produce the diesel product. Blending ratio in volume is shown in Table 3.1. Measured properties of both blending components and the diesel product, including flash point, pour point, cold filter plugging point, cloud point, viscosity, and distillation point, as well as blending ratio, are shown in Table 3.2. The product properties are calculated by both linear and nonlinear correlations. The calculated properties are compared with the measured properties of blending product to show the superiority of the proposed model.

Through Table 3.2, the result from linear model is slightly better than nonlinear when predicting Cetane Index. For flash point, pour point, CFPP, and distillation point, nonlinear model gives us much more accurate result. The validation illustrates the reliability of nonlinear models in diesel blending, which is the significant motivation of this research.

Table 3.1 Blending ratio

blending ratio(volume)	%
F1	10
F2	30
F3	15
F4	43
F5	2

Table 3.2 Measured properties of blending components and product

Property		F1	F2	F3	F4	F5	Linear	Nonlinear	Measured
Flash Point(℃)		24.0	42.0	83.0	69.0	179.0	60.7	44.4	45.5
Pour Point(℃)		-65.0	-50.0	2.5	-5.0	2.5	-23.2	-22.2	-12.5
CFPP(℃)		-50.0	-50.0	4.0	-4.0	-1.0	-21.1	-15.5	-8.0
Cetane Index		36.8	48.0	63.4	60.6	57.7	54.8	62.2	55.7
Kinematic Viscosity(40℃),mm2/s		1.284	1.300	4.416	4.858	4.327	3.356	2.110	2.371
Distillation (D86)	10%	137.2	165.4	262.6	256.9	332.2	219.8	204.4	207.5
	50%	143.8	199.2	301.8	307.9	334.9	258.5	286.4	289.1
	95%	166.2	254.8	361.6	387.6	349.7	321.0	351.0	348.2

Table 3.3 the regressed coefficients for the boiling range

	C0	C1	C2	C3	C4	C5	C6	C7
D10	-0.0504	1.6746	-0.002205	0.000029	-0.12954	-3.34E+03	-5.24E+01	43.67155
D50	3.767599	-4.40E+03	1.67E+01	-0.02055	17.93395	3.89E+06	-3.36E+08	1.15E+04
D90	2.80E+05	-2.61E+03	8.04E+00	-0.008151	9.976215	3.16E+06	-3.36E+08	-9.79E+03

3.3 Solution strategy

After refiners discovered that linear models for the diesel blending problem are not accurate, they realised that the nature of the problem is a nonlinear problem. However, the obstacle of development of nonlinear model is the complexity of the problem. Due to a large number of variables and equations, researchers tried to simplify the problem to make it easier to solve (Moro el al.1998). In the simplification, they used linear correlations which resulted in reduced accuracy for predicting the properties thereby limiting the applications of the model.

Due to the complexity of the diesel blending problem, it could be difficult to solve the nonlinear problem directly. Exponentiation arithmetic is applied in the model of Pour Point and CFPP estimation. If the planning model is solved directly by the existing solvers (CONOPT, BARON, MINOS), it would lead to infeasible.

To overcome the solving difficulty, a solution strategy is introduced. Since one of the key aspects of solving general NLP problems successfully is to provide a feasible initial point. A solution strategy that emphasised the use of a good initialisation for nonlinear diesel blending model is presented below.

Mathematically, the Nonlinear Programming (NLP) Problem can be expressed like:

$$\text{Minimize } f(x)$$

$$\text{St} \quad g(x) \leqslant 0$$

$$L \leqslant x \leqslant U$$

where x is a vector of variables that are continuous real numbers. f(x) is the objective function, and g(x) represents the set of constraints. L and U are vectors of lower and upper bounds on the variables.

When solving an NLP problem, it is highly desirable to provide initial values for all the variables as a starting point. Even though algorithms are different depending on different solvers, the initial values of variables will influence whether the problem can be solved or not and the solving time. A poor initial value may lead to more solving time and infeasible solution from the solver. On the other hand, a good initial value could allow for much quicker convergence to the optimal solution. However, due to the complexity of the diesel blending problem, it is difficult to provide a suitable initial value for all the variables.

To improve the efficiency of solving the nonlinear diesel blending model, a multi modelling and solution method is proposed as follows:

Since there are so many constraints in the diesel blending problem, it is decomposed into two parts. The first part is the objective function and the most crucial constraints that are related to the variables in the objective function (Equation 3.1, 3.2, 3.3, 3.6, 3.7, 3.8, 3.9, 3.10 and the mixing correlation of density Equation 3.11). The following parts consist of other constraints (other equations mentioned in the model).. By decomposing the model, solving a complex nonlinear problem directly is avoided. After the first part is solved, which is simple and easy to work out, the variables those are in the objective function are valued. Then, the second part is added into the model and solved. Sequentially, the others parts are added into the model and solved .

Through this method, the solver firstly solves a simple NLP problem to determine the variables in the first part. The values of the variables will be the initial point when it comes to the next step. These values are results of a part of the model, so they are more reliable than predicted arbitrarily.

3.4 Case study

To demonstrate the effectiveness of the proposed blending model, an assumed case study is shown as follows. The feedstocks properties comes from diesel streams of a refining processing Chinese Daqing Crude

Table 3.4 Feedstock availability and properties

		F1	F2	F3	F4
Avalability(t)		1500	1200	1300	800
Cetane Number		68	34	73	73
Sulphur Content(ppm)		12	8	2	8
Density(g*ml^{-1})		0.867	0.8559	0.8287	0.8162
CFPP(℃)		-15	-8	-15	4
Viscosity(mm^2/sec)		3.8	1.5	4.4	2.7
Ash Content(% (m/m))		0.003	0.1	0.01	0.008
PAH(% (m/m))		9	13	4	2
Flash Point(℃)		50	70	60	55
	10%(℃)	137.2	165.4	262.6	256.9
Distillation(D86)	50%(℃)	143.8	199.2	301.8	307.9
	90%(℃)	185.6	266.8	372.3	396.7

Four diesel intermediate feedstocks need to be blended to diesel products that can be sold directly to the market. Feedstock properties are presented in Table 3.4. Every product must satisfy the EN 590 diesel fuel product standard and the market demands simultaneously. The product specification and demands are shown in Table 3.5.

Table 3.5 Product specifications

	P1	P2	P3	P4
Cetane Number	⩾46	⩾46	⩾46	⩾46
Sulphur Content(ppm)	⩽10	⩽10	⩽10	⩽10
Density(g*ml^{-1})	0.82-0.86	0.82-0.86	0.82-0.86	0.82-0.86
CFPP(℃)	0	-5	-10	-15
Viscosity(mm^2/sec)	2-4.5	2-4.5	2-4.5	2-4.5
Ash Content(% (m/m))	⩽0.01	⩽0.01	⩽0.01	⩽0.01
PAH(% (m/m))	⩽11	⩽11	⩽11	⩽11
Flash Point(℃)	⩾55	⩾55	⩾55	⩾55
Price($/t)	1270	1290	1320	1330
Demand(t)	500	900	1150	2150

The objective of the diesel blending problem is to generate a local optimal solution that meets all the specifications and market demand for each product while maximising the overall profit. For feedstock F2, the cetane number 34 cannot meet the specification, and the CFPP (cold filter plugging point) 9℃ is not qualified for product P3 and P4. If it is blended into products, theses inferior properties need to be compensated for by premium properties from other feedstocks.

The blending ratio of each product is the key variable of the case since it determines the product properties. To predict the boiling range, parameters in Equation 3.16 and 3.17 are regressed as Table 3.6:

Diesel blending model is to maximize objective function (3.1), subject to constraints (3.2) – (3.21).

The optimised product properties are shown in Table 3.7.

Table 3.6 Parameters regressed for boiling range prediction

	10%	50%	90%
C0	-1.1221800E+03	-6.7706000E+03	-3.1739400E+03
C1	1.7772186E+01	4.2621677E+01	5.8536876E+01
C2	-5.9493070E-02	-5.1265930E-02	-2.5951042E-01
C3	6.5610000E-05	-2.8420000E-05	3.4356000E-04
C4	-4.9407090E-02	-3.0859948E-01	-5.1248600E-02
C5	-1.1602600E+04	-5.5564200E+04	-2.0435300E+04
C6	1.0337340E+06	5.0551080E+06	1.6848850E+06
C7	3.7781577E+01	2.2027610E+02	6.4706280E+01

Table 3.7 Properties of each product

	P1	P2	P3	P4
Cetane Number	54.2	52.6	58.7	66.7
Sulphur Content(ppm)	8.076	8.347	9.803	6.794
Density(g*ml^{-1})	0.836	0.841	0.852	0.846
CFPP(℃)	-3.3	-5.0	-10.0	-15.0
Viscosity(mm^2/sec)	2.000	2.000	2.591	3.523
Ash Content(% (m/m))	0.009	0.009	0.006	0.007
PAH(% (m/m))	7.521	8.354	8.762	6.901
Flash Point(℃)	60.1	60.0	55.0	55.7

From Table 3.7, by adopting the proposed model, the market demands and product specifications are both achieved, especially CFPP (cold filter plugging point) which is critical property to winter diesel grades definition. The optimisation result based on the proposed model is compared with the linear model in which linear correlation as equation (3.9) is applied to calculate all the products properties.

Table 3.8 Comparison between two results of the proposed model and LP model

	P1	P2	P3	P4
Model 1	500	900	1150	2250
Model 2	591	900	1150	2150

In Table 3.8, the production of each product from the two models is different. The result from the proposed model prefers to produce as much Product 4 as possible. However, the result from the linear model prefers to produce more Product 1. As there is difference in the recipe of the two models, the composition and products properties are also different.

The difference of the two results is due to the difference between the linear correlations and the nonlinear correlations. The less accurate linear correlations could make big difference when considering the large amount of petroleum products produced everyday all over the world.

Inaccurate correlation could result in unqualified products, which can lead to not only a financial penalty, but also potential safety hazard. Even though all the product properties based on the recipe from the linear model seem to be within the limit, when validating the product properties with the nonlinear models, some of the properties exceed the bounds of specifications. In this case, for instance, after recalculating by nonlinear correlations, the product properties of conventional model are different compared with those in the linear model result.

Table 3.9 Comparison of linear result CFPP and Validated CFPP

CFPP(℃)	Linear result	Validated
P1	0.0	-0.8
P2	-5.0	-6.3
P3	-10.0	-11.2
P4	-15.0	-16.2

Table 3.9 illustrates that the difference between the linear result and the validated property. With the diesel stream CFPP decreasing from 0 ^{o}C to -15 ^{o}C, the deviation of the linear correlation increase from about 0.8 ^{o}C to about 1.2 ^{o}C. The relative error of 5.3% cannot be neglected. Due to the inaccurate CFPP prediction, the linear model leads to a property loss in the products, which would cause a profit loss. In this case, the total profit optimised by linear model is 7.44 M$. However, the proposed nonlinear planning model could optimize the profit to 7.69 M$. With better property estimation methods, the total profit of the blending process is increased by 3.3%.

This case is solved by CONOPT in GAMS 23.5 on Dell M14 (Intel® Core™ 2.40GHz) running Windows 10. It contains 161 equations and 133 variables. The execution time is 0.004s

3.5 Summary

Diesel Product blending is one of the most important steps in refining operations. Most refining products are blended from intermediate process streams. Due to the varying properties of blending components from upstream units and tightened product specifications, the diesel product blending problem becomes more challenging for modern refiners. For predicting diesel blending properties, the investigation shows that the nonlinear models have better accuracy than the linear models. The different results of linear models and nonlinear models are validated in this chapter. To improve the feasibility of the results for diesel blending optimization, nonlinear models are necessary to predict product properties.

Good initialization is very important to solve NLP problems. In diesel blending optimisation, due to the large number of variables, it obtains infeasible result from existing solver to solve this nonconvex NLP model. A solution strategy is introduced to solve diesel blending optimization problem.

In the case study, a diesel blending problem is solved by the nonlinear model and a conventional linear model. Compared with the linear model, the nonlinear model can deliver a more accurate property prediction and a better objective, which is a higher profit in this problem.

Nomenclature

Sets

i	component index
j	product index

Parameters

$CFPP_i$	cold filter plugging point of the component i
$Cost_i$	cost of a component
$Price_j$	price of a product
R_i	residue of component i
R_j	residue of product R_j
ϵ_z	value of property z of component i
den_i	density of component i
v_i	kinematic viscosity of component i
T_F	flash point in kelvin

Continuous variables

$Profit$	profit of a process
F_i	feedstock of component i

$FB_{i,j}$ amount of component i blended into product j

P_j amount of product j

$Pr_{j,z}$ property z of product j

$x_{i,j}$ volume/mass fraction of component i in product j

T_i pour point in degrees Rankine of component i

T_b blend pour point in Rankine of product j

$CFPP_b$ cold filter plugging point of the blend in Rankine

$dens_j$ density of the mixture

x_i mass fraction of component i

VBN_i viscosity blending number of component i

$VBN_{mixture}$ viscosity blending number of mixture

$V_{mixture}$ viscosity of mixture

BI_F flash point blending index of component i

A_i average boiling temperature (℃) of component i

G_i the components i ASTM severity (T90-T10)

CI cetane index

Chapter 4 Scheduling of refinery diesel blending

4.1 Introduction

Planning and scheduling approaches for overall modeling are linked for the best combinatory solution solved for a suitable objective function (Lee et al, 1996), which has been incorporated throughout the formulation of subsequent models compiled.

The overview for planning and scheduling hierarchy is related to the other constituents involved across the network. This enables the successful function of the procedure in order to propose a feasible optimal solution relevant to the refinery process network being investigated by considering the associated limitations that constrain the relationship values.

Optimization of a refinery indicates maximizing profit potential of the site. The planning models are capable of making decisions that are fairly independent of time such as long-term contracts. Otherwise, they are less applicable for short-term needs where both the market and a plant are fluctuant. On the other hand, scheduling, which aims to achieve planning targets and ensure stable operations while satisfying the market requirements. For a scheduling plan, the optimal process variables, which come from individual or several scheduled horizon, must lie within the overall optimal solution space and within the defined constraints supplied at the beginning of the model formulation.

Review of existing diesel blending scheduling problems shows that several mathematical programming approaches are currently available for short-term blending and scheduling problems. However, in order to reduce the problem difficulty, most of the existing mathematical approaches are not ideal for the optimisation of diesel blending scheduling problems due to the complexity and accuracy requirement. As diesel takes a very important position in modern refineries and even modern industries, it is necessary to develop a model for diesel blending scheduling problem. In this Chapter, a new Mixed-Integer Non-Linear Programming (MINLP) model for optimizing diesel blending scheduling which considers all the properties that is in the product specifications and nonlinear prediction correlations. In addition, due to the difficulty in solving an MINLP problem, a robust solving algorithm is also presented

4.2 Problem definition

Scheduling is a sequence of jobs, with their start time and end time, that certain ensures constraints are met. Scheduling is carried out for minimizing cost and/or some measure of time like the overall project completion time. The diesel blending scheduling system consists of three pieces of equipment i.e. component stock tanks, blending tanks and product stock tanks as shown in Figure 4.1. These three pieces of equipment are linked together through various piping segments, flow meters and valves. The components from the component tanks are transferred to the blending (mixing) tanks according to the recipes. Thus, different products can be produced and stored in their suitable product stock tanks.

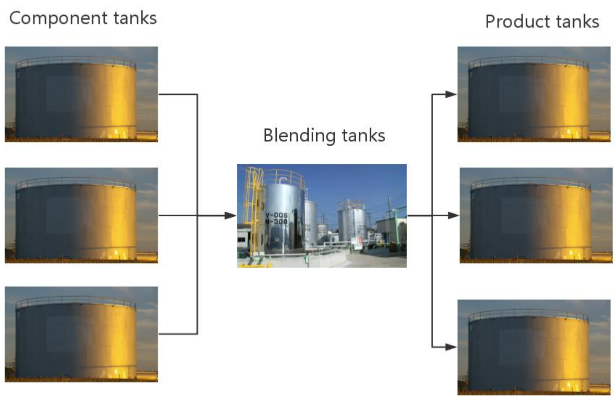


Figure 4.1 Illustration of a blending problem

The main features of the proposed method are summarized as follows:

1. A single period optimization model is developed that is able to deal with multiple product demands with the same due date while satisfying the product specifications.

2. Discrete-time representations are used in the proposed approach.

3. Binary variables are used to represent assignment decisions.

The key elements in a diesel blending planning and scheduling problem that requires attention are as follows:

Decision variables:

- Amount and type of product being produced from blending tanks in each time interval.

- Blending ratio of product blended in the blending tank in each time interval.

Parameters:

- Minimum and maximum inventory capacities for each blending tank and storage tank

- Minimum and maximum flow rate capacities for the blending tank

- Standard specifications for different types of diesel products.

Constraints:

- Blending tank can store only one product during the scheduling horizon

- Quality limitation on each product must be satisfied.

- Demand of different grade of diesel must be satisfied.
- Mass balance.

Assumptions:

- The composition requirements of products are not considered in this research.
- The input bounds of each components stream to each blender are neglected.
- The change-over cost of blenders is not considered in this research.

Another preliminary major issue during the mathematical model formulation of a scheduling problem for any process is the representation of time. The two main methods to represent time have been introduced in Chapter 2. Discrete-time representation provides a reference grid of time for all operations competing for shared resources, such as equipment items. This renders the possibility of formulating the various constraints in the scheduling problem in a relatively straightforward way (Floudas and Lin 2004). In addition, due to the variable nature of the timings of events, it becomes more challenging to model the scheduling process and the continuous-time approach may lead to mathematical models with more complicated structures compared to their discrete-time counterparts. As the great number of variables is one of the biggest challenges in optimizing diesel blending scheduling problem, to decrease model scale, discrete-time representation is applied in this work.

4.3 Mathematical model

A new nonlinear diesel blending model is presented in this section. This model is based on an assumption that the blenders have the same capacities that are available for different kind of diesel products.

Objective function: to maximum the total profit for all the diesel products.

$$Profit = \sum_{j=1}^{NP} P_j \cdot Price_{P,j} - \sum_{i=1}^{NF} F_i \cdot Price_{F,i} \qquad (4.1)$$

Subject to:

1) Operation constraint

$$\sum_j A_{j,n,t} \leq 1 \qquad \forall\, n, t \qquad (4.2)$$

Binary variable $A_{j,n,t}$ denotes that product j is blended in blender n during time interval t. Constraint 4.2 donates that only 1 product can be produced in 1 blender during 1 time interval. N is the number of available blenders.

2) Material balance for component tanks

$$FF_{i,t} + VC_{i,t-1} = VC_{i,t} + \sum_n FB_{i,n,t} \qquad \forall\, i, n, t \qquad (4.3)$$

Where $FF_{i,t}$ is the input to component i, $VC_{k,t}$ is the original amount of component in component i, $FB_{i,n,t}$ is the flowrate of component i to blender n during time interval t.

3) Material balance for blending tank

$$\sum_i FB_{i.n,t} = FP_{j,n,t} \qquad \forall j, n, t \qquad (4.4)$$

$FP_{j,n,t}$ is the flowrate or product j from blender n to product storage tank.

4) Blending tank capacity

$$VB_{min} * A_{j,n,t} \leq FP_{j,n,t} \leq VB_{max} * A_{j,n,t} \qquad \forall\, j, n, t \qquad (4.5)$$

Constraint (4.5) specifies that minimum and maximum volumetric flowrates must be satisfied when product j is blended during time interval t.

5) Other constraints

$$FB_{i,n,t} = FP_{j,n,t} * x_{i,j,n,t} \qquad \forall\, i,j,n,t \qquad (4.6)$$

where $Volume_{i,j}$ is the volume amount of component i in product j.

$$FB_{i,n,t} * den_i = xx_{i,j,n,t} \qquad \forall\, i,j,n,t \qquad (4.7)$$

where $xx_{i,j}$ is the mass amount of component i in product j.

$$FP_{j,n,t} * dens_{j,t} = yy_{j,t} \qquad \forall\, j,n,t \qquad (4.8)$$

where yy_j is the mass amount of product j and $dens_j$ is density of product j

$$\sum_i x_{i,j,n,t} * den_i = dens_{j,t} \qquad \forall\, j,n,t \qquad (4.9)$$

6) Product specification requirement

For properties that can be predicted by different nonlinear correlations

$$Pr_{j,z,t} = f(x_{i,j,t},\, \epsilon_z) \qquad \forall\, i,j,z,t \qquad (4.10)$$

For properties that can be predicted by linear correlations

$$Pr_{j,z,t} = \sum_i x_{i,j,t} * \epsilon_z \qquad \forall\, j,z,t \qquad (4.11)$$

$$Pr_{j,z,t} = \sum_i w_{i,j,t} * \epsilon_z \qquad \forall\, j,z,t \qquad (4.12)$$

7) Product demand

$$\sum_{t \le d} FP_{j,n,t} \ge \sum_{dt \le d} dd_{j,dt} \qquad \forall\, j,n \qquad (4.13)$$

The constraint above defines all the products to be achieved the market demand at the due date.

Diesel blending scheduling model is to optimise objective function (Equation 4.1) subject to equations (4.2-4.13).

4.4 Solution algorithm

As we know, an MINLP model is difficult to solve. The existing MINLP solvers can optimize some straightforward MINLP problems. However, scheduling of diesel blending problem contains large number of binary variables and massive equations, which exceeds the solving capacity of existing MINLP solvers. Therefore, a modest growth in problem size can lead to a significant increase in the computational requirements. For instance, in the case shown in section 4.4, there are more than 300 continuous variables and 24 binary variables. Besides, all existing algorithms scale exponentially in the worst case (Floudas and Lin, 2004). If the case is solved by the existing MINLP solvers (DICOPT etc.), an infeasible result will be obtained. The optimal solution cannot be obtained directly from the optimisation software. Therefore, in this work, a robust solution algorithm is developed as shown in Figure 4.2.

In a diesel blending scheduling case, the problem is divided into 2 sub-problems. The first one is the Non-Linear Programming (NLP) diesel blending planning problem. This problem is formulated and optimized using the method proposed in Chapter 3. Nonlinear blending correlations are used to predict product properties in the NLP model. Once the result is obtained, it provides the component volume fractions blended in each diesel product, which is incorporated into the next sub-problem, a Mixed-Integer Linear Programming (MILP) scheduling problem. The MILP scheduling model is developed by the method proposed in Chapter3. The blending recipe is fixed by the result from the first NLP blending model. By optimizing the MILP problem, the scheduling result for blending operation is obtained. In addition, by taking into account more operating conditions in the scheduling model, the solution from the scheduling model will be more practical to be used for daily operation. The next step is to validate the solution for the blending scheduling problem using the NLP model. This is where the iteration starts. The solution for the diesel scheduling problem is optimised in one iteration. This process will be repeated until the solution of the MILP scheduling model is equal or close enough to the solution in the previous iteration, which indicates the maximum profit is achieved in the optimal solution

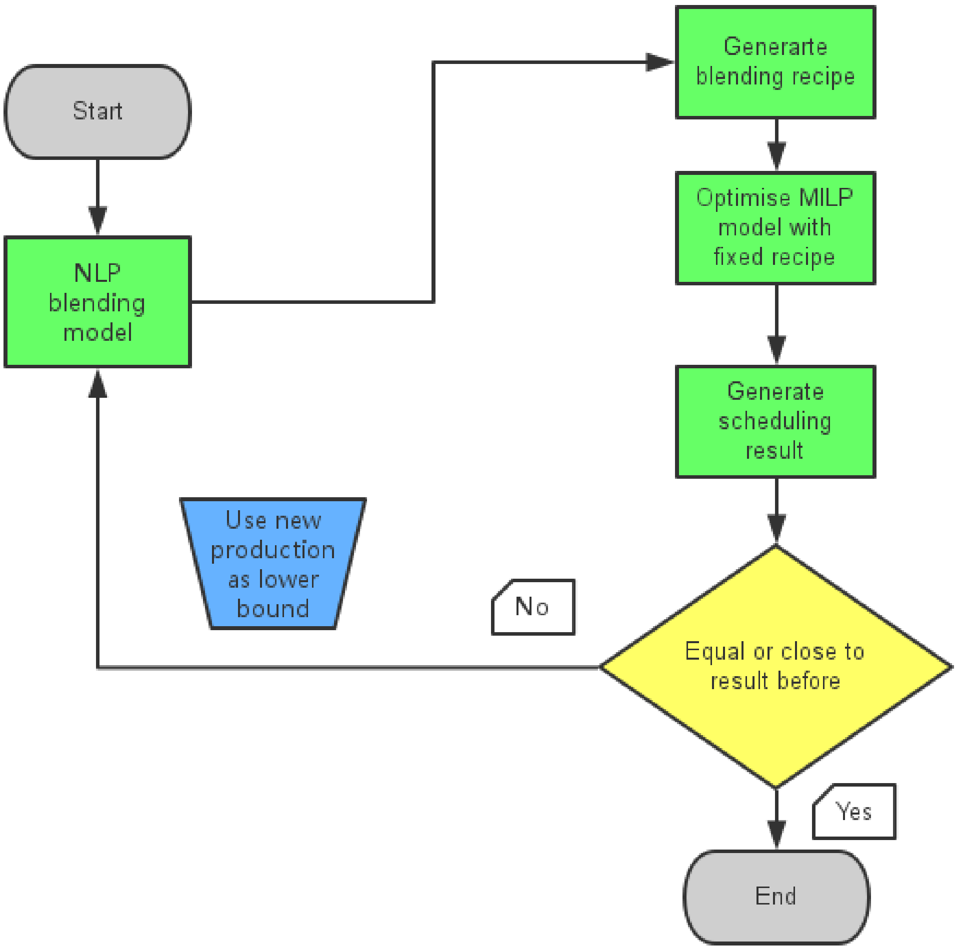


Figure 4.2 Solving Algorithm

4.5 Case study

4.5.1 Basic information

An assumed case study is presented to demonstrate the effectiveness and superiority of the proposed diesel blending scheduling model. The data of the scheduling part including inventory, requirements of product and so is referenced from Mendes and Grossmann's oil blending scheduling case (Mendes and Grossmann, 2006), while the properties are modified to satisfying the requirements of the diesel streams.

The objective of this case study is to find an optimal schedule for the blending of four components streams to produce three different grades of diesel products. The number of blenders available is 3 and the capacity of each is 5.0 Mbbl. A certain amount of feedstocks are placed in the storage tanks before the blending, The products are transferred to storage tanks every day in a fixed daily production. Properties, production and inventory limits are listed in Table 4.1 along with cost of each component. During the blending process, the inventory varies depend on production and blending recipe, but it need to be in line with the storage tank capacity range.

Table 4.1 Feedstock properties

	F1	F2	F3	F4
Cetane Number	68	34	73	73
Sulphur Content(ppm)	12	8	2	8
Density($g*ml^{-1}$)	0.867	0.8559	0.8287	0.8162
CFPP(℃)	-4	-2	-12	-10
Viscosity(mm^2/sec)	3.8	1.5	4.4	2.7
Ash Content(% (m/m))	0.003	0.1	0.01	0.008
PAH(% (m/m))	9	13	4	2
Flash Point(℃)	50	70	60	55
Cost($/bbl)	24	20	36	34
Production Rate (Mbbl/day)	1.5	3.3	2	1.4
Initial Stock (Mbbl)	4.8	2	7.5	2.2
Minimum Stock (Mbbl)	0.5	0.5	0.5	0.5
Maximum Stock (Mbbl)	10	25	25	10

Product specifications are specified in Table 4.2. Three diesel products graded by CFPP (cold filter plugging point) have different prices. This is the key variable in this case.

Table 4.2 Product specifications

	P1	P2	P3
Cetane Number	⩾46	⩾46	⩾46
Sulphur Content(ppm)	⩽10	⩽10	⩽10
Density($g*ml^{-1}$)	0.82-0.86	0.82-0.86	0.82-0.86
CFPP(℃)	0	-5	-10
Viscosity(mm^2/sec)	2-4.5	2-4.5	2-4.5
Ash Content(% (m/m))	⩽0.01	⩽0.01	⩽0.01
PAH(% (m/m))	⩽11	⩽11	⩽11
Flash Point(℃)	⩾55	⩾55	⩾55
Price($/bbl)	31	33	34

Table 4.3 allocates the daily requirements or the three grades of products. The inventory of products must be greater than the due day demand besides of the minimum inventory. The production of each product is limited because of the

blender capacity and other operation limits.

Table 4.3 Inventory and daily requirements of products

	P1			P2			P3		
Requirements (Mbbl)	MIN	MAX	LIFT	MIN	MAX	LIFT	MIN	MAX	LIFT
Day1	0.5	5	1	0.5	0.5	1.2	0.5	5	1
Day2									
Day3				0.5	5	2.5			
Day4	0.5	5	2.5	0.5	5	2.3			
Day5									
Day6									
Day7	0.5	5	3						
Day8	0.5	5	1				0.5	0.5	2.2
Inventory (Mbbl)	0.5	15		0.5	15		0.5	15	
Rate(Mbbl/day)	0.5	5		0	5		0.5	5	

In this case, the objective is to find an optimal scheduling to maximize the profit with satisfying the product specifications and daily demand during an 8-day period. The major constraints are the inventory limits for feedstocks and products, product specifications, daily demand and other operation constraints.

4.5.2 Solving process

All the solving process is operated in GAMS 23.5.

The solving algorithm proposed in this chapter is applied to optimize the diesel blending scheduling problem. Firstly, formulation as the model presented before. Secondly, the model is decomposed into 2 sub models, an NLP model for blending planning and an MILP model for scheduling. The problem is then solved by optimising the planning model. The iterative method is applied to obtain an overall optimal solution.

Firstly, the NLP blending planning model is solved by CONOPT, which contains 106 equations and 78 variables. The blending recipe is shown in Table 4.4.

Table 4.4 The First Blending Recipe from the NLP model

	P1	P2	P3
F1	0.443	0.511	0.206
F2	0.537	0.372	0.099
F3	0	0.061	0.462
F4	0.021	0.057	0.233

In Table 4.5 when the volume fractions of the same product are added together, the result of Product 1 is 1.001, same as Product 2. This is down to an approximation in GAMS, and won't affect the calculation and optimization.

Then, fix the recipe in the scheduling model as in Table 4.3. Solve the MILP problem using CPLEX, with 1380 equations, 492 single variables and 72 binary variables. Generation time is 0.032s. Through optimizing the MILP scheduling problem, new productions scheme is as Table 4.5.

Table 4.5 New Productions by the MILP model

	P1	P2	P3
Production (Mbbl)	7.5	54.0	43.7

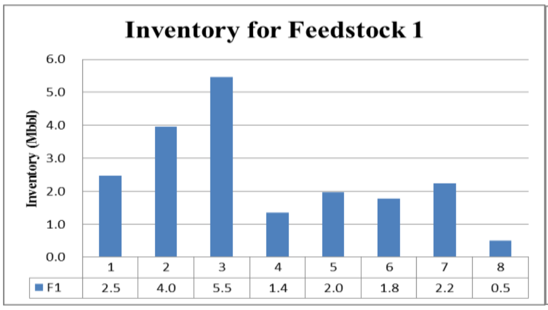
The new productions are different from the first productions due to limitations of blender capacity and operating constraints. The new productions are more in line with the practical situation and operating conditions. Afterwards, the productions in the NLP planning model are fixed and the iteration started as Figure 4.2 represents.

The optimal solution is achieved in iteration 2. The product properties are shown in Table 4.6.

Table 4.6 Productions properties of the optimal solution

	P1	P2	P3
Cetane Number	47.1	49	67.4
Sulphur Content(ppm)	9.2	8.7	6.9
Density($g*ml^{-1}$)	0.856	0.85	0.827
CFPP(℃)	-0.2	-5.4	-10.6
Viscosity(mm^2/sec)	2.000	2.000	2.773
Ash Content(% (m/m))	0.008	0.008	0.008
PAH(% (m/m))	11.000	9.984	4.413
Flash Point(℃)	59.6	60.1	60.0
Price($/bbl)	31	33	34
Production	20.84	6.50	18.20

The feedstock and product inventory is a key variable of a diesel blending scheduling problem. The inventory should be in the range of limits during the whole time horizon.



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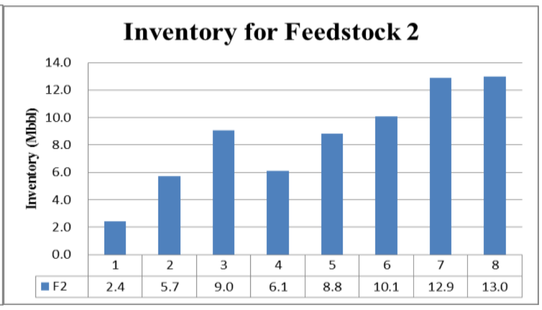

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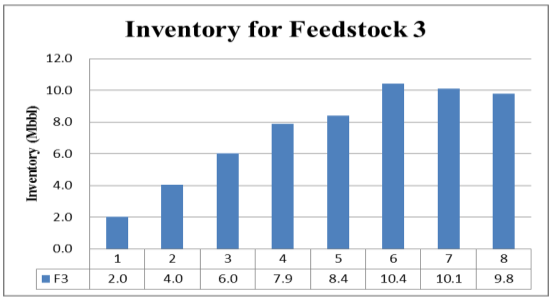

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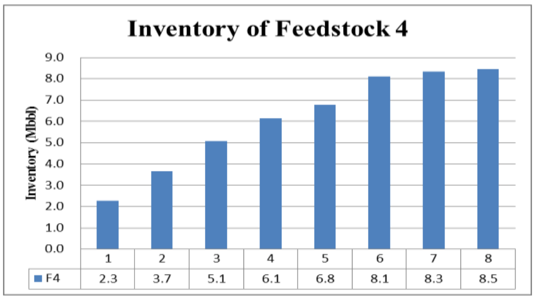

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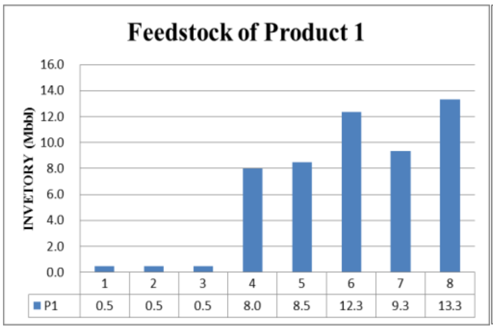
Figure 4.3 Inventories of feedstocks during the blending process



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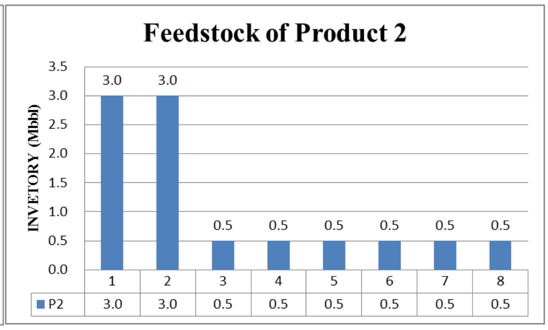

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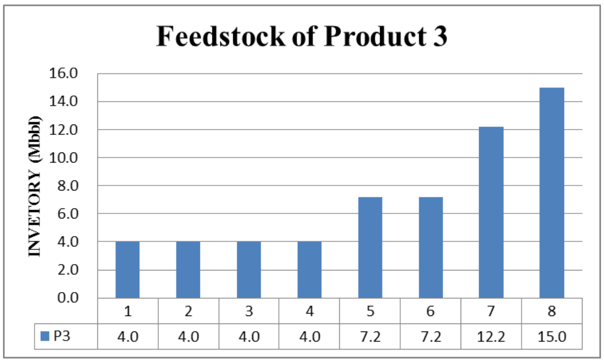

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Figure 4.4 Inventory of products during the blending process

From Figures 4.3 and 4.4, the inventory of feedstock and product varies during the process, but remains between the upper and lower bounds at all the times.

Blender	Product	1	2	3	4	5	6	7	8
n1	P1								5
	P2								
	P3	2.627				5			
n2	P1				5				
	P2	5					5	4.5	5
	P3								
n3	P1	1.5		5	4.538		0.5	0.5	
	P2		1.5						
	P3								5

Figure 4.5 Gantt Chart for the scheduling result

During the problem time period, the blender operations are as shown in Figure 4.5.

In summary, the diesel blending scheduling case has been modelled and optimized by the methods proposed in this chapter. The optimal objective is $605 Million. The market daily demand is achieved with all the product specifications satisfied.

This case is solved by CONOPT in GAMS 23.5 on Dell M14 (Intel® Core™ 2.40GHz) running Windows 10. It contains 1380 equations, 492 single variables and 72 discrete variables. The execution time is 0.032s.

4.6 Summary

In this chapter, a new MINLP model has be developed for scheduling of refinery diesel blending. This model applies nonlinear correlations for property prediction, which will make the model more accurate and complex. All the specifications from diesel product standards are included in the model, which will increase the model scale. Existing MINLP solvers are not capable of solving a nonconvex diesel blending scheduling problem which contains a large number of binary variables and equations. In order to solve the MINLP model, a new solution algorithm has been applied to decompose the MINLP problem into two parts: NLP and MILP and combine them with iterations. A case study shows that the scheduling model is feasible and this solution algorithm is effective in optimisation.

Nomenclature

Sets

i	component index
j	product index
t	time interval index
n	blender index

Parameters

$Price_j$	price of a product
$Cost_i$	cost of a component
$VC_{k,t}$	the original amount of component in component i
VB_{min}, VB_{max}	minimum and maximum volumetric flowrates
ϵ_z	value of property z of component i
$dd_{j,dt}$	market demand at the due date of product j

Binary variables

$A_{j,n,t}$	binary variable to denote that product j is blended in blender n during time interval t

Continuous variables

$Profit$	profit of a process
$FF_{i,t}$	input to component i
$FB_{i,n,t}$	the flowrate of component i to blender n during time interval t
$FP_{j,n,t}$	flowrate or product j from blender n to product storage tank
$Pr_{j,,z,t}$	property z of product j
$x_{i,j,t}$	volume/mass fraction of component i in product j

Chapter 5 Modelling and Optimisation of Gasoline Blending Scheduling

5.1 Introduction

5.1.1 Gasoline

Gasoline, also called gas or petrol, is a mixture of volatile, and flammable liquid hydrocarbons derived from petroleum, and used as fuel for internal-combustion engines. It is also used as a solvent for oils and fats. Originally a by-product of the petroleum industry (kerosene being the principal product), gasoline became the preferred automobile fuel because of its high energy of combustion and capacity to mix readily with air in a carburettor.

Gasoline is a complex mixture of hundreds of different hydrocarbons. Most are saturated and contain 4 to 12 carbon atoms per molecule. Gasoline used in automobiles boils mainly between 30 ° and 200 ° C, which is normally lower than diesel (150 °C-300 °C).

5.1.2. Gasoline blending

Similar to diesel, gasoline can be produced in various processes in a modern oil refinery. Due to the different sources of gasoline streams, they contain both superior and inferior properties. Besides, different marketing locations served by a refinery may have different requirement and regulatory specifications that may also vary seasonally. Therefore, refiners need to select optimal combinations of various intermediate gasoline intermediates in a particular blending ratio to produce on-specification products. Figure 5.1 shows a simplified petroleum flowsheet. Only a small portion of distillates from distillation unit can go directly to blending processes. Most out-streams from the distillation unit are transported to upgrading processes. The streams coming from these upgrading processes are much more valuable and are sent to blending processes.

Major gasoline components come from: distillation unit, catalytic reforming unit, fluid catalytic cracking unit, isomerisation unit, alkylation unit, and other units such as coking, hydrotreating and hydrocracker.

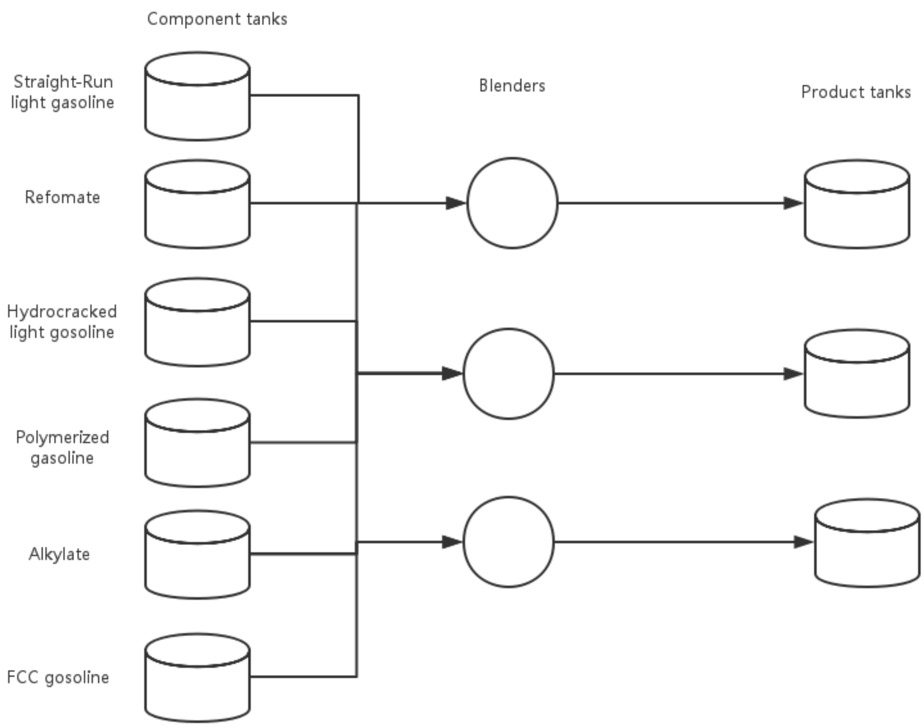

Figure 5.1 A schematic of the gasoline blending operations

In addition, different additives such as oxygenates, antioxidants, anti-rust agents, detergents, lubricants, etc. are used to further improve the gasoline products' quality to meet the product specifications.

The objective of gasoline blending is to find the optimal blending recipe to achieve a best overall profit while satisfying the environmental regulations and market demand.

From the introduction above, gasoline and diesel blending operations share a lot of similarities:

- Several feedstocks are blended into several grades of products with various specifications.
- The objective is to generate an optimal blending recipe
- Accurate prediction of product properties is the key part of the optimization due to product specifications.
- The nature of gasoline blending and diesel blending is nonlinear, but linear models are widely used to simplify the problem.

In recent years, much work has been done for gasoline blending optimization in the literature. Rigby, Lasdon, and Waren (1995) discussed successful implementation of decision support systems for off-line multi-period blending problems at Texaco. Kelly (2004) analyzed the underlying mathematical modelling of complex non-linear formulations for planning models of semi-continuous facilities where the optimal operation of petroleum refineries and petrochemical plants was mainly addressed. Numerous reformulation results and decomposition methods (e.g. column generation, Lagrangian relaxation/decomposition) have been proposed to improve the solution of lot-sizing-based production planning problems (Miller, Nemhauser, and Savelsbergh, 2003). To obtain more accurate production targets, the above formulations have also been extended to include overtime, product substitutes, productivity and capacity utilization. These extensions form the basis of many production planning systems

(Pochet and Wolsey, 2006). In addition, in industries, commercial applications such as Aspen Blend™ and Aspen PIMS-MBO™ from AspenTech are also available for dealing with online and offline blending optimization problems

However, when it comes to gasoline blending scheduling, only linear blending models have been adopted so far. Some researchers tried to apply nonlinear blending models in optimizing gasoline blending scheduling problem with many restrictions. Glismann and Gruhn (2001) proposed a two-level optimization approach where a non-linear model is used for the recipe optimization whereas a Mixed-Integer Linear Programming (MILP) is utilized for the scheduling problem. But products specifications are not considered in this model as constraints.

It is widely recognized that it is necessary to use Non-Linear Programming (NLP) models for the property prediction for gasoline blending. Therefore, it would be relevant to see whether the developed methodology for nonlinear diesel scheduling could be extended to nonlinear gasoline blending scheduling.

In this Chapter, the model is modified by using gasoline blending models to replace the diesel blending models. The scheduling part remains the same since both are product blending problem. The solving algorithm for Mixed-Integer Non-linear Programming (MINLP) problem is also employed to optimize gasoline blending scheduling problems.

5.2 Existing gasoline property correlations

There are several properties that are important in characterizing automotive gasoline such as octane number (ON), Reid vapor pressure (RVP), ASTM distillation points, viscosity, flash point, and aniline point. Ideal mixing refers to quality blending as its volumetric average (Barrow, 1961). However, most gasoline properties blend in a non-ideal and nonlinear fashion, necessitating the use of more complex blending models to predict these properties (Rusin, 1975). In this section, blending models for key properties – octane number, RVP, and ASTM distillation points - are presented and discussed.

5.2.1 Octane number

Octane numbers indicate the antiknock characteristics of gasoline or the ability of the gasoline to resist detonation during combustion in the combustion chamber. There are two types of octane number: research octane number (RON) is measured by ASTM D 908 under city condition, and, motor octane number is measured by ASTM D 357 under road conditions. RON is normally greater than MON by 6-12. Since RON and MON both are not linear properties, complex blending models are needed for accurate prediction of blended octane numbers.

Early research on the octane number of hydrocarbons showed that octane numbers of aromatics and branched iso-paraffins are higher than those of the corresponding paraffins (Lovell, 1931). The American Petroleum Institute (API) analyzed octane numbers of more than 300 hydrocarbon molecules and developed several gasoline composition based correlations (ASTM, 1958; API, 1986; Scott, E, J, 1958). Anderson (1972) developed a linear octane number prediction method for different gasoline using 31 molecular lumps based on the gas chromatographic (GC) analysis. However, a high average error around 2.8 is shown when predicting catalytically cracked naphthas due to the shortcoming of linear ON model. Since then, Researchers have been considering the nonlinear interactions between different chemical compounds of gasoline and putting emphasis on the enhancement of reliability of octane number correlations (Rusin, 1981; Habib, 1989; Cotterman, 1989). Leeuwen (1994) correlates the GC analysed gasoline composition with octane number by neural networks; Meusinger (1999) and Moros (2000) used genetic algorithms and neural networks to identify partial ONs of gasoline components based on the structural elements of the molecule. Other researches on chemical composition based ON methods include Twu and Coon (1997), and Albahri (2000). Ghosh (2006) developed a detailed composition based octane number prediction model covering variety of gasoline process streams based on the analysis of 1471 gasoline fuels with 57 hydrocarbon lumps from GC analysis. The model provides an acceptable accuracy within a standard error of 1 number for both RON and MON.

For blending index method, the simplest form of their tabulated blending indexes has be converted into the relations (Riazi, 2005):

$$BI_{RON} = \begin{cases} 36.01 + 38.33X - 99.8X^2 + 341.3X^3 - 507.2X^4 + 268.64X^5 & 11 \le RON \le 76 \\ -299.5 + 1272X - 1552.9X^2 + 651X^3 & 76 \le RON \le 103 \\ 2206.3 - 4313.64X + 2178.57X^2 & 103 \le RON \end{cases}$$

$$X = \mathrm{RON}/100 \tag{5.1}$$

5.2.2 RVP

The RVP (Reid vapour pressure) of a gasoline blend affects the gasoline performance in terms of ease of starting, engine warm-up, and rate of acceleration. Two fundamental methods for predicting blended RVP are given in Stewart et al. (1959) and Vazques-Esparragoza et al. (1992). Stewart et al. (1959) presented one of the first theoretical approaches for predicting blended RVP. The method uses component data (such as feedstock composition and component volatility), thermodynamic relationships, and a set of simplified assumptions (i.e. presence of air and water vapour are ignored, absolute pressure is taken as the RVP, volatile components are assumed to have the density of butanes, and the non-volatile components are assumed to have the thermal expansion characteristics of n-octane) to predict the blended RVP of a mixture. Vazques-Esparragoza et al. presented an iterative procedure that extended Stewart's method. In this approach, the additivity of liquid and gas volumes is assumed and a different equation of state is used. Furthermore, Vazques-Esparragoza et al. approach requires that the molar composition of feedstocks to be known. The computations required in both of these methods are complex in comparison to those required in other approaches.

The easiest blending index method for RVP prediction is developed by Chevron.

$$RVPI_i = (RVP_i)^{1.25} \tag{5.2}$$

$$RVPb = \left(\sum V_i RVPI_i\right)^{0.8} \tag{5.3}$$

5.2.3 Boiling range

For gasoline boiling range, Ethyl Corporation model mentioned in Chapter 3 can also be used here to predict D86 distillation.

$$D86_{XB} = \sum_{i=1}^{n} v_i BV_{xi} \tag{5.4}$$

$$\mathrm{BV}x_i = C0_x + C1_x A_i + C2_x A_i^2 + C3_x A_i^3 + C4_x A_i G_i + C5_x \frac{G_i}{A_i} + C6_x \frac{G_i}{A_i^2} + C7_x G_i \tag{5.5}$$

5.3 Mathematical model

Gasoline blending planning and scheduling are interactive. Planning operation deals with recipe generation according to market demand and product specifications. The result of planning model, which is the recipe, is sent to the scheduling level. Scheduling works in a more specific way. It allocates what is going to be done in each time interval, including conducting the process in terms of, where streams go and when an assignment ends. On the other hand, the feedback from the scheduling level can help the planning operationists make better decision at the planning level.

Specific to gasoline blending problem, planning level decides a blending recipe to achieve an optimal overall profit while the product specifications and market demands are satisfied. After obtaining the blending recipe, the scheduling level deals with how to achieve an optimal profit according to the recipe and market demand with specifications in restricted time and process capacity under operating constraints.

5.3.1 Planning model

Assumptions:

- The composition requirements of products are not considered in this research.
- The input bounds of each components stream to each blender are neglected.
- The change-over cost of blenders is not considered in this research.
- Flowrate limits are not considered in this research.

The objective of planning model is to maximize the profit through the process, which is equal to total sale subtracting the cost of feedstocks:

$$Profit = \sum_{j=1}^{NP} P_j \cdot Price_j - \sum_{i=1}^{NF} F_i Cost_i \tag{5.6}$$

Subject to:

4) Material balance for component tanks

$$F_i = R_i + \sum_j FB_{i,j} \qquad \forall\, i \qquad (5.7)$$

5) Material balance for product tanks

$$P_j = R_j + \sum_i FB_{i,j} \qquad \forall\, j \qquad (5.8)$$

6) Market demand of each products must be satisfied

$$P_j \geq P_j^{min} \qquad \forall\, j \qquad (5.9)$$

7) Composition concentration

In order to satisfy product qualities and market conditions, upper and lower bounds can be forced on the component concentration for different grades of gasolines

$$CC_{i,j,min} \leq FB_{i,j} \leq CC_{i,j,max} \qquad \forall i, j \qquad (5.10)$$

$CC_{i,j,min}$ and $CC_{i,j,max}$ are the minimum/maximum concentration of component i in product j.

8) Product specification requirement

For properties that can be predicted by linear correlations

$$Pr_{j,z} = \sum_i x_{i,j} * \epsilon_z \qquad \forall\, j, z \qquad (5.11)$$

$$Pr_{j,z} = \sum_i w_{i,j} * \epsilon_z \qquad \forall\, j, z \qquad (5.12)$$

For properties that can be predicted by different nonlinear correlations

$$Pr_{j,z} = f(x_{i,j},\ \epsilon_z) \qquad \forall\ i,j,z \tag{5.13}$$

To improve its applicability, this model gives priorities to the blending index methods for nonlinear properties. This is because these methods require less data or other properties. The applied models are listed in Table 5.1

Table 5.1 Applied models for nonlinear properties

Method	Property
Riazi	Octane Number
Chevron	RVP
Ethyl Corporation	Boiling Range

For planning model, the objective is to maximize Equation 5.6 subject to Equations 5.7-5.13.

5.3.2 Model validation

A verification case from an Asian refinery is presented to show the accuracy of properties prediction of blending products. Three blending components are mixed together to produce the gasoline product. Feedstock 1 is an alkylate stream, Feedstock 2 is an H/S LCN stream, and Feedstock 3 is a raffinate stream. Measured properties of blending components and gasoline product, including RON, RVP, D86 and blending ratio, are shown in Table 5.2. The linear result comes from volume based property indices and the nonlinear result comes from the correlations mentioned before. The calculated properties are compared with the measured properties of blending product to show the performance and difference between linear and nonlinear models.

Table 5.2 Gasoline blending model validation

	F1	F2	F3	Product	Linear	Nonlinear
RON	95.6	92.6	75	93.7	92.3	92.6
RVP	32	63	70	59	59.3	59.5
10%℃	82.6	51.6	51.6	53	55.6	53.07
50%℃	106.8	93.3	64	93.9	93.9	93.5
90%℃	136.6	161.6	78.5	169.9	155.1	159.5
Final℃	215.6	189.5	95.5	196.8	189.2	199.07
ratio	12.85	83.25	3.9			

Comparing the results, nonlinear model delivered better results on RON and D86. For RVP, the results are similar. In order to reduce the prediction error, it is necessary to apply nonlinear correlations in gasoline blending scheduling.

5.3.3 Scheduling model

Objective function: to maximum the total profit for all the diesel products while subtracting the .feedstock costs.

$$Profit = \sum_{j=1}^{NP} P_j \cdot Price_{P,j} - \sum_{i=1}^{NF} F_i \cdot Price_{F,i} \tag{5.13}$$

Subject to:

1) Operation constraint

$$\sum_j A_{j,n,t} \leq 1 \qquad \forall\ n,t \tag{5.14}$$

Binary variable $A_{j,n,t}$ is introduced in the model to denote whether product j is being blended in blender n during time interval t.

2) Material balance for component tanks

$$FF_{i,t} + VC_{i,t-1} = VC_{i,t} + \sum_n FB_{i,n,t} \quad \forall\ i,t \tag{5.15}$$

3) Material balance for blending tanks

$$\sum_i FB_{i.n,t} = FP_{j,n,t} \qquad \forall\, j, n, t \tag{5.16}$$

4) Component concentration

$$A_{j,n,t} \cdot CC_{i,j,t,min} \leq FB_{i.j,n,t} \leq A_{j,n,t} \cdot CC_{i,j,t,max} \qquad \forall\; j, n, t \tag{5.17}$$

$CC_{i,j,t,min}$ and $CC_{i,j,t,max}$ are the minimum and maximum concentration of component i in product j during time interval t. If product j is not processing in blender n during time interval t ($A_{j,n,t} = 0$), the flowrate of component i to blender n to produce product j during time interval t will be zero.

5) Product specification requirement

For properties that can be predicted by different nonlinear correlations

$$Pr_{j,z,min} \leq Pr_{j,z,t} = f(x_{i,j,t}, \epsilon_z) \leq Pr_{j,z,max} \qquad \forall\; j, z, t \tag{5.18}$$

For properties that can be predicted by linear correlations

$$Pr_{j,z,min} \leq Pr_{j,z,t} = x_{i,j,t} * \epsilon_z Pr_{j,z,max} \qquad \forall\, j, z, t \tag{5.19}$$

6) Product demand

$$\sum_{t \leq d} FP_{j,n,t} \geq \sum_{dt} dd_{j,dt} \qquad \forall\; j, n \tag{5.20}$$

For scheduling problem, the objective is to maximize Equation 5.13 subject to Equation 5.14-5.20.

5.4 Case study

This case study was curled from the work by Mendez (2006) and Gupta (2008). The data is modified to compose a gasoline blending scheduling problem. Five components and n-butane are blended into two grades of gasoline. Component streams are available in storage tanks with an available initial inventory, and will be produced and transferred to storage tanks daily. From the component storage tanks, the component streams can be sent to blending tanks for mixing and from blending tanks the product streams can be transferred to different product storage tanks. In addition, two kinds of additives, ethanol and alkylate, can be blended into the blends in order to improve the product quality to meet the specifications. Properties of the five component streams, n-butane stream and additives are specified in Table 5.3. For ethanol, an additional constraint is considered i.e. the volume composition should not exceed 10% in the two grades of products. Ethanol and alkylate can be purchased from the market at the price of $189/bbl and $123.9/bbl respectively.

Table 5.3 Properties of streams and additives

	Stream 1	Stream 2	Stream 3	Stream 4	Stream 5	n-butane	Ethanol	Alkylate
RON	97.2	93.8	100.7	97.6	89.3	93	107	93
MON	86.6	84.4	89.01	86.6	81.9	92	89	90
RVP(psi)	1.1	1.4	0.9	1.3	2.7	52.0	9.6	5.0
Aromatics(%)	78.1	64.3	89.9	85.5	15.2	0	0	0
Availability (bbl)	400	222	400	100	600	125		
Cost ($/bbl)	105.0	95.0	110.0	107.0	108.0	114.0	189.0	123.9
Production Rate (Mbbl/day)	1.50	3.30	2.00	1.40	4.00	1.50		
Initial Stock (Mbbl)	4.00	2.22	4.00	1.00	6.00	1.25		
Minimum Stock (Mbbl)	0.50	0.50	0.50	0.50	0.50	0.50		
Maximum Stock (Mbbl)	35.00	35.00	35.00	35.00	45.00	35.00		

The two final gasoline products can be sold at the price of $115/bbl for Gasoline 89 and $126.8/bbl for gasoline 91. The product specifications are listed in Table 5.4.

Table 5.4 Product specifications and prices

	Gasoline 89	Gasoline 91
AKI	89	91
RON	94	96
MON	84	86
RVP(psi)	6.9	6.9
Aromatics(%)	35	35
Price ($/bbl)	115	126.8

Table 5.5 allocates the daily requirements or the two grades of products. The inventory of products must be greater than the due day demand besides of the minimum inventory.

Table 5.5 Inventory and daily requirements of products

	P1			P2		
Requirements (Mbbl)	MIN	MAX	LIFT	MIN	MAX	LIFT
Day1	0.5	5.0	1.0	0.5	5.0	1.2
Day2						
Day3				0.5	5.0	2.5
Day4	0.5	5.0	2.5	0.5	5.0	2.3
Day5				0.5	5.0	5.0
Day6				0.5	5.0	5.0
Day7	0.5	5.0	3.0	0.5	5.0	5.0
Day8	0.5	5.0	1.0			
Inventory (Mbbl)	0.5	60.0		0.5	60.0	
Rate(Mbbl/day)	0.5	5.0		0.0	5.0	

The objective of this case study is to find an optimised schedule in an 8-day period while the product specifications are satisfied.

Before optimizing the problem, several assumptions are made.

- The number of blenders is assumed to be 2.

- The blending index method proposed by Riazi (2005) is applied to calculate RON for blends. Meanwhile MON can be calculated using the method proposed by Jenkins (1980)

$$MON=22.5+0.83RON-20*SG-0.12(\%O)+0.5(TML)+0.2(TEL) \qquad (5.21)$$

  SG is specific gravity and TML and TEL are the concentration of tetra methyl lead and tetra ethyl lead in mL/UK gallon. And %O is the volume fraction of olefins in the gasoline. In this case, since the densities are not provided, SG is assumed to be 0.72, a very normal SG for gasoline stream. And TEL, TML and %O are all assumed to be zero.

As nonlinear correlations are applied to predict ROM, MON, RVP of the blends, this problem has become an MINLP problem. The algorithm proposed in Chapter 4 is used to optimize this MINLP scheduling problem. It is firstly decomposed into an NLP blending planning model and MILP scheduling model. The NLP model deals with the nonlinear blending optimization. The result, which is gasoline blending recipe in this case, is transferred to the next MILP scheduling problem as a fixed recipe. After optimizing, the scheduling model returns a new production, in which blending operation constraints are considered, to the NLP planning model. By fixing the production, the NLP planning model starts the next iteration. As the MILP scheduling model deals with specific blending operations, the result from it is more realistic and practical than the planning result. After getting the feedback, the NLP model can optimize the planning problem in a higher horizon. The process continues until the result from scheduling model is the same or very close to that in last iteration. This is the optimal point of the gasoline blending scheduling problem.

The problem is solved by CONOPT in GAMS 23.5 to maximize objective function (Equation 5.6) subject to constraints (Equation 5.7-5.20). The solving process ends at iteration 2.

The optimization results are shown in Table 5.6 to Table 5.7

Table 5.6 Detailed product composition and production

Compostion	Gasoline 89 (bbl)	Gasoline 91 (mbbl)
Stream 1	0	0
Stream 2	0.443	0.358
Stream 3	0.428	0.093
Stream 4	0	0
Stream 5	0.056	0.239
n-butane	0.072	0.049
Ethanol	0	0.1
Alkylate	0	0.161
Production(Mbbl)	8	68

Table 5.7 Blended product properties (nonlinear blending)

	AKI	RON	MON	RVP(psi)	Aromatics(%)
Gasoline 89	90.1	94.0	86.1	6.9	35
Gasoline 91	91.9	96.0	87.8	6.9	35

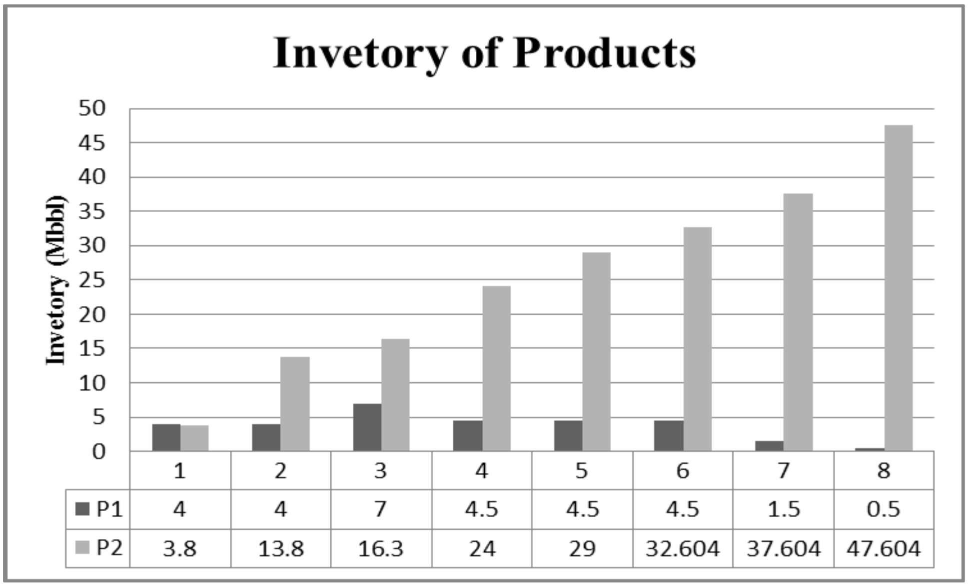

Figure 5.2 Inventory of products

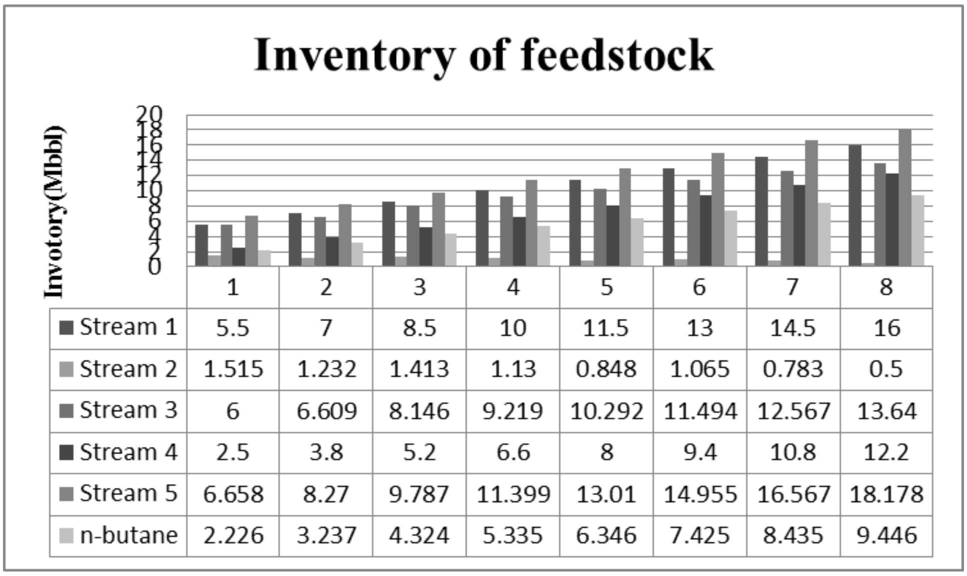

Figure 5.3 Inventory of feedstocks

From Table 5.5, since the price of Gasoline 89 is very low compared with the component cost, the local optimal solution only produces minimum amount of this product that can meet the market demand and inventory requirement.

Blender		1	2	3	4	5	6	7	8
	P1								
n1	P2	5	5	5	5	5	3.604	5	5
	P1	5		3					
n2	P2		5		5	5	5	5	5

Figure 5.4 Gantt Chart for the scheduling result

During the problem time period, the blender operations are as shown in Figure 5.4.

This case is solved by CONOPT in GAMS 23.5 on Dell M14 (Intel® Core™ 2.40GHz) running Windows 10. It contains 1171 equations, 403 single variables and 32 discrete variables. The execution time is 0.032s. The local optimal profit of this case is $ 897 Million.

5.5 Summary

In this Chapter, a new application of the proposed model is introduced. Although there have been many research on gasoline blending scheduling, nonlinear correlations and property prediction accuracy haven't receive enough attention. After modification, the model can deal with gasoline blending successfully. Due to nonlinear gasoline property prediction models, the blending scheduling model becomes an MINLP problem, which cannot be solved by existing MINLP solvers because of the complexity of the equations and the large number of variables and equations. The solving algorithm proposed in Chapter 4 is also introduced to solve MINLP gasoline blending scheduling problem. This MINLP is decomposed into a two-level optimisation problem. NLP part generates a blending recipe and fixes the nonlinear variables in the MINLP formulation, which makes it an MILP to optimise the scheduling problem. The iteration between the two-level models provides a near-optimal solution for the gasoline blending scheduling problem. to A case study is presented to prove the reliability, efficiency and superiority of the proposed model and solving algorithm.

Nomenclature

Sets

i component index

j product index

t time interval index

n blender index

Parameters

RVP_i RVP of component i

$RVPI_i$ blending index of RVP of component i

A_i average boiling temperature (℃) of component i

G_i the components i ASTM severity (T90-T10)

$Cost_i$ cost of a component

$VC_{k,t}$ the original amount of component in component i

VB_{min}, VB_{max} minimum and maximum volumetric flowrates

$dd_{j,dt}$ market demand at the due date of product j

ϵ_z value of property z of component i

Binary variables

$A_{j,n,t}$	binary variable to denote that product j is blended in blender n during time interval t

Continuous variables

RON	research octane number
MON	motor octane number
RVP	Reid vapour pressure
$RVPb$	RVP of mixture
$Profit$	profit of a process
$Price_j$	price of a product
$FF_{i,t}$	input to component i
$FB_{i,n,t}$	the flowrate of component i to blender n during time interval t
$FP_{j,n,t}$	flowrate or product j from blender n to product storage tank
$Pr_{j,,z,t}$	property z of product j
$x_{i,j,t}$	volume/mass fraction of component i in product j

Chapter 6 Conclusions and future work

6.1 Conclusions

Due to decreased oil prices and degrading qualities of crude oil, stiff market competition and stringent fuel specifications, refinery need to have smarter strategies to meet product demands and generate profit. However, diesel production blending problem has not received sufficient attention from academic researchers. Refineries widely apply Linear Programming (LP) models, which could lead to big properties and profit loss due to inaccuracy, to operate diesel blending process. More accurate property prediction methods should be adopted in diesel blending operation.

A model is developed to optimize diesel blending planning problem. Instead of linear correlations for property estimation, which is mostly used in the refining industry, nonlinear correlations for property prediction of diesel blending are applied to improve the model accuracy. The properties in the diesel product specifications are taken into account in this model. With the application of nonlinear correlations in the model, the accuracy and complexity of the problem both increase. To avoid infeasible solutions, a solution algorithm is proposed. By decomposing the model into several sub-models, the problem is solved layer by layer. The initial point of each layer comes from the upper level layer, until to a simply NLP model that can be easily worked out by the solvers. A diesel blending production case is optimized by this model. The NLP model with complex Non-Linear correlations is solved using the solution algorithm.

On the basis of the NLP model, an MINLP model for diesel blending scheduling is developed. For diesel production blending, the nature of nonlinear blending makes scheduling an MINLP problem. Existing MINLP solvers fail to solve this problem due to large number of equations and variables. To overcome the difficulties in solving an MINLP problem, a robust algorithm is successfully developed. The model is decomposed into two sub-models: NLP model for planning part and MILP model for scheduling part. The NLP model deals with the diesel blending planning optimization, which generates a blending recipe. Then, the blending recipe is delivered to the next level, MILP scheduling model as a fixed recipe. After the scheduling optimisation is performed, the new production is transferred to the NLP planning mode to modify the blending optimization. After several iterations, the overall optimal solution can be achieved. Through this algorithm, the MINLP problem which cannot be solved by existing solvers can be solved.

In addition, the model is developed for diesel production blending scheduling problem, but it can be expanded to other refinery processes, such as gasoline blending. Considering the difference between the blending model of gasoline and diesel, the proposed model needs to be modified before modelling the gasoline blending problem. However, due to the same nature of nonlinear blending, the gasoline MINLP blending scheduling problem can be optimised through the proposed solution algorithm.

In this work, NLP models are developed in diesel blending planning and scheduling. The proposed model and solution algorithm can improve the model accuracy, increase the profit and reduce the computation effort. This provides a significant improvement to the decision making procedure for refinery diesel blending operation..

6.2 Future work

As this work introduces a model for diesel product blending, it is just the first step for refining optimization. Therefore, there is a large scope of the future research.

Nonlinear blending models have been researched for years. They are more accurate than LP models in refinery optimization. But there still are potential in improving model accuracy. More industrial case studies can be applied to validate and improve the developed methodology.

Only off line blending is considered in this work, however, in line blending is also a widely used blending method in refineries. More research can be developed in refinery in line diesel blending and optimization.

To achieve an overall optimization, the methodology for diesel blending can be expanded to consider detailed upstream processes for producing more cost effective diesel blending stocks.

As a more specific process level, more research can be addressed in advanced process control for refinery diesel blending operation.

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Appendix A Diesel blending optimization in GAMS

```
sets      i     diesel feedstock    / F1, F2, F3, F4/

            j     products               / P1, P2, P3, P4/

parameters

            amount(i)     amount of diesel i (t)

                    / F1    1500

                      F2    1200

                      F3    1300

                      F4    800

                      /

            CN(i)           Cetane number of diesel i

                    / F1    68

                      F2    34

                      F3    73

                      F4    73

                      /
```

SC(i) Sulphur content of diesel i (ppm)

/ F1 12

F2 8

F3 2

F4 8

/

Den(i) Density of diesel i (g*ml-1)

/ F1 0.8670

F2 0.8559

F3 0.8287

F4 0.8162

/

PPt(i) Pour point of diesel i

/ F1 -20

F2 -14

F3 -37

F4 -5

/

CFPP(i) Could filter plugging point of diesel i

/ F1 -15

F2 -9

F3 -16

F4 3

/

v(i) viscosity of diesel i

/F1 3.8

F2 1.5

F3 4.4

F4 2.7

/

CR(i) Carbon residue of diesel i

/F1 0.2

F2 0.1

F3 0.3

F4 0.4

/

AC(i) Ash content of diesel i

/F1 0.003

F2 0.01

F3 0.01

F4 0.008

/

PAH(i) polycyclic aromatic hydrocarbons in diesel i

/F1 9

F2 13

F3 4

F4 2

/

FP(i) flash point of diesel i

/F1 50

F2 70

F3 60

F4 55

/

price(j) price of product j

/ P1 1270

P2 1290

P3 1320

P4 1330/

CNsta(j) standard Cetane number of product j

/ P1 46

P2 46

P3 46

P4 46/

SCsta(j) standard sulphur content of product j (ppm)

/ P1 10

P2 10

P3 10

P4 10/

PPtsta(j) standard Pour Point of product j

/ P1 0

P2 -10

P3 -20

P4 -35/

CFPPsta(j) standard Cold filter plugging point of product j

/ P1 0

P2 -5

P3 -10

P4 -15/

Densitylower(j) lower limit of density (g*ml-1)

/ P1 0.82

P2 0.82

P3 0.82

P4 0.82/

Densityupper(j)   upper limit of density   (g*ml-1)

/ P1   0.86

P2   0.86

P3   0.86

P4   0.86/

viscositylower(j)   lower limit of viscosity

/P1   2

P2   2

P3   2

P4   2/

viscosityupper(j)   upper limit of viscosity

/P1   4.5

P2   4.5

P3   4.5

P4   4.5 /

FPtsta(j)   standard Flash Point of product j

/ P1   55

P2 55

P3 55

P4 55/

BPI(i) Initial boiling point

/F1 131.5

F2 140.7

F3 205

F4 151.7

/

BP10(i) 10% boiling point

/F1 137.2

F2 165.4

F3 262.6

F4 256.9

/

BP30(i) 30% boiling point

/F1 139.9

F2	173.4
F3	275.6
F4	272.2

/

BP50(i) 50% boiling point

/F1	143.8
F2	199.2
F3	301.8
F4	307.9

/

BP90(i) 90% boiling point

/F1	158.5
F2	246.9
F3	349.9
F4	367.6

/

BP95(i) 95% boiling point

/F1 166.2

F2 254.8

F3 361.6

F4 387.6

/

BPF(i) Final boiling point

/F1 185.6

F2 266.8

F3 372.3

F4 396.7

/

POSITIVE VARIABLES

x(i,j) volume fraction of feed i in product j variables

yy(j) amount of product j (ton)

xx(i,j) mass of feed i in product j

dens(j) density of product j

CarbonP(j)

CNP(j)

PAHP(j)

ashP(j)

volume(i,j) volume of feed i in product j

SulphurP(j)

VBNi(i) Viscosity Blending Index of feed i

VBNj(j) Viscosity Blending Index of product j

vis(j) viscosity of product j

y(j) volume amount of product j(L)

FB(i)

s

PourP(j)

CFPPp(j)

BIF(i) blending index of flash point of feed i

BIfp(j) blending index of flash point of product j

flashp(j) flash point of product j

BVXi(i)

BVX10(i)

```
  BVX30(i)
  BVX50(i)
  BVX90(i)
  BVX95(i)
  BVXf(i)
Ai(i)
Gi(i)
BPFI(j)    Initial boiling point
  BPF10(j)    10% boiling point
  BPF30(j)    30% boiling point
  BPF50(j)    50% boiling point
  BPF90(j)    90% boiling point
  BPF95(j)    95% boiling point
  BPFF(j)    Final boiling point
;
equations
density(j)
```

densityl(j)

densityu(j)

profit

Cetanenumber1(j)

Cetanenumber2(j)

Sulphurcontent1(j)

Sulphurcontent2(j)

Cfpp1(j)

VBN1(i)

VBN2(j)

Viscosity(j)

viscositystand1(j)

viscositystand2(j)

ashcontent1(j)

ashcontent2(j)

pahydro1(j)

pahydro2(j)

BI1(i)

BI2(j)

BI3(j)

BI4(j)

A(i)

C(j)

D(i,j)

E(i,j)

G(j)

Boilingpoint2(i)

Boilingpoint4(i)

Boilingpoint5(i)

Boilingpoint9(j)

Boilingpoint11(j)

Boilingpoint12(j)

Aieq(i)

Gieq(i)

```
;

density(j)..             dens(j)=e= sum(i,den(i)*x(i,j);

densityu(j)..          dens(j)=l=densityupper(j);

densityl(j)..          dens(j)=g=densitylower(j);

profit..                     s=e=sum(j, y(j)*price(j));

Cetanenumber1(j)..      sum(i,x(i,j)*CN(i))=g=CNsta(j);

Cetanenumber2(j)..      sum(i,x(i,j)*CN(i))=e=CNP(j);

Sulphurcontent1(j)..   sum(i,xx(i,j)*SC(i)/((yy(j)+0.000001)))=l=SCsta(j);

Sulphurcontent2(j)..   sum(i,xx(i,j)*SC(i)/((yy(j)+0.000001)))=e=SulphurP(j);


Aieq(i)..                      Ai(i)=e=(BP10(i)+BP50(i)*2+BP90(i))/4;

Gieq(i)..                      Gi(i)=e=BP90(i)-BP10(i);


Boilingpoint2(i)..

BVX10(i)=e=-1120+Ai(i)*(17.77218623)+Ai(i)*Ai(i)*(-0.05949307)+Ai(i)*Ai(i)*

Ai(i)*(0.00006561)+Ai(i)*Gi(i)*(-0.04940709)+(-11600)*Gi(i)/(Ai(i)+0.000000001
```

)+(1030000)*Gi(i)/(Ai(i)*Ai(i)+0.0000001)+(37.7815769)*Gi(i);

Boilingpoint4(i)..

BVX50(i)=e=-6.77060E+3+Ai(i)*(42.62167742)+Ai(i)*Ai(i)*(-0.05126593)+Ai(i)*

Ai(i)*Ai(i)*

(-0.00002842)+Ai(i)*Gi(i)*(-0.30859948)+(-5.55642E+4)*Gi(i)/(Ai(i)+0.0000000

01)+(5.055108E+6)*Gi(i)/(Ai(i)*Ai(i)+0.0000001)+(2.202761E+2)*Gi(i);

Boilingpoint5(i)..

BVX90(i)=e=-3170+Ai(i)*(58.53687623)+Ai(i)*Ai(i)*(-0.25951042)+Ai(i)*Ai(i)*

Ai(i)*

(0.00034356)+Ai(i)*Gi(i)*(-0.0512486)+(-204000)*Gi(i)/(Ai(i)+0.000000001)+(16

80000)*Gi(i)/(Ai(i)*Ai(i)+0.0000001)+(64.70628018)*Gi(i);

Boilingpoint9(j)..   BPF10(j)=e=sum(i,x(i,j)*BVX10(i));

Boilingpoint11(j)..   BPF50(j)=e=sum(i,x(i,j)*BVX50(i));

Boilingpoint12(j)..   BPF90(j)=e=sum(i,x(i,j)*BVX90(i));

Cfpp1(j)..

```
13.45*log(cfppsta(j)+459.67)=g=log(sum(i,(((x(i,j))**1.03)*((cfpp(i)+459.67)**13.
45)+0.00000001)));

ashcontent1(j)..          sum(i,xx(i,j)*AC(i)/(yy(j)+0.00000001))=l=0.01;

ashcontent2(j)..            sum(i,xx(i,j)*AC(i)/(yy(j)+0.00000001))=e=AshP(j);

pahydro1(j)..             sum(i,xx(i,j)*pah(i)/(yy(j)+0.00000001))=l=11;

pahydro2(j)..             sum(i,xx(i,j)*pah(i)/(yy(j)+0.00000001))=e=PAHP(j);

VBN1(i)..               VBNi(i)=e=14.534*log(log(v(i)+0.8))+10.975;

VBN2(j)..                VBNj(j)=e=sum(i,(xx(i,j)/(yy(j)+0.0000001)*VBNi(i)));

viscosity(j)..         vis(j)=e=exp(exp((VBNj(j)-10.975)/14.534))-0.8;

viscositystand1(j)..   vis(j)=l=viscosityupper(j);

viscositystand2(j)..   vis(j)=g=viscositylower(j);

BI1(i)..       log10(BIF(i)+0.00001)=e=-6.1188+(2414/(FP(i)+273.15-42.6));

BI2(j)..       BIfp(j)=e=sum(i,x(i,j)*BIF(i));

BI3(j)..       log10(BIfp(j)+0.00001)=e=-6.1188+(2414/(flashp(j)+273.15-42.6));
```

```
BI4(j)..        flashp(j)=g=FPtsta(j);

A(i)..                    sum(j,xx(i,j))=l=amount(i);

C(j)..                       yy(j)=e=sum(i,xx(i,j));

D(i,j)..                  volume(i,j)=e=y(j)*x(i,j);

E(i,j)..                   volume(i,j)*den(i)=e=xx(i,j);

G(j)..               dens(j)*y(j)=e=yy(j);

yy.lo('P1')=500;

yy.lo('P2')=800;

yy.lo('P3')=700;

yy.lo('P4')=300;
```

```
option      NLP= conOPT ;

Model diesel2 /density
densityl
densityu
profit

A

C
D
E
G
```

```
/;

solve diesel2 using nlp maximazing s;



Model diesel1 /density

densityl

densityu

profit

Cetanenumber1

Cetanenumber2

Sulphurcontent1

Sulphurcontent2




Cfpp1
```

VBN1

VBN2

Viscosity

viscositystand1

viscositystand2

ashcontent1

ashcontent2

pahydro1

pahydro2

BI1

BI2

BI3

```
BI4

A

C

D

E

G

/;

solve diesel1 using nlp maximazing s;

Model blending /all/;

solve blending using nlp maximizing s ;
```

```
display yy.l,yy.m, x.l,x.m, XX.L,s.l,s.m;
```

Appendix B Diesel blending scheduling optimization in GAMS

```
sets        i       diesel feedstock      / F1, F2, F3, F4/

              j       products                    / P1, P2, P3/

              t    time interval              /1,2,3,4,5,6,7,8/

              n       blender                     /n1,n2,N3/



parameters

                  AVA(I)

                /F1               39.9

                F2                 28.4

                F3                 23.5

                  F4               13.4/

 iniinventory(i)    initial inventory of diesel i        (Mbbl)

                              / F1    4.8

                                F2    2.0

                                F3    2.6
```

```
                    F4    2.3

                    /



        Production(I)            daily production of i    (mbbl)

                   / F1    1.5

                    F2    3.3

                    F3    2.0

                    F4    1.4

                    /

         minstock(i)             minimum stock

                    / F1    0.5

                    F2 0.5

                    F3    0.5

                    F4    0.5

                    /

         maxstock(i)             maximum stock

                    / F1    10
```

F2 25

F3 25

F4 10

/

minstockJ(J) minimum stock

/ P1 0.5

P2 0.5

P3 0.5

/

maxstockJ(J) maximum stock

/ P1 15

P2 15

P3 15

/

CN(i) Cetane number of diesel i

/ F1 68

F2 34

F3 73

F4 73

/

SC(i) Sulphur content of diesel i (ppm)

/ F1 12

F2 8

F3 2

F4 8

/

Den(i) Density of diesel i (g*ml-1)

/ F1 0.8670

F2 0.8559

F3 0.8287

F4 0.8162

/

PPt(i) Pour point of diesel i

/ F1 -20

F2 -14

F3 -37

F4 -5

/

CFPP(i) Could filter plugging point of diesel i

/ F1 -4

F2 -2

F3 -12

F4 -10

/

v(i) viscosity of diesel i

/F1 3.8

F2 1.5

F3 4.4

F4 2.7

/

CR(i) Carbon residue of diesel i

/F1 0.2

F2 0.1

F3 0.3

F4 0.4

/

AC(i) Ash content of diesel i

/F1 0.003

F2 0.01

F3 0.01

F4 0.008

/

PAH(i) polycyclic aromatic hydrocarbons in diesel i

/F1 9

F2 13

F3 4

F4 2

/

FP(i) flash point of diesel i

/F1 50

F2 70

F3 60

F4 55

/

price(j) price of product j $ per bbl

/ P1 31

P2 33

P3 35

/

cost(i)

/F1 22

F2 20

F3 26

F4 24

/

CNsta(j) standard Cetane number of product j

/ P1 46

P2 46

P3 46

/

SCsta(j) standard sulphur content of product j (ppm)

/ P1 10

P2 10

P3 10

/

PPtsta(j) standard Pour Point of product j

/ P1 0

P2 -10

P3 -20

/

CFPPsta(j) standard Cold filter plugging point of product j

/ P1 0

P2 -5

P3 -10

/

Densitylower(j) lower limit of density (g*ml-1)

/ P1 0.82

P2 0.82

P3 0.82

/

Densityupper(j) upper limit of density (g*ml-1)

/ P1 0.86

P2 0.86

P3 0.86

/

viscositylower(j) lower limit of viscosity

/P1 2

P2 2

P3 2

/

viscosityupper(j) upper limit of viscosity

/P1 4.5

P2 4.5

P3 4.5

/

FPtsta(j) standard Flash Point of product j

/ P1 55

P2 55

P3 55

/

Table LIFT(j,t)

	1	2	3	4	5	6	7	8
P1	1.0			2.5			3.0	1.0
P2	1.2		2.5	2.3				
P3							1.0	2.2

Table xmilp(i,j)

	P1	P2	P3
F1			
F2			
F3			
F4			

positive variables

x(i,j) volume fraction of feed i in product j yy(j) amount of product j (MASS)

xx(i,j) mass of feed i in product j

dens(j) density of product j

y(j)

volume(i,j)

FlowrateP(j,n,t) volume of product j being blended in blender n during time slot t

FlowrateB(i,j,n,t) volume of component i being transfered to blender n during time slot t

ymilp(j)

BIfp(j) blending index of flash point of product j

SCALARS PPPPP/ 0 /

number /1/ ;

variable

s

totalpro

PourP(j)

CFPPp(j)

BIF(i) blending index of flash point of feed i

flashp(j) flash point of product j

AVAdaily(i,t)

AVARES (i,t) daily residue in inventory tank

AVARESj(j,t)

bias(j)

yy(j) amount of product j (MASS)

xx(i,j) mass of feed i in product j

dens(j) density of product j

CarbonP(j)

CNP(j)

PAHP(j)

ashP(j)

volume(i,j) volume of feed i in product j

SulphurP(j)

VBNi(i) Viscosity Blending Index of feed i

VBNj(j) Viscosity Blending Index of product j

vis(j) viscosity of product j

y(j) volume amount of product j(L)

FB(i)

binary variable

A(j,n,t) denote if product j is processed in blender during time slot t

equations

density(j)

densityl(j)

densityu(j)

profit

Cetanenumber1(j)

Cetanenumber2(j)

Sulphurcontent1(j)

Sulphurcontent2(j)

Cfpp1(j)

VBN1(i)

VBN2(j)

Viscosity(j)

viscositystand1(j)

viscositystand2(j)

ashcontent1(j)

ashcontent2(j)

pahydro1(j)

pahydro2(j)

BI1(i)

BI2(j)

BI3(j)

BI4(j)

AA(i)

B(J)

C(j)

D(i,j)

E(i,j)

F(j)

GG(j)

H

profitMILP

blendingbalance2(j,n,t)

blendingbalance3(i,j,n,t)

blendingbalance4(j)

blendingbalance5(j,n,t)

blendingbalance6(j,n,t)

blendoperation3(n,t)

D2(i,j,n,t)

*D3(i)

AVA1(i,t)

AVA2(i,t)

AVA21(i,t)

AVA22(i,t)

AVA23(i,t)

AVA24(i,t)

AVA25(i,t)

AVA26(i,t)

AVA31(j,t)

AVA32(j,t)

AVA33(j,t)

```
AVA34(j,t)

AVA35(j,t)

AVA36(j,t)

AVA3(j,t)

AVA4(j,t)

AVA5(i,t)

AVA6(i,t)

AVA7(j,t)

AVA8(j,t)

;

density(j)..              dens(j)=e=(sum(i,x(i,j)*den(i)));

densityu(j)..           dens(j)=l=densityupper(j);

densityl(j)..           dens(j)=g=densitylower(j);

profit..                        s=e=sum(j, y(j)*price(j))-sum((i,j),volume(i,j)*cost(i));

Cetanenumber1(j)..       sum(i,x(i,j)*CN(i))=g=CNsta(j);

Cetanenumber2(j)..       sum(i,x(i,j)*CN(i))=e=CNP(j);

Sulphurcontent1(j)..    sum(i,xx(i,j)*SC(i)/((yy(j)+0.000001)))=l=SCsta(j);
```

```
Sulphurcontent2(j)..    sum(i,xx(i,j)*SC(i)/((yy(j)+0.000001)))=e=SulphurP(j);




Cfpp1(j)..
13.45*log(cfppsta(j)+459.67)=g=log(sum(i,(((x(i,j))**1.03)*((cfpp(i)+459.67)**13.
45)+0.00000001)));


ashcontent1(j)..            sum(i,xx(i,j)*AC(i)/(yy(j)+0.00000001))=l=0.01;

ashcontent2(j)..               sum(i,xx(i,j)*AC(i)/(yy(j)+0.00000001))=e=AshP(j);

pahydro1(j)..               sum(i,xx(i,j)*pah(i)/(yy(j)+0.00000001))=l=11;

pahydro2(j)..               sum(i,xx(i,j)*pah(i)/(yy(j)+0.00000001))=e=PAHP(j);

VBN1(i)..               VBNi(i)=e=14.534*log(log(v(i)+0.8))+10.975;

VBN2(j)..                 VBNj(j)=e=sum(i,(xx(i,j)/(yy(j)+0.0000001)*VBNi(i)));

viscosity(j)..          vis(j)=e=exp(exp((VBNj(j)-10.975)/14.534))-0.8;

viscositystand1(j)..      vis(j)=l=viscosityupper(j);

viscositystand2(j)..      vis(j)=g=viscositylower(j);

BI1(i)..          log10(BIF(i)+0.00001)=e=-6.1188+(2414/(FP(i)+273.15-42.6));

BI2(j)..          BIfp(j)=e=sum(i,x(i,j)*BIF(i));
```

```
BI3(j)..        log10(BIfp(j)+0.00001)=e=-6.1188+(2414/(flashp(j)+273.15-42.6));

BI4(j)..        flashp(j)=g=FPtsta(j);



AA(i)..                     sum(j,volume (i,j))=l=AVA(i);

B(J)..                              sum(i,x(i,j))=e=1;

C(j)..                        yy(j)=e=sum(i,xx(i,j));

D(i,j)..                    volume(i,j)=e=y(j)*x(i,j);

E(i,j)..                     volume(i,j)*den(i)=e=xx(i,j);

F(j)..                                      sum(i,volume(i,j))=e=y(j);

GG(j)..                dens(j)*y(j)=e=yy(j);

h..                 sum(j,y(j))=l=120;

profitMILP..

          sum((j,n,t),
FlowrateP(j,n,t)*price(j))-sum((i,j,n,t),FlowrateB(i,j,n,t)*cost(i))=e=totalpro;



blendingbalance2(j,n,t)..
sum(i,FlowrateB(i,j,n,t))=e=FlowrateP(j,n,t)    ;
```

```
blendingbalance3(i,j,n,t)..
FlowrateB(i,j,n,t)=e=FlowrateP(j,n,t)*xmilp(i,j); ;

blendingbalance5(j,n,t)..
FlowrateP(j,n,t)=l=5*A(j,n,t);

blendingbalance6(j,n,t)..
FlowrateP(j,n,t)=g=0.5*A(j,n,t);

blendingbalance4(j)..
yMILP(j)=e=sum((n,t),FlowrateP(j,n,t));

blendoperation3(n,t)..                    sum((j), A(j,n,t))=l=1;
```

```
D2(i,j,n,t)..
FlowrateP(j,n,t)*xMILP(i,j)=e=FlowrateB(i,j,n,t);

*D3(i)..
Volumeres(i)=e=AVA(i)-sum((j,t),FlowrateB(i,j,t))+INIINVENTORY(I);

AVA1(i,t)..                                        AVAres(i,'1')=e=
iniinventory(i)+production(i)-sum((j,n),FlowrateB(i,j,n,'1'));

AVA2(i,t)..                    AVAres(i,'2')=e=    AVAres(i,'1')+production
(i)-sum((j,n),FlowrateB(i,j,n,'2'));

AVA21(i,t)..                   AVAres(i,'3')=e=    AVAres(i,'2')+production
(i)-sum((j,n),FlowrateB(i,j,n,'3'));

AVA22(i,t)..                   AVAres(i,'4')=e=    AVAres(i,'3')+production
(i)-sum((j,n),FlowrateB(i,j,n,'4'));

AVA23(i,t)..                   AVAres(i,'5')=e=    AVAres(i,'4')+production
(i)-sum((j,n),FlowrateB(i,j,n,'5'));

AVA24(i,t)..                   AVAres(i,'6')=e=    AVAres(i,'5')+production
```

(i)-sum((j,n),FlowrateB(i,j,n,'6'));

AVA25(i,t).. AVAres(i,'7')=e= AVAres(i,'6')+production (i)-sum((j,n),FlowrateB(i,j,n,'7'));

AVA26(i,t).. AVAres(i,'8')=e= AVAres(i,'7')+production (i)-sum((j,n),FlowrateB(i,j,n,'8'));

AVA3(j,t).. AVAresj(j,'2')=e= AVAresj(j,'1')+sum(n,FlowrateP(j,n,'2'))-LIFT(j,'2');

AVA31(j,t).. AVAresj(j,'3')=e= AVAresj(j,'2')+sum(n,FlowrateP(j,n,'3'))-LIFT(j,'3');

AVA32(j,t).. AVAresj(j,'4')=e= AVAresj(j,'3')+sum(n,FlowrateP(j,n,'4'))-LIFT(j,'4');

AVA33(j,t).. AVAresj(j,'5')=e= AVAresj(j,'4')+sum(n,FlowrateP(j,n,'5'))-LIFT(j,'5');

AVA34(j,t).. AVAresj(j,'6')=e= AVAresj(j,'5')+sum(n,FlowrateP(j,n,'6'))-LIFT(j,'6');

AVA35(j,t).. AVAresj(j,'7')=e= AVAresj(j,'6')+sum(n,FlowrateP(j,n,'7'))-LIFT(j,'7');

```
AVA36(j,t)..                                              AVAresj(j,'8')=e=
AVAresj(j,'7')+sum(n,FlowrateP(j,n,'8'))-LIFT(j,'8');



AVA4(j,t)..                                               AVAresj(j,'1')=e=
sum(n,flowrateP(j,n,'1'))-LIFT(j,'1');



AVA5(i,t)..                  AVAres(i,t)=g=minstock(i);

AVA6(i,t)..                AVAres(i,t)=l=maxstock(i);

AVA7(j,t)..                 AVAresj(j,t)=g=minstockj(j);

AVA8(j,t)..                AVAresj(j,t)=l=maxstockj(j);




y.lo('p1')= 7.5;

y.lo('p2')= 6.0;

y.lo('p3')=3.2;



Model diesel2 /density
```

densityl

densityu

profit

*avalable

B

AA

F

C

D

E

GG

h/

solve diesel2 using nlp maximizing s;

Model diesel1 /density

densityl

densityu

profit

Cetanenumber1

Cetanenumber2

Sulphurcontent1

Sulphurcontent2

*avalable

Cfpp1

VBN1

VBN2

Viscosity

viscositystand1

viscositystand2

ashcontent1

ashcontent2

pahydro1

pahydro2

BI1

BI2

BI3

BI4

AA

F

C

D

E

GG

B

/;

```
solve diesel1 using nlp maximazing s;

display y.l,y.m, x.l,x.m, XX.L,s.l,s.m,volume.l;

xmilp(i,j)=x.L(i,j);

MODEL SCHEDULING /profitMILP, blendingbalance2,blendingbalance4,

blendingbalance3

blendingbalance5,

blendingbalance6,

blendoperation3,

D2,

*D3,

*avalable

AVA1,AVA2,AVA3

AVA4

AVA21

AVA22

AVA23

AVA24
```

```
AVA25

AVA26

AVA31

AVA32

AVA33

AVA34

AVA35

AVA36

AVA5

AVA6

AVA7

AVA8

/;

solve Scheduling using MIP maximizing totalpro;

display totalpro.l,totalpro.m,y.l,y.m,flowrateB.l,flowratep.l,A.l,ymilp.l,XMILP;

WHILE       (((PPPPP < totalpro.l)),

            PPPPP = totalpro.l;
```

```
*                  Pj(j)=    ymIlp.l(j);

                 number= number+1;

                 y.lo(j)=ymilp.l(j);

                 y.up(j)=ymilp.l(j);

solve diesel2 using nlp maximazing s;

solve diesel1 using nlp maximazing s;

*solve blending using nlp maximizing s ;

xmilp(i,j)=x.L(i,j);

display      x.l,xmilp, TOTALPRO.L;

solve Scheduling using MIP maximizing totalpro;

DISPLAY                                              TOTALPRO.L,FLOWRATEP.L,PPPPP,
y.l,x.l,number,flowratep.l,A.L,avares.l, AVARESJ.L;      )



display totalpro.l,y.l,x.l,number,flowratep.l,A.L,avares.l, AVARESJ.L;
```