Biodiesel production from castor oil seeds cultivated in constructed wetlands

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Abstract
With the escalating demand for renewable energy and the imperative to mitigate environmental degradation, there is increasing interest in biodiesel as a sustainable substitute of fossil fuels. The present study presents a comparative evaluation of biodiesel production from castor seeds cultivated in two distinct environments: conventional agricultural fields and rice mill effluent-fed constructed wetlands. Castor (Ricinus communis L.), a non-edible oilseed crop known for its resilience and high oil content, was assessed for seed quality, oil yield, trans esterification efficiency, fuel properties and kinetic and thermodynamic parameters. Wetland-grown seeds, found to be with marginally poorer yield (82%) and quality, demonstrated significant potential for biodiesel production while simultaneously contributing to wastewater remediation. Kinetic modelling confirmed pseudo-first-order reaction behaviour, with agricultural oil exhibiting a higher rate constant (0.0034 min^{-1}) than wetland oil (0.0025 min^{-1}).

Agricultural seeds, on the other hand, yielded superior oil content (50%) and biodiesel conversion (94%), with favourable physicochemical properties such as lower acid value, enhanced cold flow and higher flash point. Thermodynamic analysis revealed higher activation energy and enthalpy for agricultural oil, indicating more efficient conversion. The dual functionality of constructed wetlands, biomass generation and effluent treatment, positions them as a viable strategy for circular economy integration.

Keywords: Biodiesel, Castor seeds, Wetland cultivation, Rice mill effluent, Transesterification, Sustainable energy.

Introduction

The rising global energy demand, coupled with the environmental impacts of fossil fuel consumption, has intensified the search for sustainable alternatives such as biodiesel. Biodiesel, produced through the transesterification of vegetable oils and animal fats, has emerged as a promising renewable fuel due to its biodegradability, lower toxicity and reduced greenhouse gas emissions compared to petroleum diesel[15]. Among various non-edible oilseed crops, castor (*Ricinus communis L.*) is considered a potential feedstock because of its high oil content (40–55%), adaptability to marginal lands and the industrial significance of ricin oleic acid[19].

In India, castor is widely cultivated in arid and semi-arid regions, with Gujarat, Rajasthan and Andhra Pradesh being major contributors[24]. However, the cultivation of castor in conventional agricultural systems requires substantial land and water resources, which often compete with food crops. To address this challenge, alternative cultivation methods have been explored, including the use of wastewater-irrigated constructed wetlands. Rice mill effluent, which is generated in large quantities during parboiling and polishing processes, contains high organic load and nutrients but also poses risks of eutrophication and groundwater contamination if untreated[21,26]. The integration of oilseed crops such as castor into constructed wetlands irrigated with rice mill effluent offers a dual advantage wastewater remediation and biomass generation for biofuel production.

However, the quality of seeds and oil derived from such stressed environments can differ significantly from conventionally grown counterparts. Previous studies have shown that environmental stress, wastewater composition and cultivation conditions can influence oil yield, fatty acid composition and subsequent biodiesel properties[19,20]. Therefore, a comparative analysis of castor seeds cultivated under agricultural and effluent-fed wetland systems is crucial for evaluating their potential as viable biodiesel feed stocks.

The present study investigates the production of biodiesel from castor seeds grown in rice mill effluent-based wetlands compared to conventional agricultural fields. It assesses differences in seed quality, oil yield, transesterification efficiency, fuel properties and kinetic parameters, thereby providing insights into the feasibility of utilizing wastewater-grown castor seeds for sustainable biodiesel production.

Material and Methods

Procurement of Castor Oil-seed: Castor oil seeds used for the present study were procured from two primary sources: traditional agricultural fields and rice-mill effluent-based constructed wetlands. Fig. 1(a) shows that seeds collected from agricultural fields are typically obtained from castor plants cultivated under standard agronomic practices, using fresh water irrigation and controlled fertilization. These seeds were found to exhibit uniform size, color and oil content, likely because of optimal growth conditions. In contrast, fig. 1(b) shows that seeds collected from constructed wetlands are derived from castor plants exposed to rice mill effluent. The specification of the wetland used for growth of the castor was studied and observed variability in seed appearance, size, color and even oil content compared to their agricultural counterparts.

(a) (b)

Figure 1: (a) Castor seeds from agricultural field (b) Castor seeds from Rice-Mill Effluent based wetland

This was expected by dint of variation in associated microhabitats because of the variable growth of the plants being grown in nutrient-rich yet stressed environments in the latter.

After harvesting, seeds from both sources were cleaned with fresh water to remove debris, broken pods and immature seeds. Drying is typically carried out under direct sunlight by spreading the seeds on clean tarpaulin sheets or trays in a single layer. This sun drying process continued for five days, with occasional stirring to ensure uniform drying. Proper drying was carried out in view of reducing the seed moisture content (to about 8% of seed weight), being an essential requirement for safe storage of the seed as well as oil extraction.

For storage, the dried seeds were packed in breathable materials such as gunny (with paper lining). The storage room was maintained to be cool, dry and well-ventilated to avoid fungal growth and to preserve seed quality. The seeds were labelled clearly, indicating whether they are from agricultural fields or wetland sources along with the date of harvest.

Production of Castor Oil: Castor oil production via cold-press milling was initiated with dehulling, where the seed hulls were mechanically removed to improve oil yield and reduce fiber[17]. This was achieved using a huller that applied shear and friction to separate kernels. The kernels were subjected to cold pressing, a method in which heat application was avoided to preserve antioxidants, ricin oleic acid and oil integrity[8]. Cold pressing had commonly been carried out in screw press mills rated 3–7.5 HP, with small-scale systems processing 20–30 kg kernels per hour on a 5 HP press, yielding 35–40% oil[12]. Pressing duration ranged from 20–30 minutes depending on kernel hardness, moisture and throughput. Operating conditions had been maintained below 50 °C to retain nutritional and oxidative stability[15].

The extracted oil had varied in quality: agricultural seeds had yielded golden-yellow, translucent oil, while effluent-fed wetland seeds had produced darker oil due to micronutrient residues[26]. Hulls had been fibrous and light brown, whereas the deoiled cake is dark brown, protein-rich and mineral-rich. These by-products were used as organic fertilizers or detoxified for animal feed applications.

Sample Characterization – Seed Quality Parameters: To assess the quality and characteristics of castor seeds obtained from agricultural fields and constructed wetlands irrigated with rice mill effluent, several physico-chemical parameters had been analysed including oil content, hull weight, moisture content, protein content and 100-seed weight. Oil content (%) had been determined by cold-press extraction where pre-cleaned and dehulled seeds had been mechanically pressed in a local cold press mill and the yield percentage had been calculated from initial seed weight, preserving oil structure[8,16]. Hull weight (%) had been measured by manually dehulling 100 seeds, drying hulls, weighing and calculating hull-to-seed ratio as an indicator of kernel proportion[17].

Moisture content (%) had been determined by oven-drying 5 g of seeds at 105 ± 2 °C for 24 h, cooling, reweighing and applying the AOAC formula. Protein content (%) of defatted meal had been measured via the Kjeldahl method, where 0.5g of deoiled seed meal had been digested, distilled and titrated and nitrogen content had been converted to crude protein using factor 6.25[24]. The 100-seed weight had been obtained by randomly selecting and weighing 100 seeds from each group using an electronic balance, providing an indicator of size and maturity[4]. All experiments had been conducted in triplicate and results had been expressed as mean ± standard deviation.

Trans-esterification of Castor Oil

Base- catalyzed Trans-esterification and Acid-catalyzed Trans Esterification (Production of Biodiesel from Castor Oil Seeds): Castor oil seeds obtained from agricultural or wetland fields were subjected to oil extraction, resulting in crude oil and a by-product, de-oiled cake. The extracted oil was filtered to remove impurities, yielding raw castor oil. This oil was then processed via transesterification (figure 2) using two different catalytic routes: base-catalysed (using methanol with NaOH or ethanol with KOH) and acid-catalysed (using concentrated H_2SO_4). Both processes were carried out at 50–70°C for 3 hours. Following the reaction, the bio-diesel was separated from the glycerol by-product. The crude bio-diesel was washed with hot water at 40°C to remove residual contaminants and then subjected to a drying step. The final product obtained was pure bio-diesel, which was subsequently analyzed for its physicochemical properties.

Transesterification of Castor Oil: Procedure and Operating Parameter Influence: The trans-esterification of castor oil (figure 3) is a critical step in converting triglycerides into biodiesel (fatty acid methyl esters, FAMEs) and glycerol. This reaction involves reacting castor oil with an alcohol (methanol or ethanol) in the presence of a catalyst (base or acid), under controlled temperature and agitation. Both base-catalyzed and acid-catalyzed methods were explored to understand process efficiencies and biodiesel yields. In both the processes, two stages were involved: Stage1: mixing of the alcohol to castor oil in presence of catalyst (NaOH or KOH) at higher temperature (45-70°C) and stage 2: gravitational settling of trans-esterification products (i.e. Biodiesel and Glycerin). After settling, biodiesel and glycerol were distinctly separated. Biodiesel appeared as a clear yellow layer, while glycerol was dark brown and viscous. Washing and drying of biodiesel were done to remove methanol, residual catalyst and soap.

Base-Catalyzed trans esterification: In the base-catalyzed method, trans-esterification was carried out using either sodium hydroxide (NaOH) with methanol or potassium hydroxide (KOH) with ethanol. Preheated castor oil (to 50–60 °C) was mixed with a pre-prepared solution of catalyst (0.5% to 2% w/w of oil) dissolved in alcohol (methanol or ethanol, with 6:1 molar ratio to oil). The reaction was conducted in a round-bottom flask equipped with a mechanical stirrer, thermometer, condenser and heating mantle. The mixture was stirred continuously for 60–120 minutes depending on the trial. After completion, the mixture was allowed to settle in a separating funnel for 12 hours. Two layers were formed: the upper biodiesel layer and the lower glycerol layer[8].

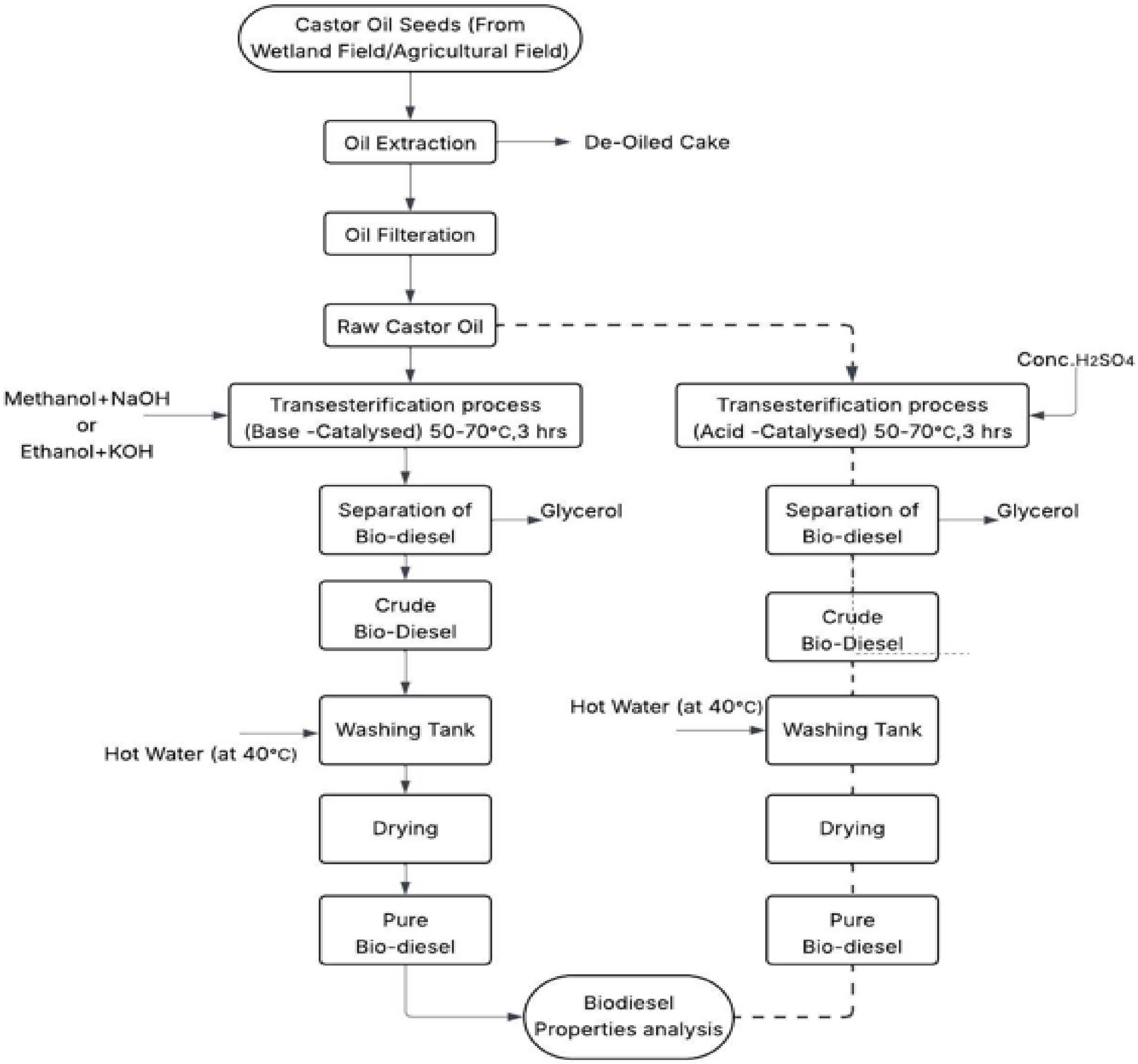

Figure 2: Process Flow Chart of Base- catalyzed Trans-esterification and Acid-catalyzed Trans Esterification

Table 1
Rationale in Selection of Process Parametric Ranges in Trans esterification Process

Parameter	Rationale
Catalyst Type and Concentration	NaOH generally provided higher conversion rates and faster reactions than KOH. Excess catalyst (>1.5%) led to soap formation, reducing biodiesel yield[14].
Alcohol Type and Molar Ratio	Methanol was more effective than ethanol due to higher polarity and reactivity. A 6:1 alcohol-to-oil molar ratio was optimal; excess alcohol complicated recovery[6].
Temperature	Optimal temperature range was 55–65 °C. Higher temperatures near methanol's boiling point (64.7 °C) accelerated the reaction but required a proper condensation setup[13].
Time	Reaction time of 60–90 minutes was generally sufficient. Longer times showed minimal improvements and risked reverse reactions or degradation[9].
Stirring Speed	Mixing at 300–600 rpm improved reactant contact. Excessive stirring led to emulsion formation in some cases[22].

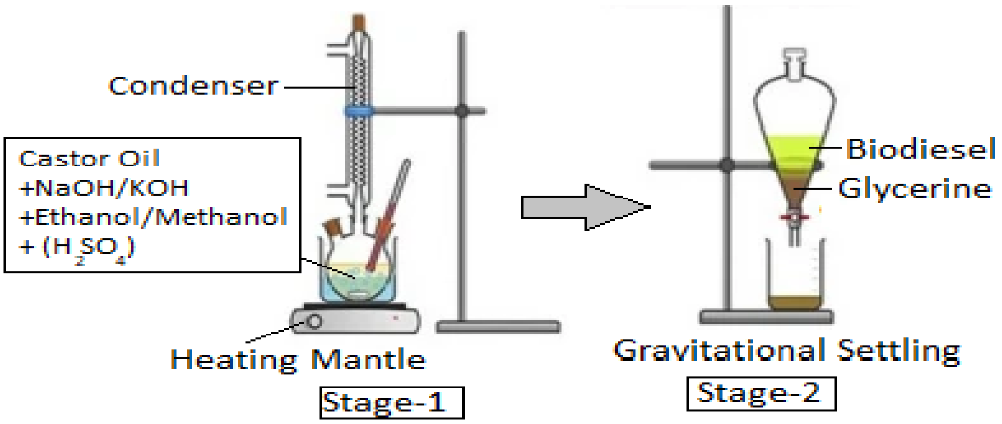

Figure 3: Schematic diagram of Transesterification

Acid-Catalyzed Trans esterification: In the acid-catalyzed method, sulfuric acid (H_2SO_4) was used as the catalyst with methanol. This method is particularly effective when the oil contains a high amount of free fatty acids. The acid catalyst (1–2% v/v of oil) was mixed with methanol and added to castor oil (molar ratio 6:1 to 12:1) and the reaction was conducted at 60–65 °C for up to 4–6 hours under reflux conditions. After the reaction, the mixture was cooled and left to settle, followed by washing and drying of the biodiesel layer[3].

Rationale in Selection of Process Parametric Ranges in Transesterification Process: Table 1 outlines key parameters influencing the transesterification of castor oil to biodiesel. NaOH is preferred as catalyst, though excess (>1.5%) promotes soap formation. Methanol with a 6:1 molar ratio ensures higher conversion and easier separation. An operating temperature of 55–65 °C accelerates the reaction near methanol's boiling point. Reaction time of 60–90 minutes achieves efficient conversion without degradation. Stirring at 300–600 rpm improves mixing while higher speeds risk emulsification.

Characterization of the Biodiesel

Properties, protocols, standards, purpose and equipment used: The biodiesel samples produced from castor oil (from both agricultural and wetland fields) were characterized based on key physicochemical properties to evaluate their suitability as alternative fuels. Each property was assessed using standardized protocols and calibrated instruments, as outlined in table 2.

The biodiesel samples derived from castor oil cultivated in agricultural and wetland environments had been characterized using standardized protocols to assess their suitability as alternative fuels (Table 2). Biodiesel yield (%) had been calculated as the proportion of methyl esters obtained relative to initial oil mass, thereby evaluating trans-esterification efficiency[11]. Kinematic viscosity at 40 °C had been measured using a Redwood viscometer following ASTM D445, since higher viscosity had been linked with poor atomization and injector fouling[6]. Acid value, reflecting free fatty acids and fuel stability, had been determined by titration with potassium hydroxide according to ASTM D664[16]. Density at 15 °C had been measured using a digital density meter in line with ASTM D4052 to assess its influence on energy content and combustion[24]. Flash point had been identified by the Pensky-Martens closed cup method (ASTM D93) as a safety indicator for storage and handling[19]. Cold flow properties (cloud and pour points) had been determined visually during controlled cooling, using ASTM D2500 and ASTM D97, to evaluate low-temperature operability[11]. All measurements had been performed in accordance with ASTM D6751, EN 14214 and CAN/CGSB-3.524 standards to confirm biodiesel quality and applicability.

Table 2
Rationale and Protocols of Assessment Biodiesel Characteristics

S.N.	Property	Purpose	Protocol Standard	Equipment Used
1	Biodiesel Yield (%)	Determines efficiency of trans esterification process	Gravimetric method (calculation)[5]	Analytical balance
2	Kinematic Viscosity (at 40°C) (centistokes)	Indicates fuel flow behaviour and atomization characteristics	ASTM D445[2]	Redwood Viscometer No. 1 / Ubbelohde Viscometer
3	Acid Value (mg KOH/g)	Measures free fatty acid (FFA) content; indicates fuel stability and quality	ASTM D664[2]	Burette, conical flask, titration setup
4	Density (g/cm³)	Affects combustion efficiency and injector performance	ASTM D4052[2]	Digital Density Meter (DMA 35 or similar)
5	Flash Point (°C)	Assesses safety in handling, storage and transport	ASTM D93[2]	Pensky-Martens Closed Cup Tester
6	Cold Flow Properties	Determines low-temperature operability of the biodiesel	ASTM D2500 (Cloud Point), ASTM D97 (Pour Point)[1]	Refrigerated bath, test jars

Estimation of Equilibrium constant (k) from Kinetics Study of Biodiesel Yield from Castor Oil (Agricultural field *vs* Constructed Wetland field): To evaluate the reaction kinetics and determine the order and rate constant of the trans-esterification process in biodiesel production, experiments were conducted using castor oil obtained from both agricultural and wetland field sources. For each trial, 1000 g of crude castor oil had been pre-treated to reduce the free fatty acid (FFA) content by subjecting it to acid-catalysed esterification with sulphuric acid (H_2SO_4) at 3wt% of oil. Following this pre-treatment, base-catalysed trans-esterification was carried out by adding 15 g of sodium hydroxide (NaOH) along with methanol at a 10:1 molar ratio (methanol to oil). The reaction mixture stirred under controlled temperature conditions ranging from 45°C to 70°C and samples were drawn at regular intervals between 10 and 60 minutes to monitor biodiesel yield and study reaction kinetics.

At each time point, the yield of biodiesel (Yt) was determined gravimetrically and expressed as a percentage of the theoretical maximum yield (Ym). The extent of conversion (Xt) was calculated by the formula:

$$Xt = \frac{Yt}{Ym} \quad (1)$$

To identify the reaction order, the experimental data was fitted to integrated rate expressions. A pseudo-first-order kinetic model was assumed since methanol had been used in excess and its concentration remained effectively constant. For the first-order reaction model, the linear form is:

$$\ln(1 - Xt) = -kt \quad (2)$$

while for second-order kinetics, the following expression had been considered:

$$\frac{1}{1-Xt} = 1 + kt \quad (3)$$

Plots of $\ln(1 - Xt)$ and $\frac{1}{1-Xt}$ versus time were generated and the linearity of the trends was assessed to evaluate order of the reaction, which corresponds to better linear correlation of the trend line (also represented by higher R2 value). The rate constant (k) was calculated from the slope of the linear fit.

All experiments were conducted at a constant temperature of 60°C for the kinetic analysis. The reaction was terminated by placing the mixture in an ice bath, after which the samples had been centrifuged and analyzed gravimetrically for biodiesel yield.

To determine the thermodynamic properties of the base-catalyzed trans-esterification process for castor oil sourced from both agricultural fields and wetland systems, reaction rate constants (k, in min^{-1}) were experimentally measured at five different temperatures: 45°C, 55°C, 60°C, 65°C and 70°C (318 K, 328 K, 333 K, 338 K and 343 K). The rate constants were determined by fitting time-dependent biodiesel yield data to a suitable kinetic model, assuming pseudo-first-order bbehavior.

For thermodynamic analysis, the Eyring equation, derived from transition state theory, was employed in the linearized form:

Eyring Equation and Thermodynamic Parameters:

The Eyring equation:

$$k = \frac{k_B T}{h} exp\left(\frac{\Delta S}{R}\right) exp\left(-\frac{\Delta H}{RT}\right) \quad (4)$$

Taking natural logs:

$$ln\left(\frac{k}{T}\right) = ln\left(\frac{k_B}{h}\right) + \frac{\Delta S}{R} - \frac{\Delta H}{R}\frac{1}{T} \quad (5)$$

where k is the rate constant at temperature T (min^{-1}), T is the absolute temperature (K), k_B is the Boltzmann constant (1.380649 × 10^{-23} J/K), h is Planck's constant (6.62607015 × 10^{-34} J·s), R is the universal gas constant (8.314 J/mol·K), ΔH is the enthalpy of activation (J/mol) and ΔS is the entropy of activation (J/mol·K).

From the linear plot of $ln\left(\frac{k}{T}\right)$ versus $\frac{1}{T}$, the slope and intercept are determined:

Slope=$-\frac{\Delta H}{R}$ and intercept = $ln\left(\frac{k_B}{h}\right) + \frac{\Delta S}{R}$

At each temperature, the standard Gibbs free energy of activation (ΔG)was calculated using:

$$\Delta S = \Delta H - T\Delta S. \quad (6)$$

All logarithmic values were natural logarithms (ln) and units were consistently maintained at

k: min^{-1},T: K, ΔH (J/mol), ΔS J/mol·K, ΔS J/mol

Results and Discussion

Influence of Growing Environment on Castor Seed Quality Parameters: Agricultural vs. Wetland Cultivation: The comparative assessment (Fig. 4) of castor seeds from agricultural fields versus constructed wetlands revealed notable differences in their physical and chemical characteristics. Seeds from agricultural fields had demonstrated higher oil content (50%) compared to wetland-grown seeds (45%), aligning with reported ranges of 47–53% under favorable conditions[19]. Agricultural seeds had also exhibited greater protein content (20% vs. 18%), higher 100-seed weight (29 g vs. 26 g) and superior visual quality with uniform luster, whereas wetland seeds had appeared dull and variable. Wetland-grown seeds had shown higher moisture content (7% vs. 6%) and increased hull percentage (28% vs. 25%), likely due to wastewater exposure affecting plant metabolism and seed development[21]. Such differences were consistent with studies showing that environmental stress could alter oil yield and fatty acid composition, particularly ricinoleic acid, which determines castor oil's industrial value[19]. Physically, the smaller seed size and reduced weight of wetland samples had indicated stress responses and their lower oil content had agreed with literature on irrigation effects from unconventional water sources[21].

Despite quality differences, the resilience of castor plants to wastewater conditions had justified their use in constructed wetlands for remediation. The resultant oil varied in color and viscosity, where agricultural seeds had yielded golden-yellow, translucent oil, while wetland seeds had produced darker oil due to micronutrient residues or metabolites from effluent[26]. Hulls were fibrous and light brown, while the deoiled cake is dark brown, granular and nutrient-rich, often utilized as organic fertilizer or detoxified for animal feed.

Yield and Quality Parameters of Castor Seeds: The bar graph (Fig. 4) illustrates a comparative evaluation of castor oil seed characteristics between seeds sourced from agricultural and wetland fields. Seeds cultivated in agricultural fields consistently outperform those from wetland environments across all measured parameters. The oil content is visibly higher in agricultural seeds, reaching around 50%, while wetland seeds fall slightly behind at approximately 45%. This suggests that agricultural conditions are more favourable for oil accumulation in castor seeds.

In terms of hull weight, agricultural seeds show a lower proportion compared to wetland seeds, indicating a greater proportion of usable seed material in the former. The moisture content also reflects better post-harvest stability in agricultural seeds, which show a lower percentage than wetland seeds, suggesting improved storability and reduced susceptibility to spoilage. When assessing nutritional value, agricultural seeds again have the advantage, exhibiting higher protein content relative to wetland-grown seeds. These results collectively highlight that castor seeds from agricultural fields possess better oil yield potential, nutritional quality and physical attributes than those grown in wetlands, possibly due to more controlled growing conditions and absence of contaminating effluents.

Seeds cultivated in agricultural fields consistently exhibit higher oil content, with approximately 50% oil yield per 100 seeds, compared to about 45% from wetland-grown seeds. This reduction in oil yield from wetland environments is accompanied by a noticeable increase in hull weight percentage, suggesting that seeds from constructed wetlands develop thicker or heavier hulls, potentially as a physiological response to environmental stress or differences in nutrient availability.

Moisture content is also elevated in seeds from constructed wetlands, indicating that these seeds may retain more water, possibly due to the higher humidity and waterlogged conditions typical of wetland environments. This increased moisture could affect both storage stability and oil extraction efficiency. Protein content, while only slightly reduced in wetland-grown seeds compared to those from agricultural fields, still reflects the overall trend of diminished seed quality associated with wetland cultivation.

These observed differences align with literature indicating that environmental factors such as nutrient composition, water availability and potential contaminants in constructed wetlands can influence seed development, oil biosynthesis and overall seed composition. The data suggest that while constructed wetlands offer a sustainable approach for resource recovery and environmental management, there is a tradeoff in terms of reduced oil yield and altered seed composition when compared to conventional agricultural production systems. This interpretation is supported by the graphical assessment provided (Fig. 4) and corroborated by studies on the impact of non-traditional irrigation and cultivation environments on oilseed crop quality.

Variation in Castor Seed Oil Yield Properties: The comparative (table 3) study of castor seeds from agricultural and wetland fields revealed distinct post-extraction differences. Agricultural seeds showed lower hull weight (22.5%) than wetland seeds (25.0%), indicating thicker hull development under stress conditions. Moisture content was higher in wetland seeds (7.0%) compared to agricultural ones (6.0%), affecting both oil extraction and storage stability. Oil yield declined in wetland-grown seeds (33.0%) relative to agricultural seeds (38.0%), reflecting environmental impacts on biosynthesis. De-oiled cake was slightly higher in wetland seeds (35.0%) than agricultural seeds (33.5%), consistent with lower oil recovery. Overall, wetland cultivation supported castor growth but produced seeds were of lower oil yield, higher hull and moisture and increased deoiled cake, aligning with reported effects of non-traditional environments on oilseed crops.

Physical Characteristics of Castor Oil: The table 4 shows in variation in physical and chemical properties of castor oil from agricultural fields and constructed wetlands revealed clear differences due to cultivation environment. Agricultural oil exhibited higher density (0.953–0.944 g/ml) and viscosity (154.678 mm²/s) than wetland oil (0.938–0.929 g/ml; 148.512 mm²/s), reflecting greater fatty acid content. It also showed lower pour point (–11 °C vs. –9 °C) and higher flash point (266 °C vs. 225 °C), indicating better cold flow and thermal stability.

Molecular weight was slightly higher (928.3 vs. 924.1 g/mol) and color differences were noted: pale yellow for agricultural versus brownish wetland oil. Calorific value was greater for agricultural oil (36.319 vs. 35.289 MJ/kg), while moisture was higher (6.74% vs. 5.32%) and ash content was lower (2.4% vs. 3.2%). Overall, agricultural oil demonstrated superior quality whereas wetland oil showed higher ash and darker color, consistent with non-traditional cultivation effects[25].

Biodiesel Yield from Agricultural Seed Oil via (Base-Catalyzed Trans-esterification): Table 5 shows the results of base-catalysed transesterification evaluating methanol concentration effects on biodiesel yield from agricultural and wetland castor oil. In this study, 1000 g of castor oil had reacted with 15 g NaOH at 45–70°C for 60 minutes, with methanol varied from 100 to 300 g. Increasing methanol increased biodiesel yield and reduced unreacted oil, while glycerine had remained relatively stable.

Agricultural oil yields rise from 760 g to 930 g at 200–250 g methanol, with unreacted oil dropped from 160 g to 20 g. Wetland oil produced lower yields, 600–820 g, with unreacted oil decreasing from 330 g to ~100 g. Glycerine production remained similar for both sources. These results indicated higher conversion efficiency of agricultural oil due to greater purity and favourable fatty acid profile, whereas wetland oil contained more impurities or altered composition.

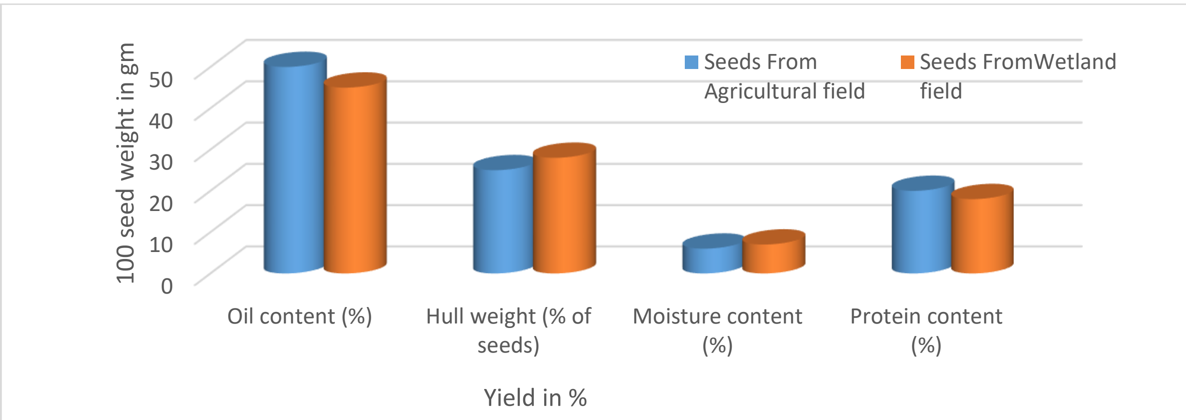

Figure 4: Assessment of Castor Oil seeds characteristics (Agricultural Field vs. Constructed Wetland seeds)

Table 3
Assessment of Castor Oil Seed to Oil Yield

S.N.	Parameters	Seeds From Agricultural field (Mean ± SE)	Seeds From Wetland (Mean ± SE)
1	Hull weight (%)	22.5 ± 1.0	25.0 ± 1.2
2	Moisture Content (%)	6.0 ± 0.3	7.0 ± 0.4
3	Castor oil yield (%)	38.0 ± 1.5	33.0 ± 1.3
4	De-oiled Cake (%)	33.5 ± 1.2	35.0 ± 1.4

Both oils were benefited from increased methanol, with optimal yields at 200–250 g for agricultural oil and 250–300 g for wetland oil. The findings had aligned with literature emphasizing alcohol-to-oil ratio and feedstock quality for efficient biodiesel production[11,15]. Constructed wetland castor oil had emerged as a viable, sustainable feedstock with environmental and resource recycling benefit.

Comparative Evaluation of Biodiesel Yield from Agricultural and Rice Mill Effluent-Based Wetland Castor Oil via Base-Catalyzed Tran-esterification: The figure 5 presents the base-catalysed transesterification on castor oil from agricultural fields and rice mill effluent wetlands. The experiment used 1000 g of oil with 15 g KOH at 45–70°C for 60 minutes, varying ethanol from 184.3 g to 921.4 g. Increasing ethanol increased biodiesel yield for both oil sources. Agricultural oil had yielded 700 g initially, rising to 870 g at maximum ethanol, while wetland oil started at 550 g and reached 770 g. Unreacted oil decreased from 220 g to 33 g in agricultural oil and from 380 g to 144 g in wetland oil. Glycerine remained relatively constant (80–97 g for agricultural, 70–86 g for wetland).

Table 4
Variation in Physical characteristics of Castor Oil

S.N.	Properties	Units	Agricultural field	Wetland field
1	Density at 15°C	(g/ml)	0.953	0.938
2	Density at 30°C	(g/ml)	0.944	0.929
3	Viscosity at 40°C	mm2/s	154.678	148.512
4	Pour point	°C	-11	-9
5	Flashpoint	°C	266	225
6	Molecular Weight	(g/mol)	928.3	924.1
7	Color	nil	Pale yellow	Brown Yellow
8	Calorific Value	(MJ/kg)	36.319	35.289
9	Moisture Content	%	6.74	5.32
9	Ash Content	%	2.4	3.2

Table 5
Effect of Methanol Content on Yield of Biodiesel from Castor Seeds

Sample No.	Methanol weight (gm)	Agricultural Seed Oil			Wetland Seed Oil		
		Biodiesel weight (gm)	Glycerine (gm)	Unreacted Oil (gm)	Biodiesel weight (gm)	Glycerine (gm)	Unreacted Oil (gm)
1	100	760	80	160	600	70	330
2	150	840	90	70	680	80	240
3	200	**930**	95	20	800	85	115
4	250	**930**	95	20	**820**	85	95
5	300	920	90	20	**820**	80	100
Note: 1000 gm of Castor oil with 15 gm of NaOH at Temperature of 45-70°C for 60 minutes							

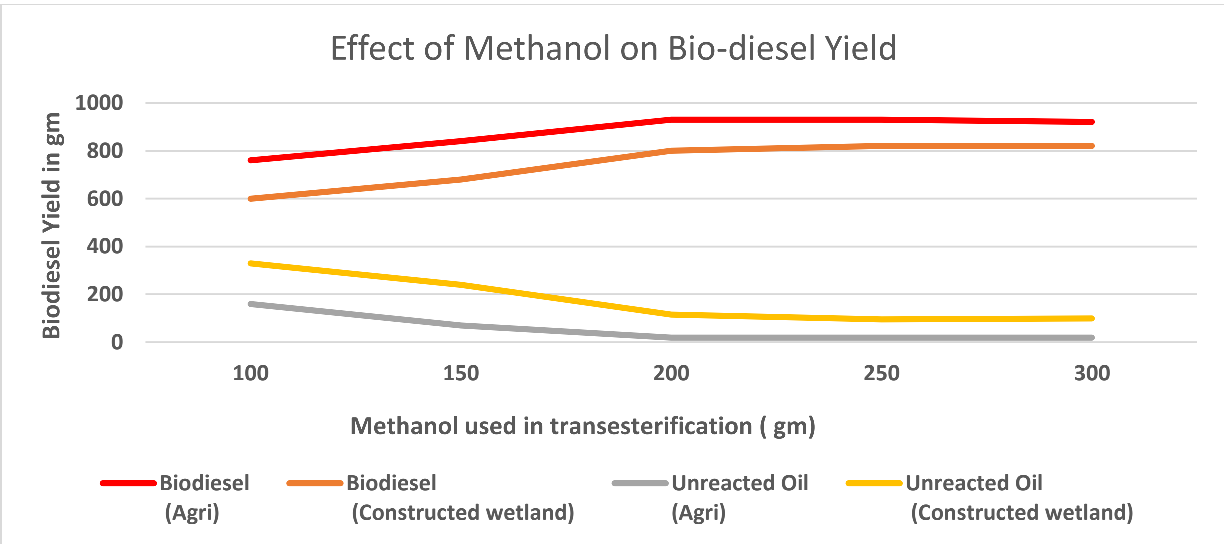

Figure 5: Bio-diesel yield comparison by Methanol-Transestrification process (Agri vs. Wetland)

Table 6
Biodiesel Yield by Acid Catalyst (H_2SO_4)

Sample No.	Methanol weight (gm)	AGRICULTURAL SEED OIL			WETLAND SEED OIL		
		Biodiesel weight (gm)	Glycerine (gm)	Unreacted Oil (gm)	Biodiesel weight (gm)	Glycerine (gm)	Unreacted Oil (gm)
1	100	800	90	110	670	78	252
2	150	840	90	70	680	80	240
3	200	920	95	20	800	85	115
4	250	930	95	20	820	85	95
5	300	**940**	95	20	**820**	85	95
Note:1000 gm of Castor oil +15 gm of NaOH +H_2SO_4 (3 wt% of oil) at Temperature of 45-70°C for 60 minutes.							

Lower conversion in wetland oil had been attributed to impurities, altering fatty acid profiles, or higher free fatty acids. Nevertheless, wetland oil had shown potential for biodiesel, offering environmental and resource recycling benefits. These findings aligned with literature emphasizing alcohol-to-oil ratio and feedstock quality for efficient biodiesel production[11,15]. Overall, agricultural oil had been more efficient, but wetland-derived oil had remained a viable sustainable alternative.

Parametric optimization of Biodiesel Yield using Acid Catalyst (H_2SO_4): Table 6 presented results of acid-catalysed methanol transesterification on castor oil from agricultural and wetland seeds. The process used 1000 g of oil with 15 g NaOH and 3% H_2SO_4 at 45–70°C for 60 minutes, increasing methanol from 100 g to 300 g. Increasing methanol enhanced biodiesel yield for both oil types. Agricultural oil had risen from 800 g to 940 g, with unreacted oil dropping from 110 g to 20 g; glycerine had remained 90–95 g. Wetland oil had yielded 670–820 g biodiesel, with unreacted oil decreasing from 252 g to 95 g and glycerine 78–85 g. Lower conversion in wetland oil was attributed to impurities or altered fatty acid composition. Nevertheless, both oils benefited from higher methanol, with wetland oil still achieving substantial yields. These results aligned with literature emphasizing alcohol-to-oil ratio and feedstock quality in optimizing biodiesel production[11,15]. Overall, agricultural oil was more efficient, but wetland-derived oil had remained a viable sustainable alternative.

Comparative Analysis of Methanol and Sulfuric Acid Effects on Biodiesel Yield from Agricultural and Constructed Wetland Castor Oil: The graph (Fig. 6) illustrated the effect of increasing methanol, with H_2SO_4 as catalyst, on biodiesel yield and unreacted oil for agricultural and constructed wetland castor oil. As methanol had increased from 100 g to 300 g, biodiesel yield had risen for both oils. Agricultural oil consistently produced higher yields, with unreacted oil decreasing more sharply than in wetland oil. Constructed wetland oil had shown higher unreacted oil at all methanol levels, indicating lower conversion efficiency. The superior performance of agricultural oil was attributed to higher purity and favourable fatty acid composition, while wetland oil contained more impurities or altered profiles due to environmental stress. Both oils were benefited from increased methanol, with wetland oil still achieving substantial yields at higher concentrations. These results aligned with literature emphasizing alcohol-to-oil ratio and feedstock quality in optimizing biodiesel[11,15]. Overall, agricultural oil remained more efficient, but constructed wetland oil proved to be a viable and sustainable alternative.

Variation in Characteristics of Biodiesels from Agricultural and Wetland Castor Sources: Table 7 shows comparison between biodiesel from castor plants grown in agricultural fields and constructed wetlands. Biodiesel yield was higher for agricultural castor (94%) than wetland castor (82%). Kinematic viscosity at 40°C was slightly lower for agricultural biodiesel (5.5 cSt) than wetland biodiesel (5.8 cSt), indicating better flow. Acid value is much lower in agricultural biodiesel (0.481 mg KOH/g) versus wetland biodiesel (1.2 mg KOH/g), suggesting superior fuel quality. Density has shown a minor difference, 0.94 g/cm³ for agricultural and 0.96 g/cm³ for wetland biodiesel.

Flash point was higher for agricultural biodiesel (160°C) than wetland (140°C), implying safer handling. Cold flow properties were better for agricultural biodiesel and poor for wetland biodiesel. Overall, agricultural castor biodiesel had demonstrated superior yield, quality and safety, while wetland biodiesel remained a viable sustainable alternative[11,15].

Kinetics of Biodiesel Yield (Maximum yield Trans-esterification Process)

Order of Esterification Reaction for Agricultural field castor to Bio-diesel: Figure 7 explains to find the order of reaction for converting agricultural field castor oil to biodiesel investigated using 1000 g of castor oil, 15 g of NaOH and H_2SO_4 (3 wt% of the oil) at temperatures ranging from 45°C to 70°C, with reaction times varying from 10 to 60 minutes, to determine the reaction order and rate constant. For the agricultural field castor oil, the maximum biodiesel yield (Ym) was approximately 3.67% and the reaction was described by a pseudo-first-order model with a rate constant of 0.0034 min^{-1}. In contrast, for wetland field castor oil, which had a higher initial FFA content (8.05% compared to 1.81% in agricultural oil), a slightly lower maximum yield (3.65%) had been obtained and the rate constant had been lower at 0.0025 min^{-1}, despite being processed under identical conditions. These variations had been attributed to the higher FFA and likely higher water content in wetland oil, which had caused slower reaction rates and reduced yields due to soap formation during base catalysis.

The findings validated the use of a pseudo-first-order kinetic model for the trans-esterification of castor oil under excess methanol conditions and had demonstrated the significant influence of FFA levels and feedstock quality on the reaction rate and overall yield.

Order of Esterification Reaction for wetland field castor to Bio-diesel: Figure 8 shows the order of the esterification reaction for converting wetland field castor oil to biodiesel studied using 1000 g of castor oil, 15 g of NaOH and H_2SO_4 (3 wt% of the oil) at a temperature range of 45–70°C for varying reaction times from 10 to 60 minutes to determine the reaction order and rate constant.

The plots (Figures 7 and 8) compare reaction order for biodiesel production from agricultural and wetland castor oil. Three models were analyzed: zero-order (x_1), pseudo-first order (ln(1-Y)) and second-order (1/1-x) versus reaction time. For agricultural biodiesel, the pseudo-first order model had the best fit (R^2 = 1) while zeroth- and second-order fits were weaker (R^2 = 0.274 and 0.9991). Wetland biodiesel showed a similar trend, with pseudo-first order R^2 = 1 and slightly lower fits for zeroth and second order (R^2 = 0.2991 and 0.9995).

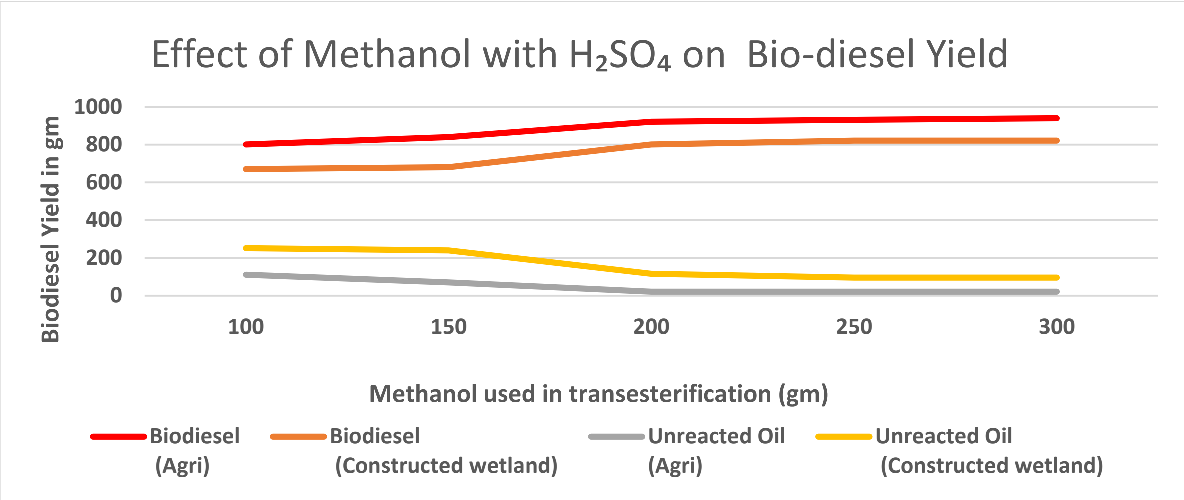

Figure 6: Role of H_2SO_4 in Optimized Biodiesel Yield by Methanol-Transestrification process

Table 7
Properities of Biodiesel (Agri vs. Wetland)

S.N.	Property	Agricultural Field Castor - Biodiesel	Wetland Field Castor - Biodiesel
1	Biodiesel Yield (%)	94	82
2	Kinematic Viscosity (at 40°C) centistokes	5.5	5.8
3	Acid Value (mg KOH/g)	0.481	1.2
4	Density (gm/cm^3)	0.94	0.96
5	Flash Point (°C)	160	140
6	Cold Flow Properties	Better	Poor

Table 8
Trans esterification Reaction Kinetics: Time-Based Variation of Yield

Time (min)	Yield (Yt)%	Xi = (Yt/Ym)	ln(1-Xt)	1/(1-Xt)
0	0.00	0	1	0.367879
10	3.34	3.627414	0.966	0.380602
20	3.26	3.539583	0.932	0.393765
30	3.18	3.454689	0.898	0.407384
40	3.10	3.372632	0.864	0.421473
50	3.03	3.293319	0.83	0.436049
60	2.96	3.216657	0.796	0.45113

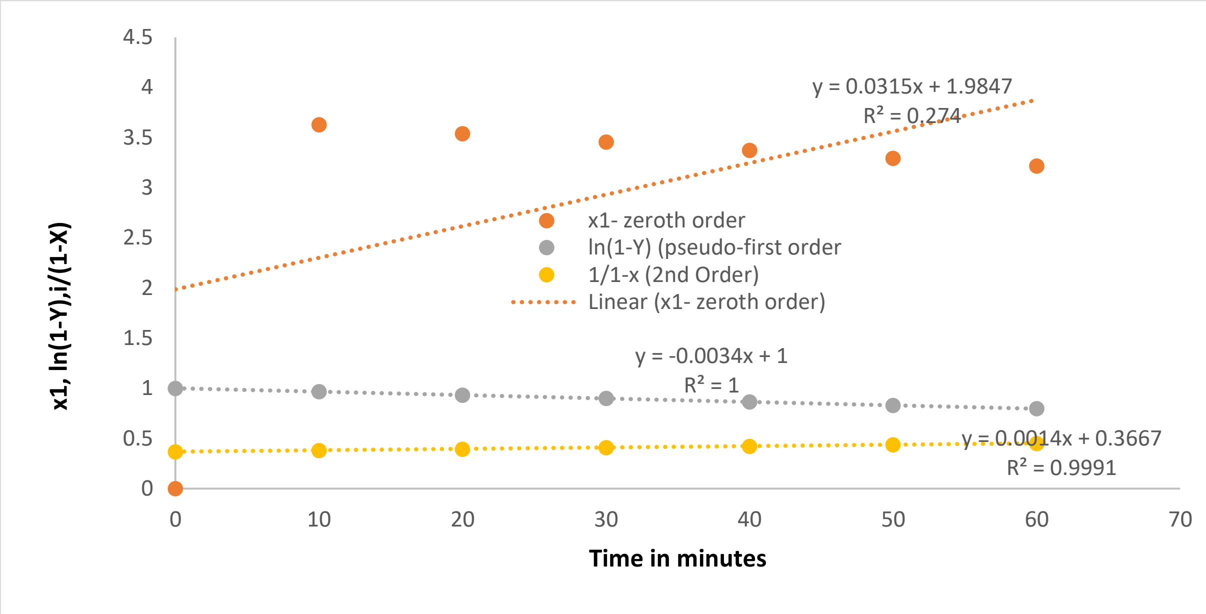

Figure 7: Plot for finding Order of Reaction for agricultural field based biodiesel production

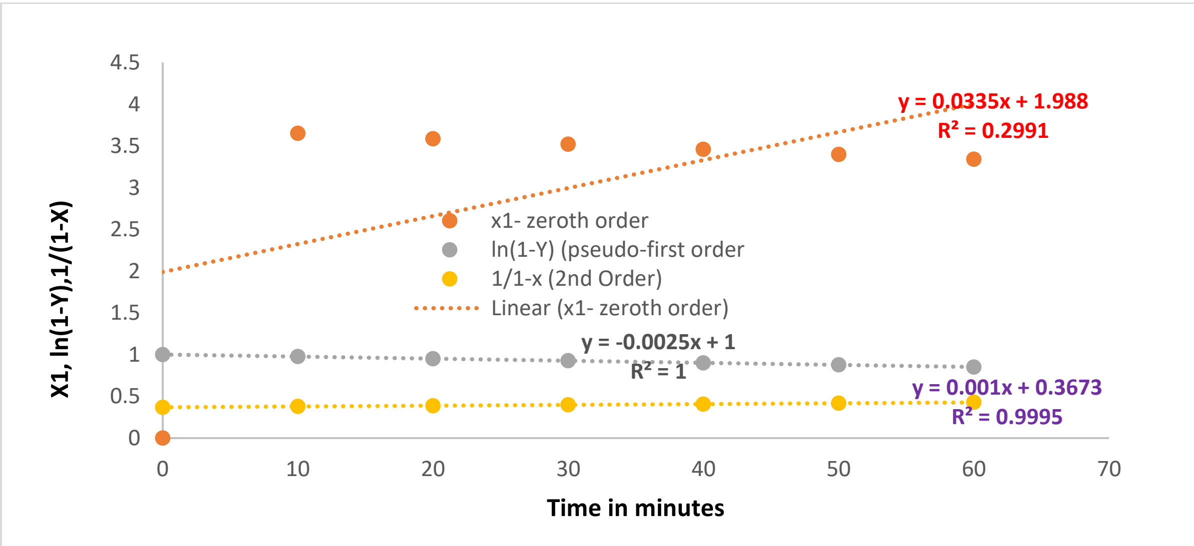

Figure 8: Evaluation of Order of Reaction for constructed wetland field based biodiesel production

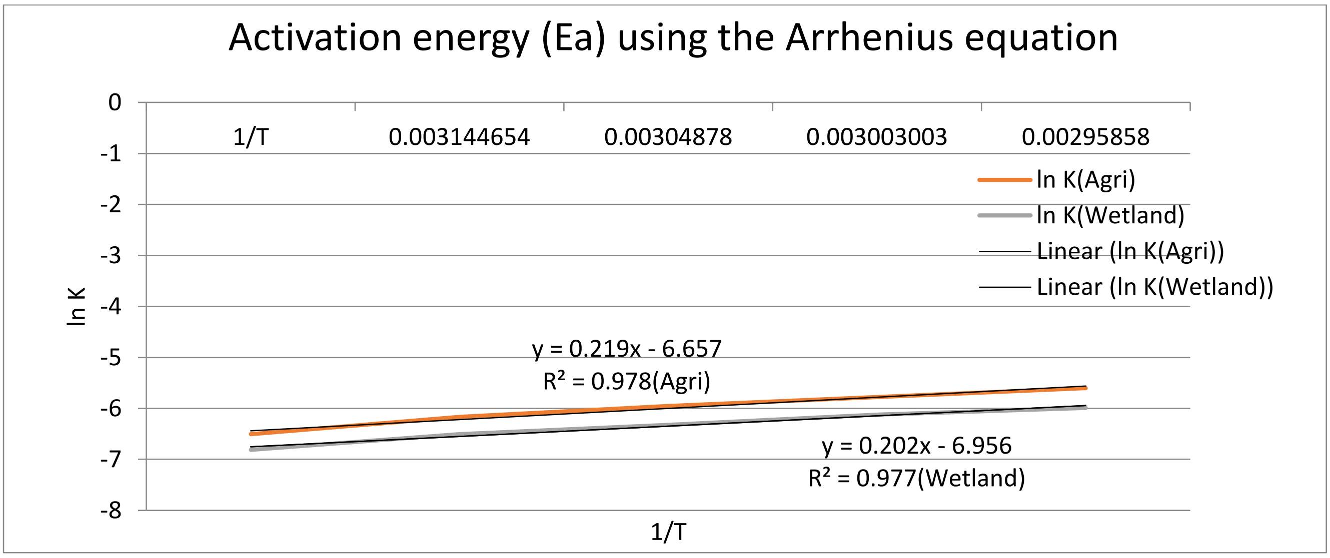

Figure 9: Plot for finding Activation energy (Ea) using the Arrhenius equation

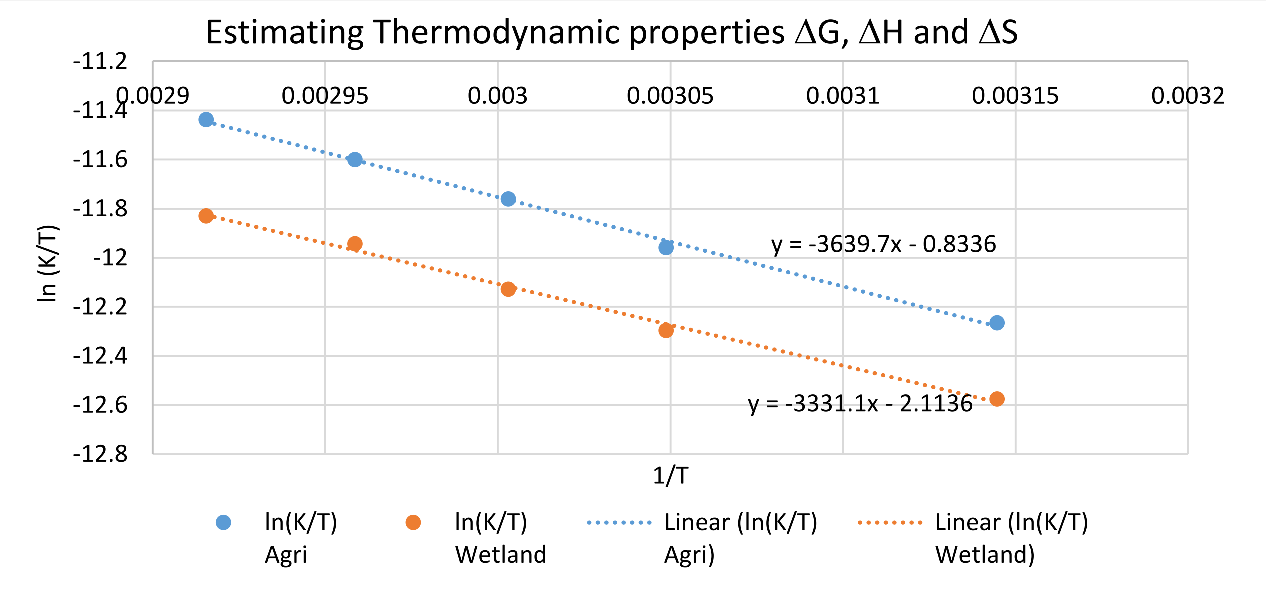

Figure 10: Estimating Thermodynamic Properties

Table 9
Data for Calculation of Kinetics of Trans-esterification of Castor Oil

Time (min)	Yield (Yt)%	Xi = (Yt/Ym	ln(1-Xt)	1/(1-Xt)
0	0.00	0	1	0.367879
10	3.36	3.651167	0.975	0.377192
20	3.30	3.58571	0.95	0.386741
30	3.24	3.521868	0.925	0.396531
40	3.18	3.459603	0.9	0.40657
50	3.13	3.398875	0.875	0.416862
60	3.07	3.339647	0.85	0.427415

Table 10
Kinetic Parameters for Agri and Wetland Castor Oil Trans-esterification

System	Initial FFA (%)	Methanol: Oil Ratio	Catalyst (%)	Temp (°C)	Processing Time (min)	Order of Reaction	Rate Constant (k, min^{-1})
Agricultural Field Castor Oil	1.81	10:01	10% H_2SO_4	60	120	Pseudo-first order	0.0034
Wetland Field Castor Oil	8.05	10:01	10% H_2SO_4	60	120	Pseudo-first order	0.0025

Table 11
Thermodynamic property of Biodiesel production (Agri vs wetland)

Oil type	Ea (kJ mol^{-1})	ΔH (kJmol^{-1})	ΔS (J mol^{-1} K^{-1})	ΔG @333 K (kJ mol^{-1})	Arrhenius R^2	Eyring R^2
Agricultural	33.0	30.3	−204.5	98.35	0.9977	0.9973
Wetland	30.4	27.7	−215.1	99.33	0.9958	0.9950

These results indicate that the trans-esterification reaction follows pseudo-first order kinetics for both feed stocks. Second-order models also show high linearity but are slightly less precise. Zero-order fits were consistently poor. Overall, kinetic behaviour is similar across sources, confirming that pseudo-first order kinetics best describes castor biodiesel production, consistent with literature reports[11,15].

Comparative Kinetic Parameters Analysis of Biodiesel Production from Agricultural and Wetland Castor Oil: Table 10 compares key process parameters and kinetics for biodiesel production from agricultural versus wetland castor oil under identical conditions: methanol-to-oil ratio 10:1, 10% H_2SO_4 catalyst, 60°C and 120 min reaction time. Agricultural castor oil has a much lower initial FFA (1.81%) than wetland oil (8.05%), indicating higher quality and lower pre-treatment needs. Both sources follow pseudo-first order kinetics, but the rate constant is higher for agricultural oil (0.0034 min^{-1}) than wetland oil (0.0025 min^{-1}), reflecting faster conversion. The combination of low FFA and higher rate constant demonstrates superior efficiency, yield and product quality for agricultural castor oil. These findings align with biodiesel literature highlighting the importance of low FFA and favorable kinetics for optimal synthesis[11,15].

Thermodynamic and Activation Energy Analysis of Biodiesel Production from Agricultural and Wetland Castor Oil: Figures 9 and 10 reveal biodiesel production from agricultural and wetland castor oil show activation energy (Ea) and thermodynamic properties (ΔH, ΔS, ΔG). Arrhenius plots (ln K vs. 1/T) reveal strong linearity for both oils (R^2 = 0.978 and 0.977), with slightly higher Ea for agricultural oil (slope 0.219 vs. 0.202). ln (K/T) vs. 1/T plots indicate higher enthalpy change (ΔH) and more negative entropy (ΔS) for agricultural oil, reflecting greater energy absorption and molecular reorganization. Overall, both oils follow similar kinetic and thermodynamic trends, but agricultural oil shows marginally higher energy requirements and superior reaction efficiency. These results support optimized biodiesel synthesis and align with literature on thermodynamic-kinetic interplay[11,15].

Finding Thermodynamic property ΔG, ΔH and ΔS:
Using Van't Hoff Equation (for thermodynamics):

$$ln\left(\frac{K}{T}\right) = -\frac{\Delta H}{R}\frac{1}{T} + \frac{\Delta S}{R} \quad (7)$$

In this form $y = mx + c$,
where slope $=\frac{\Delta H}{R}$,
Intercept $=\frac{\Delta S}{R}$.

Table 11 summarizes the thermodynamic and kinetic parameters derived from Arrhenius and Eyring analyses for the transesterification of agricultural and wetland castor oils. The activation energy (Ea) was obtained from the slope of ln(k) versus 1/T (Arrhenius plots), while the enthalpy (ΔH‡) and entropy (ΔS‡) of activation were derived from Eyring plots of ln(k/T) versus 1/T. The Gibbs free energy of activation (ΔG‡) was calculated at 333 K using the relation ΔG = ΔH– TΔS. Both oils exhibited strong linear correlations ($R^2 > 0.99$), indicating reliable kinetic modeling. Results show that agricultural oil has slightly higher Ea and ΔH but a marginally lower Δ‡ than wetland oil, suggesting that although more energy is required to initiate the reaction, the overall efficiency is comparable or superior to that of wetland oil. Negative entropy values for both systems indicate a more ordered transition state.

Conclusion

The studies present the technical viability and environmental significance of producing biodiesel from castor seeds cultivated in both agricultural and constructed wetland systems. The biodiesel derived from agricultural seeds exhibited superior physicochemical characteristics including lower viscosity, reduced acid value and better cold flow and thermal stability, making it highly suitable for commercial applications. In fact, agricultural castor seeds consistently outperformed their wetland counterparts in terms of oil yield, biodiesel conversion efficiency and fuel quality, owing to optimal growth conditions and lower free fatty acid content.

On the other hand, the constructed wetland system, irrigated with rice mill effluent, demonstrated a compelling alternative by offering dual benefits: effective wastewater treatment and biomass production for biofuel. Despite slightly lower yields and slower reaction kinetics, wetland-grown castor seeds produced biodiesel of acceptable quality, with significant environmental advantages. The kinetic and thermodynamic analyses validated the pseudo-first-order nature of the transesterification process and revealed that agricultural oil had a more favourable reaction profile.

The studies proposed a hybrid approach to biodiesel feedstock cultivation, leveraging high-yield agricultural systems for efficiency and integrating constructed wetlands for sustainability and resource recovery. This dual strategy not only enhances energy security but also aligns with global goals for environmental stewardship and circular economy development.

References

1. ASTM, Standard Test Method for Cloud Point of Petroleum Products, ASTM D2500, ASTM International, West Conshohocken, PA **(2001)**

2. ASTM, Standard Test Method for Pour Point of Petroleum Products, ASTM D97, ASTM International, West Conshohocken, PA **(2005)**

3. Canakci M. and Van Gerpen J.H., Biodiesel production via acid catalysis, *Transactions of the American Society of Agricultural Engineers*, **42**, 1203 **(1999)**

4. Chauhan B.S. and Maheshwari R.C., Performance evaluation of small-scale biodiesel production units, *Renewable Energy*, **115**, 430 **(2018)**

5. Demirbas A., Biodiesel from waste cooking oil via base-catalytic and supercritical methanol transesterification, *Energy Conversion and Management*, **50**, 923 **(2009)**

6. Freedman B., Butterfield R.O. and Pryde E.H., Transesterification kinetics of soybean oil, *Journal of the American Oil Chemists' Society*, **61**, 1638 **(1984)**

7. Fukuda H., Kondo A. and Noda H., Biodiesel fuel production by transesterification of oils, *Journal of Bioscience and Bioengineering*, **92**, 405 **(2001)**

8. Gandure J., Moyo L. and Maseka K., Evaluation of cold press extraction methods for castor oil, *International Journal of Sustainable Energy*, **40**, 317 **(2021)**

9. Gui M.M., Lee K.T. and Bhatia S., Feasibility of edible oil vs. non-edible oil vs. waste edible oil as biodiesel feedstock, *Energy*, **33**, 1646 **(2008)**

10. Knothe G. and Steidley K.R., Kinematic viscosity of biodiesel fuel components and related compounds. Influence of compound structure and comparison to petrodiesel fuel components, *Fuel*, **84**, 1059 **(2005)**

11. Knothe G., Van Gerpen J. and Krahl J., The Biodiesel Handbook, AOCS Press, Champaign, Illinois, 311 **(2015)**

12. Kumar S., Reddy S.R. and Rao B.S., Castor oil biodiesel: a sustainable non-edible source for renewable fuel, *Renewable and Sustainable Energy Reviews*, **72**, 608 **(2017)**

13. Lam M.K., Lee K.T. and Mohamed A.R., Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: a review, *Biotechnology Advances*, **28**, 500 **(2010)**

14. Long Dang Thanh, Thuy Nguyen Thi Thu, Co Nguyen Quang, Phat Phan Nhat and Long Nguyen Tien, Genetic diversity of some peanut cultivars based on SSR and rapd molecular markers in Vietnam, *Res. J. Biotech.*, **18**, 97 **(2023)**

15. Ma F. and Hanna M.A., Biodiesel production: a review, *Bioresource Technology*, **70**, 1 **(1999)**

16. Manorama K. and Chinnamma K., Effect of cold pressing conditions on castor oil yield and properties, *Journal of Oilseeds Research*, **37**, 112 **(2020)**

17. Mehta P., Verma A. and Patel S., Mechanical oil extraction methods and their effect on yield and quality of castor oil, *Industrial Crops and Products*, **145**, 111911 **(2020)**

18. Munack A., Schroder O., Krahl J. and Bunger J., Comparison of relevant gas emissions from biodiesel and fossil diesel fuel, *Agricultural Engineering International: CIGR Journal*, **3**, 143 **(2001)**

19. Parthiban R., Baskar R. and Kumar S., Characterization of castor oil biodiesel and optimization of transesterification parameters, *International Journal of ChemTech Research*, **12**, 207 **(2019)**

20. Patel R.M., Patel D.M., Shah K.P. and Patel D.A., Synthesis of Polyketones and their Antimicrobial Study, *Res. J. Chem. Environ.*, **3(2)**, 47 **(1999)**

21. Patel V.R., Patel D.A. and Patel H.K., Influence of irrigation sources on oil yield and quality of castor seeds, *Journal of Oilseeds Research*, **33**, 45 **(2016)**

22. Patil P.D., Deng S., Rhodes J.I. and Lammers P.J., Conversion of waste cooking oil to biodiesel using ferric sulfate catalyst, *Waste Management*, **32**, 1343 **(2012)**

23. Rakopoulos C.D., Antonopoulos K.A., Rakopoulos D.C., Hountalas D.T. and Giakoumis E.G., Comparative performance and emissions study of a direct injection diesel engine using blends of diesel fuel with vegetable oils or biodiesels of various origins, *Energy Conversion and Management*, **47**, 3272 **(2006)**

24. Rao P.V., Reddy K.H. and Devi K.L., Trends in castor production in India, *Indian Journal of Agricultural Sciences*, **91**, 1123 **(2021)**

25. Singh R.K. and Singh A., Castor oil: properties, production and applications, *Res. J. Chem. Environ.*, **14**, 71 **(2010)**

26. Tripathi A. and Dubey S., Environmental implications of rice mill effluent discharge and its treatment technologies, *Journal of Environmental Management*, **302**, 114060 **(2022)**.

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