Solid Waste Management in Petroleum Refineries

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Abstract: Waste management became focus of attention of many researchers and scientists in the last half century due to its vital importance. Waste management covered waste source reduction in general, by recycling, reusing, composting, incineration with or without energy recovery, fuel production and land filling. A common approach of waste management models were for specific problems with a limited scope (like assignment of generating sources to landfills, transfer stations sitting, site selection for landfills, etc.). Integrated models have been developed more recently. The latest dynamic network flow models with nonlinear costs for waste management used multi-objective mixed integer programming approach for the management of existing facilities in an industrial complex waste management system. The application of multi-objective mixed integer programming techniques was for reasoning the potential conflict between environmental and economic goals and for evaluating sustainable strategies for waste management. Material recycling exhibited huge indirect benefits in an economic sense, although the emphasis of environmental quality as one of the objectives in decision-making has been inevitably driven the optimal solution toward pro-recycling programs. The enhancement of this modeling analysis by using the grey and fuzzy system theories as uncertainty analysis tools could prove highly beneficial. A multi-objective optimization model based on the goal programming approach was applied for proper management of solid waste generated by the petroleum industries in the state of Kuwait. The analytic hierarchy process, a decision-making approach, incorporating qualitative and quantitative aspects of a problem, has been incorporated in the model to prioritize the conflicting goals usually encountered when addressing the waste management problems of the petroleum industries. An optimization model was formulated based on the goal programming technique to minimize the set of deviations from pre-specified multiple goals, which were considered simultaneously but were weighted according to their relative importance. Ten years of solid waste data have been collected from local petroleum industries and processed with different treatment options with economical constraints to provide the best possible solution to be implemented for the specified objectives to be accomplished.

Key words: Solid waste management, spent catalyst, sludge, hazardous waste, multi-objective model

INTRODUCTION

The high rate of growth of petroleum products processing have resulted in the generation of enormous amount of waste that poses a serious threat to environmental quality on the mother earth and its inhabitants. The depletion of natural resources reinforces the need to utilize the reminder in the most efficient way. Thus wastes are regarded as valuable asset as far as resources are concerned and its management is of great importance.

Refinery operations are generally divided into four basic categories: Fuel Production; By-product Processing; Ancillary Operations and Waste Management. Fuel production encompasses those operations which manufacture petroleum products such as gasoline, polymers and coke. By-product processing covers refinery operations that convert used materials and/or undesirable petroleum constituents into saleable or reusable end products. Ancillary Operations are those activities which support refinery functions and recover energy. Finally, waste Management deals with the recovery of useable materials from refinery waste

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streams, the disposal of solid and hazardous wastes and the treatment of wastewaters generated by refinery operations.

Waste management today is made difficult and costly by the increasing volumes of waste produced, by the need to control potential serious environmental and health effects of disposal. Many mathematical models have been developed to study the treatment of hazardous wastes by physical, chemical, thermal and biological processes. Additionally, mathematical programming techniques such as linear programming, dynamic programming and network models have been used to aid in managing the logistical aspects, such as finding the optimal location and size of facilities, of hazardous and non-hazardous wastes. In managing and planning the logistical aspects of hazardous waste systems, multiple goals, such as community and environmental control goals, those have different priorities have to be taken into consideration.

Economic optimization for the system planning of solid waste management was first applied\(^1\) in the late sixties in California, USA. Until the earlier eighties, the issue of increasing environmental concerns and the emphasis on material recycling have gradually changed the focus of solid waste management. Recent research programs into solid waste management system planning frequently emphasize that both socioeconomic and environmental considerations have to be evaluated simultaneously to provide a set of total solutions regarding waste recycling, facilities sitting and systems operation.

The integrated models incorporated simplified descriptions of the system and were subject to many limiting assumptions: weak disaggregation of material flows, one processing option of each type, sites dedicated to one particular processing or land filling technology, only one time period, recyclables/organics collections rarely taken into account, poor (or no) description of markets for recyclables, a single waste generating source, insufficient user’s control on the accuracy of the investment cost functions, etc.. Gottinger\(^2\) proposed a dynamic network flow model with nonlinear costs for waste management and facility-sitting decisions. Shekdar et al.\(^3\) described a dynamic goal programming model for the management of existing facilities in a waste system. A multi-objective mixed integer programming approach was proposed by Caruso et al.\(^4\) for the study of a regional system over a single time period. An interesting dynamic mixed integer programming model incorporating a large set of technologies and dealing with financial and air pollution constraints was presented by Chang et al.\(^5\). The preceding model has been transformed into a multi-objective one by Chang and Wang\(^6\). It takes four different criteria into account, three of them being environmental functions. Revenues from sales to markets are taken into account in the dynamic mixed integer programming model of Baetz and Neebe\(^7\). The model has a limited choice of technologies and only one new land filling site may be developed. A multi-period and multi-regional model developed by Everett and Modak\(^8\) has some interesting distinguishing features. Amongst them, there is the consideration of aggregated and disaggregated flows of materials and of a number of collection options for the components of the waste stream. The model does not deal with capacity addition. A very detailed static nonlinear programming model, MIMES/WASTE, has been proposed by Sundberg et al.\(^9\) to address municipal and regional problems. The main objective of the model is cost minimization but emission control is integrated in the model via explicit restrictions and fees. Recycling and energy production goals may also be imposed. The model of Ljunggren\(^10\) is an extension of MIMES/WASTE to national problems.

The approach of optimal waste minimization in a petroleum refinery was addressed by Takama et al.\(^11\). Their approach was to reuse and make use of regeneration opportunities. Wang and Smith\(^12\) discussed the minimization of wastewaters in the process industries. They pointed out that there are three possibilities for reducing wastewater, reuse, regeneration and regeneration recycling. Fletcher and Johnston\(^13\) and Harries\(^14\) described a waste auditing approach that involves a detailed analysis of a company’s processes and wastes aimed at minimizing, a meliorating or even eliminating discharges from unit processes to establish waste management. Duke\(^15\) indicated that waste minimization played a key role in US planning for hazardous waste management. He examined the effectiveness of waste minimization policies and regulations. Extensive pollution prevention programs in the industrial sectors have been adapted to minimize solid wastes generation\(^16,20\).

Waste minimization can be achieved by elimination of solid and hazardous waste generation through changes in product design and manufacturing technology\(^21\). Keen\(^22\) addressed new regulations that require a waste minimization program to be in place.

**Petroleum industries waste:** This research effort is directed towards the development and testing of a multi-objective planning model based on the goal programming approach for the proper treatment and disposal of solid wastes generated by Kuwaiti oil and petrochemical industries. All of the oil and
petrochemical industries are located at the Shuaiba Industrial Area (SIA) in Kuwait. The SIA is located about 50 km south of Kuwait City. It accommodates most of the large-scale industries in Kuwait. The total area of the SIA (both eastern and western sectors) is about 22.98 million m². Fifteen plants are located in the eastern sector and 23 in the western sector, including two petrochemical companies, three refineries, two power plants, a melamine company, an industrial gas corporation, a paper products company and, two steam electricity generating stations, in addition to several other industries. Currently, approximately 70 percent of the total land area in the SIA’s eastern sector is occupied by industrial facilities. Approximately 30 percent of the total land in the SIA’s western sector is occupied by industrial facilities.

The estimated waste generated was based on the amount of that generated by all plants working at maximum capacity, i.e. about 240,000 t/y, of significance in terms of solid waste are the Petrochemical Industries Company (PIC), the Kuwait National Petroleum Company (KNPC), the Shuaiba Refinery (Sh R), KNPC Mina Abdulla Refinery (MAB), KNPC Mina Ahmadi Refinery (MAA), the Liquefied Petroleum Gas Plant (LPG), Kuwait Melamine Industries (KMI) and other small industries. The estimated solid wastes generated in the SIA include inert wastes, garbage and both incinerable and non-incinerable hazardous wastes. Inert wastes consist primarily of wood, demolished materials, scrap materials, paper and cardboard and construction materials.

Incrinable hazardous solid wastes includes from both wastewater treatment and petroleum process units, tank bottom sludges from crude product storage tanks, Non-incinerable hazardous solid wastes consist mainly of catalysts that are used in many processing operations in the refineries. The catalysts used in the refinery are typically composed of metals such as platinum, cobalt, copper, molybdenum, iron, zinc, nickel and aluminum on inert support materials. The metal contents of catalysts and wastes generated in the SIA are show in Table 1.

There are three main categories for treating solid wastes from the petroleum refining breakdown hazardous chemicals. These units are designed to handle specific type(s) of waste to be treated. The final stream could be a less toxic waste aqueous stream which could be further processed to separate the liquid phase from the solid phase. Thermal treatment units usually consist of two sections; the incinerator and the adsorber. The incinerator provides the thermal energy while the absorber removes the contaminants from the flue gas. Each of these technologies offers advantages over the others while there are disadvantages associated with all of them. In petroleum refining, all wastes must be treated in order to achieve the required criteria for disposal.

Thermal treatment unit operate at very high temperatures, usually 8004000°F, to Shuaiba Industrial Area (SIA) in 2006.

There are also non incineration alternatives for thermally treating hazardous wastes. These processes involve oxidation, reduction and/or pyrolysis environments to destroy the organic component of the waste matrix, but generate significantly less flue gases than incineration. Some of the industrially available technologies include: Rotary kiln oxidation, Fluidized bed incarnation and Liquid injection incarnation. Most widely used chemical treatment technology today is Stabilization. Stabilization is generally used to extract leachable metals prior to landfilling. In the refinery solid waste environment, streams that may require stabilization include: contaminated soils and incinerator ash. Physical treatment technologies employ gravity separation techniques in order to separate the liquid phase from the solid phase in aqueous environments. Some of these processes are capable of capturing some of the fine solid that are in the mixtures.

Solidification can be accomplished by a chemical reaction between the waste and solidifying reagents or by mechanical processes. Contaminant migration is often restricted by decreasing the surface area exposed to leaching and/or by coating the wastes with low-permeability materials. The technologies are not regarded as destructive techniques; rather, they eliminate or impede the mobility of contaminants.

**Model description:** The model is based upon a general hierarchy of waste, flowing a source to a thermal...
treatment plant or a chemical treatment plant or a third party. If a thermal unit is chosen, then the next tier is a chemical unit. Following a chemical unit is a physical processing unit. The hierarchy ends at a landfill which follows a physical treatment unit. This hierarchy is shown in the following Fig. 1.

Based on available refinery data a model is developed and tested to minimize the transportation, processing, disposal and capital costs for the management of solid wastes produced from various facilities and having many processing and disposal routes. The objective function that must be minimized is composed of mainly four different sections. The first section is the transportation cost. The cost of transporting waste is given as dollars per mass unit of waste. This cost rate is multiplied by the total amount of waste that is transported would give the cost of transporting the waste. Transportation costs are incurred anytime there is a transfer of waste from one node to the other node.

The second section of the objective function is the processing costs. Each facility that is operating will incur a processing cost. This cost is based upon utilities, manpower and other operating costs.

Disposal costs are the third section to the objective function. These costs are imposed when one is disposing of waste in a landfill. Third party costs are incurred when a decision is made to exercise a contractual agreement with a third party.

Lastly, capital costs are incurred when a new facility is opened. These costs are incurred only in the case of a new facility. Capital costs are based upon the facility type and capacity of the facility. The overall objective equation is given as follows.

Objective Function:

\[ \text{Minimize } z = \sum_{j \in B} \left( \sum_{i \in B} f_{ij} \right) \]

Processing costs

\[ + \sum_{j \in B} \left( \sum_{i \in B} f_{ij} \right) \]

Third party treatment costs

\[ + \sum_{j \in B} \left( \sum_{i \in B} f_{ij} + \sum_{j \in B} f_{ij} \right) \]

Disposal costs

\[ + \sum_{j \in B} A_j y_j + \sum_{j \in B} A_j y_j + \sum_{j \in B} A_j y_j + \sum_{j \in B} A_j y_j \]

Capital costs

\[ (1) \]

**Constraints:** The design model is constrained on several parameters. Firstly, each node must satisfy a mass balance equation. This states that all the mass going into a node must equal an efficiency value multiplied by the output.

**Material balance on thermal units**

\[ \sum_{j \in B} f_{ij} t_{ij} = F_i \]

\[ (2) \]

**Mass balance on chemical units**

\[ \sum_{j \in B} f_{ij} = a_j \sum_{k \in B} f_{jk} \]

\[ (3) \]
Mass balance on physical units

\[ \sum_{i \in q} f_{ik} + \sum_{j \instp} f_{jk} = a_{ik} \sum_{m \in spp} f_{km} \]  (4)

There is also capacity limitation at each of the facilities which must be satisfied. Logic states that once the capacity of a facility is reached, then a decision must be made. First option is to open a new facility to handle the rest of the waste. The second decision is whether to neglect the first facility and just consider another facility.

**Landfill capacity constraint**

\[ \sum_{m \in sl} f_{ml} + \sum_{j \in ss} f_{jl} \leq C_i Y_j \]  (6)

**Thermal unit capacity constraint**

\[ \sum_{i \in B} f_{ij} \leq C_j Y_j \]  (7)

**Chemical unit capacity constraint**

\[ \sum_{i \in B} \sum_{j \in tsp} f_{ik} \leq C_k Y_k \]  (8)

**Physical unit capacity constraint**

\[ \sum_{k \in sep} f_{km} \leq C_m Y_m \]  (9)

As an extra limitation, there can only one type of each facility. This constraint was set to in order to achieve a non complex solution. The mathematical formulations of these constraints are as flows:

At most build one thermal treatment unit, \( \sum_{p \in pr} Y_{pi} \leq 1 \), one chemical treatment unit, \( \sum_{v \in ov} Y_{vi} \leq 1 \), one physical unit, \( \sum_{w \in wp} Y_{wi} \leq 1 \) and one landfill unit, \( \sum_{x \in xp} Y_{xi} \leq 1 \).

**Results and Discussion:** The model was applied successfully to a typical petroleum industrial complex, which had eight different waste streams with a known quantity of waste generated that fall into the following categories:

- F037 (Refinery Sludge = 12,870 t/y), F038 (Refinery Emulsified Sludge = 7,890 t/y)
- K048 (Dissolved Air Floatation Float = 8,258 t/y), K049 (Slop Oil Emulsion Solids = 9,265 t/y), K051 (Heat Exchanger Sludge = 11,360 t/y), K052 (API Separator Sludge = 8,563 t/y), K062 (Tank Bottoms = 9,566 t/y)
- Cat (Spent Catalyst = 10,790 t/y)

The objective was to view the best method of treating these wastes in the most economical fashion. The model is requested to explore many possible combinations of treatment technologies in order to achieve the required pacification to dispose of these materials.

The effectiveness of each treatment is a factor of the inherent capability of the treatment technology, the size and cost of the equipment. In the treatment hierarchy, twelve possible thermal treatment units have been defined. In addition, the model was asked to consider the possibility of allowing a third party to dispose of some of the waste. The model considered the following technologies:

- Liquid Injection (LJ1)
- Fluidized Bed Process (FB1, FB2, FB3 & FB4)
- Molten Glass Process (MG1)
- Wet Oxidation Process (WO1, WO2, WO3 & WO4)
- Rotary Kiln (RK1 and RK2)
- Third Party Treatment (CON)
- Catalyst Recovery by High Thermal Treatment (HTT)

Continuing with the hierarchy, the model explored the best chemical treatment unit from a list that was provided. Similar to the thermal treatment units, the effectiveness of each treatment is a factor of the inherent capability of the treatment technology, the size and cost of the equipment. The following is the list of the considered chemical treatment technologies:

- Organic Extraction (OE1)
- Solvent Extraction (SE1)

Physical treatment units were the following item on the hierarchy. The following are the list of the considered physical treatment units:
Lastly, the model was requested to consider a list of possible landfills and land treatment facilities. There were specific criteria for sending waste to either a landfill or a land treatment. This criterion was a factor of the waste stream and the amount of treatment it has received. The following are the list of the landfills and land treatment available facilities:

- Landfill (LF1 & LF2)
- Land Treatment (LT1)

The model was asked to determine the optimized route from the waste streams to the landfills/land treatment. The model was run using GAMS. The following Fig. gives a flow diagram of all possible combination considered.

### Thermal Units

| Units | WO1 | WO2 | WO3 | WO4 | RK1 | RK2 |
|-------|-----|-----|-----|-----|-----|-----|
| Capacity (t/y) | 600 | 100 | 900 | 5,400 | 100 | 4,820 |
| Efficiency | 68% | 80% | 68% | 75% | 62% | 71% |

### Contracts

| Units | LJ1 | FB1 | FB2 | FB3 | FB4 | MG1 | CON |
|-------|-----|-----|-----|-----|-----|-----|-----|
| Capacity (t/y) | 196 | 795 | 179 | 295 | 45,000 | 256 | 1,000,000 |
| Efficiency | 75% | 94% | 94% | 94% | 94% | 94% | 100% |

### Chemical units

| Units | SE1 | OE1 |
|-------|-----|-----|
| Capacity (t/y) | 60,000 | 1,250 |
| Efficiency | 70% | 75% |

### Landfills

| Units | LF1 | LF2 | LT1 |
|-------|-----|-----|-----|
| Capacity (t/y) | 10,000 | 15,000 | 100,000 |

### Waste to thermal transportation cost ($/ton)

| LJ1 | FB1 | FB2 | FB3 | FB4 | MG1 |
|-----|-----|-----|-----|-----|-----|
| F037 | 70 | 71 | 72 | 74 | 197 | 76 |
| F038 | 76 | 79 | 77 | 84 | 177 | 78 |
| K048 | 79 | 73 | 77 | 78 | 95 | 78 |
| K049 | 72 | 75 | 79 | 74 | 79 | 76 |
| K051 | 74 | 72 | 79 | 73 | 90 | 78 |
| K052 | 72 | 77 | 70 | 80 | 81 | 71 |
| K062 | 70 | 79 | 77 | 76 | 70 | 70 |

### Waste to high temperature treatment unit transportation cost ($/ton)

| CAT |
|-----|
| 88 |

### Waste to chemical transportation cost ($/ton)

| SE1 | OE1 |
|-----|-----|
| K049 | 89 |
| K051 | 81 |
| K052 | 88 |
| K062 | 87 |

### Thermal to chemical transportation cost ($/ton)

| SE1 | OE1 |
|-----|-----|
| LJ1 | 127 |
| FB1 | 95 |
| FB2 | 121 |
| FB3 | 147 |
| FB4 | 151 |
| MG1 | 120 |
| W01 | 121 |
| W02 | 118 |
| W03 | 98 |
| W04 | 101 |
| RK1 | 121 |
| RK2 | 99 |

### Chemical to physical transportation cost ($/ton)

| EN1 | ST1 |
|-----|-----|
| SE1 | 121 |
| OE1 | 144 |

### Physical separation units

| Units | EN1 | ST1 |
|-------|-----|-----|
| Capacity (t/y) | 35,000 | 50,000 |
| Efficiency | 90% | 90% |

Fig. 2: All the available processing routes for the model
The above data defines the problem and describes the structure of the refinery under study. The flow scheme for this integrated solid waste management system is shown schematically in Fig. 3.

It is also assumed that the management of the integrated solid waste system has special goals to achieve such as minimizing the cost of managing the system and improving its operating efficiency. The management also likes to satisfy, as much as possible, the needs and multiple goals of several groups involved in the management of these wastes. Among these groups are the public, local government and waste generators. These multiple goals can be related to environmental control aspects, objections to building of treatment stations and landfills at certain locations, restrictions related to traffic flow of vehicles and the need of waste generators to haul the waste away from their plants.

Ten years of real solid waste data from the petroleum industries are obtained and annual average is worked out as 67,772 tons consisting of refinery sludge, refinery emulsified sludge, dissolved air floatation float, slop oil emulsion solids, heat exchanger sludge, API separator sludge and tank bottoms. There is an extra 10,790 t/y of spent catalyst generated through various processes in the refinery that has to be disposed safely. Various thermal treatment technologies, liquid injection, fluidized bed process, molten glass process, wet oxidation process, rotary kiln and an option to use third party treatment have been considered. Spent catalyst can only be treated in high temperature treatment process to reduce the risk of seepage of heavy metals in the water table.

Fig. 3: An integrated solid waste management system for the petroleum/petrochemical industries

Fig. 4: Optimal solution
The results of model solution provide the management with information about the extent of solid waste removal from the various sections. The model predicts the optimum route and provide a level of savings in financial resources allocated to run the transportation fleet and operate the solid waste treatment facilities, the extent of facilities utilization, energy production and level of recycling.

The results of the model (Fig. 4) proves that it can be used to address many of the problems and issues associated with the management of solid waste systems such as the need for solid waste removal from the various petrochemical plants, the efficient utilization of facilities, systems cost control and the control of environmental pollution.

The refinery sludge and slop oil emulsion is economically treated by wet oxidation process (WO4) but due to its capacity constraint the remainder refinery sludge is sent to fluidized bed process (FB4). Fluidized bed processes (FB1, FB3 and FB4) are economically used for processing refinery emulsified sludge, tank bottoms and slop oil emulsions. Dissolved air flotation and heat exchanger sludge were economically treated in fluidized bed process (FB4). Wet oxidation process (WO2) is the most economical choice for treatment of API separator sludge. However due to its limited capacity, the remainder is treated in fluidized bed process (FB4). Spent catalyst is subjected to high temperature treatment process where deposited coke is burnt reducing the total mass that has to be sent to the landfill.

In thermal treatment section undergoing various treatment processes and recovering the desired components total solid waste was reduced by about 22%. The most cost effective choice was fluidized bed process (FB4) for most of the handled wastes due to its size resulting into low cost per unit of waste processed.

Chemical treatment is applied to certain thermally treated waste, either organic extraction process or solvent extraction process. Most of the treated waste is sent to solvent extraction process due to its large capacity and associated low cost. There is further reduction in the final mass of processed solid waste about 30%.

For physical treatment encapsulation unit and stabilization unit are used in parallel. The major portion of treated waste is subjected to encapsulation unit treatment while one tenth is treated in stabilization unit. There is about 10% further reduction in the total mass of treated solid waste. All the spent catalyst is treated in the high thermal treatment unit and prior to be disposed to land treatment unit. The treated wastes in the physical treatment section are also sent to two landfills and remainder is disposed to land treatment unit.

All the spent catalyst (10,725 t/ year) treated in the high thermal treatment unit was sent to land treatment before its disposal. The other wastes treated in the physical treatment section are sent to both the landfills (10,000 t/ year to landfill1 and 15,000 t/ year to landfill2) and remaining part (9,404 t/ year) to land treatment unit. The model chose this not only to reduce the cost of treating, but also the cost of the disposing the landfilling these wastes.

**CONCLUSION**

The application of the model to actual solid waste data of petroleum industries has facilitated in choice of treatment processes, their capacities and appropriate routing of waste streams regarding the most cost effective management of solid industrial waste. The present model provides the efficient utilization of all available facilities emphasizing on the control of environmental pollution and the most cost effective management strategies for industrial waste.

With reference to available data and waste management facilities the choice of fluidized bed processes and wet oxidation process ascertains the use of the most efficient intermediate handling units to make the waste management highly cost effective. The preference of solvent extraction unit over organic extraction for API separator waste is based on space velocity/residence time. The cost effectiveness for this chemical treatment process has been influenced by capacity and operation time. In physical treatment process, the model provides the optimum use of the encapsulation unit with high cost stabilization unit to satisfy all the defined constraints in the industrial waste management exercise. The computed results reveal that the present model is a viable tool and can be efficiently used to assist in making appropriate decisions regarding the petroleum industries solid waste.

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