The importance of distillation columns continues to increase both in the traditional petro-chemical industry and in the sustainable sector with renewable resources and energy. The key role they play in the chemical and petrochemical industries and the quest to make them more energy efficient has made distillation process a high priority for all stake holders in the industries. For instance there are about 40,000 distillation columns in the US alone. These consume about 40-60% of the total energy usage in the chemical and petrochemical industries and 6% of the total US energy. Also, major costs of operations second only to the cost of crude in the refinery is energy and 35% of these is consumed in the crude distillation unit. Usually the order of economic importance in the control of distillation column is product quality, process throughput and utility reductions and often traded off between them has to be made. This paper presents a new methodology for optimising the efficiency of the crude distillation unit without trading off the product quality and process throughput. The method uses a neural network based strategy for the modelling and optimisation of distillation columns incorporating the second law of thermodynamics. Second law analysis indicates how well a system is performing compared to the optimum possible performance and hence gives a good indication of the actual energy use of a process. Real time optimisation of distillation columns is made feasible by using neural network models which can be quickly developed from process operation data. The computation time in neural network model evaluation is very short making them ideal for real-time optimisation. Bootstrap aggregated neural networks are used in this study for enhanced model accuracy and reliability. Aspen HYSYS was used for the simulation of the distillation systems. Neural network models for exergy efficiency and product quality are developed from simulated process operation data and are used to maximise exergy efficiency while satisfying product quality constraints. There is great potential for energy recovery in the analysed processes. The recoverable energy is a sum of internal and external exergy losses. The economic analysis of the recoverable energy reveals the energy saving potential of the method. The green house gas (GNG) analysis also affirms it's sustainability nature. It is expected that the application of the methods will aid the design and operation of energy efficient crude distillation column.